COMPREHENSIVE ORGANOMETALLIC CHEMISTRY

The Synthesis, Reactions and Structures of Organometallic Compounds

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The Synthesis, Reactions and Structures of Organometallic Compounds

Volume 1

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Preface

Although the discovery of the platinum complex that we now know to be the first π-alkene complex, $K[PtCl_3(C_2H_4)]$, by Zeise in 1827 preceded Frankland's discovery (1849) of diethylzinc, it was the latter that initiated the rapidly developing interest during the latter half of the nineteenth century in compounds with organic groups bound to the elements. This era may be considered to have reached its apex in the discovery by Grignard of the magnesium reagents which occupy a special place because of their ease of synthesis and reactivity. With the exception of trimethylplatinum chloride discovered by Pope, Peachy and Gibson in 1907 by use of the Grignard reagent, attempts to make stable transition metal alkyls and aryls corresponding to those of main group elements met with little success, although it is worth recalling that even in 1919 Hein and his co-workers were describing the 'polyphenylchromium' compounds now known to be arene complexes.

The other major area of organometallic compounds, namely metal compounds of carbon monoxide, originated in the work starting in 1868 of Schützenberger and later of Mond and his co-workers and was subsequently developed especially by Hieber and his students. During the first half of this century, aided by the use of magnesium and, later, lithium reagents the development of main group organo chemistry was quite rapid, while from about 1920 metal carbonyl chemistry and catalytic reactions of carbon monoxide began to assume importance.

In 1937 Krause and von Grosse published their classic book 'Die Chemie der Metallorganischen Verbindungen'. Almost 1000 pages in length, it listed scores of compounds, mostly involving metals of the main groups of the periodic table. Compounds of the transition elements could be dismissed in 40 pages. Indeed, even in 1956 the stimulating 197-page monograph 'Organometallic Compounds' by Coates adequately reviewed organo transition metal complexes within 27 pages.

Although exceedingly important industrial processes in which transition metals were used for catalysis of organic reactions were developed in the 1930s, mainly in Germany by Reppe, Koch, Roelen, Fischer and Tropsch and others, the most dramatic growth in our knowledge of organometallic chemistry, particularly of transition metals, has stemmed from discoveries made in the middle years of this century. The introduction in the same period of physical methods of structure determination (infrared, nuclear magnetic resonance, and especially single-crystal X-ray diffraction) as routine techniques to be used by preparative chemists allowed increasingly sophisticated exploitation of discoveries. Following the recognition of the structure of ferrocene, other major advances quickly followed, including the isolation of a host of related π-complexes, the synthesis of a plethora of organometallic compounds containing metal–metal bonds, the characterization of low-valent metal species in which hydrocarbons are the only ligands, and the recognition from dynamic NMR spectra that ligand site exchange and tautomerism were common features in organometallic and metal carbonyl chemistry. The discovery of alkene polymerization using aluminium alkyl–titanium chloride systems by Ziegler and Natta and of the Wacker palladium–copper catalysed ethylene oxidation led to enormous developments in these areas.

In the last two decades, organometallic chemistry has grown more rapidly in scope than have the classical divisions of chemistry, leading to publications in journals of all national chemical societies, the appearance of primary journals specifically concerned with the topic, and the growth of annual review volumes designed to assist researchers to keep abreast of accelerating developments.

Organometallic chemistry has become a mature area of science which will obviously continue to grow. We believe that this is an appropriate time to produce a comprehensive review of the subject, treating organo derivatives in the widest sense of both main group and transition elements. Although advances in transition metal chemistry have appeared to dominate progress in recent years, spectacular progress has, nevertheless, also been made in our knowledge of organo compounds of main group elements such as aluminium, boron, lithium and silicon.

In these Volumes we have assembled a compendium of knowledge covering contemporary organometallic and carbon monoxide chemistry. In addition to reviewing the chemistry of the elements individually, two Volumes survey the use of organometallic species in organic synthesis and in catalysis, especially of industrial utility. Within the other Volumes are sections devoted to such diverse topics as the nature of carbon–metal bonds, the dynamic behaviour of organometallic compounds in solution, heteronuclear metal–metal bonded compounds, and the impact of organometallic compounds on the environment. The Volumes provide a unique record, especially of the intensive studies conducted during the past 25 years. The last Volume of indexes of various kinds will assist readers seeking information on the properties and synthesis of compounds and on earlier reviews.

As Editors, we are deeply indebted to all those who have given their time and effort to this project. Our Contributors are among the most active research workers in those areas of the subject that they have reviewed and they have well justified international reputations for their scholarship. We thank them sincerely for their cooperation.

Finally, we believe that 'Comprehensive Organometallic Chemistry', as well as providing a lasting source of information, will provide the stimulus for many new discoveries since we do not believe it possible to read any of the articles without generating ideas for further research.

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Structural and Bonding Relationships among Main Group Organometallic Compounds

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1.1 INTRODUCTION

1.1.1 General Considerations

Although this series of volumes, as the adjective 'comprehensive' in the title implies, is intended to provide a reasonably full account of organometallic chemistry, the purpose of this introductory chapter is to indicate the salient structural and bonding features of main group organometallic compounds by use of illustrative examples rather than by a comprehensive coverage. It is hoped that this will convey some feeling not only for the reasons why certain organometallic compounds have rather peculiar structures, but also for the relative stabilities and reactivities of the various types of compound, characteristics relevant to some of the chapters of Volumes 7 and 8 as well as to the other chapters in the present volume and Volume 2, to which the reader is referred for further details of specific systems.

The definition of organometallic compound used here is that which is most commonly used:[1–8] we shall be concerned with compounds in which the organic groups or residues are attached to metal atoms by metal–carbon bonds. Also in conformity with common practice, we shall include in our discussion some systems that strictly should be described as 'organometalloidal', for example organo-boron, -silicon, -germanium and -arsenic systems. By doing so, we shall be considering together as one family the organo derivatives of elements more electropositive than carbon. Like metal–carbon bonds, metalloid–carbon bonds in general have a polarity $M^{\delta+}—C^{\delta-}$, which is one of the characteristic features that distinguish organometallic compounds from other types of organic compound, in which carbon is found at the positive end of bonds to nonmetallic elements like nitrogen, oxygen, fluorine, chlorine or bromine.

This bond polarity makes the organic groups R in metal alkyls or aryls, MR_n, carbanionic in character, susceptible to attack by electrophiles, while the metal atoms themselves are susceptible to nucleophilic attack, not only on account of their positive charges, but also because they generally have vacant orbitals that can accommodate electronic charge from nucleophiles. This in turn is because most (though not all) metal atoms have more valence shell orbitals than electrons, so when the electrons are paired off in bonds to alkyl or aryl groups, the surplus orbitals remain empty, or else find limited use in multicentre metal–carbon bonding, one pair of electrons being associated with two or more metal atoms as well as one carbon atom, instead of being shared between just one metal and one carbon atom.

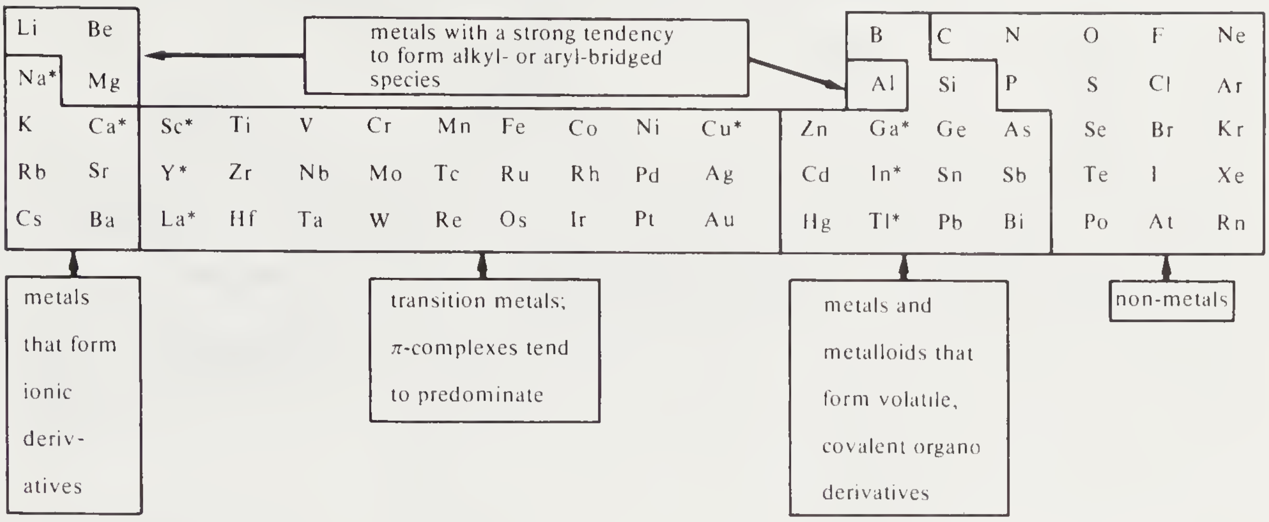
These characteristics of organometallic systems, which are discussed in more detail below, may be contrasted with those of other types of organic compound in which the atoms of non-metallic elements like nitrogen, oxygen or the halogens (which have more valence shell electrons than orbitals) generally possess lone pairs of electrons and function as the sites for attack by electrophiles.

In the following sections we outline the manner in which organometallic compounds can be broadly classified according to their structural types, and consider some thermochemical aspects of organometallic chemistry relevant to the synthesis, stability and reactivity of organometallic compounds. Attention is then focused on the various types of structural unit that are found among main group organometallic systems, and the special bonding problems they pose: organometallic chemistry has provided a rich territory for theoreticians in search of stimulating problems.

1.1.2 The Main Structural Types

Although, as indicated above, a bond polarity $M^{\delta+}—C^{\delta-}$ is a general characteristic of organometallic systems, the degree of this polarity, and the tendency of systems to adopt associated structures involving multicentre metal–carbon bonding, are characteristics that vary markedly with the metal. Since they are reflected in the bulk properties of metal alkyls and aryls, they form a convenient basis for the classification of organometallic compounds, as illustrated in Figure 1.[5,7]

For example, the metal–carbon bonds in alkyl derivatives of the less electropositive metals and metalloids like boron, silicon, germanium and arsenic are only slightly polar. Such derivatives are typically 'organic' in their bulk properties: low melting, volatile, soluble in non-polar solvents. The boiling temperatures of the methyl derivatives given in Table 1[5] show, for instance, that these derivatives are much more volatile than most other derivatives of these elements. Thus trimethylborane, BMe_3 (b.p. −22 °C), has a volatility similar to that of the comparable alkane isobutane, $CHMe_3$ (b.p. −12 °C), while the boiling points of the tetramethyls, MMe_4, of the Group IV elements (M = C, Si, Ge, Sn and Pb) show only a slight increase with molecular mass down the



*metals that also participate in alkyl- or aryl-bridging

Figure 1 Types of organometallic compound

Table 1 The Boiling Temperatures (°C) of the Methyl Derivatives MMe_n of Some Metals and Metalloids

MMe_2		MMe_3		MMe_4		MMe_3	
Be	$220^{a,b}$	B	−22	C	10	N	3
Mg	$—^{b}$	Al	126^{c}	Si	27	P	40
Zn	44	Ga	56	Ge	43	As	52
Cd	106	In	136	Sn	77	Sb	79
Mg	93	Tl	147^{a}	Pb	110	Bi	110

[a] Extrapolated boiling temperature. [b] Unlike their Group II congeners, which have discrete molecular structures MMe_2, the dimethyl derivatives of beryllium and magnesium have associated polymeric structures $(MMe_2)_n$ in the solid phase. The volatility of $(MgMe_2)_n$ is too low to allow a meaningful boiling/sublimation temperature to be quoted. [c] Trimethylaluminium crystallizes and vaporizes as the dimer Al_2Me_6.

group. Some representative structures of these molecular methyl derivatives are shown in Figure 2a. Note that the trimethyl derivatives of the Group V metals arsenic, antimony and bismuth are unusual among main group metal alkyls in possessing lone pair electrons on their metal atoms.

In contrast to these systems, organo derivatives of the most electropositive metals like sodium or potassium are essentially ionic, M^+R^-. These exceedingly reactive substances have salt-like properties such as high melting temperatures, low volatilities, and low or negligible solubilities in non-polar, noncoordinating solvents like pentane or hexane. Between these two extremes are systems with highly polar but nevertheless essentially covalent metal–carbon bonds, the polarity of which acts as a source of reactivity; these systems include such useful reagents as lithium alkyls, magnesium alkyls and aryls (Grignard reagents), and aluminium alkyls. It is these same metals that show the most marked tendency to indulge in multicentre bonding: their alkyls and aryls adopt associated structures (Figure 2b) in which the bonding power of pairs of electrons is spread over more than just two atoms. Since the study of such systems has done much to clarify our understanding of chemical bonding in general as well as metal–carbon bonding in particular, and since these associated structures serve as models for the intermediates or transition states in many organic reactions, particular attention will be focused on them in the present survey.

A third category of structure (Figure 2c) found occasionally among main group organometallic compounds, though much more often among transition metal derivatives (see Volumes 3–6), is that of metal–hydrocarbon π-complexes. In these the metal atom or ion is located above the plane of a set of carbon atoms in an unsaturated organic ligand like an alkene or alkyne, a cyclopentadienyl ring, or a benzyl residue, making use of the π-bonding electrons of the ligand to bond strongly to two or more of the ligand carbon atoms.

These various structural types can conveniently be distinguished by indicating the number of carbon atoms through which a particular ligand coordinates to a metal (the *hapticity* of the ligand, designated either by h^n or η^n in the formula), and the number of metal atoms to which that ligand bonds. For example, when a monovalent organic residue like an alkyl or aryl group bonds terminally to a single metal atom through just one of its carbon atoms, its mode of attachment is referred

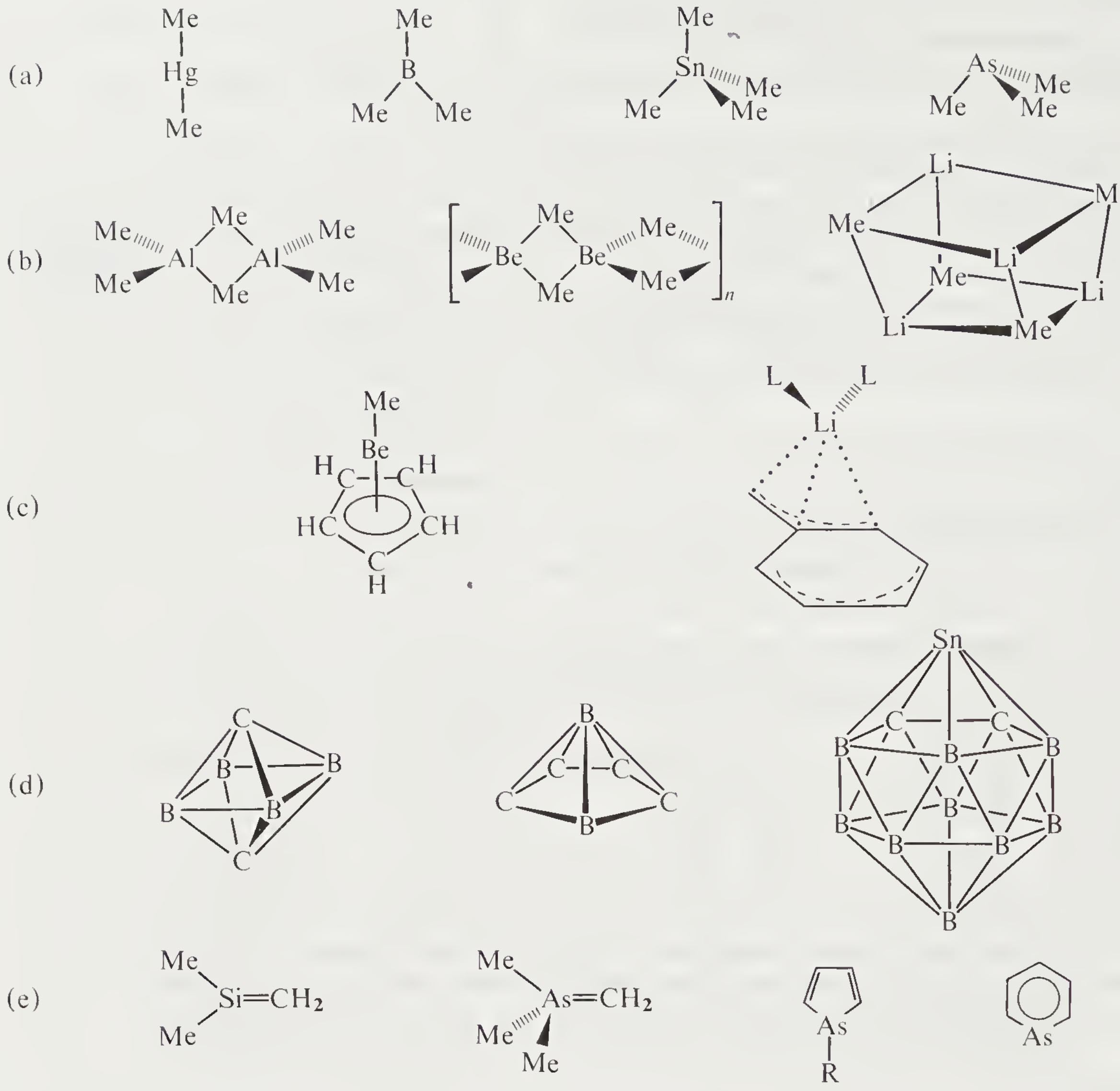


Figure 2 Some representative structures of main group organometallic compounds. (a) Molecular structures of the monomeric metal methyls $HgMe_2$, BMe_3, $SnMe_4$ and $AsMe_3$. (b) The associated structures of $(AlMe_3)_2$, $(BeMe_2)_n$ and $(LiMe)_4$, *i.e.* $Al_2Me_4(\mu_2\text{-}Me)_2$, $[Be(\mu_2\text{-}Me)_2]_n$ and $[Li(\mu_3\text{-}Me)]_4$. (c) The metal–hydrocarbon π-complexes $BeMe(\eta^5\text{-}C_5H_5)$ and $Li(\eta^3\text{-}CH_2C_6H_5)\cdot N(CH_2CH_2)_3N$. (d) The carboranes and metallacarboranes $C_2B_4H_6$, $C_4B_2H_6$ and $Sn(\eta^5\text{-}C_2B_9H_{11})$; each carbon and boron atom has one terminal hydrogen atom attached (not shown). (e) Species containing metal–carbon multiple bonds

to as monohapto (h^1 or η^1) or σ-bonded. When a similar monovalent group bridges two metal atoms, as do two of the six methyl groups of hexamethyldialuminium, Al_2Me_6 (Figure 2b), its mode of bonding is referred to as μ_2. The methyl ligands of tetrameric methyllithium, $(LiMe)_4$, bridge three metal atoms (Figure 2b) and so are referred to as μ_3-bonded. The cyclopentadienyl residue in cyclopentadienyl(methyl)beryllium, $MeBe(C_5H_5)$ (Figure 2c), is h^5 (or η^5) bonded.

Examples of a fourth category of structure among main group organometallic compounds are shown in Figure 2d. These are carboranes[9] and metallacarboranes,[10] mixed cluster systems containing carbon and boron atoms or carbon, boron and metal atoms in their polyhedral molecular skeletons. The development of our understanding of how their molecular skeletons are held together by relatively few electrons (like bridged metal alkyls, they are electron deficient[11] in the sense that they contain fewer bond pairs than bonding atom contacts) has provided a welcome stimulus to bonding theories and allowed us to recognize the family relationships that link metal–hydrocarbon π-complexes with boron hydride and metal carbonyl clusters on the one hand, and carbocations and small ring hydrocarbon systems on the other.[12] These points will be illustrated in Section 1.6 below.

One further category of compound that is little represented in main group organometallic chemistry, though of increasing importance in transition metal chemistry, is that of species containing metal–carbon multiple bonds (Figure 2e). Carbene complexes, $L_nM{=}CR_2$, or carbyne complexes, $L_nM{\equiv}CR$, where M is a main group metal of Groups I–IV, are generally unstable to association, *e.g.* equation (1). Evidently their multiple bonds represent a less strong bonding arrangement than the greater number of single bonds that form when they oligomerize or poly-


(1)

merize. The monomers are known only as highly reactive short-lived intermediates in certain reactions. Monomeric arsenic, antimony and bismuth ylides, $R_3MCR'_2$, analogues of Wittig reagents $R_3PCR'_2$, are known, however, and these same metal atoms have been incorporated adjacent to carbon atoms in unsaturated ring systems like arsabenzene (*cf.* pyridine, see Figure 2e) and arsoles (*cf.* pyrroles), though the aromaticity of these ring systems is markedly less than that of their nitrogen analogues. The metal–carbon bonds in the ylides are perhaps better represented by the canonical form $L_n\overset{+}{M}—\overset{-}{C}R_2$ rather than $L_nM{=}CR_2$.

Further elaboration of these structural and bonding aspects will be found below after a brief survey of thermochemical aspects of main group organometallic chemistry in Section 1.2.

1.2 THERMOCHEMICAL ASPECTS

1.2.1 General Considerations

The usefulness of many organometallic compounds as reagents, and their reactivity towards oxidizing agents, acids, water and assorted multiply-bonded compounds, reflects the relative weakness of metal–carbon bonds compared with metal–nitrogen, –oxygen or –halogen bonds. Most metal alkyls and aryls, MR_n, are thermodynamically (though not necessarily kinetically) unstable to hydrolysis to metal hydroxide, $M(OH)_n$, and hydrocarbon, RH, and also, like organic compounds in general, are unstable to oxidation to metal oxide, carbon dioxide and water. Many are also thermodynamically unstable with respect to their constituent elements (M, C and H_2) or to the mixture of hydrogen, hydrocarbons and metal that normal thermal decomposition would afford. Some, like the simpler alkyls and aryls of lithium, magnesium, zinc, boron and aluminium, are so reactive to oxygen and/or moisture as to need protection from the atmosphere. Such compounds need to be prepared, characterized, stored and used under controlled atmosphere conditions, *e.g.* in apparatus filled with dry nitrogen or argon, or under vacuum. Others, although thermodynamically unstable with respect to oxidation and hydrolysis, nevertheless survive exposure to air and moisture only because there is no easy route by which such reactions can proceed. In order to appreciate the category into which specific compounds fall, it is helpful to consider some of the considerable body of thermochemical data now available on organometallic compounds.[6,13,14]

1.2.2 Enthalpies of Formation and Bond Enthalpies

The standard molar enthalpies of formation (ΔH°_f) and metal–carbon average molar bond enthalpies (E_m(M—C)) of some gaseous metal methyls, MMe_n, of main group metals M are given in Table 2. The group trends in ΔH°_f are illustrated in Figure 3. From Table 2 and Figure 3 it is apparent that decomposition of these compounds into the metal or metalloid M, carbon and hydrogen would be an exothermic process for such heavy metal alkyls as $HgMe_2$, $PbMe_4$ and $BiMe_3$ (*i.e.* $-\Delta H^\circ_f$ is negative), and also for $ZnMe_2$, $CdMe_2$ and $InMe_3$. However, for such compounds as BMe_3, $AlMe_3$, $SiMe_4$ and $GeMe_4$, the process would be endothermic ($-\Delta H^\circ_f$ is positive).

The metal–carbon average molar bond enthalpies (or bond enthalpy terms), E(M—C) in Table 2, represent the average enthalpy terms associated with the metal–carbon bonds of MMe_n, such that the enthalpy change for the disruption of these compounds into metal atoms and methyl

Table 2 Standard Molar Enthalpies of Formation (ΔH°_f/kJ mol^{-1}) and Metal–Carbon Average Molar Bond Enthalpies (E_m(M—C)/kJ mol^{-1}) of Some Gaseous Metal Methyls MMe_n

Group II, MMe_2			*Group III*, MMe_3			*Group IV*, MMe_4			*Group V*, MMe_3		
M	ΔH°_f	E_m	M	ΔH°_f	E_m	M	ΔH°_f	E_m	M	ΔH°_f	E_m
—	—	—	B	−123	365	C	−167	358	N	−24	314
—	—	—	Al	−81	274	Si	−245	311	P	−101	276
Zn	50	177	Ga	−42	247	Ge	−71	249	As	13	229
Cd	106	139	In	−173	160	Sn	−19	217	Sb	32	214
Hg	94	121	Tl	—	—	Pb	136	152	Bi	194	141

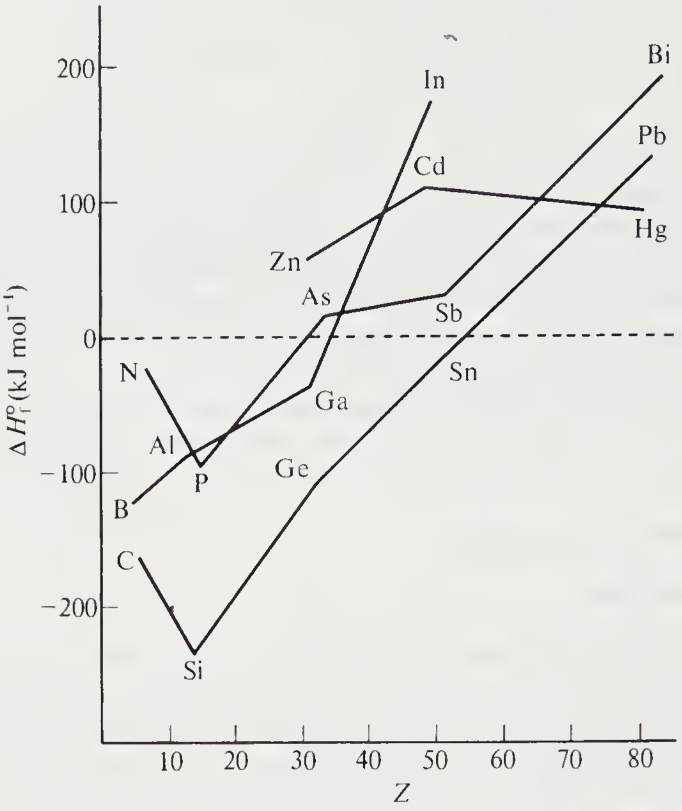


Figure 3 Group trends in the standard molar enthalpies of formation, ΔH_f°, of some gaseous metal methyls

radicals is equal to nE(M—C). The manner in which they vary with M is worth noting. Boron-carbon bonds are slighly stronger than carbon-carbon bonds, but the larger Group III metals form M—C bonds that get progressively weaker as the group is descended. Similar group trends are to be seen in Groups II, IV and V: within each group, the metal-carbon bonds get weaker as they get longer.

1.2.3 Thermal Stability

The above thermochemical data provide a rough guide to the thermodynamic stability of these metal alkyls, in the absence of free energy data for specific reactions, but have to be used with caution if an indication of thermal stability is required. Generally, metal alkyls decompose, when heated, into assorted hydrocarbons, some hydrogen and the metal (or metal hydride), rather than into the constituent elements, so the enthalpies of formation of the hydrocarbon products must be taken into account.

As an example of how the identities of the hydrocarbons produced can influence the enthalpy change associated with the decomposition of a metal alkyl, one can consider different possible modes of decomposition of tetramethyllead, $PbMe_4$, which normally generates ethane *via* methyl radicals:[15]

$$PbMe_4(g) \rightarrow Pb(s) + 2C_2H_6(g)$$

Since the standard molar enthalpy of formation of ethane, ΔH_f°, is -85 kJ mol^{-1},[6] the enthalpy change for this decomposition reaction is -307 kJ mol^{-1}. The reaction is thus highly exothermic, some 170 kJ mol^{-1} more so than the hypothetical decomposition into the elements in their standard states. Moreover, since the reaction generates more gaseous molecules than it consumes, it would be expected to be accompanied by an increase in entropy. With $T\Delta S$ positive and ΔH negative, ΔG $(= \Delta H - T\Delta S)$ would also be negative, implying that $PbMe_4$ is thermodynamically very unstable with respect to these products.

Other possible decomposition reactions are as follows:

$$PbMe_4(g) \rightarrow Pb(s) + 2MeH(g) + C_2H_4(g) \quad \Delta H = -235 \text{ kJ mol}^{-1}$$

$$PbMe_4(g) \rightarrow Pb(s) + 2H_2(g) + 2C_2H_4(g) \quad \Delta H = -33 \text{ kJ mol}^{-1}$$

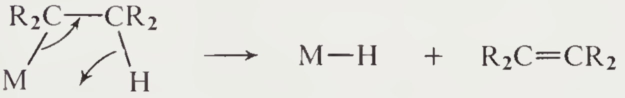
These are clearly thermodynamically less likely reactions, and in practice hydrogen, methane and ethylene feature only as minor decomposition products.

It is apparent that the enthalpy change associated with such decomposition reactions varies markedly with the hydrocarbons formed. Decomposition into metal and alkanes, rather than into hydrogen and alkenes, appears the thermodynamically more likely reaction. Compounds like $CdMe_2$, $InMe_3$ and $BiMe_3$, as well as $PbMe_4$, are all thermodynamically unstable species, whereas species like BMe_3 or $SiMe_4$, with large negative values of ΔH_f°, are stable. Nevertheless, all the compounds in Table 2 are isolable, and can be stored at normal temperatures without decomposition. This is because there is no route of low enough activation energy by which they can decompose: their decomposition reactions are kinetically controlled.

A likely mechanism for the decomposition of a metal methyl derivative, MMe_n, is homolytic dissociation of a metal–carbon bond, generating the radicals $[MMe_{n-1}]\cdot$ and $Me\cdot$. The energy required for this process, the bond dissociation enthalpy, will normally exceed, by some 50 kJ mol^{-1}, the bond enthalpy term, $E(M—C)$, given in Table 2. Thus, although the complete decomposition of several of these compounds is a highly exothermic process, the first step in the decomposition, homolytic cleavage of a metal–carbon bond, requires so much energy as to occur only at elevated temperatures. Pyrolytic decomposition of tetramethyllead, the least stable tetramethyl derivative of the Group IV metals, sets in at about 265 °C, and the bond dissociation enthalpy, $D(Me_3Pb—Me)$, is 205 kJ mol^{-1} (*cf.* $E(M—C)$ = 152 kJ mol^{-1}).[16,17]

It was the thermal decomposition of alkyls of such metals as lead, zinc and bismuth, at *ca.* 450 °C in a stream of nitrogen or hydrogen at low pressure, that was the method first used to demonstrate the formation and short-lived existence of alkyl radicals in the gas phase.[18]

Metal–carbon bond dissociation is by no means the only mechanism by which metal alkyls or aryls can decompose thermally. One important source of thermal instability is the presence of a hydrogen atom attached to the β-carbon atom of a metal alkyl. Such a β-attached hydrogen atom can migrate to the metal atom, allowing elimination of alkene (equation 2). This type of reaction, like the homolytic M—C bond cleavage, involves loss of the metal–carbon bond energy, and also involves cleavage of a C—H bond (for which $E(C—H)$ is *ca.* 408 kJ mol^{-1}). However, set against these lost bond energies are the gain in carbon–carbon bond energy (*ca.* 198 kJ mol^{-1}) and the energy of the new M—H bond, which is generally some 10–20% stronger than the metal–carbon single bond.[13] Such a reaction therefore generally offers a lower energy alternative to simple homolytic bond cleavage, and it is not surprising that metal alkyls containing β-attached hydrogen atoms (n-alkyls and branched derivatives $L_nM—CH_2CHR_2$) are thermally less stable than methyl or neopentyl derivatives or even aryls (which would generate arynes in giving similar reactions).



(2)

Such β-elimination reactions will clearly be facilitated by the presence on the metal of a vacant orbital to accommodate the metal–hydrogen bond pair, and so are much more important in the alkyl chemistry of metals of Groups I–III than of the Group IV metals, which in the tetraalkyls, MR_4, are effectively coordinatively saturated. Derivatives of Group II or III metal atoms can, however, be stabilized by adduct formation with Lewis bases. Adducts $MR_2{\cdot}2L$ (M = Be, Mg or Zn, L = a Lewis base) and $M'R_3{\cdot}L$ (M′ = B, Al, Ga, In or Tl) are appreciably more stable, thermally, than the free alkyls MR_2 or $M'R_3$. The simple ethyl or higher n-alkyl derivatives MR_n of transition metals, which have nine valence shell orbitals, undergo β-elimination reactions so readily as to render such species effectively inaccessible, though ethyl derivatives in which the remaining valences are occupied in bonding to polyhapto ligands are known, and β-elimination reactions are turned to particularly good effect in many catalyst systems[19] (see Volumes 3, 7 and 8 in particular, but also Volumes 4–6).

The availability of low-energy vacant metal orbitals can also facilitate the decomposition of metal alkyls and aryls by accommodating electrons promoted from metal–carbon bonding orbitals, thereby weakening the metal–carbon bonds, or by allowing α-hydrogen transfer, modes of decomposition that are also more important in transition metal chemistry than in main group chemistry. Tetramethyltitanium, $TiMe_4$, for example, decomposes above about −78 °C; contrast $PbMe_4$, which decomposes above about +265 °C, and $SiMe_4$, which is stable to above +500 °C.

1.2.4 Stability to Oxidation and Hydrolysis

Despite the general thermodynamic instability of organometallic compounds with respect to oxidation and hydrolysis, compounds vary markedly in their reactivity to oxygen and water. The thermodynamic instability to oxidation arises because of the large free energies of formation of the metal oxides, carbon dioxide and water. The enthalpy of combustion of gaseous dimethylzinc, a spontaneously flammable compound, is *ca.* -1920 kJ mol^{-1}. Tetramethyltin, which is air-stable, has an enthalpy of combustion (to solid SnO_2 and gaseous CO_2 and H_2O) of -3590 kJ mol^{-1}. The differing reactivities of these two compounds is a further feature attributable to differences of coordination. Like $ZnMe_2$, the lighter alkyls of the metals Li, Na, Be, Mg, Zn, B, Al, Ga, In and Tl are spontaneously flammable, as indeed are trialkyls of the Group V metals As, Sb and Bi. Kinetic reactivity to oxidation by air is thus associated with the presence of empty low-lying orbitals, like the 4*p* orbital of $GaMe_3$, or with a lone pair of electrons, as in $SbMe_3$. The Group IV tetraalkyls like $SnMe_4$ possess neither of these features and so resist oxidation at normal temperatures.

The reactivity of these metal alkyls towards water resembles their sensitivity to oxidation, and is similarly rationalized in terms of the metal coordination state. Thus the alkyls and aryls of the Group I and II metals, and of Zn, Cd, Al, Ga and In, are readily hydrolyzed, some with explosive violence. In contrast, the trialkylboranes are unaffected by water at normal temperatures, although their coordinatively unsaturated boron atoms afford sites for nucleophilic attack. This unreactivity is attributed to the very slight polarity of boron–carbon bonds. The alkyls and aryls of the Group IV and Group V metals are also kinetically inert to hydrolysis by water.

1.2.5 Energetics of Some Exchange Reactions

The enthalpies of formation listed in Table 2 allow one to calculate the enthalpy changes of the exchange reactions:

$$\mathrm{M + M'R \rightarrow MR + M'}$$

which can be used for the synthesis of one organometallic compound from another. Such reactions are likely to be of preparative use if the enthalpy change is large and negative, *i.e.* if they are strongly exothermic, which will be the case when a compound with weak metal–carbon bonds, such as a lead or mercury alkyl, is used as the reagent. The figures (ΔH, kJ mol^{-1}) for some reactions involving dimethylmercury are as follows:[5–7]

$$\mathrm{HgMe_2(g) + M(s) \rightarrow MMe_2(g) + Hg(l)} \qquad \mathrm{Zn}, -38;\ \mathrm{Cd}, +17$$

$$\tfrac{3}{2}\,\mathrm{HgMe_2(g) + M(s) \rightarrow MMe_3(g)} + \tfrac{3}{2}\,\mathrm{Hg(l)} \qquad \mathrm{Al}, -228;\ \mathrm{Ga}, -178;\ \mathrm{In}, +33$$

$$\mathrm{2HgMe_2(g) + M(s) \rightarrow MMe_4(g) + 2Hg(l)} \qquad \mathrm{Sn}, -205;\ \mathrm{Pb}, -49$$

Metals that can be alkylated or arylated in this manner by organomercurials include the alkali metals, the alkaline earths, zinc, aluminium, gallium, tin, lead, antimony and bismuth.

A more commonly used route to metal alkyls and aryls involves the reaction of a metal alkyl or aryl with the halide of the metal concerned:

$$\mathrm{MX + M'R \rightarrow MR + M'X}$$

Discussion of the energetics of these reactions requires a knowledge of the standard enthalpies of formation of the halides. Figures for some chlorides are given in Table 3,[5–7] which also lists their differences from the enthalpies of formation of the metal methyls. These differences effectively measure the enthalpy change when a methyl group is replaced by a chlorine atom on the metal in question. The more exothermic this process is, the better is that metal alkyl as a methylating agent. The less exothermic this process is (or the more endothermic), the more suitable

Table 3 Standard Molar Enthalpies of Formation of Some Metal Chlorides ($\Delta H_f^\circ(\mathrm{MCl}_n)$/kJ mol^{-1}) and their Differences from the Standard Molar Enthalpies of Formation of the Metal Methyls MMe_n

Group II, MCl_2			*Group III*, MCl_3			*Group IV*, MCl_4			*Group V*, MCl_3		
M	ΔH_f°	*diff.*[a]	M	ΔH_f°	*diff.*[a]	M	ΔH_f°	*diff.*[a]	M	ΔH_f°	*diff.*[a]
—	—	—	B	−403[b]	−94	C	−135[c]	8	—	—	—
—	—	—	Al	−705	−206	Si	−687[c]	−112	P	−320[c]	−75
Zn	−416	−236	Ga	−525	−162	Ge	−690[c]	−146	As	−305[c]	−107
Cd	−391	−250	In	−537	−236	Sn	−511[c]	−123	Sb	−382	−138
Hg	−230	−162	Tl	—	—	Pb	−314[b]	−113	Bi	−379	−170

[a] The figures in the difference columns relate to the enthalpy difference in kJ *per mole of methyl group*, *i.e.* diff. = $(1/n)\,[\Delta H_f^\circ(\mathrm{MCl}_n) - \Delta H_f^\circ(\mathrm{MMe}_n)]$. [b] Relates to gaseous MCl_n. [c] Relates to liquid MCl_n. Remaining ΔH_f° figures relate to solid MCl_n.

is the chloride of that metal or metalloid as a species to be alkylated. Of the metals in Table 3, zinc, cadmium, aluminium and indium appear likely to provide the best alkylating reagents, though the cadmium and indium alkyls can be excluded on the grounds of lesser availability. Zinc and aluminium alkyls, like lithium alkyls and Grignard reagents RMgX, are particularly useful for the alkylation of chlorides of less electropositive metals (as a generalization, the exchange reaction between an alkyl derivative of one metal and the halide of another pairs the halogen with the more electropositive metal).

The enthalpies of formation of metal alkyls and halides exemplified by the data in Tables 2 and 3 can incidentally be used, in conjunction with data for alkyl halides, to estimate the enthalpy changes, and so the feasibility, of reactions between metals and alkyl halides as routes to alkylmetal halides, *e.g.* Grignard reagents RMgX. Such reactions are thermodynamically feasible for electropositive metals like Li, Na, Mg, Zn or Al, and tend to proceed smoothly once started, though initiation may prove troublesome.

1.3 COMPOUNDS WITH METAL–CARBON SINGLE BONDS

1.3.1 Some Representative Structures

In the vast majority of main group organometallic compounds, the metal–carbon bonding consists only of single bonds linking alkyl or aryl groups to the metals in question. These are the types of bond whose energies were the subject of the previous section. In themselves, they pose no valence problem, since each can be assigned an electron pair, accommodated in an orbital resulting from the overlap of one carbon orbital and one metal orbital. Structural interest in such systems tends to be metal-centered, attaching to the state of coordination of the metal atoms, which in turn tends to be determined primarily by the atoms other than carbon in the metal coordination sphere.

These points are illustrated by the examples in Figures 4 and 5. For example, the simple dialkyls and diaryls of zinc, ZnR_2 (Figure 4), are volatile, covalent, monomeric species with a CZnC bond angle of 180°. The shape is readily rationalized in terms of the usual Valence Shell Electron Pair Repulsion arguments,[20] the two bond pairs being as far apart as possible, with *sp* hybridization of the metal atom, which has two spare valence shell orbitals. These spare orbitals confer Lewis acidity on the zinc dialkyl, which can form adducts ZnR_2L (with planar coordination; L = a Lewis base) or ZnR_2L_2 (with tetrahedral coordination). Derivatives ZnRX, where X is an electronegative atom or group (halogen, OR, SR, NR_2 or PR_2) adopt associated structures, exemplified by dimers $(ZnRX)_2$, in which the atom or group X bridges two metal atoms by supplying a total of three electrons for bonding, or cubane-type tetramers $(ZnRX)_4$ in cases where the group X can act as a formal source of five electrons (*e.g.* when X = OR).

Further examples of systems with metal–carbon single bonds are shown in Figure 5. With a

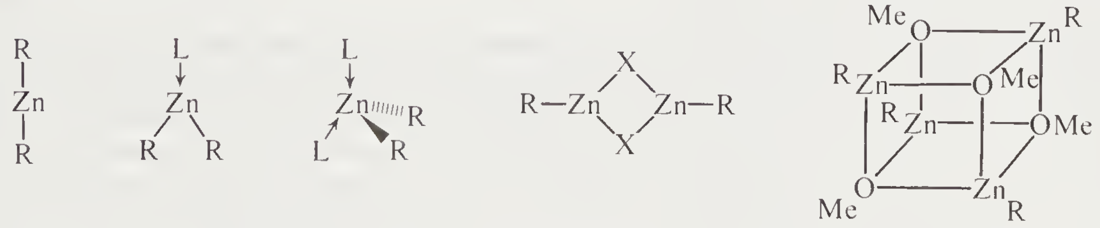


Figure 4 Some organozinc structural types: ZnR_2, ZnR_2L, ZnR_2L_2, $(RZnCl)_2$ and $(RZnOMe)_4$

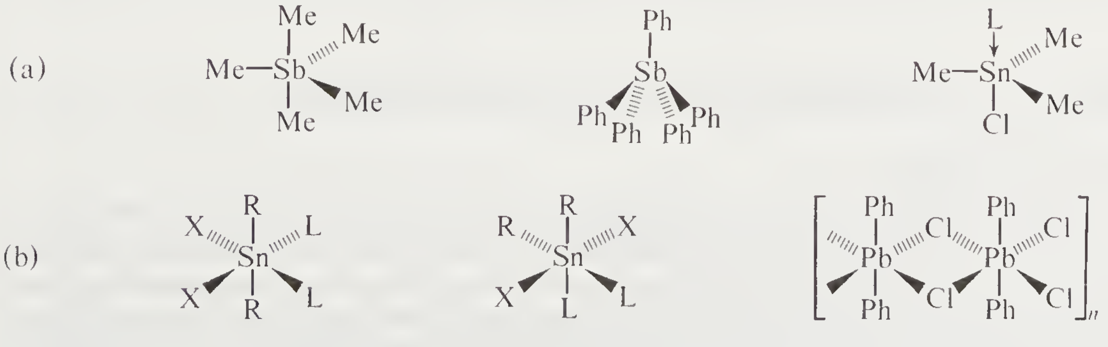


Figure 5 Structures of some organometallic compounds with more highly coordinated metal atoms: (a) $SbMe_5$, $SbPh_5$, $SnMe_3Cl{\cdot}L$; (b) *trans*-$R_2SnX_2{\cdot}2L$, *cis*-$R_2SnX_2{\cdot}2L$ and Ph_2PbCl_2

minimum of four metal valence shell orbitals normally available, metal coordination numbers up to four can be rationalized readily enough in terms of electron pair bonds and sp, sp^2 or sp^3 hybridization. Higher coordination numbers require the use of d orbitals, three-centre bonds or secondary bonding. For example, $sp^3d_{x^2-y^2}$ hybridization can be invoked to explain the unusual square pyramidal coordination of the metal atoms in $SbPh_5$[21] (five-coordination usually involves a trigonal bipyramidal arrangement of ligands about the metal, explicable in terms of $sp^3d_{z^2}$ hybridization). The relatively long metal–halogen bonds in dialkyllead halides R_2PbX_2, with linear RPbR units perpendicular to their $(PbX_2)_n$ chains, may be rationalized in terms of three-centre X···Pb···X bonding, while the weak M···X bonds commonly found in Group IV compounds MR_3X, where X is a halogen or pseudohalogen, fall into the category of secondary bonding.[22] Detailed discussion of such species is beyond the scope of the present work, since interest in them is occasioned mainly by their M—X bonding, while their singly bonded alkyl or aryl groups play a subsidiary role, occupying spare metal valences.

1.3.2 Bond Lengths of Metal–Carbon Single Bonds

Recent improvements in techniques for structure determination, especially X-ray crystallography, have led to the accumulation of a useful stock of data on interatomic distances in organometallic systems, particularly involving such metals as magnesium, zinc, mercury, aluminium, silicon and tin, though some metals remain comparatively neglected. The average lengths of metal–carbon single bonds, between four-coordinate metal and carbon atoms, are given in Table 4, which also lists the four-coordinate metal covalent radii implied by these data, assuming a covalent radius for tetrahedrally coordinated carbon of 77 pm. Organometallic compounds are particularly suited to the determination of metal single bond covalent radii since they are the least polar singly bonded species normally formed by metals.

Table 4 Typical Metal–Carbon Bond Lengths (d/pm)[a] and Implied Single Bond Covalent Radii (r/pm)[b] of Some Main Group Metals and Metalloids

	Group II			*Group III*			*Group IV*			*Group V*[d]	
M	d	r	M	d	r	M	d	r	M	d	r
Be	179	102	B	156	82	C	154	77	N	147	70
Mg	219	142	Al	197	120	Si	188	111	P	187	110
Zn	196	119	Ga	198	121	Ge	195	118	As	196	119
Cd	211[c]	134	In	223	146	Sn	217	140	Sb	212	135
Hg	210[e]	133	Tl	225	148	Pb	224	147	Bi	226	149

[a] Values of d quoted are average values of the lengths of single bonds attaching tetrahedrally coordinated carbon atoms terminally to tetrahedrally coordinated metal atoms. [b] $r = d - 77$. [c] Value for $CdMe_2$. [d] Values of d and r quoted for Group V elements relate to pyramidally coordinated atoms. [e] Few organomercurials contain tetrahedrally coordinated metal atoms. The value of d quoted is the median value for organomercurials in general, which show a wide spread of Hg—C distances.

Despite the comparative wealth of data on organo derivatives of some metals, the metal–carbon bond lengths have rarely been determined with sufficient precision to allow their sensitivity to such factors as the metal and carbon atom coordination numbers to be explored. The marked dependence of carbon–carbon single bond lengths on the carbon coordination numbers is a familiar feature of structural organic chemistry. Typical values are 154 pm for a single bond between two four-coordinate carbon atoms, 148 pm for a single bond between two three-coordinate carbon atoms, and 138 pm for a single bond between two two-coordinate carbon atoms. Shorter bonds than those listed in Table 4 are to be expected for coordination numbers below four, while higher coordination numbers imply greater expected interatomic distances.

1.4 COMPOUNDS WITH BRIDGING ALKYL OR ARYL GROUPS

1.4.1 General Considerations

A well-established feature[23] of the organometallic chemistry of such metals as lithium,[24] copper,[25–28] beryllium,[29] magnesium and aluminium[30–32] is the tendency of their alkyl and aryl derivatives to adopt associated structures by forming three-centre or even four-centre electron pair bonds. The simpler alkyl derivatives of these metals, MR_n (R = Me, Et, Pr^n), are associated through bridging alkyl groups in which the metal-attached carbon atoms have a coordination number greater than four. Similar bridging alkyl groups have been found in the organometallic chemistry of various other metals,[33] including yttrium and the lanthanons Dy, Ho, Er and Yb. Several other metals M (*e.g.* Ti, Ta, Cr) and metalloids (*e.g.* B) form mixed bridges MRM′ to main group metals M′ such as Li, Mg or Al.[34] Further metals can be expected to be added to the list of examples as suitable alkyl derivatives are structurally characterized.

The metals that show the strongest tendency to form such bridges are located in the Periodic Table (Figure 1) between those that form essentially ionic alkyls M^+R^- or $M^{2+}(R^-)_2$ (the heavier alkali metals and alkaline earths), and those that form covalent monomeric molecular alkyls MR_n. They are relatively electropositive (Pauling electronegativity in the range *ca.* 1.0–1.5) and form cations with a high charge: radius ratio, and so are highly polarizing. The associated structures allow the metal atoms to make as effective use as possible of their valence shell orbitals, one or more of which would remain unused if association did not occur.

The types of structure adopted, and the bonding rationales for them, are conveniently discussed by considering first some alkyl-bridged aluminium systems $Al_2R_4(\mu_2\text{-}R)_2$, as these illustrate three-centre M_2C bonding in its simplest form and allow direct comparison with related two-centre M—C bonds in the same molecules. Similar three-centre M_2C bonds feature in derivatives of transition metal and lanthanon members of Group III and of copper, and account for the polymeric structures of beryllium dialkyls and magnesium dialkyls. The dominant structural feature of lithium alkyls, however, consists of triangles of metal atoms capped by triply bridging alkyl groups, *i.e.* four-centre two-electron M_3C bonds. These allow each lithium atom to use at least three atomic orbitals: if restricted to three-centre M_2C bonding the metal atoms of unsolvated alkyls $(LiR)_n$ could become only two-coordinate, using only two orbitals apiece.

1.4.2 Bridged Organoaluminium Systems[11,30–32]

Although some indication that aluminium alkyls, AlR_3, are associated was obtained from very early work on these systems more than a century ago (too early for the valence problems they posed to be recognized immediately),[35] it was only in 1941 that the dimeric nature of trimethylaluminium, $(AlMe_3)_2$, was established by gas density measurements,[36] which also showed that the enthalpy of dissociation, $(AlMe_3)_2 \rightarrow 2AlMe_3$, was about 84 kJ mol^{-1}. That the structure was bridged like that of aluminium chloride, Al_2Cl_6, rather than ethane-like was soon deduced from its vibrational spectra,[37–39] although it was not at first clear whether the hydrogen atoms of the bridging methyl groups played a vital role in the bridging, *i.e.* whether bridging occurred through Al· · ·C· · ·Al links or through Al—C· · ·H· · ·Al links (Figure 6). It was known, for example, that the degree of association of aluminium alkyls, AlR_3, in inert solvents decreases in the sequence R = Me > Et > Pr^i > Bu^t, the *t*-butyl derivative being monomeric; one interpretation was that association occurred through Al—C· · ·H· · ·Al links, and so became progressively more difficult, and finally impossible, as the α-hydrogen atoms were replaced by methyl groups. The earliest X-ray crystallographic studies on $(AlMe_3)_2$[40,41] did not locate the hydrogen atoms, so although they were strongly suggestive of symmetrical Al· · ·C· · ·Al bridges, the data were arguably[42,43] nevertheless compatible with the involvement of hydrogen atoms in unsymmetrical Al—C· · ·H· · ·Al bridges. However, further low-temperature X-ray crystallographic work[44] located the hydrogen atoms of the bridging methyl groups with sufficient precision to establish the symmetrically bridged Al· · ·C· · ·Al structure, which was also indicated by ^{27}Al NQR studies.[45]

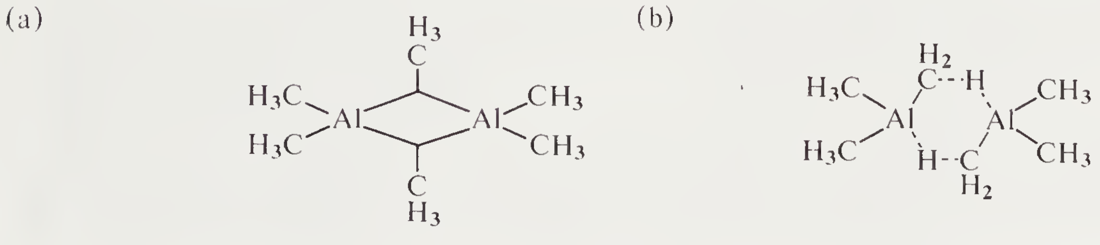


Figure 6 Bridge bond types considered possible for Al_2Me_6. (a) The symmetrical Al· · ·C· · ·Al bridges established by structural studies. (b) The hypothetical Al—C· · ·H· · ·Al bridges excluded by X-ray[44] and NQR[45] studies

The structure is illustrated in Figure 7. The greater length of the bridging Al—C links than the terminal bonds, the acute angle at the bridging carbon atom, and the orientation of the bridging methyl groups, with the hydrogen atoms pointing away from the Al· · ·Al axis, all support the bonding description shown in Figure 6a, with normal two-centre electron pair bonds linking the metal atoms to the terminal methyl groups and the carbon atoms to their substituent hydrogen atoms, and with two three-centre Al_2C links in the bridging region formed by overlap of the four metal and two carbon sp^3 hybrid AOs available. This type of $(Al—C)_2$ bridge bonding is com-

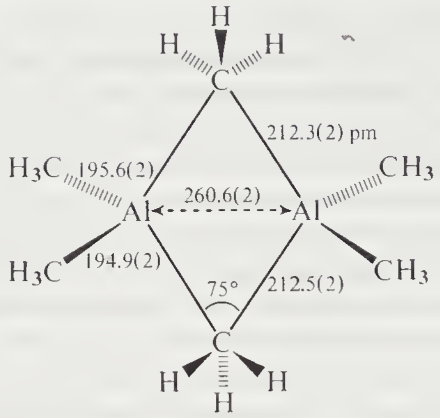


Figure 7 Molecular structure of crystalline hexamethyldialuminium, Al_2Me_6[44]

monly referred to as electron deficient in that there are fewer bond pairs than points of contact between bonded atoms. However, the bridge region is *not* electron deficient in the sense that more electrons could be accommodated without structural change: Al_2Me_6 contains precisely the right number of electrons to fill all the bonding MOs. Adding an extra pair of electrons would cause the structure to change to an ethane-like model, $[Me_3Al—AlMe_3]^{2-}$, with a single metal–metal bond and exclusively terminally attached methyl groups.

The relatively short metal–metal distance across the $(AlC)_2$ ring of Al_2Me_6 and the acute angle at carbon (Figure 7) can be seen as consequences of the cross-ring metal–metal bonding that is an implicit feature of the three-centre bonded description; the AOs of one metal atom combine in phase not only with the bridging carbon sp^3 hybrid AOs, but also with the corresponding AOs of the other metal atom. Expressed in terms of localized MOs, the $(AlC)_2$ ring contains two pairs of electrons, one σ-bonding, the other π-bonding with respect to metal–metal interactions.[5,11,46,47]

These distinctive features of the structure of Al_2Me_6 can be better appreciated if one compares its two-bond pair $(AlC)_2$ ring with the four-bond pair $(AlN)_2$ ring of the compound $Al_2Me_4(\mu\text{-}NMe_2)_2$[48] and with the three-bond pair AlNAlC ring of the mixed bridge compound $Al_2Me_4(\mu\text{-}Me)(\mu\text{-}NMe_2)$,[49] the structures of which are shown in Figure 8. Figure 9 compares the localized MO bonding descriptions of the rings in these three compounds. As the number of AOs supplied by the bridging atoms increases, so does the number of bridge-bonding MOs. However, although both bridge-bonding MOs in the case of Al_2Me_6 are metal–metal bonding in character, Figure 9 shows the metal–metal *antibonding* character of the extra bridging MO of $Al_2Me_5(NPh_2)$ and of the two extra bridging MOs of $Al_2Me_4(NMe_2)_2$. The manner in which the metal–metal distance increases in the sequence $Al_2Me_6 < Al_2Me_5NPh_2 < Al_2Me_4(NMe_2)_2$ reflects the progressive filling of these MOs, and so loss of Al· · ·Al bonding, from a formally double metal–metal bonding interation in Al_2Me_6, through a formally single metal–metal bonding interaction in $Al_2Me_5NPh_2$, to zero in $Al_2Me_4(NMe_2)_2$.

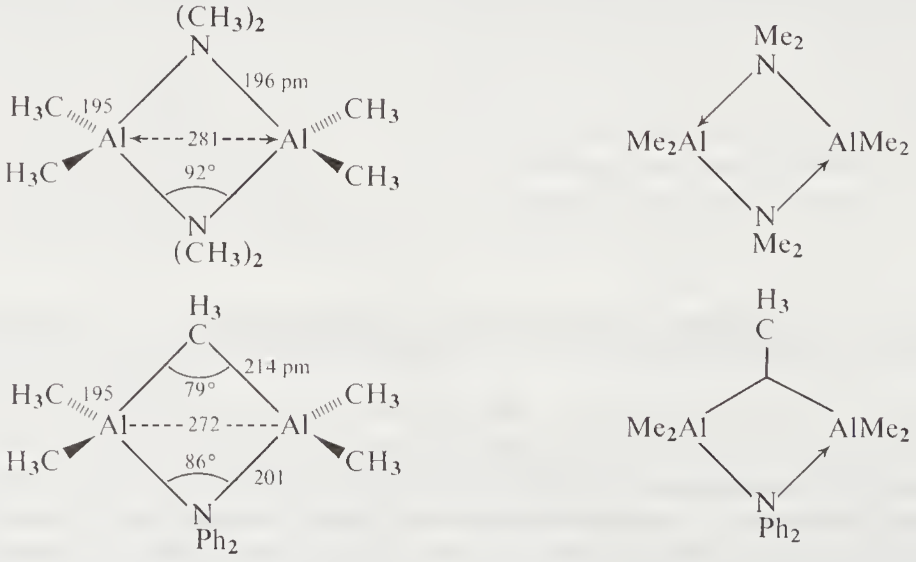


Figure 8 Structures and bonding of the compounds (a) $Al_2Me_4(\mu_2\text{-}NMe_2)_2$[48] and (b) $Al_2Me_4(\mu_2\text{-}Me)(\mu_2\text{-}NPh_2)$[49]

Figure 9 Influence on the bridge bonding MOs of the number of AOs supplied by the bridging atoms in some organoaluminium species. (a) Each bridging atom (X) supplies one AO, *e.g.* $Al_2Me_4(\mu_2\text{-}Me)_2$. (b) One bridging atom (X) supplies one AO, the other (Y) supplies two, *e.g.* $Al_2Me_4(\mu_2\text{-}Me)(\mu_2\text{-}NPh_2)$. (c) Each bridging atom (Y) supplies two AOs, *e.g.* $Al_2Me_4(\mu_2\text{-}NMe_2)_2$

A further feature of the MOs shown in Figure 9 that is worth noting is that there is no net bonding interaction across the ring perpendicular to the metal· · ·metal axis for any of these systems, *i.e.* between X and X in Figure 9a, between X and Y in Figure 9b or between Y and Y in Figure 9c.

The metal–metal distances across the $(AlX)_2$ or $(AlY)_2$ rings in these compounds should not be taken to imply that the bridge itself progressively weakens as the metal–metal distance increases. The stability to dissociation into monomers increases in the sequence $Al_2Me_6 < Al_2Me_5(NPh_2) < Al_2Me_4(NMe_2)_2$, *i.e.* as the total number of bonding electrons associated with the bridge increases. The decreasing stability to dissociation within the series of alkyls $Al_2Me_6 > Al_2Et_6 > Al_2Pr^i_6$ already noted probably reflects the decreasing capacity of an alkyl group to bridge two aluminium atoms as its bulk increases. (The dissociation enthalpies for the process $Al_2R_6 \rightarrow 2AlR_3$ are *ca.* 84 kJ mol^{-1} for R = Me, *ca.* 71 kJ mol^{-1} for Al_2Et_6 and *ca.* 34 kJ mol^{-1} for $Al_2Bu^i_6$;[50,51] the enthalpy change in solution is sensitive to the solvent used, *e.g.* being less in toluene than in cyclopentane because the former preferentially solvates the monomer.) In Lewis base solvents, aluminium alkyls are monomeric.

Structural studies on other dimers $(AlR_3)_2$ or mixed systems $(AlR^1_2R^2)_2$ have thrown further light on the relative bridging capacities of different groups R, and have consistently revealed Al· ·C· ·Al but not Al—C· ·H· ·Al bonding interactions. In the cyclopropyl derivative $Al_2Pr^c_6$, for example, the orientation of the bridging cyclopropyl groups (Figure 10) clearly precludes

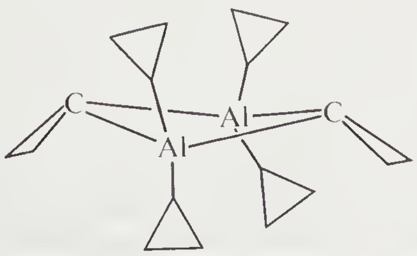
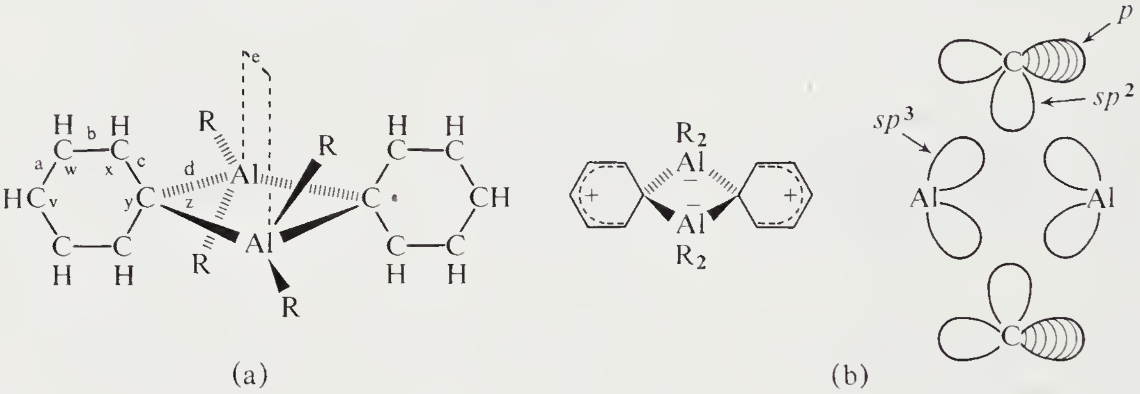


Figure 10 Structure of the tricyclopropylaluminium dimer, Al_2(cyclo-Pr)$_6$[52]

Al—C· · ·H· · ·Al bonding.[52] When phenyl groups act as bridges between aluminium atoms (which they do more effectively than methyl groups: the mixed derivative $Al_2Me_4Ph_2$[53] has phenyl, not methyl, bridges), Al—C—H· · ·Al bonding interactions are not possible, because the bridging carbon atom has no hydrogen substituent.

The structures of two such systems, $Al_2Ph_4(\mu\text{-}Ph)_2$ and $Al_2Me_4(\mu\text{-}Ph)_2$, are illustrated in Figure 11.[53] In both cases the plane of the bridging phenyl group is perpendicular to the $(AlC)_2$ ring plane, so the bridging carbon atom is surrounded by a distorted tetrahedron of two carbon and two aluminium atoms. The ring CCC angle at this carbon atom (angle *y* in Figure 11a) is significantly lower than the hexagonal angle of 120°, and the ring C—C bonds it forms are slightly longer (*c* in Figure 11a) than normal phenyl ring bonds, as if electronic charge were drained from the ring into the Al—C bonds (Figure 11b).



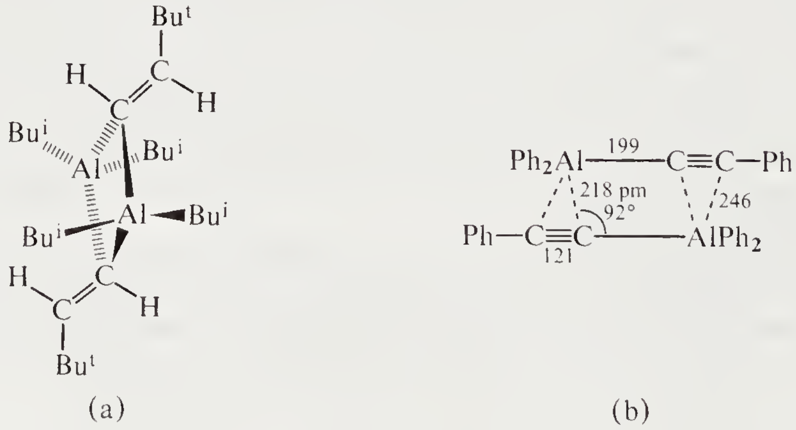
(a) (b)

Figure 11 Skeletal features of the phenyl-bridged aluminium compounds Al_2Ph_6 and $Al_2Me_4(\mu_2\text{-}Ph)_2$. (a) Structure: interatomic distances (pm) and bond angles[53]

	a	b	c	d	e	v	w	x	y	z
$Al_2Ph_4(\mu_2\text{-}Ph)_2$	139	140	142	218	270	118°	120°	123°	114°	77°
$Al_2Me_4(\mu_2\text{-}Ph)_2$	138	141	142	213	268	121°	120°	122°	116°	78°

(b) Bonding: valence bond representation (left); metal and carbon AOs available (right)

Two further types of bridge that have been structurally characterized and are worth noting briefly are those formed by alkenyl and alkynyl groups, —CH=CHR and —C≡CR. Both types of group can use their π-systems to strengthen the $(AlC)_2$ ring bonding as phenyl groups can, so both form stronger bridges than do alkyl groups. Details of the structures of $Al_2Bu_4(\mu\text{-}CH{=}CHBu^t)_2$[54] and of $Al_2Ph_4(\mu\text{-}C{\equiv}CPh)_2$[55] are given in Figure 12. The orientation of the alkenyl bridging groups in the former allows a bonding description like that for bridging phenyl groups. However, the alkynyl groups of $Al_2Ph_4(\mu\text{-}C{\equiv}CPh)_2$ (Figure 12b) bridge in an unsymmetrical manner, effectively by σ-bonding to one metal atom while π-bonding (see Section 1.5 below) to the other. The related compound $Al_2Me_4(\mu\text{-}C{\equiv}CMe)_2$ has a very similar unsymmetrically bridged structure.[56]



(a) (b)

Figure 12 The structures of (a) $Al_2Bu^i_4(\mu_2\text{-}CH{=}CHBu^t)_2$[54] and (b) $Al_2Ph_4(\mu_2\text{-}C{\equiv}CPh)_2$.[55] Al· · ·Al is 268 pm in (a) and 299 pm in (b)

The structural data for these various bridged aluminium systems are summarized in Table 5, which includes data for the halides $Al_2Me_2Cl_2(\mu\text{-}Cl)_2$,[57] Al_2Cl_6[58] and Al_2Br_6[59] for the purpose of comparison. From Table 5 the characteristic features of electron deficient bridges between aluminium atoms are seen to be (i) relatively short (*ca.* 260–270 pm) metal–metal distances, (ii) acute bond angles at the bridging carbon atoms, and (iii) longer bridge bonds than terminal bonds.

Table 5 Interatomic Distances and Angles in Some Bridged Organoaluminum Systems

	Interatomic distances (pm)[a]			*Angles* (°)			
Compound	$Al—C_\mu$	$Al—C_t$	$Al\cdots Al$	$AlC_\mu Al$	$C_\mu AlC_\mu$	C_tAlC_t	*Ref.*
Al_2Me_6	212	195	261	76	104	123	44
$Al_2Pr^c_6$	208	193	262	78	97	115	52
Al_2Ph_6	218	196	270	77	104	115	53
$Al_2Me_4(\mu\text{-}Ph)_2$	213	198	268	78	101	122	53
$Al_2Bu^i_4(\mu\text{-}CH{=}CHBu^t)_2$	211	198	268	79	101	129	54
$Al_2Ph_4(\mu\text{-}C{\equiv}CPh)_2$	209	194	299	92	88	—	55
$Al_2Me_4(\mu\text{-}Me)(\mu\text{-}NPh_2)$	214	195	272	79	98	117	49
$Al_2Me_4(\mu\text{-}NMe_2)_2$	[196]	195	281	[92]	[88]	116	48
$Al_2Me_2Cl_2(\mu\text{-}Cl)_2$	[226]	193	321	[91]	[89]	[125]	57
Al_2Cl_6	[221]	[206]	340	[100]	[80]	[118]	58
Al_2Br_6	[238]	[228]	314	[82]	[98]	[115]	59

[a] Where there are two distinct $Al—C_\mu$ or $Al—C_t$ distances in a particular compound, the interatomic distances quoted are average values for that compound. Distances and angles in parentheses relate to bridging or terminal atoms other than carbon.

It is worth noting that this last feature is not by itself indicative of electron deficient bonding. Even systems in which both the bridging and terminal bonds are formally single bonds, *e.g.* Al_2Cl_6 or Al_2Br_6, have longer bridge bonds than terminal bonds.[58,59] This is in part because non-bonding electron or internuclear repulsions will necessarily be greater if a group occupies a bridging site as opposed to a terminal one. However, a second factor is that the property that allows a ligand to function as a three-electron bridging group, the possession of a lone pair of electrons, also allows such a ligand to form multiple bonds when terminally bound to a coordinatively unsaturated metal. The terminal Al—Cl bonds of Al_2Cl_6 or Al—Br bonds of Al_2Br_6 probably have bond orders greater than unity.[60]

NMR studies have been used to explore the solution behaviour of bridged organoaluminium systems,[23] *e.g.* to determine the ease with which bridging and terminal groups exchange sites in species $(AlR_3)_2$, or to identify the bridging groups in mixed derivatives $(AlR'R''_2)_2$, *etc.*[30,61,62] Such studies have shown a decreasing capacity for bridging in the sequence $R_2N > RO > Cl > Br > PhC{\equiv}C > RCH{=}CH \approx Ph > Me > Et > Pr^i > Bu^t$. Bridging by three-electron ligands is thus stronger than bridging by the one-electron ligands that are the main concern here. The relative bridging capacities of the alkyl groups are the reverse of the sequence expected from inductive effects, and presumably reflect bulk effects.

1.4.3 Bridged Organo Derivatives of Gallium, Indium and Thallium

The heavier Main Group III elements have little tendency to form electron deficient bridges involving carbon atoms. Their trimethyl derivatives MMe_3 for example, like trimethylborane, are monomeric in the gas phase and apparently also in the liquid, although mass spectroscopic studies[63] on $GaMe_3$ have indicated the presence of such ions as $Ga_2Me_5^+$ and $Ga_3Me_9^+$. In the crystal, X-ray diffraction studies have shown the indium[64] and thallium[65] compounds to be monomeric, though their trigonal planar molecules are packed in a manner consistent with very weak $M\cdots C$ bonding along the MMe_3 three-fold axes (the M—C distances for $InMe_3$ are: intramolecular, 216, 212 and 215 pm; intermolecular, 310 and 360 pm;[64] for $TlMe_3$: intramolecular, 222, 230 and 234 pm; intermolecular, 316 and 331 pm[65]).

The alkenyl and alkynyl derivatives of these metals are associated, probably through bridges of the types shown in Figure 12. The triphenyl derivatives MPh_3 (M = Ga or In) crystallize as monomers MPh_3, though as in the case of the methyl derivatives, the packing of the monomers is indicative of weak association through $M—C—C\cdots M$ or $M—C—C—C\cdots M$, but not $M\cdots C\cdots M$, bonds, *i.e.* it involves the *ortho* or *meta* carbon atoms of the phenyl groups.[66]

Some $M\cdots C\cdots M$ bonding is indicated, however, by the structures of the cyclopentadienyl-indium(I) and -thallium(I) compounds $M(C_5H_5)$, in which there are slightly puckered $\cdots M(C_5H_5)M(C_5H_5)M(C_5H_5)\cdots$ chains with the ring perpendicular to the $M\cdots M$ axes (Figure 13).[67] The bonding in these structures may be regarded as predominantly ionic, with the $C_5H_5^-$ anions and M^+ cations stacked in a manner that nevertheless reflects the stereochemical significance of the 'lone pair' of electrons on each metal atom, suggesting some covalent metal–ring interaction. The carbon atoms are five-coordinate, forming three normal bonds in the plane of the ring (to the two neighbouring carbon atoms and the substituent hydrogen atom) and two very

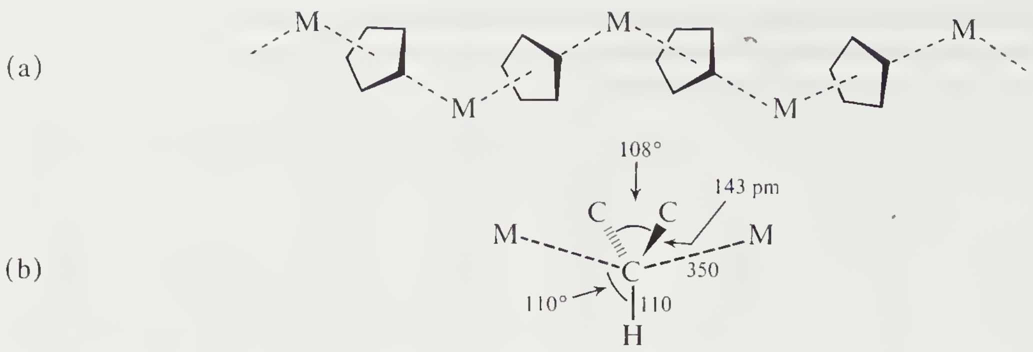


Figure 13 (a) The puckered chain structures of $In(C_5H_5)$ and $Tl(C_5H_5)$.[67] (b) The coordination at carbon

long bonds (the In—C distance is *ca.* 350 pm; the Tl—C distance, not determined, is presumably longer) at an angle of about 70° to the plane of the ring. Similarly coordinated carbon atoms are to be found in dicyclopentadienyllead, $Pb(C_5H_5)_2$ (which also contains $\cdots M(C_5H_5)M(C_5H_5)M(C_5H_5)\cdots$ chains, the remaining cyclopentadienyl groups being terminally bound, pentahapto, one on each metal atom)[68] and in the sodium cyclopentadienide $Na(C_5H_5)(Me_2NCH_2CH_2NMe_2)$,[69] though the metal–carbon bonding in this last compound can have little covalent character. However, the bonding in the gallium(III) derivative $GaMe_2(C_5H_5)$, which is also polymeric, is more localized in character.[70] The bridging cyclopentadienyl groups are tilted with respect to the metal–metal vectors in such a manner as to bring one carbon atom near to one gallium atom, and a second (non-adjacent) carbon atom near to the second of the bridged gallium atoms on the other side of the ring.

1.4.4 Bridged Alkyl Derivatives of Rare Earth Elements

The capacity of metals at the left-hand side of the transition series to participate in MCM three-centre bonds has been demonstrated in species of formulae $(\eta^5\text{-}C_5H_5)_2M(\mu\text{-}Me)_2M(\eta^5\text{-}C_5H_5)_2$[71] and $(\eta^5\text{-}C_5H_5)_2M(\mu\text{-}Me)_2AlMe_2$[72] (M = an element such as Y, Dy Ho, Er or Yb). Their structures (Figure 14) show how the monomeric coordinatively unsaturated (14-electron) species $(\eta^5\text{-}C_5H_5)_2MMe$ resemble $AlMe_3$ in being able to dimerize by forming methyl bridges, or to associate with similar species. Although the interatomic distances in these derivatives have not been determined with sufficient precision to allow detailed discussion, their metal–methyl carbon bonds are of a length consistent with a three-centre bonded description of their $(MC)_2$ or $\overline{\mathrm{MCAlC}}$ rings.

Figure 14 Methyl-bridged derivatives of the rare earths $(\eta^5\text{-}C_5H_5)_2M(\mu_2\text{-}Me)_2M(\eta^5\text{-}C_5H_5)_2$ and $(\eta^5\text{-}C_5H_5)_2M(\mu_2\text{-}Me)_2AlMe_2$. The interatomic distances and angles cited relate to the ytterbium compounds

1.4.5 Group II Derivatives

Of the Group II elements, only beryllium and magnesium show a strong tendency to form bridged alkyls. The alkaline earths calcium, strontium and barium are sufficiently electropositive to form alkyl derivatives that are essentially ionic. Zinc, cadmium and mercury tend to form monomeric, molecular alkyls and aryls MR_2, although zinc, having a covalent radius of 131 pm and electronegativity 1.66, like gallium may be regarded as having properties that are on the borderline of those needed to form stable bridged alkyls.

If Group II metals like beryllium or magnesium are to use all four valence shell orbitals by forming electron deficient alkyl bridges, then in derivatives MR_2 both alkyl groups R need to be in bridging sites, and the structures are necessarily polymeric. The simpler alkyls of beryllium and magnesium are of this type (see Figure 15). The methyl derivatives of both beryllium[73] and magnesium[74] have been the subjects of X-ray crystallographic studies, which although not locating the hydrogen atoms, have revealed the relatively short metal–metal distances and acute angles at the bridging carbon atoms that also characterize $AlMe_2Al$ bridges. The resemblance is underlined by the structure adopted by the mixed metal derivative $Mg(AlMe_4)_2$ (Figure 16).[75]

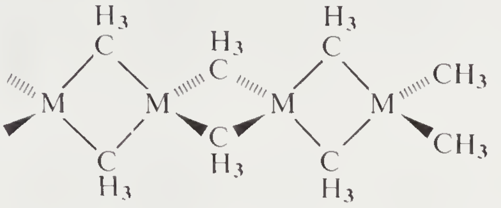


Figure 15 The polymeric structures of $(BeMe_2)_n$ [73] and $(MgMe_2)_n$[74]

	M—C (pm)	M···M (pm)	MCM angle
$(BeMe_2)_n$	193	209	66°
$(MgMe_2)_n$	224	272	75°

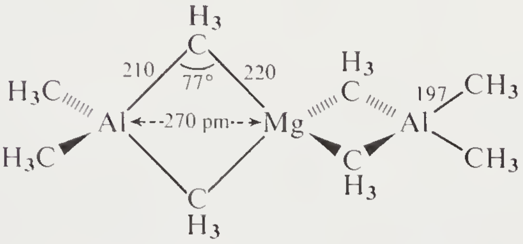


Figure 16 The structure of $Mg(AlMe_4)_2$[75]

The polymeric nature of the simple beryllium or magnesium dialkyls or diaryls has made them less convenient subjects for study than aluminium alkyls, causing them to have low volatility and low solubility in inert solvents. However, the relative bridging capacities found in aluminium chemistry hold also in Group II. The bulkier dialkyls are oligomers or even monomers. Di-*t*-butylberyllium, $BeBu^t_2$, for example, is volatile and monomeric, with a Be—C bond length of 170 pm in the linear CBeC skeleton.[76] Gaseous $BeMe_2$ also contains linear molecules with the same Be—C bond length.[77]

The propynyl derivative $[BeMe(C{\equiv}CMe)(NMe_3)]_2$ (Figure 17),[78] as expected, associates through bridging alkynyl rather than methyl groups, but unlike the bridging alkynyl groups of $[AlPh_2(C{\equiv}CPh)]_2$, they are orientated almost perpendicular to the metal–metal axis. Significantly, the metal–metal distance in this compound (233 pm) is longer than that in $(BeMe_2)_n$, and the ring metal–carbon distances are shorter than those in $(BeMe_2)_n$. The bis(propynyl) derivative $[Be(C{\equiv}CMe)_2NMe_3]_2$[79] crystallizes with two types of dimeric molecule in the lattice, one similar to that shown in Figure 17, the other with a nearly rectangular $(BeC)_2$ ring, of sides 176 and 204 pm, involving bridging by π-bonded propynyl groups like those in $Ph_2Al(C{\equiv}CPh)_2$ (Figure 12b).

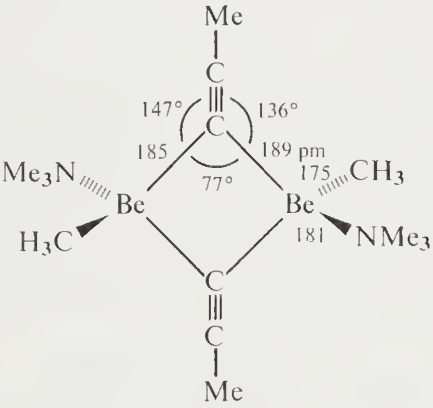


Figure 17 The structure of the alkynyl-bridged derivative $[BeMe(NMe_3)(\mu_2\text{-}C{\equiv}CMe)]_2$

When compared with the data for related $(BeX)_2$ bridged systems, involving other bridging atoms such as hydrogen,[80] nitrogen,[79,81,82] oxygen[79,83] or chlorine,[84] the shapes of these bridged beryllium systems (Table 6) show a rather less clear distinction between electron deficient and electron precise systems than was the case for the aluminium systems listed in Table 5. Although the two shortest metal···metal distances (Table 6) relate to the only two compounds containing

Table 6 Interatomic Distances and Angles in Some Bridged Beryllium Systems

		Coordn. no.		*Interatomic distances* (pm)			*Angle* (°)	
Compound	X	Be	X	Be—X	Be···Be	X···X	BeXBe	*Ref.*
$(NaOEt_2)_2(Et_2BeH)_2$	H	4	4	140	220	173	104	80
$[BeMe_2]_n$	C	4	5	193	209	324	66	73
$[BeMe(C{\equiv}CMe)(NMe_3)]_2$	C	4	3	185, 189	233	293	77	78
$[Be(C{\equiv}CMe)_2(NMe_3)]_2$	C	4	3	184, 190	232	294	77	79
$[Be(C{\equiv}CMe)_2(NMe_3)]_2$	C	4	3	176, 204	255	283	84	79
$[Be(N{=}CBu^t_2)_2]_2$	N	3	3	168	223	252	83	81
$[Be(NMe_2)_2]_3$	N	3, 4	4	165, 178	230	255	84	82
$[BeH(NMeC_2H_4NMe_2)]_2$	N	4	4	175, 176	232	262	83	79
$Be_3Cl_2(\mu\text{-}OBu^t)_4$	O	3, 4	3	154, 164	223	225	89	79
$[BeBr(OBu^t)(OEt_2)]_2$	O	4	3	162	230	228	91	79
$[BeMe(OSiMe_3)]_4$	O	4	4	173	243	247	89	83
$[BeCl_2]_n$	Cl	4	2	202	263	305	82	84

bridging one-electron ligands, the hydrogen-bridged $(NaOEt_2)_2(Et_2BeH)_2$[80] and the methyl-bridged $(BeMe_2)_n$,[73] some of the systems containing three-electron bridging ligands have quite short metal···metal distances (see, for example, the ketimino-bridged compound $[Be(N{=}CBu^t_2)_2]_2$[81] and the alkoxy-bridged $Be_3Cl_2(OBu^t)_4$[79]). One striking feature of the data in Table 2 is the extent to which the angle at the bridging atom, BeXBe, reflects the identity of X, being most acute when X = C, *ca.* 83–84° when X = N, and *ca.* 90° when X = O, varying remarkably little with the coordination numbers of Be and X.

The organo derivatives of beryllium and magnesium that have been most widely studied are of the formula type RMX, where X is a potential three-electron ligand (halogen, OR, NR_2) and therefore functions as the bridging unit when these associate. The sequence of bridging capacities noted above in connection with aluminium systems clearly holds for beryllium and magnesium too, and indeed may be regarded as applicable for organometallic systems in general.

Though the simpler zinc alkyls ZnR_2 are not associated, bridged species clearly feature in their exchange reactions. The capacity of zinc to participate in multicentre bonding involving carbon is illustrated by the structure of crystalline $Zn(Me)(C_5H_5)$,[85] in which the $\cdots Zn(C_5H_5)Zn(C_5H_5)Zn(C_5H_5)\cdots$ chains are held together by bridging cyclopentadienyl groups tilted at some 65° with respect to the metal···metal vectors, allowing them to bond trihapto to one metal, dihapto to the next in the chain. The bonding is thus intermediate in character between that in $In(C_5H_5)$[67] (Figure 13) and that in $GaMe_2(C_5H_5)$.[70]

1.4.6 Organolithium Compounds

Organolithium compounds differ from the bridged organo derivatives of the second and third group elements already discussed in that they generally associate through triply bridging hydrocarbyl groups, using four-centre Li_3C bonds. These make better use of the few electrons available than three-centre Li_2C bonds would. For example, methyllithium exists in solution and in the crystal as the tetramer $(LiMe)_4$, the structure of which (Figure 18) was deduced from X-ray powder data.[86] In the tetramer the four lithium atoms are at the corners of a regular tetrahedron, shown by broken lines in Figure 18. The carbon atoms are located over the centres of the four tetrahedral faces, so they in turn define the corners of a second tetrahedron which, together with the first, generates a distorted cubic Li_4C_4 skeleton, shown by the full lines in Figure 18.

Within this skeleton, the metal–carbon bonding may be treated conveniently in terms of four localized four-centre Li_3C bonds, one over each face of the Li_4 tetrahedron. Each carbon atom

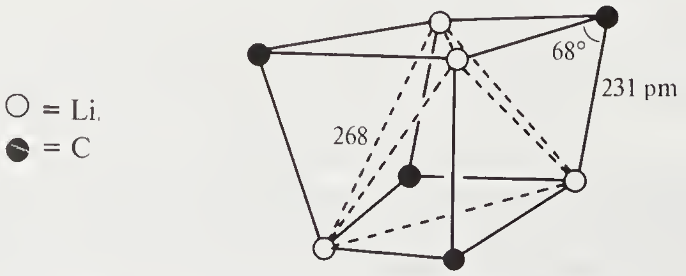


Figure 18 The distorted cubic Li_4C_4 skeleton of the methyllithium tetramer, $(LiMe)_4$

contributes an sp^3 hybrid atomic orbital to overlap the three sp^3 hybrid atomic orbitals supplied by the three lithium atoms in the capped face, all four hybrid orbitals being orientated so that they point towards the centre of the Li_3C trigonal pyramid.

While using three valence shell orbitals for the skeletal bonding, each metal atom still has one vacant sp^3 hybrid atomic orbital pointing outwards away from the centre of the Li_4 tetrahedron. This orbital is responsible for the relatively strong intermolecular bonding in solid methyllithium, which is relatively involatile and insoluble in hydrocarbon solvents. However, it dissolves readily enough in coordinating solvents, or in solutions of Lewis bases L, from which tetrameric adducts $(LiMe{\cdot}L)_4$ can be isolated. In these the Li_4C_4 skeleton of $(LiMe)_4$ is intact, the Lewis base molecules occupying the vacant coordination sites, one on each metal atom. A single-crystal X-ray study[87] of one such adduct, $(LiMe)_4{\cdot}2TMEDA$ (where TMEDA is here acting as a bridge between $(LiMe)_4$ units), has afforded mean interatomic distances in the Li_4C_4 skeleton of Li· · ·Li, 257 pm, and Li· · ·C, 226 pm (*cf.* the less precise values of 268 and 231 pm respectively obtained from the powder study[86] on uncoordinated methyllithium).

This ability of the methyllithium molecule to accommodate four Lewis base molecules without cleavage or change of symmetry can be contrasted with the behaviour of the alkylaluminium dimers $(AlR_3)_2$, which have no vacant orbitals with which to function as Lewis acids without bridge opening.

Since the filled cluster molecular orbitals of $(LiMe)_4$ involve in-phase combinations of the metal atomic orbitals, they are clearly metal–metal bonding in character, though because lithium and carbon differ markedly in electronegativity, the bonding electrons in the Li_3C trigonal pyramids will necessarily tend to be centred nearer to the carbon atom than to the lithium atoms, making the Li—C bonding more important than the Li· · ·Li bonding, a conclusion that appears to be supported by the results of Raman[88] and lithium NMR[89,90] spectroscopic studies on various tetrameric lithium alkyls $(LiR)_4$. Moreover, the view of the bonding as involving four discrete four-centre bonds appears more helpful in interpreting the ESR spectra[91] of radicals such as $CH_2Li_4Me_3$ than one involving four fully delocalized bond pairs associated with the whole skeleton. The degree of metal–metal bonding in the filled MOs of $(LiMe)_4$ is nevertheless reflected in the relatively short metal–metal distance therein (257 pm: *cf.* 267 pm in the diatomic molecule Li_2, and 304 pm in lithium metal), and also in the persistence of the Li_4 cluster during the fragmentation of methyllithium in the mass spectrometer.

The higher alkyls of lithium adopt structures similar to that of $(LiMe)_4$, with the invariably bridging alkyl groups located over the triangular faces of the metal clusters. Tetramers like that of $(LiMe)_4$ are particularly common, though the bulkier the alkyl group the less the interaction between tetramers in the crystal. *t*-Butyllithium, $(LiBu^t)_4$, for example, is readily soluble in hydrocarbon solvents, and is much more volatile than methyllithium. Ethyllithium[92] crystallizes in the form of tetramers, $(LiEt)_4$, associated into strips (rather than three-dimensionally as in $(LiMe)_4$) and dissolves in hydrocarbons as the hexamer, $(LiEt)_6$, a species also detected in the mass spectrum. The structure of this hexamer inferred from NMR studies[93] consists of a distorted octahedron of lithium atoms, with six of the eight triangular faces bridged by the alkyl groups, the remaining two faces being opposite each other.

Such a structure was subsequently established for cyclohexyllithium, $(LiC_6H_{11})_6$, by an X-ray crystallographic study.[94] The salient features are illustrated in Figure 19. The arrangement of the six lithium atoms (Figure 19a) may be viewed either as a slightly folded chair shape or as a distorted octahedron in which two opposite faces have edges of length 297 pm, while the remaining triangular faces (which are the ones bridged by the cyclohexyl groups) have one edge of this length and two shorter edges of average length 240 pm. The bridging carbon atoms of the cyclohexyl groups (Figure 19b) are located above the midpoints of the long edges, and form bonds of length 218 pm to the lithium atoms of these edges and a slightly longer bond (230 pm) to the third lithium atom. The bonding in the Li_3C unit can be described in terms of a four-centre bond rather like that in $(LiMe)_4$, though since two of the Li· · ·C interactions are stronger than the third, the bonding is intermediate in character between μ_2 and fully symmetrical μ_3. A further interesting feature of the structure is that the α-hydrogen atoms of the cyclohexyl groups, and half of the β-hydrogen atoms, are orientated in a manner that brings them close to the side of the lithium atoms away from the molecular skeleton. The three distinct Li· · ·H distances average 200 (α-C—H), 209 (β-C—H) and 233 pm (β-C—H), which distances may be compared with the intermolecular Li· · ·H distance of *ca.* 223 pm in $(LiMe)_4$.[86]

Interestingly, the trimethylsilyl derivative $(LiSiMe_3)_6$[95] adopts a structure very similar to that of $(LiC_6H_{11})_6$, with triply bridging Me_3Si groups, showing that both the Group IV elements, carbon and silicon, can take part in four-centre Li_3X bonding. Perhaps slightly more surprisingly, the lithio-ketimine $(LiN{=}CBu^t_2)_6$[96] also adopts a folded-chair hexameric structure containing

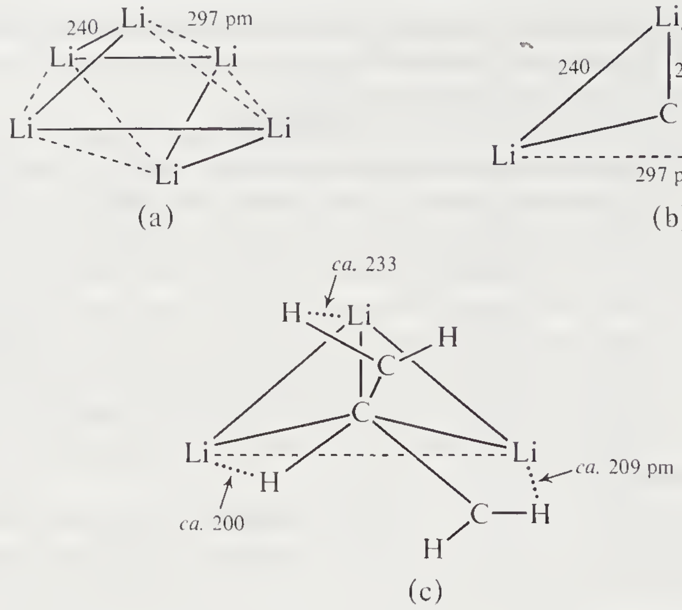


Figure 19 Features of the molecular structure of the cyclohexyllithium hexamer, $(LiC_6H_{11})_6$.[94] (a) The folded-chair (distorted octahedral) arrangement of the six metal atoms. (b) The three lithium atoms near to each carbon atom. (c) The C—H···Li interactions involving hydrogen atoms attached to the α- and β-carbon atoms

triply bridging ketimino nitrogen atoms, despite having twice as many electrons for skeletal bonding as has $(LiC_6H_{11})_6$ or $(LiSiMe_3)_6$ (the ketimino group $N{=}CBu^t_2$ functions as a source of three electrons) and providing the first example of electron deficient bridging through the nitrogen atom of an organonitrogen ligand.

Though rarer than triply bridging alkyl groups, doubly bridging alkyl groups are known in organolithium chemistry, either in the case of bulky alkyl derivatives or in cases where chelating bases restrict the number of bonding interactions available to the lithium atoms. The bicyclobutane derivative $(LiC_4H_5{\cdot}TMEDA)_2$, for example, contains μ_2-bicyclobutyl ligands in its dimeric structure (Figure 20),[97] which is of interest in providing the first example of a bridging tertiary alkyl group (the bridging carbon atom is one of the bridgehead carbons). Clearly, in this case, as in the case of phenyl bridges, there can be no doubt that bridging occurs through M···C···M, not M—C···H···M, bonding interactions. The comparative length of the Li···C and Li···Li distances in $(LiC_4H_5{\cdot}TMEDA)_2$ (Figure 20; *cf.* Figures 18 and 19) can be attributed to the effect of the chelating TMEDA ligands in restricting the extent of the Li···C and Li···Li interactions.

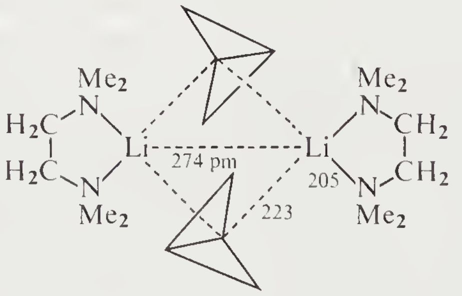


Figure 20 The structure of the dimeric bicyclo[1.1.0]butan-1-yllithium–tetramethylethylenediamine adduct

The strong tendency of lithium to form alkyl bridges, reflected in its preference for triply bridged rather than doubly bridged structures as illustrated above, is also apparent in the structures of lithium organometallate complexes Li_xMR_y, where M is a metal or metalloid that may itself have only a very slight capacity for forming MRM three-centre-bonded bridges in its own binary alkyls MR_{y-x}. For example, although boron alkyls, BR_3, do not associate to form dimers, $(BR_3)_2$, like their aluminium counterparts, they nevertheless can function as Lewis acids and form tetraalkylborates, $M^+BR_4^-$, in which the groups R can play a bridging role between M and B. Methyl bridges between boron and lithium atoms, for example, are a particularly interesting feature of the structure of the tetramethylborate $LiBMe_4$, which has been the subject of a single-crystal neutron and X-ray diffraction investigation.[98] Two types of bridging methyl group are present. One involves a linear B—C···Li arrangement of the skeletal atoms that places all three methyl hydrogen atoms within *ca.* 223 pm of the lithium atom (the C· · ·Li distance of 236 pm is the same as that between tetramers in $(\mathrm{LiMe})_4$). The other involves bent (82°) B—C· · ·Li arrangements in the form of $\mathrm{B}(\mu\text{-}\mathrm{CH}_3)_2\mathrm{Li}$ four-membered ring systems that superficially appear to be reminiscent of the $\mathrm{Al}(\mu\text{-}\mathrm{CH}_3)_2\mathrm{Al}$ ring system in $\mathrm{Al}_2\mathrm{Me}_6$. However, the BCLiC rings in LiBME_4 are slightly puckered, and the orientations of the methyl groups are such as to place two hydrogen atoms of each within *ca.* 212 pm of the lithium atoms.

Among the heavier alkali metals, sodium forms organo derivatives that are intermediate in character between covalent (electron deficient) and ionic. Thus whereas methylsodium crystallizes, like methyllithium, in tetramers, ethylsodium adopts a double-layer structure in which the methylene groups of the alkyl residues have a trigonal pyramidal array of sodium atoms or ions as near neighbours.[99] Methylpotassium adopts a nickel arsenide type structure, in which the methyl groups, effectively as carbanions CH_3^- and presumably with the expected pyramidal geometry, are surrounded by a trigonal prismatic array of potassium ions.[100]

1.4.7 Bridged Organocopper Systems

Copper is another metal with a strong tendency to indulge in multicentre metal–carbon bonding. Studies on its trimethylsilylmethyl derivative $\mathrm{CuCH}_2\mathrm{SiMe}_3$ (chosen because the neopentyl type of structure avoids the problems of thermal instability that stem from β-attached hydrogen, and the bulk favours oligomer rather than polymer formation) have shown that it crystallizes as the tetramer, $(\mathrm{CuCH}_2\mathrm{SiMe}_3)_4$ (Figure 21a),[101] in which a square planar arrangement of metal atoms is held together by bridging silylmethyl groups. The bond angles (CuCCu, 74°; CCuC, 164°) are consistent with the bonding interpretation of linearly (*sp*) hybridized copper atoms involved in three-centre CuCCu bonds. The Cu· · ·Cu distance of 242 pm is short enough to allow significant overlap of the metal orbitals with the carbon sp^3 hybrid orbital, but is not regarded as indicative of direct unassisted metal–metal bonding. If the metal atoms had been able to make use of more atomic orbitals, a more compact structure, like the Li_4 or Li_6 arrangements discussed above, might have been expected. The apparently similar tetramer $(\mathrm{CuOBu^t})_4$ (Figure 21b)[102] has significantly longer Cu· · ·Cu distances (271 pm), as expected for electron precise, as opposed to electron deficient, bridging.

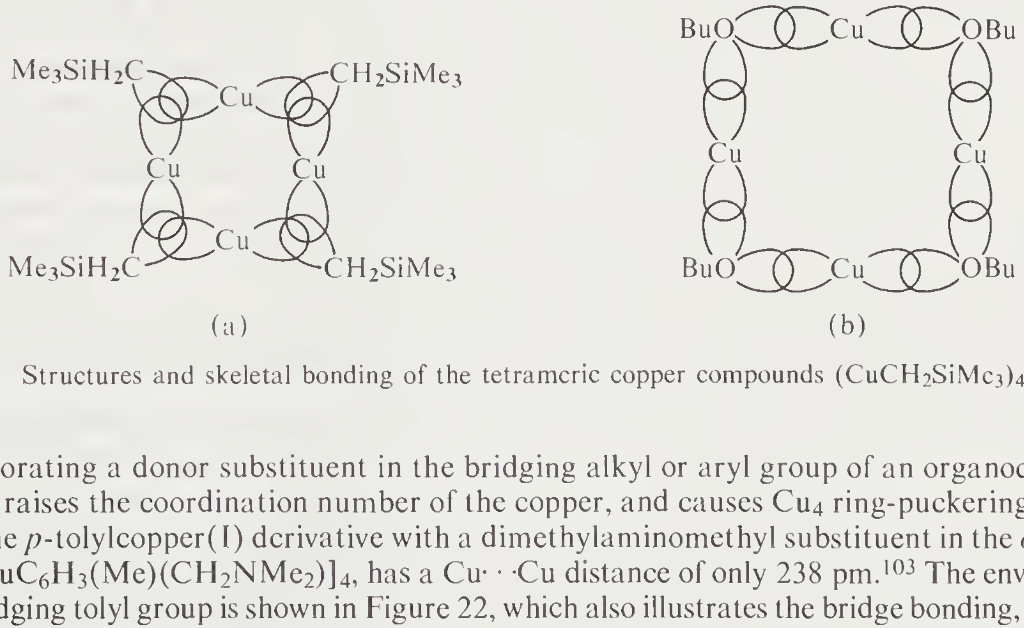


Figure 21 Structures and skeletal bonding of the tetrameric copper compounds $(\mathrm{CuCH}_2\mathrm{SiMe}_3)_4$ and $(\mathrm{CuOBu^t})_4$

Incorporating a donor substituent in the bridging alkyl or aryl group of an organocopper(I) tetramer raises the coordination number of the copper, and causes Cu_4 ring-puckering. For example, the *p*-tolylcopper(I) derivative with a dimethylaminomethyl substituent in the *ortho* position, $[\mathrm{CuC}_6\mathrm{H}_3(\mathrm{Me})(\mathrm{CH}_2\mathrm{NMe}_2)]_4$, has a Cu· · ·Cu distance of only 238 pm.[103] The environment of the bridging tolyl group is shown in Figure 22, which also illustrates the bridge bonding, involving three copper atoms, found in some 2-dimethylaminophenylcopper(I) derivatives.[104,105]

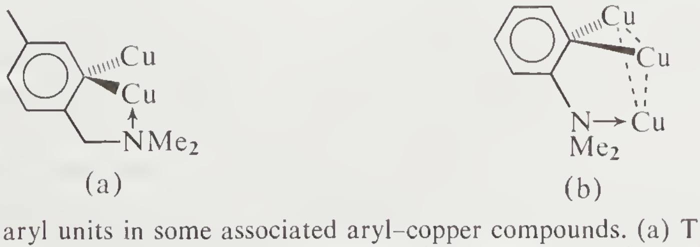


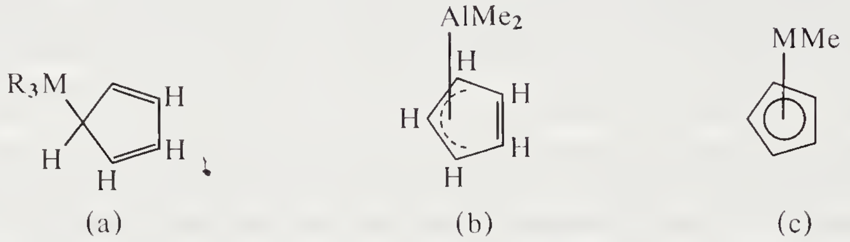
Figure 22 The bridging aryl units in some associated aryl–copper compounds. (a) The edge-bridging 2-(dimethylaminomethyl)phenyl ligand of the tetramer $[\mathrm{CuC}_6\mathrm{H}_3(\mathrm{Me})\mathrm{CH}_2\mathrm{NMe}_2]_4$, which contains a butterfly-shaped Cu_4 skeleton. (b) The face-bridging dimethylaminophenyl ligand of the Cu_6 clusters in $(\mathrm{CuC}_6\mathrm{H}_4\mathrm{NMe}_2)_4(\mathrm{CuX})_2$ (X = Br or C≡CTol), which contain distorted octahedral Cu_6 skeletons

1.5 METAL–HYDROCARBON π-COMPLEXES

1.5.1 *Tri-* and *Penta-hapto* Cyclopentadienyl Derivatives

Organometallic compounds in which a metal atom bonds to an unsaturated organic ligand by means of the carbon–carbon π-bonding electrons of the latter are far rarer in main group organometallic chemistry than in transition metal chemistry. Detailed discussion of such systems is therefore more appropriate as a prelude to transition metal systems (see Volume 3, Chapter 19). However, the present survey would be incomplete without brief mention of a few representative main group systems and some comments on their bonding implications.

Most known main group metal–hydrocarbon π-complexes are cyclopentadienyl complexes.[106] The cyclopentadienyl group C_5H_5, which as the anion $C_5H_5^-$ is an aromatic ring system with a planar regular pentagonal structure, can bond to metals in a variety of ways, some of which are illustrated in Figure 23. Towards Group IV metals in the form of trialkyl derivatives MR_3 (M = Si, Ge, Sn or Pb), the cyclopentadienyl group acts as a σ-bonding ligand. The unit MR_3 effectively replaces one hydrogen atom of the parent cyclopentadiene, bonding to only one ring carbon atom, though extensive spectroscopic studies on systems $R_3MC_5H_5$ have shown them to be fluxional, the unit MR_3 migrating very readily round the ring.[107]



(a) (b) (c)

Figure 23 Structures of some main group metal cyclopentadienyl derivatives: (a) $R_3M(\eta^1\text{-}C_5H_5)$ (M = Si, Ge, Sn, Pb); (b) $Me_2Al(\eta^3\text{-}C_5H_5)$; (c) $MeM(\eta^5\text{-}C_5H_5)$ (M = Be, Zn)

Derivatives of aluminium, zinc and beryllium, however, contain π-bonding cyclopentadienyl groups. For example, the aluminium derivative $AlMe_2(C_5H_5)$ is monomeric in the gas phase, with a *trihapto* cyclopentadienyl ligand,[108] while the beryllium[109] and zinc[110] compounds $MMe(C_5H_5)$ in the gas phase have *pentahapto* cyclopentadienyl ligands (Figure 23).

These structures can be rationalized in terms of the numbers of electrons that the ligand contributes to the metal valence shell. The Group IV elements in the derivatives $MR_3(C_5H_5)$ can accommodate eight electrons altogether in their four valence shell orbitals; the trialkyl unit MR_3 therefore requires only one electron from the cyclopentadienyl ligand, to which it accordingly bonds in a σ fashion. The dialkylaluminium unit $AlMe_2$, by contrast, requires three more electrons to complete the octet on the metal, and so bonds to three carbon atoms of the cyclopentadienyl ligand (each ring carbon atom can supply the one electron it would otherwise use for ring π-bonding). The beryllium and zinc units MMe, which in themselves contain only three electrons in the metal valence shell, require five more to fill the available orbitals, and so bond to all five metal valence shell electrons.

The orientations of the metal alkyl units with respect to the cyclopentadienyl ligands in these compounds are those that maximize the overlap of the metal and ligand orbitals. In the dimethylaluminium cyclopentadienide, $AlMe_2(C_5H_5)$, for example, the V-shaped dimethylaluminium residue will bond most strongly to the three ring carbon atoms if orientated as shown in Figure 24a, when the two available metal orbitals (an sp^2 hybrid pointing towards the ring, and a p-orbital parallel to the ring plane, perpendicular to the AlR_2 unit) point towards these carbon atoms. The combinations of metal and ligand orbitals that account for the bonding are shown in Figure 24b.

The metal–carbon bonding in the *pentahapto*-cyclopentadienyl complexes $BeMe(C_5H_5)$ and $ZnMe(C_5H_5)$ resembles that in ferrocene, except that d-orbitals play no significant part. These complexes may be viewed as complexes of cationic units MMe^+ with cyclopentadienide anions $C_5H_5^-$. The latter have three filled π-bonding orbitals (Figure 24c) that neatly match the symmetries of the three vacant metal orbitals (an sp hybrid pointing towards the centre of the C_5H_5 ring, and a pair of p-orbitals tangential to this), so allowing all three π-bonding pairs to contribute to the metal–ligand bonding.

The polymeric structure of the zinc compound $ZnMe(C_5H_5)$ in the crystal has already been remarked on.[85] Though in the polymer the cyclopentadienyl groups perform a bridging role, their

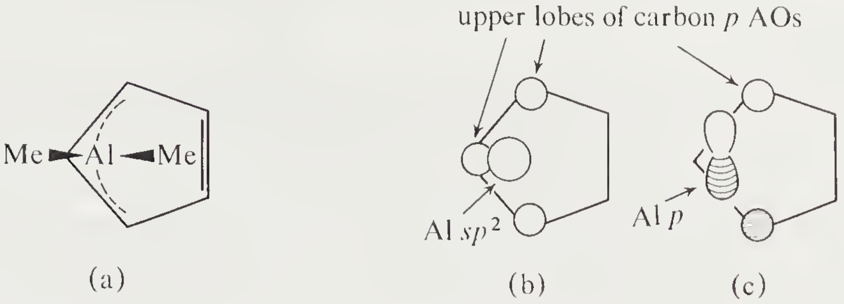


Figure 24 Orientation of the $AlMe_2$ unit with respect to the cyclopentadienyl ring in $Me_2Al(\eta^3\text{-}C_5H_5)$, and the orbitals involved in bonding to the cyclopentadienyl ring, all shown in plan

total hapticity remains five as expected: they coordinate *dihapto* to one, and *trihapto* to the other, of the two metal atoms they bridge.

Similar links between structures and electron numbers are shown by other main group metal cyclopentadienyl derivatives,[110] and much more extensively by transition metal cyclopentadienyls. There are exceptions in cases where the bonding is essentially ionic, when a *pentahapto* mode of coordination to the metal ion may be adopted when an electron count might suggest a different mode. For example, this is true of the sodium cyclopentadienide $Na(C_5H_5)$TMEDA, which contains $Na(TMEDA)^+$ cations and $C_5H_5^-$ anions in puckered chains, the anions bonding *pentahapto* to each of the two metal ions they bridge.[111]

1.5.2 Lithium Derivatives of Unsaturated Hydrocarbons

The manner in which lithium ions can interact with the π-electron clouds of aromatic hydrocarbons has been revealed by a systematic study[112] of some aryllithium systems in which chelating bases, particularly TMEDA, were used to limit the number of lithium orbitals available to bond to the hydrocarbon residues. Some representative structures are shown in Figure 25.

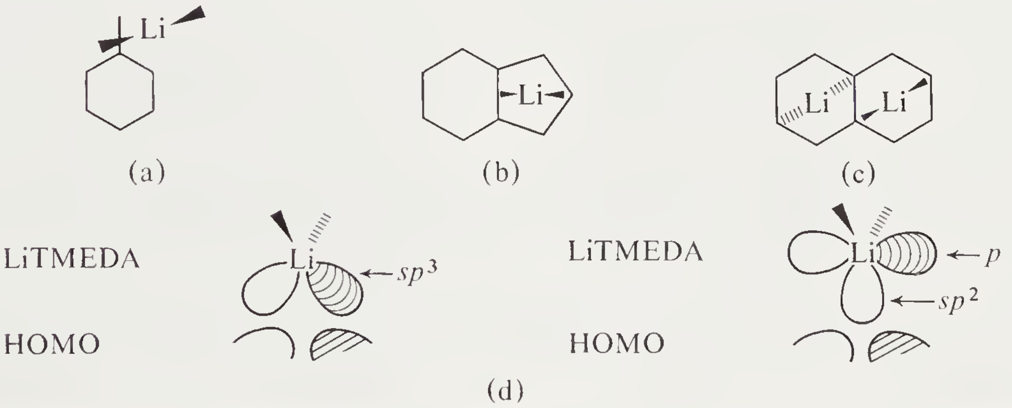
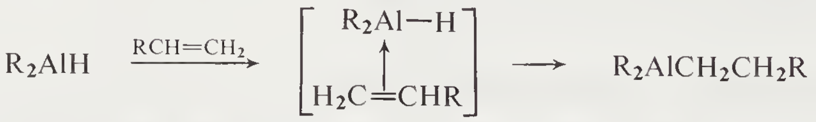


Figure 25 Orientation of the LiL_2 unit (L = a Lewis base) with respect to the organic residue in some unsaturated organolithium compounds. (a) The benzyllithium–triethylenediamine complex, $LiCH_2Ph{\cdot}N(CH_2CH_2)_3N$. (b) The indenyllithium–tetramethylethylenediamine complex, Li(indenyl)·TMEDA. (c) The naphthalene complex Naph·$(LiTMEDA)_2$. (d) Orbitals of the LiL_2 unit orientated in a manner to bond with the HOMO of the unsaturated organic ligand

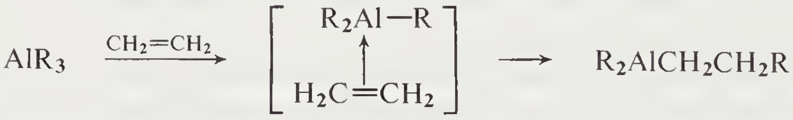
The $Li(TMEDA)^+$ cation, like the $AlMe_2^+$ cation referred to in the previous section in the discussion of the structure of $AlMe_2(C_5H_5)$, has two vacant metal orbitals with which to interact with an anionic organic residue. These orbitals (Figure 25) can be regarded either as two of a set of four sp^3 hybrid metal orbitals, lying in a plane perpendicular to the LiN_2 plane, or as one *p*-orbital perpendicular to that plane, and an sp^2 hybrid orbital in that plane. Clearly, this last orbital, pointing towards the unsaturated ligand (or the in-phase combination of the two available sp^3 hybrid orbitals) can interact with a suitable symmetric π-orbital of the ligand whatever the orientation of the LiN_2 unit. However, the *p*-orbital (or the out-of-phase combination of the sp^3 hybrid orbitals) can be used effectively for metal–ligand bonding only if the lithium atom lies over a node in a suitable ligand orbital, with the TMEDA ligand suitably orientated (Figure 25). In practice it has been found that the Li(TMEDA) unit is located over a node in the HOMO of the organic ligand in such compounds as indenyllithium(TMEDA),[113] bifluorenylbis[lithium(TMEDA)],[114] and bis[lithium(TMEDA)] naphthalenide[115] or anthracenide.[115] The position of the lithium in the benzyllithium–triethylenediamine adduct $LiCH_2Ph{\cdot}N(C_2H_4)_3N$[116] shows the same feature.

1.5.3 Other Systems

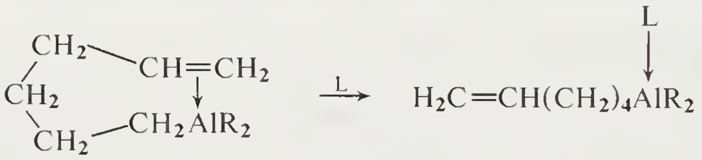
Complex formation between main group metals and alkenes is almost certainly an important first step in the preparation of metal alkyls from alkenes and metal hydrides, *e.g.* equation (3). Similar alkene complexes are also believed to feature in the 'growth' reactions of metal alkyls, reactions that are important in the oligomerization and polymerization of alkenes (equation 4). However, the stabilities of such complexes to dissociation or rearrangement are generally too low to allow their isolation. Evidence of their existence has nevertheless been obtained by the simple device of anchoring the alkene function to the metal atom in question, by means of a suitable length alkyl chain to allow π-complex formation. For example, weak complexing between the alkene function and the metal atom in hexenylalanes, $R_2Al(CH_2)_4CH{=}CH_2$, has been detected by IR and ^1H NMR spectroscopic studies,[117] which showed a lower alkene stretching frequency, $\nu(C{=}C)$, and deshielded vinylic protons compared with the values obtained when a Lewis base L was added to destroy the π-complex (equation 5). Such internal π-complexes clearly feature in the cyclization reactions readily undergone by ω-alkenylalanes (equation 6). This type of reaction has been used to convert α,ω-dienes into cyclic alkenes, with organoaluminium hydrides as catalysts (equation 7).[118] The detailed stereochemistry and kinetics of various other reactions between organoaluminium compounds and alkenes or alkynes are likewise interpretable in terms of π-complex formation as a key step.[119,120]



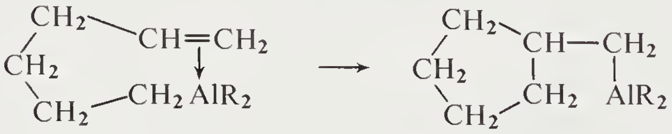
$$R_2AlH \xrightarrow{RCH{=}CH_2} \left[\begin{array}{c} R_2Al{-}H \\ \uparrow \\ H_2C{=}CHR \end{array}\right] \longrightarrow R_2AlCH_2CH_2R \tag{3}$$



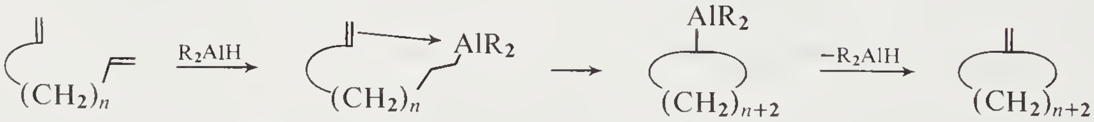
$$AlR_3 \xrightarrow{CH_2{=}CH_2} \left[\begin{array}{c} R_2Al{-}R \\ \uparrow \\ H_2C{=}CH_2 \end{array}\right] \longrightarrow R_2AlCH_2CH_2R \tag{4}$$



(5)

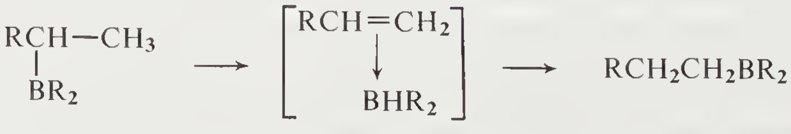


(6)



(7)

Similar examples could be drawn from the organometallic chemistry of many other main group metals and metalloids, *e.g.* the hydroboration of alkenes and alkynes is believed to involve π-complex formation as a first step,[121] and the rearrangement reactions of organoboranes, which under moderate conditions show high stereospecificity, most likely involve intermediates of a π-complex type rather than separate alkene and boron hydride molecules (equation 8). Many other reactions of organometallic compounds are believed to proceed through related intermediates. Clearly, π-complex formation is very important in main group organometallic chemistry even though few π-complexes are isolable.



$$\begin{array}{l} RCH{-}CH_3 \\ | \\ BR_2 \end{array} \longrightarrow \left[\begin{array}{c} RCH{=}CH_2 \\ \downarrow \\ BHR_2 \end{array}\right] \longrightarrow RCH_2CH_2BR_2 \tag{8}$$

In representing the bonding in metal–hydrocarbon π-complexes such as the alkene complexes of aluminium and boron just discussed, we have shown the donation of electronic charge from the alkene π-orbital to a suitable vacant metal orbital by a dative bond arrow. An alternative way of depicting the bonding, that underlines its relationship to the three-centre bonding of alkyl bridge bonds (and the number of electrons involved), is to show a two-centre link between the alkene carbon atoms and a three-centre link between them and the main group metal atom (Figure 26).

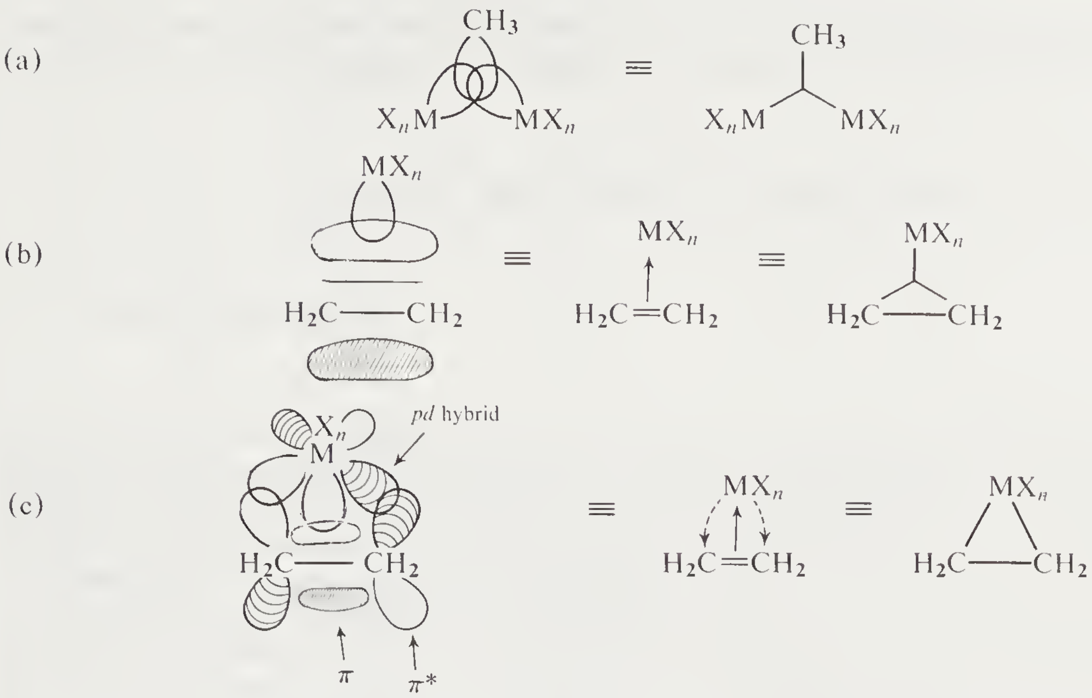


Figure 26 Triatomic bonding arrangements common in organometallic systems. (a) An alkyl bridge bond: three atoms, three AOs, two electrons. (b) A main group metal–alkene π-complex: three atoms, five AOs, four electrons. (c) A transition metal–alkene π-complex: three atoms, six AOs, six electrons

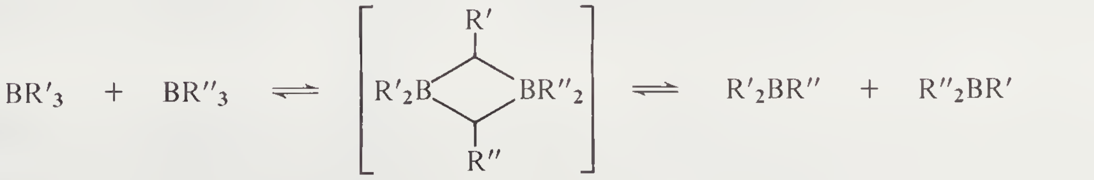
In the π-complex the main group metal atom is thus linked by a three-centre, two-electron bond to two carbon atoms which are otherwise linked to each other by a two-centre, two-electron bond. The three atoms are thus held together by two pairs of electrons, in contrast to the one pair of electrons in a typical MCM alkyl bridge bond. The important difference between the two systems is that, whereas each of the three atoms involved in an alkyl bridge bond supplies only one atomic orbital for the bonding, in the π-complex each of the two carbon atoms provides two atomic orbitals for the skeletal bonding.

Yet a third bonding arrangement is possible if each of the three atoms can supply two orbitals and two electrons for bonding, when three two-centre bonds can link the three atoms together. This cyclopropane-type of bonding holds for transition metal–alkene π-complexes, which differ from their main group metal counterparts in that transition metals can contribute a filled d-orbital to help with the metal–ligand bonding. Conventionally,[122,123] this is shown as releasing electronic charge into the alkene π^*-orbital, reducing the C—C bond order from two to one, and adding a second electron pair to those involved in metal–carbon bonding. These points are illustrated in Figure 26. A more detailed discussion of the bonding between transition metal atoms and unsaturated hydrocarbons is to be found in Chapter 19 of the present work (Volume 3).

1.6 CARBORANES AND METALLACARBORANES

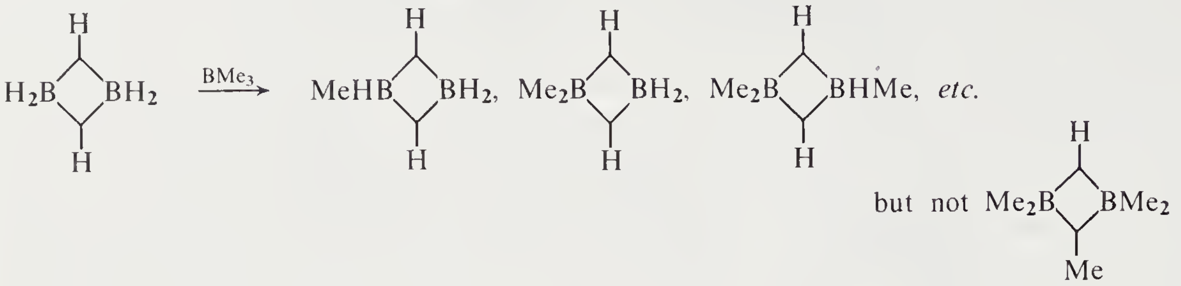
1.6.1 Introduction

Unlike their aluminium analogues, the trialkyls and triaryls of boron, BR_3, do not form dimers, B_2R_6, in the condensed phase, although exchange of alkyl groups between different boron alkyls, BR'_3 and BR''_3, occurs easily enough to suggest that bridged transition states, if not intermediates, are readily accessible species in such reactions (equation 9). Evidently the greater bond energy expected for a bridged dimer, B_2R_6, would not be sufficient to offset the greater non-bonded repulsions involved.



$$BR'_3 + BR''_3 \rightleftharpoons \left[R'_2B \overset{R'}{\underset{R''}{\diamond}} BR''_2 \right] \rightleftharpoons R'_2BR'' + R''_2BR' \qquad (9)$$

Three-centre bridge-bonding between boron atoms, but with hydrogen atoms rather than alkyl groups doing the bridging, is of course a familiar feature of boron hydride chemistry,[124] and indeed the observation that reactions between trimethylborane and diborane generated mono-, di-, tri-and tetra-methyldiboranes $B_2H_{6-n}Me_n$ (n = 1–4), but not the pentamethyl derivative B_2HMe_5, provided an early pointer to the bridged structure of diborane (equation 10).



(10)

It was with the discovery of carboranes,[9] mixed hydrides of carbon and boron in which atoms of both elements are incorporated in the electron deficient molecular skeleton, that the capacity of boron to form three-centre bonds involving carbon was first demonstrated. The first examples were prepared by reactions between alkenes or alkynes and boron hydrides in attempts to synthesize alkyl derivatives of the latter, and were soon found to have structures based on polyhedral arrangements of carbon and boron atoms held together remarkably well by relatively few electrons. The structural pattern to which they conform, reflecting the numbers of electrons available for bonding, has turned out to be relevant to a wide range of other systems, linking boron hydride clusters on the one hand with metal clusters, metal–hydrocarbon π-complexes and carbocations on the other,[12] and so will be considered in some detail here.

1.6.2 The Structural Pattern

The best known series of carboranes has the general formula $C_2B_{n-2}H_n$, where n = 5–12. Their structures are illustrated in Figure 27.[12,125,126] They consist of exclusively triangular-faced polyhedral arrangements of the n constituent CH and BH units, each orientated so that the substituent (*exo*) hydrogen atoms point radially outwards away from the roughly spherical surface on which the carbon and boron atoms lie. As prepared from alkynes and boron hydrides, they tend to have the carbon atoms occupying adjacent polyhedral vertices, but isomerize when heated to place the carbon atoms preferentially in the sites of low coordination number,[126] *e.g.* in equatorial positions in the case of the pentagonal bipyramidal $C_2B_5H_7$, or in the capping sites in the tricapped trigonal prismatic $C_2B_7H_9$ and bicapped square antiprismatic $C_2B_8H_{10}$. An isoelectronic and isostructural series of anionic boranes $B_nH_n^{2-}$ is also known, together with a few monocarba members of the series $[CB_{n-1}H_n]^-$ (see examples in Table 7).[125] In view of their closed polyhedral structures, these boranes and carboranes are referred to as *closo* clusters.

Table 7 *Closo*, *nido* and *arachno* Carboranes and Boranes

No. of skeletal bond pairs	*No. of polyhedron vertices*	*Parent polyhedron*	*closo*	*Examples nido*	*arachno*
6	5	trigonal bipyramid	$C_2B_3H_5$	—	$B_3H_8^-$
7	6	octahedron	$C_2B_4H_6$	$C_2B_3H_7$	B_4H_{10}
			CB_5H_7	B_5H_9	$[C_4H_6]^a$
			$B_6H_6^{2-}$	—	—
8	7	pentagonal bipyramid	$C_2B_5H_7$	$C_xB_{6-x}H_{10-x}$ x = 0–4)	B_5H_{11}
			$B_7H_7^{2-}$	—	—
9	8	dodecahedron	$C_3B_5H_7$	—	B_6H_{12}
			$C_2B_6H_8$	—	—
			$B_8H_8^{2-}$	—	—
10	9	tricapped trigonal prism	$C_2B_7H_9$	$C_2B_6H_{10}$	—
			$B_9H_9^{2-}$	B_8H_{12}	—
11	10	bicapped square antiprism	$C_2B_8H_{10}$	$C_2B_7H_{11}$	B_8H_{14}
			$CB_9H_{10}^-$	$B_9H_{12}^-$	—
			$B_{10}H_{10}^{2-}$	—	—
12	11	octadecahedron	$C_2B_9H_{11}$	$C_2B_8H_{12}$	$C_2B_7H_{13}$
			$CB_{10}H_{11}^-$	CB_9H_{13}	B_9H_{15}
			$B_{11}H_{11}^{2-}$	$B_{10}H_{14}$	—
13	12	icosahedron	$C_2B_{10}H_{12}$	$C_4B_7H_{11}$	$B_{10}H_{14}^{2-}$
			$CB_{11}H_{12}^-$	$C_2B_9H_{11}^{2-}$	$B_{10}H_{15}^-$
			$B_{12}H_{12}^{2-}$	$CB_{10}H_{13}^-$	—

[a] Bicyclobutane.

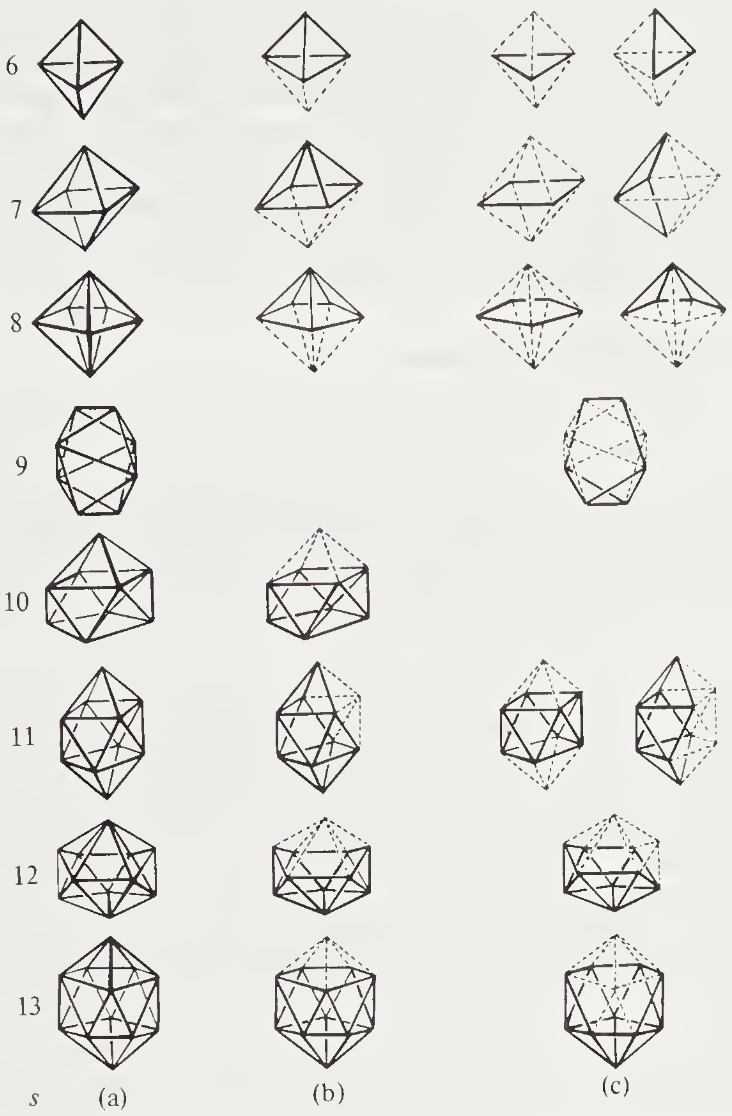


Figure 27 The polyhedral shapes of (a) *closo*, (b) *nido* and (c) *arachno* carboranes and related clusters; s = number of skeletal electron pairs; (a) *closo* species are $C_2B_{n-2}H_n$, $B_nH_n^{2-}$, *etc.*; (b) *nido* species are $C_2B_{n-2}H_{n+2}$, B_nH_{n+4}, *etc.*; (c) *arachno* species are $C_2B_{n-2}H_{n+4}$, B_nH_{n+6}, *etc.* The one *exo* hydrogen atom attached to each skeletal atom in these species, and the *endo* hydrogen atoms of the *nido* and *arachno* species, have been omitted for clarity

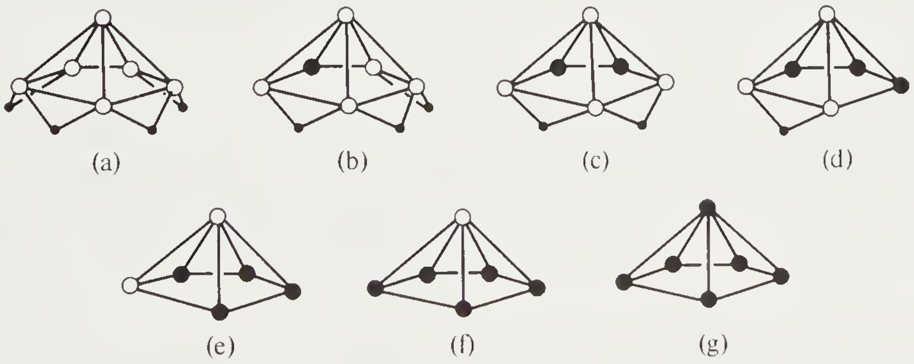


Figure 28 The pentagonal pyramidal shapes of the series of *nido* carboranes $C_xB_{6-x}H_{10-x}$, $[C_5Me_5BI]^+$ and $[C_6Me_6]^{2+}$ formally related to hexaborane(10), B_6H_{10}: (a) B_6H_{10}; (b) CB_5H_9; (c) $C_2B_4H_8$; (d) $C_3B_3H_7$; (e) $C_4B_2H_6$; (f) $[C_5Me_5BI]^+$; (g) $[C_6Me_6]^{2+}$. The *endo* hydrogen atoms of the compounds $C_xB_{6-x}H_{10-x}$ (x = 0–3) bridge adjacent basal boron atoms. Each skeletal atom also has one *exo* substituent (H, Me or I) which is not shown

More open structures, though based on the same series of polyhedra, are adopted by carboranes of formulae $C_2B_{n-2}H_{n+2}$ and $C_2B_{n-2}H_{n+4}$. The former, like the isoelectronic boranes B_nH_{n+4}, have structures based on polyhedra with $(n + 1)$ vertices, one of which is left vacant. They are referred to as *nido* species ('nest-like'). The latter, and the isoelectronic boranes B_nH_{n+6}, have structures based on polyhedra with $(n + 2)$ vertices, two of which are left vacant. They are referred to as *arachno* species ('cobweb-like'). The shapes defined by these polyhedral fragments are shown in Figure 27. Again, the carbon atoms preferentially occupy the sites of lower coordination number.[126] The extra (*endo*) hydrogen atoms lie roughly on the same sphere as the skeletal carbon and boron atoms, generally surrounding the open face of the polyhedral fragment, either terminally bound to adjacent boron atoms or in bridging sites between pairs of boron atoms. These points are illustrated (Figure 28) by the structures of the isoelectronic series of *nido* clusters formally related to hexaborane(10), B_6H_{10}. These include the carboranes CB_5H_9, $C_2B_4H_8$, $C_3B_3H_7$, $C_4B_2H_6$ and the cationic $[C_5BH_6]^+$ and $C_6H_6^{2+}$, all of which are known either as the parent species or as derivatives. The *endo* hydrogen atoms bridge B···B links, but not B···C or C···C links.

1.6.3 The Bonding in Carborane-type Clusters

It was noted in the previous section that the atoms in carboranes and related borane structures effectively lie on two concentric spheres. One (*exo*) hydrogen atom attached to each carbon or boron atom lies on the outer sphere, and is held there by a normal two-centre electron pair bond to the carbon or boron atom. Any remaining (*endo*) hydrogen atoms, and all of the carbon and boron atoms, lie on the inner sphere, and it is the number of electrons available for holding together these inner-sphere atoms that controls the shape of the carborane. These electrons are commonly referred to as the skeletal or framework electrons. Their number is easily calculated from the molecular formula. Expressing the molecular formula as $(CH)_a(BH)_bH_c$, then the number of skeletal bonding electrons will be $(3a + 2b + c)$, since each CH unit can furnish three electrons and each BH unit can supply two electrons. Thus *closo* carboranes of general formulae $C_2B_{n-2}H_n$, *i.e.* $(CH)_2(BH)_{n-2}$, contain $(2n + 2)$ skeletal bonding electrons, that is $(n + 1)$ skeletal bond pairs. *Nido* carboranes of formulae $C_2B_{n-2}H_{n+2}$ contain $(n + 2)$ skeletal bond pairs while *arachno* carboranes $C_2B_{n-2}H_{n+4}$ contain $(n + 3)$ skeletal bond pairs. For all three structural types, *closo*, *nido* and *arachno*, the structure is based on a polyhedron with a number of vertices one fewer than the number of skeletal bond pairs available (Table 7).[12,125]

These electron numbers are such as to make localized bonding treatments of the skeletal bonding difficult or unsatisfactory for most carboranes, particularly the *closo* species, though Lipscomb's elegant localized two- and three-centre bonded descriptions of the bonding in neutral *nido* and *arachno* boranes[127] has proved particularly helpful in dealing with these species. For *closo* boranes $B_nH_n^{2-}$ and carboranes $C_2B_{n-2}H_n$, the $(n + 1)$ pairs of skeletal electrons available would have to be assigned to three two-centre (polyhedral edge) bonds and $(n - 2)$ three-centre (polyhedral face) bonds in order to ensure that each boron and carbon atom was involved in the three skeletal bonds their valences require. These numbers of bonds are ill-suited to the numbers of edges $(3n - 6)$ and faces $(2n - 4)$ possessed by these n-vertex polyhedra. Nevertheless, the average bond order of the polyhedral edge bonds, readily assessed by dividing the number of bond pairs $(n + 1)$ by the number of edges $(3n - 6)$, is seen to be quite low, ranging from 7/12 for the octahedral $B_6H_6^{2-}$ or $C_2B_4H_6$ to 13/30 for the icosahedral $B_{12}H_{12}^{2-}$ or $C_2B_{10}H_{12}$. Carborane and borane clusters are remarkably robust species considering that the links between their atoms are essentially half-bonds.

Although localized bond treatments provide but poor descriptions and no explanation of the skeletal bonding in *closo* boranes and carboranes, the numbers of electrons involved are readily explicable using MO treatments.[127–133] The high temperatures commonly used to synthesize *closo* boranes and carboranes, and their failure to change shape when subsequently irradiated or heated quite strongly, show that the polyhedral shapes they adopt must be those that make best use of the electrons available. MO treatments[127–133] have shown that the polyhedra in Figure 27 have appropriate symmetries to generate $(n + 1)$ bonding MOs from the $3n$ AOs available (each of the n skeletal atoms can provide three atomic orbitals for skeletal bonding: one is an *sp* hybrid AO pointing radially away from the *exo* hydrogen atom, towards the centre of the cluster; the other two are *p* AOs perpendicular to this, tangentially orientated with respect to the surface of the skeletal sphere; see Figure 29). Of the $(n + 1)$ skeletal bonding MOs, one unique orbital of A symmetry arises from a fully in-phase combination of the radially orientated AOs. The remaining n bonding MOs arise from combinations of the tangentially orientated surface *p* AOs, stabilized where appropriate by suitable symmetry combinations of radial AOs.

Interestingly, the number of skeletal bonding MOs remains at one more than the number of polyhedron vertices, even when not all of the vertices are occupied by skeletal carbon or boron atoms. The square pyramidal-shaped skeleton of the *nido* carborane $C_2B_3H_7$ or borane B_5H_9, for example, generates seven skeletal bonding MOs, just as does the octahedral $C_2B_4H_6$ or $B_6H_6^{2-}$. The shapes of *nido* and *arachno* boranes and carboranes are thus understood as placing their skeletal atoms in the positions that generate the right number of bonding MOs to accommodate

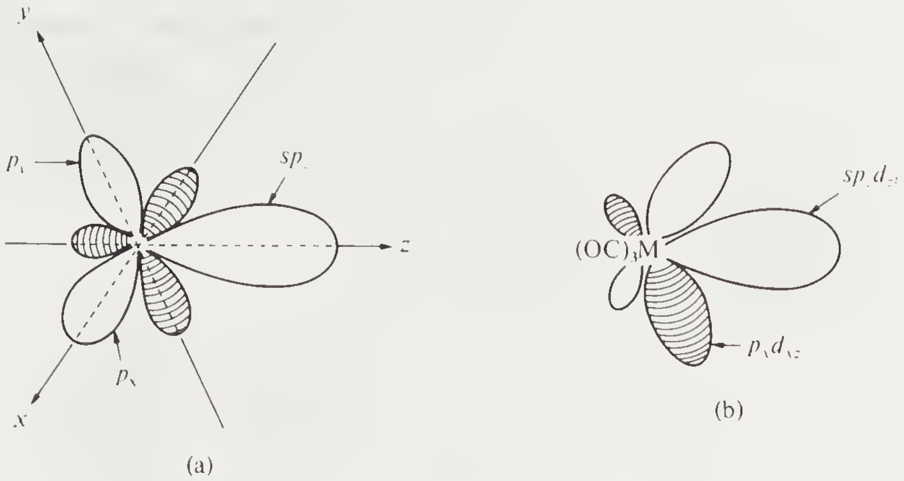


Figure 29 The orbitals that (a) BH or CH units and (b) $Fe(CO)_3$ or $Co(\eta^5\text{-}C_5H_5)$ units can use for skeletal bonding in clusters. (a) The radially orientated *sp* hybrid and tangentially orientated *p* AOs of a BH or CH unit. (b) The radially orientated d_{z^2} and tangentially orientated *pd* hybrid AOs of an $Fe(CO)_3$ or $Co(\eta^5\text{-}C_5H_5)$ unit (the tangential p_yd_{yz} orbital is not shown)

their skeletal electrons. Adding extra electron pairs to boranes and carboranes causes their skeletal atoms to move to more open arrangements, effectively based on progressively larger polyhedra with progressively more vertices left vacant. Examples of a further series, referred to as *hypho* (net-like) species, are known, with $(n + 4)$ skeletal bond pairs holding together n skeletal atoms effectively occupying all but three of the vertices of the appropriate $(n + 3)$-vertex polyhedra.

The carboranes and boranes thus have structures that depend systematically on the numbers of electrons they contain. Since the electron numbers can be deduced from molecular formulae, it is possible to predict the likely structures of new compounds from their formulae.

1.6.4 Metallacarboranes

The relevance of carborane chemistry to other areas of cluster chemistry became apparent with the synthesis and structural characterization of metallacarboranes, cluster compounds that incorporate metal, carbon and boron atoms in their polyhedral skeletons.[10] They were first prepared by using cationic metal fragments to plug the gap in anionic *nido* carboranes. For example, base degradation was used to remove a boron atom from the *closo* icosahedral carborane $C_2B_{10}H_{12}$, generating the *nido* anion $C_2B_9H_{11}^{2-}$, which was found to coordinate to metal ions that regenerated the icosahedron (equation 11 and Figure 30).[134] This work had many repercussions, because it demonstrated the following points: (i) that a BH unit of a carborane could be replaced by various metal units, exemplified by the species $[Fe(\eta^5\text{-}C_5H_5)]^+$ and $[Fe(\eta^5\text{-}C_2B_9H_{11})]$ above; (ii) that a metal ion could bond to the two carbon atoms and three boron atoms of the pentagonal face of the *nido* anion $[C_2B_9H_{11}]^{2-}$ in the same way that it could bond to the cyclopentadienide anion $C_5H_5^-$, forming metallocene-type products; and (iii) that a metal atom could link together two polyhedral clusters by occupying a common vertex of both.

$$\begin{tikzcd}
 & & {[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_{11})]^-} \\
C_2B_{10}H_{12} \arrow[r, "\text{i, NaOR/ROH}", "\text{ii, NaH}"'] & C_2B_9H_{11}{}^{2-} \arrow[ur, "Fe^{2+}/C_5H_5^-"] \arrow[dr, "Fe^{2+}"] & \\
 & & {[Fe(\eta^5\text{-}C_2B_9H_{11})_2]^{2-}}
\end{tikzcd} \qquad (11)$$

It soon became apparent that such units as $Fe(CO)_3$, $Co(\eta^5\text{-}C_5H_5)$, $Ni(PR_3)_2$, $BeNMe_3$, AlR, GaR, Sn and Pb and other species isoelectronic with these could replace one or more of the BH units of carboranes in mixed metal, carbon and boron clusters. What these units had in common was that, like a BH unit, they contained four electrons too few to fill the valence shell of their metal atoms. The main group units contained four valence shell electrons rather than the eight expected for a closed-shell configuration, while the transition metal units were 14-electron systems, four

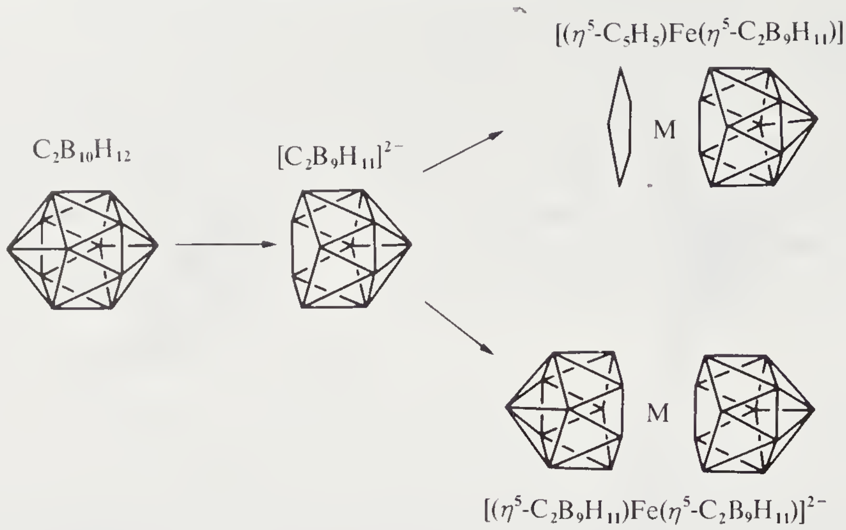


Figure 30 Icosahedral and icosahedral-fragment species involved in the first syntheses of metallacarboranes

short of the usual 18.[135] If required to make three AOs available for cluster bonding, each would therefore function as a source of two skeletal bonding electrons. Main group units like $BeNMe_3$, AlR, GaR, Sn or Pb, like a BH unit, could provide a radially orientated *sp*- or *p*-orbital and a pair of tangentially orientated *p*-orbitals (Figure 29). Transition metal units could provide a set of orbitals with similar lobal characteristics: a radially orientated d_{z^2} or hybrid orbital, and a pair of *pd* hybrid orbitals (Figure 29). Though not identical to the orbitals supplied by main group units, these latter orbitals, having similar energies and spatial and lobal characteristics, would be able to make a very similar contribution to the cluster bonding. The term 'isolobal' has been coined to describe the relationship between such transition metal units and their main group counterparts.[136,137]

In addition to the units already listed, capable of replacing the BH units of carboranes, a second series of metal-containing units was found to be capable of furnishing three orbitals and three electrons for cluster bonding, and so of replacing the CH units of carboranes. They included the species $Co(CO)_3$, $Ni(\eta^5\text{-}C_5H_5)$, $Cu(PR_3)_2$, BCO, P, As and Sb. Further units are to be found among the representative examples of metallacarborane formulae listed in Tables 8 and 9.[10,134,138]

Table 8 Examples of Metalla-carboranes and -boranes with *closo* Structures[10,134,138]

N[a]	*Shape*	*Examples*
6	octahedron	$C_2B_3H_5CoCp$; $C_2B_3H_5Fe(CO)_3$; $B_4H_6(CoCp)_2$; $B_3H_5(CoCp)_3$
7	pentagonal bipyramid	$C_2B_4H_6ML_n$ [ML_n = $Fe(CO)_3$, CoCp, $Ni(PPh_3)_2$, $Pt(PEt_3)_2$, GaR]; $C_2B_3H_5(ML_n)_2$ [ML_n = $Fe(CO)_3$, CoCp]; $C_3B_3H_5MeMn(CO)_3$; $C_4BH_3R_2\{Mn(CO)_3\}_2$
8	dodecahedron	$C_2B_4H_4Me_2SnCoCp$; $B_4H_4(CoCp)_4$; $B_4H_4(NiCp)_4$
9	tricapped trigonal prism	$C_2B_6H_8ML_n$ [ML_n = CoCp, $Mn(CO)_3^-$, $Pt(PMe_3)_2$]; $C_2B_5H_7(CoCp)_2$; $[CB_7H_8CoCp]^-$; $[Co(\eta^5\text{-}C_2B_6H_8)_2]^-$
10	bicapped square antiprism	$C_2B_7H_9CoCp$; $C_2B_7H_7Me_2Fe(CO)_3$; $C_2B_6H_8(CoCp)_2$; $[Co(\eta^5\text{-}C_2B_7H_9)_2]^-$; $CB_7H_8CoCpNiCp$; $[B_9H_9NiCp]^-$
11	octadecahedron	$C_2B_8H_{10}ML_n$ [ML_n = CoCp, $IrH(PPh_3)_2$]; $[Co(\eta^5\text{-}C_2B_8H_{10})_2]^-$; $C_2B_7H_9(CoCp)_2$; $[CB_9H_{10}CoCp]^-$
12	icosahedron	$C_2B_9H_{11}ML_n$ [ML_n = CoCp, $Pt(PR_3)_2$, $Ni(PR_3)_2$, $Fe(CO)_3^-$, Ge, Sn, Pb, Tl^-, AlEt, $BeNMe_3$, $Ru(CO)_3$, $RhH(PEt_3)_2$]; $[M(\eta^5\text{-}C_2B_9H_{11})_2]^{x-}$ (M = Fe^{II}, Co^{III}, Ni^{IV}); $[M(\eta^5\text{-}CB_{10}H_{11})_2]^{y-}$ (M = Co^{III}, Ni^{IV}); $C_2B_8H_{10}(CoCp)_2$; $C_2B_7H_9(CoCp)_3$; $CB_9H_{10}AsCoCp$
13	1,6,5,1 polyhedron	$C_2B_{10}H_{12}CoCp$; $C_2B_9H_{11}(CoCp)_2$
14	bicapped hexagonal antiprism	$C_2B_{10}H_{12}(CoCp)_2$; $C_4B_8H_8Me_4(FeCp)_2$

[a] *N* = number of skeletal atoms.

Table 9 Some Metalla-carboranes and -boranes with *nido* Structures[10,134,138]

N[a]	*Shape*	*Examples*
4	butterfly	$B_3H_8Mn(CO)_3$
5	square pyramid	$B_4H_8Fe(CO)_3$; B_4H_8CoCp; $B_3H_7[Fe(CO)_3]_2$
6	pentagonal pyramid	$B_5H_{10}FeCp$; B_5H_9CoCp; $C_2B_3H_7Fe(CO)_3$; $C_2B_3H_7CoCp$; $C_2B_2R_4SFe(CO)_3$; $C_3B_2R_5NiCp$; $C_4BH_5Fe(CO)_3$
7	hexagonal pyramid	$C_5H_5BPhMn(CO)_3$; $B_2Me_2N_2Me_2C_2Et_2Cr(CO)_3$; $B_3N_3Et_6Cr(CO)_3$
9	capped square antiprism	$B_5H_5(NiCp)_4$; $C_2B_6H_6R_2Pt(PR_3)_2$
10	decaborane type	$C_2B_7H_{11}CoCp$; $C_2B_7H_9Me_2Ni(PR_3)_2$; $B_9H_{13}CoCp$
11	icosahedral fragment	$[(B_{10}H_{12})_2Zn]^{2-}$; $[B_{10}H_{12}NiCp]^-$; $B_9H_{10}SPtH(PEt_3)_2$

[a] *N* = number of skeletal atoms.

Like boranes and carboranes, metalla-boranes and -carboranes thus have shapes that reflect the numbers of electrons available for skeletal bonding, *closo* for *n* atoms and $(n + 1)$ bond pairs, *nido* for $(n + 2)$ bond pairs and so on. For new compounds the probable shape can be deduced from an electron count, *i.e.* from the molecular formula. The number of electrons likely to be available for skeletal bonding can be calculated by summing the valence shell electrons on the cluster atoms, adding electrons from ligands (counted in the usual way), and subtracting two for each main group element and 12 for each transition metal in the cluster (the numbers of electrons not involved in cluster bonding). For example, the metallacarborane of formula $CB_7H_8Co(\eta^5\text{-}C_5H_5)Ni(\eta^5\text{-}C_5H_5)$ contains 10 cluster atoms (one carbon, two transition metal atoms and seven boron atoms). These collectively have 44 valence shell electrons. The eight hydrogen and two cyclopentadienyl ligands contribute a further 18 electrons, making a total of 62 electrons. Deducting $8 \times 2 + 2 \times 12$, *i.e.* 40 electrons for cluster non-bonding roles (they bond the ligands to the cluster), we are left with 22 electrons, *i.e.* eleven pairs, for skeletal bonding. The *closo* structure is thus intelligible.

Tables such as Tables 10 and 11 have been drawn up to help with skeletal electron counting, showing the electron contributions various groups may make, though they must be used with caution. For example, though a $Co(CO)_4$ unit may formally be a source of five electrons for skeletal bonding, it is more likely to act as a monovalent substituent on the periphery of a cluster than to be embedded in the cluster polyhedron, unless some of the carbonyl groups act as bridges to neighbouring atoms. More generally among transition metal systems, the 18-electron rule that is the basis for the electron contributions in Table 11 may not hold: some of the nine valence shell orbitals may remain empty, or be only half-filled. Main group metalla-carboranes and -boranes, however, tend to have the structures predicted by the electron contributions listed in Table 10.

Table 10 Skeletal Electron Contributions $(v + x - 2)$[a] made by Main Group Cluster Units

Group number (= *v*)	*Element*	*Cluster unit* M (*x* = 0)	MR (*x* = 1)	MR_2 *or* ML (*x* = 2)
1	Li, Na	—	0	1
2	Be, Mg, Zn, Cd	0	1	2
3	B, Al, Ga, In, Tl	1	2	3
4	C, Si, Ge, Sn, Pb	2	3	4
5	N, P, As, Sb, Bi	3	4	—
6	O, S, Se, Te	4	5	—
7	F, Cl, Br, I	5	—	—

[a] *v* = number of valence shell electrons on M; *x* = number of electrons from ligands; R = a one-electron ligand, L = a two-electron ligand.

Table 11 Skeletal Electron Contributions ($v + x - 12$)[a] that Transition Metal Cluster Units May Make

Number of valence shell electrons, v	*Transition metal*	*Cluster unit*			
		ML_2[b] ($x = 4$)	$M(\eta^5\text{-}C_5H_5)$ ($x = 5$)	ML_3 ($x = 6$)	ML_4 ($x = 8$)
6	Cr, Mo, W	—	−1	0	2
7	Mn, Tc, Re	−1	0	1	3
8	Fe, Ru, Os	0	1	2	4
9	Co, Rh, Ir	1	2	3	5
10	Ni, Pd,[c] Pt[c]	2	3	4	—

[a] x = number of electrons from ligands. [b] L = a two-electron ligand. [c] The tendency of these elements to form 16-electron complexes may boost their skeletal electron contribution by 2.

1.6.5 Relationship to Metal–Hydrocarbon π-Complexes and Other Organic Systems

Once the shapes of boranes and carboranes had shown how polyhedral aggregates of n tervalent units like BH or CH units could make effective use of such limited numbers of electrons as n, $(n + 1)$ or $(n + 2)$ bond pairs, and metallacarboranes had shown how wide was the range of metal-containing units that could be incorporated in such polyhedral aggregates, it became apparent that carboranes and boranes provided the structural and bonding pattern to which many other systems could be expected to conform. Of particular interest for organometallic chemistry was the close relationship that emerged between carboranes and metal–hydrocarbon π-complexes.[134] In the same way that metallacarboranes can be regarded as clusters of BH, CH and ML_n units, where ML_n is a metal atom M with assorted ligands L attached, so metal–hydrocarbon π-complexes can be treated as clusters of CH and ML_n units, held together by the electrons they contribute together with any extra electrons from the *endo* hydrogen atoms of any CH_2 groups present.

As a simple example, the *pentahapto* cyclopentadienylberyllium complex $MeBe(\eta^5\text{-}C_5H_5)$,[109] the structure of which (Figure 23) was rationalized in Section 1.5.1 above in terms of the donation of five electrons to the metal valence shell by the cyclopentadienyl ligand, can alternatively be regarded as a *nido* pentagonal pyramidal cluster of one apical BeMe unit (supplying one skeletal electron) and five basal CH units (supplying three skeletal electrons apiece). With six skeletal atoms and eight skeletal bond pairs it has the expected structure for a member of the same species as the carboranes shown in Figure 28.

The pentagonal cyclopentadienyl anion itself, $C_5H_5^-$, can be regarded as a cluster of five CH units held together by eight electron pairs, and so classified as an *arachno* cluster of the carborane type. Indeed, typical aromatic ring systems in general can be regarded as *arachno* members of the carborane cluster family. The square shape of the cyclobutadienyl dianion $C_4H_4^{2-}$, for example, is an appropriate shape for a four-atom seven-bond pair cluster. Benzene and related six-membered aromatic ring systems are similarly classifiable as *arachno* species when it is recognized that the hexagonal bipyramid is an eight-vertex polyhedron which, like the D_{2d} dodecahedron of $B_8H_8^{2-}$, has a suitable shape to generate nine skeletal bonding MOs. (For these *arachno* aromatic systems, the $(n + 3)$ skeletal bond pairs counted as holding their n ring atoms together include the n σ-bonding pairs as well as the three pairs associated with the π-system of the ring.[12])

These and other metal–hydrocarbon systems with shapes that clearly reflect the carborane structural pattern are illustrated in Figure 31 and listed in Table 12.[12,134–152] Metallocenes like ferrocene, $Fe(\eta^5\text{-}C_5H_5)_2$, in which a metal atom is sandwiched between two cyclopentadienyl rings, may be regarded as pairs of *nido* clusters sharing a common apex occupied by the metal atom, which contributes three orbitals for skeletal bonding to each of the two clusters it is shared between. Thus in ferrocene itself, six electrons in the metal valence shell are effectively cluster non-bonding, accommodated in three atomic orbitals, while three orbitals are used in bonding to each cyclopentadienyl ring. The iron atom thus contributes one electron to each of the two pentagonal pyramidal cluster units to supplement the 15 skeletal electrons supplied by the five CH units, giving each *nido* cluster the requisite total of 16 electrons. This treatment is thus very

Table 12 Classification of Metal–Hydrocarbon π-Complexes, Aromatic Systems and Various Hydrocarbons as Carborane-type Clusters

Fundamental polyhedron	*b*	*closo species* ($a = b - 1$)	*Ref.*	*nido species* ($a = b - 2$)	*Ref.*	*arachno species* ($a = b - 3$)	*Ref.*
Trigonal bipyramid	6	$(CPh)_2\{Fe(CO)_3\}_3$	135	$(CPh)_2\{Co(CO)_3\}_2$	136	$(CH_2)_2Pt(PPh_3)_3$	—
				$(CPh)_2(NiCp)_2$	137	$(CH_2)_3$	—
				tetrahedrane	—		
Octahedron	7	$(CEt)_2Co_4(CO)_{10}$	138	$(CPh)_4CoCp$	139	(π-allyl)$Co(CO)_3$	—
				$C_5H_5^+$	140–145	C_4H_6 (bicyclobutane), $C_4H_4^{2-}$	—
Pentagonal bipyramid	8	$(CPh)_4Fe_3(CO)_8$	146	CpBeMe	109	$(\eta^4\text{-}CH_2{=}CHCH{=}CH_2)\text{-}Fe(CO)_3$	—
				$CpMn(CO)_3$	147	$C_5H_5^-$	—
				$C_6Me_6^{2+}$	148		
				$(\eta^5\text{-}C_5Me_5)BI^+$	149		
Hexagonal bipyramid	9	—	—	$(\eta^6\text{-}C_6H_6)_2Cr$	150	benzene	—
D_{2d} dodecahedron	9	—	—	—	—	benzvalene; $Me_2Al(\eta^3\text{-}C_5H_5)$	108
Heptagonal bipyramid	10	—	—	$(\eta^7\text{-}C_7H_7)V(CO)_3$	151	$C_7H_7^+$	—

a = number of skeletal atoms. b = number of skeletal bond pairs.

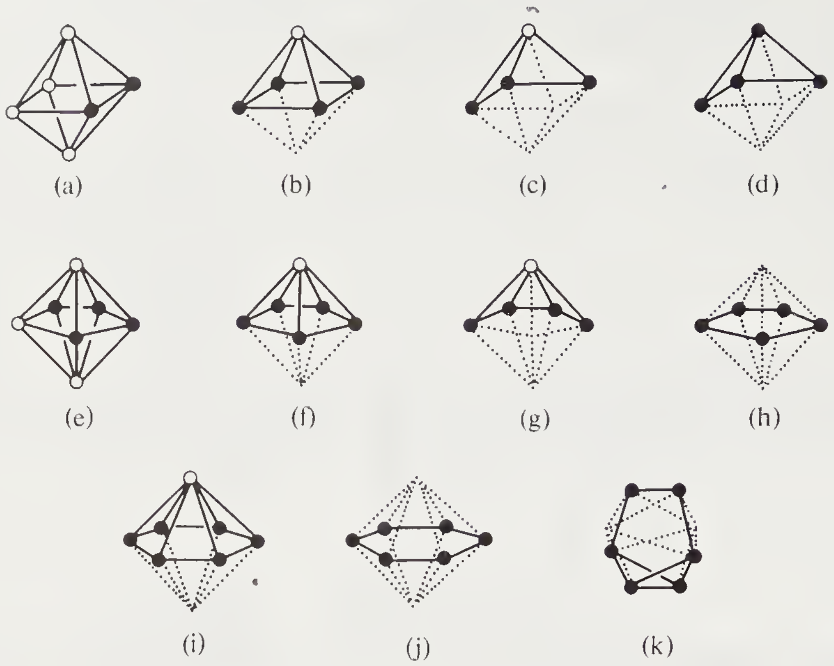


Figure 31 The polyhedral skeletal shapes of some metal–hydrocarbon π-complexes, and of some hydrocarbons, showing their relationship to boranes and carboranes: (a) *closo* $C_2Et_2Co_4(CO)_{10}$; (b) *nido* $(\eta^4\text{-}C_4Ph_4)Fe(CO)_3$; (c) *arachno* $(\eta^3\text{-allyl})Co(CO)_3$; (d) *arachno* C_4H_6 (bicyclobutane); (e) *closo* $(CPh)_4Fe_3(CO)_8$; (f) *nido* $(\eta^5\text{-}C_5H_5)Mn(CO)_3$; (g) *arachno* $(\eta^4\text{-}CH_2CHCHCH_2)Fe(CO)_3$; (h) *arachno* $[C_5H_5]^-$; (i) *nido* $(\eta^6\text{-}C_6H_6)Cr(CO)_3$; (j) *arachno* C_6H_6 (benzene); (k) *arachno* C_6H_6 (benzvalene). Open circles represent metal atoms; filled circles represent carbon atoms; substituents are not shown

similar to the description of ferrocene as $C_5H_5^-Fe^{2+}C_5H_5^-$ for the purpose of electron counting, though this should not be taken to imply that the metal–ligand bonding is ionic: the Fe^{2+} cation uses its six vacant orbitals to bond strongly to the π-electrons of the two aromatic rings.

Other systems worth noting are the carbocations $C_5H_5^+$[140–145] and $C_6Me_6^{2+}$,[148] whose pyramidal shapes are those appropriate for *nido* sets of n CH (or CMe) units held together by $(n + 2)$ bond pairs; the butterfly shape of bicyclobutane, C_4H_6 (*cf.* B_4H_{10}); and the manner in which benzvalene, C_6H_6, has an *arachno* shape clearly relatable to the dodecahedron of $B_8H_8^{2-}$, with two highly coordinated vertices left vacant.[12] Further examples that illustrate the close family relationships between carboranes, metallacarboranes, metal–hydrocarbon π-complexes and neutral and ionic hydrocarbons are to be found in refs. 11, 12 and 134–152.

1.6.6 Relationship to Other Cluster Systems

In the previous section we considered the relationship of carboranes and metallacarboranes with metal–hydrocarbon π-complexes and with various other organic systems, all containing one or more skeletal carbon atoms. That boron and/or carbon atoms are not essential constituents of clusters with carborane-type structures and electron numbers has been amply demonstrated in two other areas of cluster chemistry worthy of brief mention here, *viz.* in transition metal carbonyl cluster chemistry, and in clusters of the heavier metals of Main Groups IV and V.

From Tables 8–11 it is apparent that the BH units of boranes or carboranes can in principle be replaced by such units as $M(CO)_3$ (M = Fe, Ru or Os), $M(\eta^5\text{-}C_5H_5)$ (M = Co, Rh or Ir), $Ni(PR_3)_2$, Ge, Sn or Pb, each of which can act as a source of three AOs and two electrons for skeletal bonding, while the CH units of carboranes can be replaced by such units as $Co(CO)_3$, $Ni(\eta^5\text{-}C_5H_5)$, As, Sb or Bi. Complete replacement of all the BH and CH groups of carboranes by such metal atom units would thus lead to metal clusters of predictable shapes. For example, similar structures to the *closo* polyhedra of the borane anions $B_nH_n^{2-}$ might be expected for hypothetical metal carbonyl cluster anions $[M_n(CO)_{3n}]^{2-}$ (M = Fe, Ru or Os) or isoelectronic species $H_2M_n(CO)_{3n}$ or $M_n(CO)_{3n+1}$, for mixed metal carbonyl clusters $M'_2M''_{n-2}(CO)_{3n+1}$ (M′ = Co, Rh or Ir; M″ = Fe, Ru or Os), or for anionic clusters M_n^{2-} of the Group IV metals Ge, Sn or Pb.

Most known metal carbonyl clusters[153] are tri- or tetra-nuclear species $M_3(CO)_x$, $M_4(CO)_y$, *etc.*, for which analogies with borane systems are of little value. However, there is an increasing number of clusters of rather higher nuclearity for which analogy with boranes has proved helpful in understanding their structures.[154] Early examples included the compounds $H_2Ru_6(CO)_{18}$,[155] $Rh_6(CO)_{16}$[156] and $Ru_6C(CO)_{17}$ (Figure 32b),[157] each of which has a total of 86 valence shell electrons associated with its six metal atoms, which are located at the vertices of an octahedron. Localized two-centre bond descriptions of these clusters are unsatisfactory; they contain two electrons too many to allow each metal atom to form four skeletal bonds, one along each octahedral edge. However, if each metal atom is assumed to form three skeletal bonds (in MO terms, to contribute three AOs to the skeletal basis set), then these octahedral systems would be classified as six-atom, seven-bond pair *closo* clusters (*cf.* $C_2B_4H_6$). Many further 86-electron octahedral metal carbonyl clusters are known.[125,154,158]

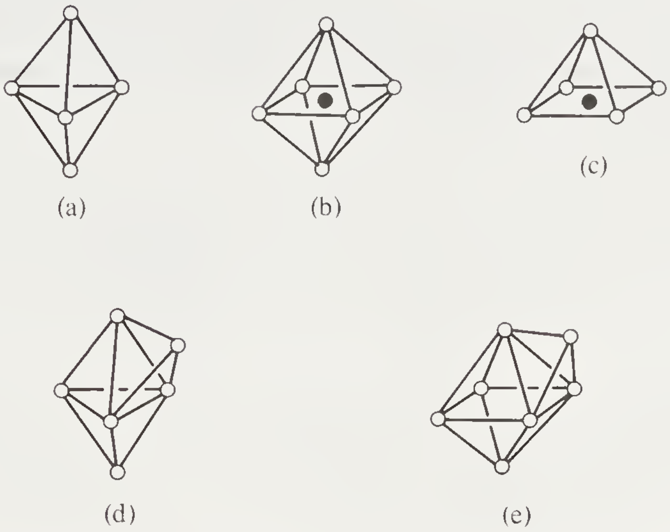

(a) (b) (c) (d) (e)

Figure 32 The skeletal shapes of some metal clusters formally related to carboranes and boranes: (a) *closo* Sn_5^{2-}, $Os_5(CO)_{16}$ (*cf.* $C_2B_3H_5$); (b) *closo* $Ru_6C(CO)_{17}$ (*cf.* $C_2B_4H_6$); (c) *nido* $Fe_5C(CO)_{15}$ (*cf.* B_5H_9); (d) capped *closo* $Os_6(CO)_{18}$; (e) capped *closo* $[Rh_7(CO)_{16}]^{3-}$

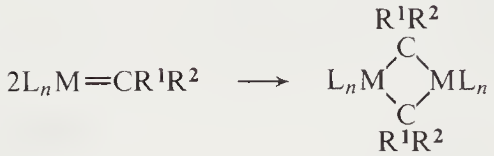
The *closo* trigonal bipyramidal structures of the osmium carbonyl clusters $Os_5(CO)_{16}$ (Figure 32a)[159] and $HOs_5(CO)_{15}^-$[160,161] (formally five-atom six-bond pair clusters related to $C_2B_3H_5$) and *nido* square pyramidal structures of the iron group carbonyl carbides $M_5(CO)_{15}C$[162,163] (formal analogues of B_5H_9) provide further examples of the relevance of the carborane structural pattern to metal carbonyl cluster chemistry. There are, however, many metal carbonyl clusters with no carborane counterparts, including series of n-atom, n-bond pair clusters with capped polyhedral structures; their skeletons are based on polyhedra with $(n-1)$ vertices, as would be expected from the electron count. The extra metal atom caps a triangular face where it can use spare metal electrons. Comparable capping of the faces of carborane polyhedra is unlikely, since their carbon and boron atoms, unlike the metal atoms of metal carbonyl clusters, have no spare electrons with which to bond to a capping atom. Examples include $Os_6(CO)_{18}$, which has a capped trigonal bipyramidal structure,[164] and $Os_7(CO)_{21}$, with a capped octahedral structure.[165] More detailed discussion of such systems is to be found in refs. 12, 125, 153, 154 and 158 and references cited therein.

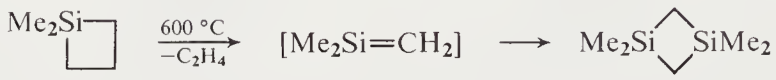
A more direct analogy with carboranes is to be found in the cluster chemistry of such main group metals as tin, lead and bismuth.[167,168] *Closo* structures have been found for anionic tin and lead clusters of general formula M_n^{2-}[167] (*cf.* $B_nH_n^{2-}$) and for certain cationic bismuth clusters exemplified by the trigonal bipyramidal Bi_5^{3+},[168] while *nido* structures appear likely for clusters M_n^{4-} (M = Ge, Sn or Pb). Such systems are as yet less readily accessible than their carborane counterparts, so few have been isolated and characterized. However, here, as in metal carbonyl cluster chemistry, analogies with carboranes and metallacarboranes have stimulated the development of new synthetic methods as well as providing the basis for the rationalization of structures. Carboranes and metallacarboranes appear likely to occupy a focal point in cluster chemistry in future.

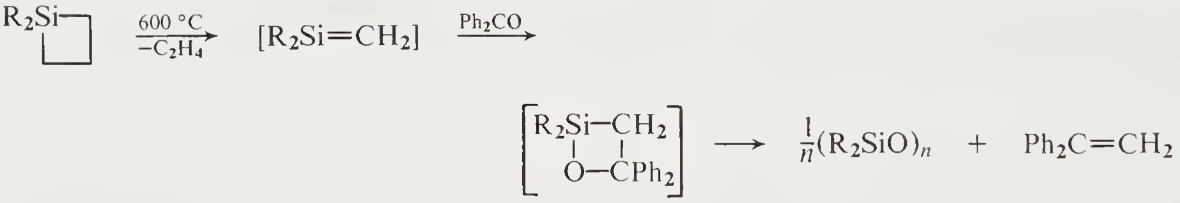
1.7 COMPOUNDS CONTAINING METAL–CARBON MULTIPLE BONDS

1.7.1 Carbene Complexes

Complexes containing carbene units CR^1R^2 terminally attached to main group metal atoms are far rarer than their transition metal counterparts. They are unknown among derivatives of metals and metalloids of Groups I–IV except as short-lived species. This is because they are thermodynamically much less stable than associated structures in which the M=C double bonds of the carbene complexes are replaced by pairs of M—C single bonds, and there is normally no significant kinetic barrier to the association reaction shown in equation (12). For example, pyrolysis of 1,1-dimethylsilacyclobutane generates 1,1,3,3-tetramethyldisilacyclobutane in a reaction believed to involve the methylene derivative $Me_2Si{=}CH_2$ as an intermediate (equation 13).[169,170] The same intermediate is believed to feature in the gas-phase thermal decomposition reactions of Me_3SiH,[171] $Me_3SiSiMe_3$[172] and Me_4Si.[173] Its reactions reflect a strong polarity of the $Si^{\delta+}{=}CH_2{}^{\delta-}$ bond, *e.g.* equation (14).[174] That the methylene complex has a singlet, π-bonded electronic configuration rather than a triplet diradical structure $Me_2\dot{S}i—\dot{C}H_2$ is supported by the rate at which it is evidently formed in such pyrolysis reactions, and by the type of reaction it undergoes with trichlorosilane $SiHCl_3$, when it attacks the Si—Cl bonds (the most polar) rather than the Si—H bond (the weakest).[175]


(12)


(13)


(14)

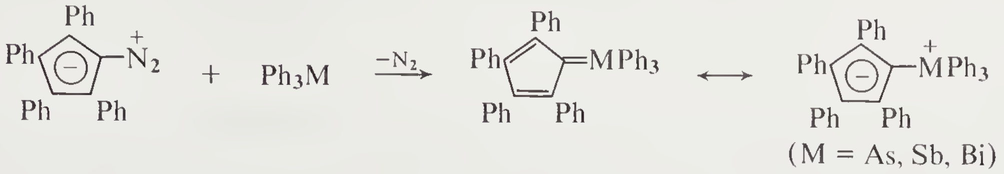
The energy of the Si=C double bond in $Me_2Si{=}CH_2$ is believed to exceed that of the Si—C single bonds by only *ca.* 150 kJ mol^{-1}.[176] Even smaller differences are expected between the M=C and M—C bond energies of germanium, tin and lead. In view of this, the preparation of compounds $R_2M{=}CR'_2$ (M = Si, Ge, Sn or Pb) that are stable in the condensed phase appears unlikely unless the substituents R and R′ are so very bulky as to prevent dimerization.

A different situation obtains with the Group V metals arsenic, antimony and bismuth, all of which are known to be capable of forming carbene complexes in the form of ylides, $R_3MCR'_2$. Though less readily accessible and thoroughly documented than their phosphorus analogues $R_3PCR'_2$ (Wittig reagents), many such arsenic compounds have been prepared and characterized.[177] The compound Me_3AsCH_2, for example, has been synthesized by the sequence of reactions shown in equation (15). Judging by their ^1H NMR spectra (the methylene protons absorb at very high field) and their Lewis base character (the methylene carbon is readily protonated[178] or attacked by other Lewis acids MX_n, which form adducts $R_3AsCH_2MX_n$), the As=C double bonds of derivatives R_3AsCH_2 are highly polar, better represented by the canonical form $R_3\overset{+}{A}s—\overset{-}{C}H_2$ than by the form $R_3As{=}CH_2$, though this should not be taken to imply non-planarity at the

$$Me_3As \xrightarrow[120\ °C]{ClCH_2SiMe_3} [Me_3AsCH_2SiMe_3]^+Cl^- \xrightarrow[-LiCl,\ BuH]{LiBu^n}$$

$$Me_3AsCHSiMe_3 \xrightarrow[-(Me_3Si)_2O]{Me_3SiOH} Me_3AsCH_2 \qquad (15)$$

methylene carbon atom. An ylide structure appears likely for the tetraphenylcyclopentadiene derivative $Ph_3AsC_5Ph_4$ and its antimony and bismuth analogues (equation 16).[179]

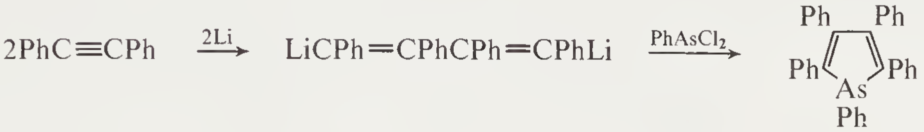


(16)

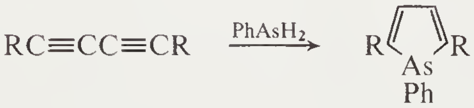
1.7.2 Unsaturated Ring Systems with Metal–Carbon Multiple Bonding

Opportunities for metal–carbon multiple bonding involving arsenic, antimony and bismuth also arise when these metals are incorporated in five- or six-membered ring systems related to pyrrole and pyridine. Most attention has been paid to the arsenic compounds, the arsoles (or arsenoles, analogues of pyrroles) and arsenins (or arsabenzenes, analogues of pyridine).[180]

Arsoles can be prepared from dienes or diynes as shown in equations (17) and (18).[181,182] They contain planar AsC_4 rings but have pyramidal coordination at arsenic,[183] implying localization of the arsenic lone pair electrons on the metal atom rather than the delocalization expected if arsoles were aromatic. However, the barrier to inversion is some 40–60 kJ mol^{-1} lower than that of normal tertiary arsines R_3As, suggesting that there is some stabilization of the planar transition state.[184] Photoelectron spectroscopic studies on 1-phenyl-2,5-dimethylarsole support a localized diene structure, with little interaction between the arsole and phenyl rings.[185]

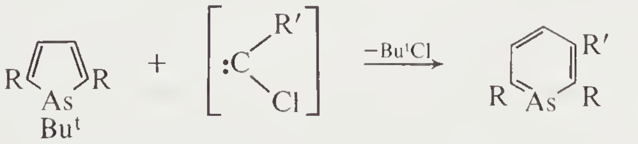


(17)

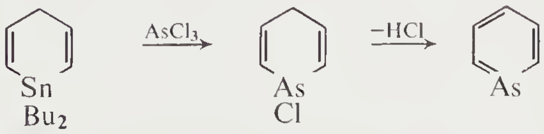


(18)

Arsenins can be prepared by the insertion of carbenes into arsoles, *e.g.* equation (19).[186] The parent compound is accessible by the reaction sequence[187] shown in equation (20). The less stable antimony analogue can be prepared similarly from $SbCl_3$. Arsenin is a colourless air-sensitive compound whose photoelectron, UV and NMR spectra are consistent with an aromatic structure (*cf.* pyridine),[188] which is supported by theoretical treatments.[188–190] Structural evidence of aromaticity has come from a study of the 2,3,6-triphenyl derivative $AsC_5H_2Ph_3$, which contains a planar AsC_5 ring, with ring interatomic distances of 187 (As—C) and 141 pm (C—C) (*cf.* 196 pm for a typical As—C single bond).[191]

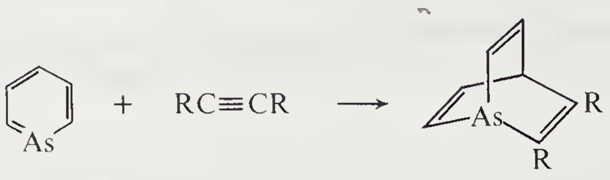


(19)



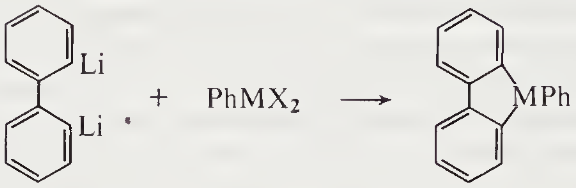
(20)

The ready reactions of arsenins with alkynes or benzyne to form arsabarrelenes reflect in part the greater energy of three As—C single bonds than of two As$\overset{\cdots}{=}$C bonds of order 1.5 (equation 21).[192,193] A preference to form single bonds (to other arsenic atoms) rather than multiple bonds to carbon is also apparent from the spontaneous dimerization reactions shown by arsaanthracenes.[194–197]



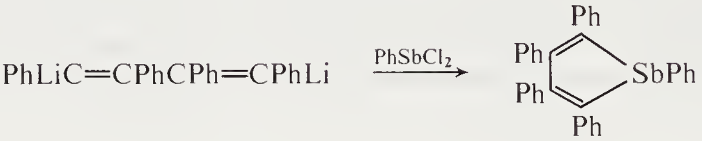
(21)

Antimony and bismuth heterocycles analogous to the above arsenic compounds have been prepared by similar reactions, *e.g.* equations (22)–(24).[181,198] Like the analogous arsoles, the five-membered antimony and bismuth ring systems react as dienes, with negligible aromatic character, while multiple $M\overset{\cdots}{-}C$ bonding in the six-membered rings is evidently weak.[192]

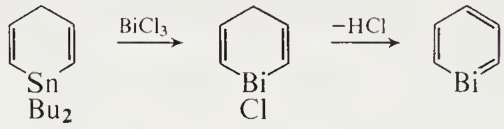


(22)

M = Sb, Bi



(23)



(24)

1.8 CONCLUSION

The intention of this survey has been to note the various types of metal–carbon links found among main group organometallic systems, and to discuss their bonding implications. The commonest type of link, the metal–carbon single bond, has received but scant attention here because it poses no particular bonding problem. However, it was noted how its polarity and strength[6,14] varied systematically with thc position of the element in the Periodic Table, and how these variations, considered in conjunction with the electronic configuration of the metal (whether it was coordinatively saturated, or possessed spare orbitals or electrons), allowed one to rationalize such matters as the ease of preparation of specific compounds and their thermal or oxidative stability and reactivity.[5,7]

Particular attention has been paid here to systems commonly referred to as electron deficient,[11] in which sets of atoms are held together by fewer electrons than would be needed to allocate a pair to each two-centre link. The development of our understanding of such systems has been due in the main to work on organometallic systems, supplemented by work on boranes, to which organometallic systems are anyway closely related. The three- or four-centre bridge bonds used to describe the associated structures of certain metal alkyls show how spare orbitals can be made good use of when few electrons are available, and provide models for the bonding arrangements possible when atoms or groups are transferred from one site to another during reactions in areas that may be quite remote from organometallic chemistry.

The concept of multicentre bonding was also seen to be particularly helpful in understanding the bonding interactions that can occur between certain metals and unsaturated hydrocarbons, interactions that main group metals in general indulge in less effectively than transition metals because they lack the spare electrons the latter can use for back π-bonding to unsaturated ligands. The polyhedral structures of carboranes[9] and metallacarboranes[10] can also be rationalized in terms of two- and three-centre bonds, though a generally more helpful overall picture of their bonding is obtained if one focuses attention on the total number of electrons that occupy their delocalized skeletal orbitals, rather than on the details of the precise distribution of these electrons.[12] This approach incidentally facilitates the comparison of carboranes with various other cluster and ring systems, illustrating their three-dimensional aromatic nature, and enabling these one-time chemical rule-breakers to be seen now as pattern-makers for a sizeable and rapidly developing area of chemistry, shedding useful light on such apparently diverse topics as the structure, bonding and reactions of nonclassical carbocations, the synthesis and structures of new metal clusters, and the interactions between unsaturated molecules and metal clusters or metal surfaces. Elaboration of these themes will be found in several subsequent chapters in the present work.

In contrast to these many and varied electron deficient organometallic systems, species containing multiple metal–carbon bonds are relatively rare in main group organometallic chemistry, because they make less effective use of the available orbitals than do associated singly bonded structures. They have accordingly been dealt with only briefly here.

In concentrating almost exclusively on the bonding in systems whose structures have been established by X-ray crystallographic methods, we have hardly touched on the rapidly accumulating literature concerned with the structures and bonding of hypothetical organometallic systems. Theoretical calculations on various hypothetical systems have already drawn attention to such fascinating subjects as the novel atom arrangements that appear possible for molecules Li_xC_y, the probable influence of metal substituents on the structures and bonding of carbocations, and the striking structural and bonding consequences of permetallating certain simple unsaturated hydrocarbons.[199–204] Such subjects are only just beginning to attract experimental attention,[205–207] and no structural information is yet available. However, they appear likely to feature as areas of substantial experimental as well as theoretical work in future editions of the present set of volumes.

Acknowledgement. This chapter draws substantially on material and approaches from refs. 5–12, 125, 154 and 158 and notably those of G. E. Coates,[1,2,5,8] whose own writings brought helpful order to organometallic chemistry during its explosive growth.

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2

Alkali Metals

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2.1 INTRODUCTION

2.1.1 Literature

There are a number of pertinent reviews and books on aspects of the chemistry of organoalkali metal compounds. General consideration is given in a volume in the Houben-Weyl series,[1] a book by Schlösser entitled ‘Polare Organometalle’,[2] and a chapter in the Coates, Green and Wade book on ‘Organometallic Compounds’.[3] General aspects of organolithium compounds are exclusively featured in a book by Wakefield,[4] published in 1974, while earlier reviews by Schlosser in 1964 are concerned with sodium and potassium compounds.[5] Polyamine-chelated alkali metal compounds featured in a volume of the American Chemical Society series, ‘Advances in Chemistry’;[6] topics included preparation, properties, structures and applications as metallating agents.

Metallations by organo-lithium[7] and -sodium[8] have also been reviewed. Earlier reviews on preparations of organolithiums by Gilman and coworkers are also highly recommended.[9] Heteroatom substituted organolithiums featured in other reviews.[10] Structures have featured in a number of reviews by Brown[11] and one by Oliver.[12]

The methyl derivatives were included in a general survey of the chemistry of methyl organometallics.[13]

Considerations of the effects of ion pairing in carbanionic, including aromatic radical anion and dianion, species have also been presented.[14,15]

Finally, annual surveys of the literature appear in the series ‘Organometallic Chemistry’[16] and in the *Journal of Organometallic Chemistry*.[17]

2.1.2 Trends in the Properties of the Elements

These are given in Table 1.

Table 1 Trends in Some Selected Properties of the Alkali Metals

Metal	*Electronic configuration*	*Electro-negativity*[a]	*I.p.* (eV)[b]	*Covalent*[b] *radii* (Å)	*Ionic*[b] *radii* (Å)
Li	[He]2*s*	0.97	5.390	1.35	0.60
Na	[Ne]3*s*	1.01	5.138	1.54	0.95
K	[Ar]4*s*	0.91	4.339	1.96	1.33
Rb	[Kr]5*s*	0.89	4.176	2.11	1.48
Cs	[Xe]6*s*	0.86	3.893	2.25	1.69

[a] Allred–Rochow scale. [b] Data published by E. H. Sargeant and Co., Chicago.

2.2 GENERAL CONSIDERATIONS

2.2.1 Structures and Bonding

These are specifically discussed in the appropriate section for each type of compound considered. In general, alkyl- and aryl-lithium compounds can exist[4] as aggregates in the solid state, in solution and in the gas phase, aggregation decreasing with size of the organic group and in stronger solvating media. The analogous alkali metal compounds are also aggregated[5] in solution; fewer crystal structures have been determined and as they have negligible vapour pressure, no vapour phase studies have been performed. Polymetallated[6] species, *e.g.* C_5Li_4 and CLi_4, are known. The methyl derivatives of potassium, rubidium and caesium have an ionic structure (nickel arsenide type)[19] in the solid state, whereas tetrameric methyllithium[20] is adjudged in the majority view to be an electron deficient compound with methyl groups bridging lithium atoms. (Less details have been presented for methylsodium, but it was considered to be similar to methyllium.) Other bridging groups have been recognized (see Section 2.4.1). There is some difference of opinion regarding the bonding in organolithium compounds. In one corner there is the view (that of Streitwieser) that the carbon–lithium bond is an essentially ionic bond and that, for example, the strucure (methyllithium)$_4$ comprises[21] interpenetrating tetrahedra of methyl anions and lithium cations. The proponents of the other view, headed ny Schleyer[22] and co-workers, emphasize the multicentred covalent nature of lithium bonding (with of course some partial ionic or polar character). Such multicentred bonding utilizes the lithium 2*p*-orbitals. However, Schleyer,[22] while preferring his model, has also indicated that the general features of compounds, even compounds such as $C_3H_{4-n}Li_n$, the lithiated derivatives of propyne, and also $(CH_2Li_2)_2$ can be arrived at using an ionic model. Ionic bonding in methyllithium suggests interaction of CH_3^- with Li^+. A totally ionic structure for CLi_4, *i.e.* C^{4-} and four Li^+, appears most unlikely; back donation of electron density lithium would result in CLi_4 being more covalent than CH_3Li.

For delocalized carbanionic systems,[14,15] *e.g.* benzylic and allylic species as well as the radical anions and dianions, ion pairs exist in the ethereal, hydrocarbon and other media normally employed. The ion pairing of R^-,M^+ in most cases can be divided into two categories: (i) contact or tight ion pairs (t.i.p.) with essentially one solvent shell around the RM unit; and (ii) solvent separated ion pairs (s.s.i.p.) in which some solvent molecules have penetrated between R^- and M^+. These can be considered as stages along the pathway from a covalently bonded compound to free ions (equation 1). Normally in the solvents employed and at the concentrations of RM used, especially for NMR studies, free ions can be ignored. However, aggregates may play a role.

$$\mathrm{R{-}M} \rightleftharpoons \underset{\text{t.i.p.}}{\mathrm{R^-,M^+}} \rightleftharpoons \underset{\text{s.s.i.p.}}{\mathrm{R^-\|M^+}} \rightleftharpoons \underset{\text{free ions}}{\mathrm{R^- \; + \; M^+}} \qquad (1)$$

Structures in solution have been investigated by a variety of spectroscopic techniques; UV, IR and NMR (including ^{7}Li NMR)[18] have most frequently been employed.

2.2.2 Stability

2.2.2.1 Configurational stability

Configurationally rigid *sp*^{3}-hybridized alkyl alkali metal compounds and vinylic-lithiums are known. These are discussed in Sections 2.4.2.5 and 2.6.3. Reactions with proton sources, carbon dioxide and alkylating agents normally proceed with predominant retention of configuration, whereas halogens lead to inversion.

2.2.2.2 Thermal decomposition

Thermal[23,24] decomposition of organoalkali metal compounds may occur *via* α- and preferably β-elimination modes (equations 2 and 3). The possibility of radical involvement has been mainly rejected except for potassium and sodium compounds. Ease of decomposition has been found to be potassium > sodium $\geq$ lithium. Thermal decompositions of $CH_3CHCH(CH_3)Li$ and crotyllithium,[25] $CH_3CH{\cdots}\overset{-}{C}H{\cdots}CH_2,Li^+$, both provide mixtures of butene and *cis*- and *trans*-but-2-enes. More involved thermal reactions occur with the methyl derivatives; solvent-free methyllithium gives CH_4 and CH_2Li_2 at 250 °C; at higher temperatures, $LiC{\equiv}CLi$, LiH and Li are obtained. At −25 °C methyl-sodium and -potassium also provide dimetallated ethyne.[23] Phenyl-lithium and -sodium also provide dimetallated species.[23]

$$BuLi \xrightarrow[\text{octane}]{\text{boiling}} \underset{95\%}{CH_3CH_2CH{=}CH_2} + \underset{5\%}{BuH} + LiH \qquad (2)$$

$$CH_3CH_2Na \xrightarrow{90\ ^\circ C} CH_2{=}CH_2 + NaH \qquad (3)$$

Perfluoroalkyllithiums readily thermally decompose by β-LiF elimination; perfluoroneopentyllithium, $(CF_3)_3CCF_2Li$, having no β-fluorines, is more stable and only decomposes near 0 °C *via* an α-elimination process.[26]

Synthetically useful carbenoids, $RR'C(M)X$ (X = halogen), and arynoids, *e.g.* *o*-MC_6H_4X, eliminate MX by α- and β-processes, respectively, to give carbene, CRR', and benzyne derived products. These decompositions have been extensively studied.[27]

2.2.2.3 Oxidative stability[28]

All organoalkali metal compounds are highly reactive towards oxygen and hence all traces of oxygen should be excluded. Methyl, ethyl and phenyl derivatives actually ignite in air. In general, potassium and sodium compounds are more easily oxidized than the lithium analogues. A simple two-step scheme fits the findings for alkyl compounds, *e.g.* Scheme 1. $(BuLi)_4$ in Et_2O at − 78 °C gave BuOOH, while in benzene, $(BuLi)_6$ provided BuOH, both after hydrolysis. The products normally obtained are alcohols. However, the mechanism of step (i), the formation of the hydroperoxide salt, is a complex one, especially as the organoalkali metal compounds can exist as aggregates. A number of proposals have been considered, *e.g.* radical chain mechanisms in which the radicals $R\cdot$ or $R_nM_n^{\,\dot{+}}$ are chain carriers (Scheme 2).

$$RM + O_2 \xrightarrow{\text{i}} RO_2M$$

$$RO_2M + RM \xrightarrow{\text{ii}} 2ROM$$

Scheme 1

$$R_nM_n + O_2 \longrightarrow O_2^{\,\dot{-}} + R_nM_n^{\,\dot{+}}\ (\text{or } R\cdot + R_{n-1}M_n^{\,\dot{+}})$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot \xrightarrow{R_nM_n} (RO_2)R_{n-1}M_n + R\cdot$$

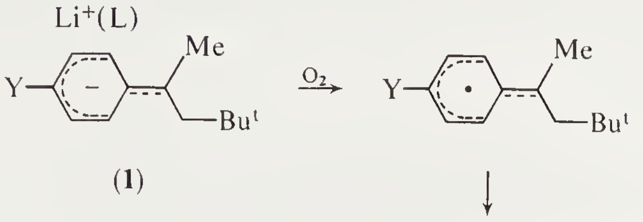
$$R_nM_n^{\,\dot{+}} + O_2 \longrightarrow RO_2\cdot + R_{n-1}M_n^{+}$$

$$RO_2\cdot + R_nM_n \longrightarrow RO_2^{-} + R_nM_n^{\,\dot{+}}$$

$$RO_2^{-} + R_{n-1}M_n^{+} \longrightarrow (RO_2)R_{n-1}M_n$$

Scheme 2

Clearly the stability of the radical species and the reaction conditions are of paramount importance. Evidence for radical intermediates has been found in a number of studies, *e.g.* (i) oxidation of neophyllithium, $PhCMe_2CH_2Li$ (tetrameric in paraffin solutions), provides some $HOCMe_2CH_2Ph$, due to the intermediacy of $\cdot CMe_2CH_2Ph$, formed by phenyl migration in the primary radical $PhCMe_2CH\cdot$; of interest is that the rearranged alcohol is suppressed in Et_2O, in which dimers of $PhCMe_2CH_2Li$ exist;[29] (ii) oxidation of the monomeric complexed s.s.i.p. *t*-benzylic species (**1**) at −30 °C yields an alkene and an alkane, disproportionation products of the intermediate radical (Scheme 3);[30] (iii) oxidation of diphenylmethylsodium (equation 4);[28b] and (iv) oxidation of 1-alkenyllithiums at −78 °C, which provides lithium enolates with partial loss of stereochemistry;[31] step (iii) was shown to proceed with retention of configuration (Scheme 4).



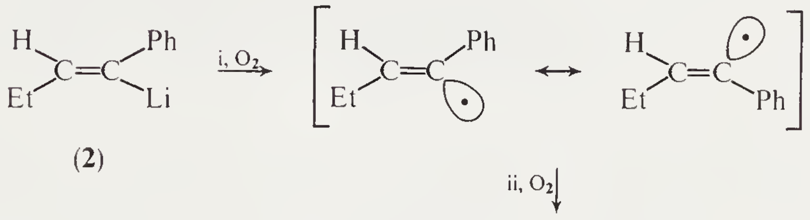
(**1**)

p-$YC_6H_4C(Bu^t){=}CH_2$ +

p-$YC_6H_4CBu^tMeH$

Scheme 3

$$2Ph_2CHNa + O_2 \xrightarrow{\text{liquid } NH_3} Na_2O_2 + Ph_2CHCHPh_2 \qquad (4)$$



(**2**)

$$(Z)\text{- and }(E)\text{-EtCH=CPh(OLi)} \xleftarrow[\text{retention}]{\text{iii, (2)}} (Z)\text{- and }(E)\text{-EtCH=CPh}(O_2Li)$$

Scheme 4

Electrochemical oxidation potentials of various organolithiums in THF and THF/HMPT have been measured by cyclic voltammetry. Some dependencies on the temperature and amount of HMPT were noticed, *e.g.* as the temperature and amount of HMPT were increased, so E_p became more negative. Values in volts *vs.* SCE were: Ph_3CLi (−1.33), Ph_2CHLi (−1.37), $PhCH_2Li$ (−1.45) and allyllithium (−1.40), all at 25 °C in THF solution; CpLi (−0.37), PhLi (−0.34), $CH_2{=}CHLi$ (−0.57), MeLi (0.72) and BuLi (−1.41), all at −62 °C in 30% HMPT.[32]

2.2.2.4 Protonation and hydrolytic stability

Organoalkali metal compounds, RM, are very readily hydrolyzed and react readily with a variety of proton sources to give the hydrocarbon, RH. Interactions with carbon acids (equation 5), which lead to metal–hydrogen exchanges, are useful preparative routes and are discussed in Section 2.3.2.

$$RM + R'M \rightleftharpoons RH + R'H \qquad (5)$$

Protonation of configurationally rigid organoalkali metal compounds proceeds with retention.

(*i*) *Enthalpies of reaction with proton sources and bond strengths*

Enthalpies of reaction of organolithiums with ethanol[33] (Table 2) and with aqueous HBr[34] (Table 3) have been reported. (The enthalpy of reaction of Bu^tLi with HBr is independent of the medium, indicating a cancelling out of solvation effects on LiBr and the organolithium.) Owing to the differences in aggregations, a detailed discussion of the trends was considered unwarranted. However, the bond strengths, obtained from the enthalpy of reaction data (Table 3), do correlate with the stabilities of the anions, R^-; for the alkyl and aryl derivatives the stronger C—Li bond is found for the more acidic hydrocarbon, RH. For allyl and benzyl, delocalization weakens the lithium–carbon bond. The heat of formation data should be compared with the calculated values of ΔH_1 (at 4-31G/5-21G levels) for the isodesmic reactions (equation 6) from Schleyer and co-workers: ΔH (kJ mol^{-1}) for RLi = $HC{\equiv}CLi$ (−137.5); $CH_2{-}\bar{C}H{-}CH_2,Li^+$ (−97.4), $CH_2{=}CHLi$ (+3.3) and CH_3CH_2Li (20.9); a similar but shorter sequence was constructed by Streitwieser *et al.*[35]

Table 2 Enthalpies of Protonation (ΔH_r) of Organolithiums by Ethanol in Diethyl Ether Solution[33]
$RLi + EtOH \rightarrow RH + EtOLi$

Compound (*RLi*)	ΔH_r (kJ mol^{-}$^{)}$
$(EtLi)_4$	−270.0
$(PhLi)_2$	−246.6
$[Me{-}C(Li){=}CH_2]$[a]	−278.8
$[(E)\text{-}MeCH{=}CHLi]_4$	−217.4
$(CH_2\overset{\cdots}{-}\bar{C}H\overset{\cdots}{-}CH_2,Li^+)_n$[b]	−212.8

[a] Dimers and tetramers. [b] *n* varies from 2 to over 12 as concentration is varied from 0.1 to 1.6 M (based on monomer).

Table 3 Enthalpies[34] of Reaction (ΔH_r) of Organolithiums with Hydrogen Bromide, Enthalpies of Formation of Solvent-free Organolithiums (ΔH_f) and Calculated bond Dissociation Energies
$RLi + HBr(g) \rightarrow RH(l) + LiBr(s)$

Compound	*Medium*	ΔH_r (kJ mol^{-1})	ΔH_f (kJ mol^{-1})	*D*(R—Li) (kJ mol^{-1})
MeLi	ether	−322.3	−74.8	256.7
EtLi	pet. ether[a]	−355.3	−55.2	198.6[b]
Pr^iLi	pet. ether	−359.5	−57.7	179.7
BuLi	ether	−352.4	−109.1[d]	201.5[c]
BuLi	pet. ether	−352.4	—	—
Bu^sLi	pet. ether	−373.7	−87.8	165.5
Bu^tLi	pet. ether	−376.2	−92.0	148.4
$CH_2\overset{\cdots}{-}\bar{C}H\overset{\cdots}{-}CH_2,Li$	pet. ether[a]	−306.8	−5.9	192.7
$PhCH_2Li$	pet. ether[a]	−318.9	17.6	181.0
p-MeC_6H_4Li	pet. ether[a]	−307.2	5.9	—
PhLi	pet. ether[a]	−316.0	51.4	262.9
p-ClC_6H_4Li	pet. ether[a]	−310.2	7.5	—

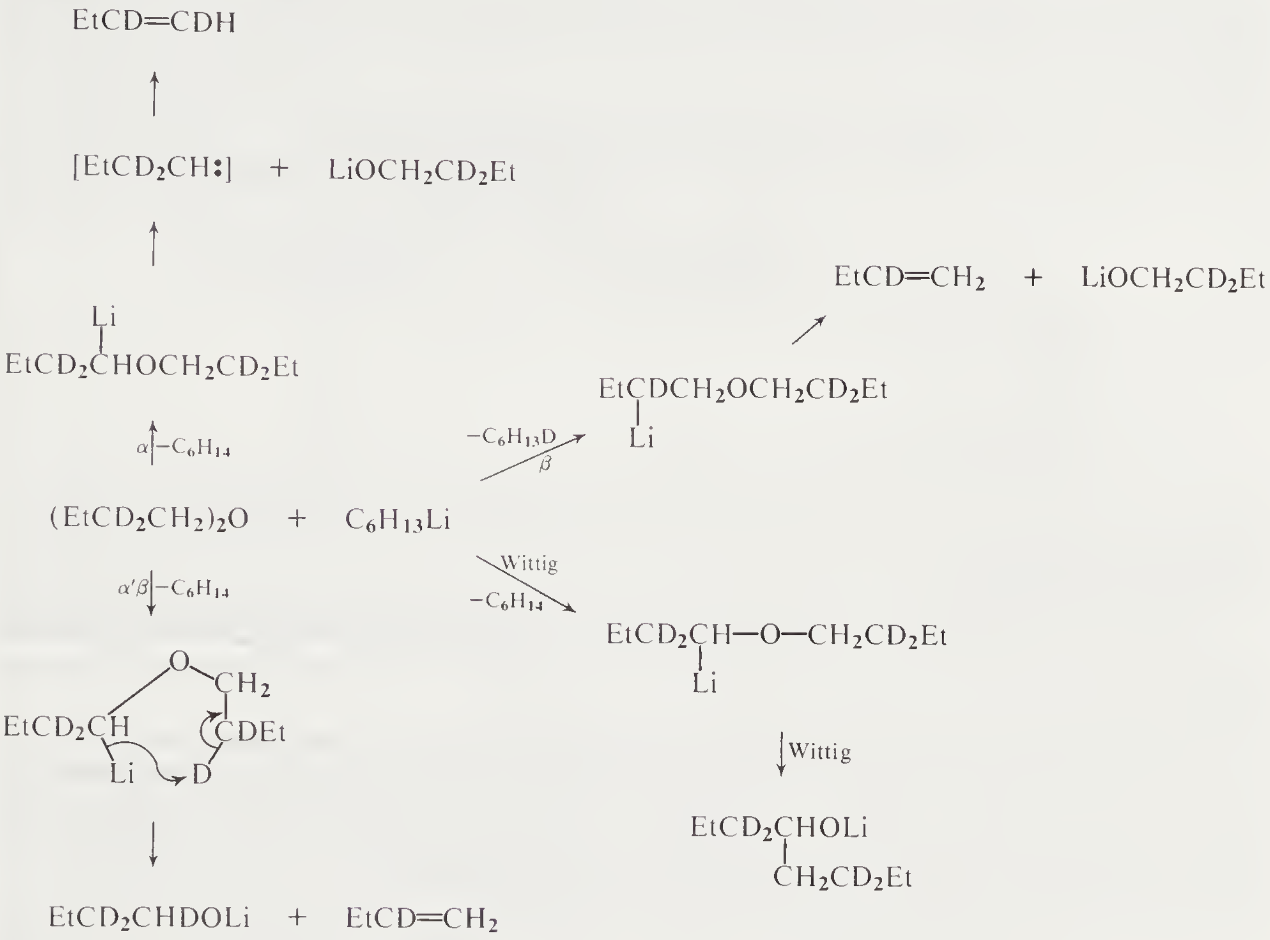
[a] Suspension. [b] 209 ± 10.0. [c] 247.9 ± 12.5 kJ mol^{-1} (H. A. Skinner, *Adv. Organomet. Chem.*, 1964, **3**, 49). [d] −131.3 ± 2.9 kJ mol^{-1} (P. O. Powell and C. T. Mortimer, *J. Chem. Soc.*, 1961, 3793); −133.8 ± 7.1 kJ mol^{-1} (Y. A. Lebedov, E. A. Miroshinchenko and A. M. Chaxin, *Dokl. Akad. Nauk SSSR*, 1962, **145**, 1288).

$$RH \quad + \quad CH_3Li \quad \longrightarrow \quad RLi \quad + \quad CH_4 \tag{6}$$

(*ii*) *Reaction with solvents*

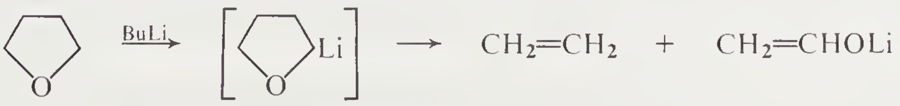
The organoalkali metal compounds have been variously reported to deprotonate solvents, in particular ethers, *e.g.* equation (7). A most elaborate study was undertaken by Maercker[36] to establish the mechanism of the reaction for a number of ethers. Using deuterium labelled ethers, α-, β- and α',β-eliminations were identified, as well as a Wittig rearrangement which becomes important when all the elimination mechanisms become less favoured due to steric hindrance. These modes are illustrated in Scheme 5 for the reaction of $(C_2H_5CD_2CH_2)_2O$ with $C_6H_{13}Li$.

$$Et_2O + RLi \longrightarrow RH + CH_2{=}CH_2 + LiOCH_2CH_3 \qquad (7)$$



Scheme 5 Mechanisms for reaction of $(EtCD_2CH_2)_2O$ with $C_6H_{13}Li$

Tetrahydrofuran is readily cleaved by alkyllithiums,[37] *e.g.* the half-life of *n*-butyllithium in THF at 35 °C is only 10 min. The mechanism involves initial deprotonation at the α-site, followed by a ${}_{\pi}4_s + {}_{\pi}2_s$ symmetry allowed cycloreversion (equation 8). Methyl substitution in the β-position of THF tends to increase the life-time of *n*-butyllithium (*e.g.* $t_{1/2}$ at 35 °C is 70 min for 3,4-Me_2-THF) probably due to the decreasing polarity of the ether. With an α-methyl substituent, deprotonation also occurs in the methyl group. Thus 2-Me-THF provides, in addition to propene and the lithium enolate of acetaldehyde (analogous to equation 8), 2-$LiCH_2$-THF.



(8)

Addition of the eliminated ethylene to the organolithium can also occur to give $R(CH_2CH_2)_nLi$ compounds. Indeed the mixture of reaction products can become most complex, *e.g.* benzyllithium in THF adds to ethylene to give $PhCH_2CH_2CH_2Li$, which subsequently undergoes an intramolecular 1,3-proton shift to $Ph\bar{C}HCH_2CH_3,Li^+$.[38] The latter then can participate in reaction with THF or with $CH_2{=}CH_2$.

These cleavage reactions are general reactions of ethers;[39] in addition to cleavage by organolithiums, cleavage by the other organoalkali metals can result.

The chelating agent TMED is often used with BuLi to provide a more powerful metallating system. However, it too can be metallated in solution by RLi derived from RH having a pK_a value greater than 35, *e.g.* toluene.[40] The stability of RLi–TMED (1 : 1) adducts is relatively good, but this is significantly reduced in the presence of excess TMED.

Reaction of alkyllithiums, but not benzyllithium, with HMPT, another ligand used to enhance the metallating ability, also occurs.[41]

2.2.3 Relative Reactivities of Organolithiums

Sequences of reactivity of organolithiums in various reactions have been obtained; Table 4 provides two examples. In addition, the qualitative sequence vinyl > alkyl > aryl > alkynyl, towards the electrophilic species chlorine, triethylsilyl chloride or acetic acid, has been indicated.[42]

Table 4 Relative Reactivities of Organolithium Reagents[2]

RLi	*Relative Reactivities* *Metallation of Ph_3CH in THF solution at 22 °C*	 *Addition to $PhCH{=}CH_2$ in THF at 20 °C*
$(MeLi)_4$	1	1
$(CH_2{=}CHLi)$	2.5	0.8
$(PhLi)_2$	5.5	1.6
$(BuLi)_4$	13	5.3
$CH_2{\cdots}\bar{C}H{\cdots}CH_2,Li^+$	51	2.0
$(PhCH_2Li)$	250	2.8

2.2.4 Radical Reactions

In addition to reactions with electrophilic species, reactions of organoalkali metals can also occur homolytically,[43] as shown in the reactions with oxygen and also with peroxides,[44] such as $RO{-}OBu^t$.

Reactions with a variety of π-acceptors, such as benzophenone, azobenzene and nitrobenzene, occur by single-electron transfer mechanisms to give anion radicals. In addition, free radical reactions with σ-acceptors, such as alkyl halides, have been recognized either by trapping an intermediate radical, *e.g.* $Bu^t\cdot$ by nitrosobenzene[43] in equation (9), or by detection of CIDNP effects as in the reaction of substituted benzyl halides with butyllithium.[45]

$$BuLi\cdot TMED \quad + \quad Bu^tI \quad \xrightarrow{PhH} \quad [Bu^t\cdot] \quad \xrightarrow{PhNO} \quad Ph(Bu^t)NO\cdot \qquad (9)$$

Reaction of alkyllithiums with titanium(IV) chloride also provides alkyl radicals.[43]

2.2.5 Carbanionic Rearrangements[46]

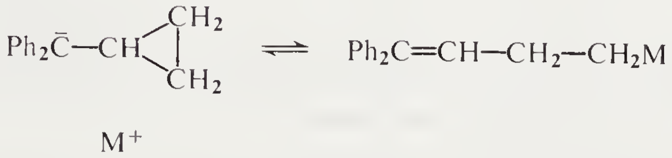
Concerted 1,*n*-sigmatropic migrations of aryl (e.g. 1,2- and 1,4-), vinyl[46] and acetylenic[47] groups can occur in organoalkali metal compounds. Migration of alkyl, benzyl and hydrogen also occurs but only under special circumstances and then may do so by a fragmentation–recombination pathway. Other groups known to migrate in carbanions are the allyl and trimethylsilylmethyl groups.

An example of a 1,2-aryl migration is given in equation (10); the ease of the rearrangement depends markedly on the metal cation, *e.g.* for (**3**), M = Li migrates at 0 °C, for Na and K (in DME) at −50 °C and for Cs at −65 °C, and on the aryl group, *e.g. p*-biphenylyl > phenyl > *p*-tolyl (≫ Me). A bridged ion is considered as a species along the reaction pathway and in some cases it may have sufficient stability, *e.g.* the spiro ion (**4**) is stable to 65 °C, to be characterized by NMR spectroscopy or by derivatization. Generally in THF, lithium of all the alkali metals is best able to stabilize localized open-chain carbanionic species, *e.g.* (**5**; M = Li), whereas the heavier alkali metal cations allow more delocalization of charge in carbanions and so favour the spiro carbanions, *e.g.* (**4**).

$$\underset{(\mathbf{3})}{\mathrm{Ph_3CCH_2M}} \xrightarrow{\mathrm{THF}} \mathrm{PhCH_2\bar{C}Ph_2,M^+} \qquad (10)$$

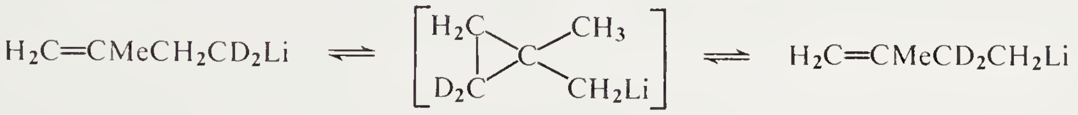
(**5**) (**4**) (11)

The cyclopropylmethyl–homoallyl carbanion interconversion has also been studied.[49] In the cyclopropyldiphenylmethyl–(4,4-diphenyl-3-butenyl) anion system (equilibrium 12), the thermodynamically preferred anion for both potassium and lithium cations in THF is the delocalized cyclopropyldiphenylmethyl anion, in contrast to the localized homoallylic anion for lithium in the poorer solvating medium diethyl ether.



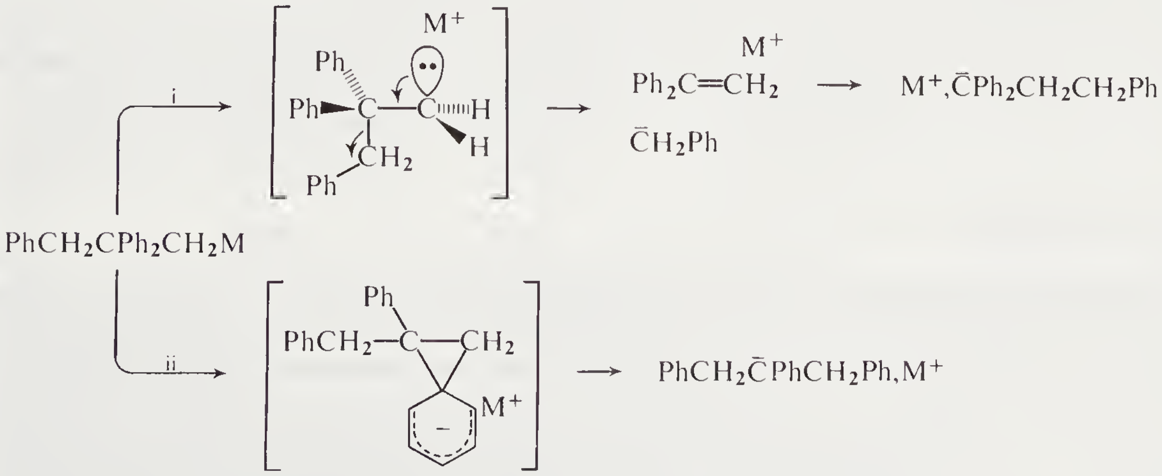
(12)

For the less resonance-stabilized system $H_2C{=}CMeCH_2CD_2Li$, no cyclopropylmethyl product could be obtained. However, scrambling of deuteriums clearly indicated some lifetime, if only a short one, of a cyclopropylmethyl anion on the reaction pathway (equation 13). The rate of deuterium scrambling increases in the solvent order cyclopentane < Et_2O < THF and in the presence of TMED and indicates that s.s.i.p. species are important.



(13)

Two distinct modes of rearrangement occur with $PhCH_2CPh_2CH_2M$: (i) migration of the $PhCH_2$ group in an elimination–addition sequence and (ii) phenyl migration involving a bridged intermediate (Scheme 6). Low temperature, good solvating media, crown ethers and small cations, *i.e.* conditions suitable for s.s.i.p. (see Section 2.5.3.4) favour the benzyl migration. The transition state for benzyl migration must involve well separated negative and positive charges and hence has a strong need for solvation; in the transition state leading to phenyl migration the negative and positive centres are close.[50]



i, M = Li in THF at 0 °C; ii, M = Cs in THF, 65 °C, or M = Cs in THF/crown ether, −75 °C

Scheme 6

2.2.6 Detection, Estimation and Derivatization[51]

A number of colour tests have been devised by Gilman for the estimation of organolithium compounds;[51a] a general test (colour test 1) involves treatment of a solution of the organometallic compound with a solution of $(p\text{-}Me_2NC_6H_4)_2CO$ (Michler's ketone), followed by hydrolysis and reaction with iodine. A blue or green colour would indicate a positive test. Two recent methods of estimation are worthy of attention: these employ titration of the organometallic solution with 2,5-$(MeO)_2C_6H_3CH_2OH$ (colour change: colourless to red)[52a] and $(PhCH_2)_2C{=}CNNHSO_2C_6H_4Me\text{-}p$ (colour change: colourless to orange).[52b]

The position of the metal in an organoalkali metal and also the yields have often been determined by derivatization using carbonation or by trimethylsilylation. Caution has been expressed[53] regarding the use of CO_2/H_2O for the determination of yields of RM since as well as the primary product RCO_2H appreciable yields of ketones R_2CO and alcohols R_3COH may be produced. Thus not all the RM finishes up as RCO_2H, the species normally determined. Concern has also been expressed regarding the use of Me_3SiCl since the trimethylsilyl derivatized product is most prone to metallation by any surviving metallating agent. Use of Me_2SO_4 or D_2O does not suffer from such disadvantages.

2.3 GENERAL FORMATIONS OF ORGANOALKALI METAL COMPOUNDS

2.3.1 From Organic Halides and the Alkali Metals[1,2]

This direct method (equation 14) has proved of particular value for lithium compounds; some examples are listed in Table 5; for the other alkali metals the use is more limited. Various forms of lithium have been used as indicated in the table; in addition, lithium vapours have also been employed (Section 2.3.7). In contrast, for sodium and potassium, finely divided metal, metal dispersions[54] or amalgams with high-speed stirring appear necessary to obtain good yields of the appropriate organometallics.[5]

$$RX + 2M \longrightarrow RM + MX \qquad (14)$$

The most significant drawback to these reactions is coupling of RX to give R—R dimers (the Wurtz coupling). This coupling becomes increasingly easier as the electropositivity of the metal increases and becomes particularly serious for sodium and the heavier alkali metals; it also becomes more important in the halide sequence: chloride, bromide and iodide.

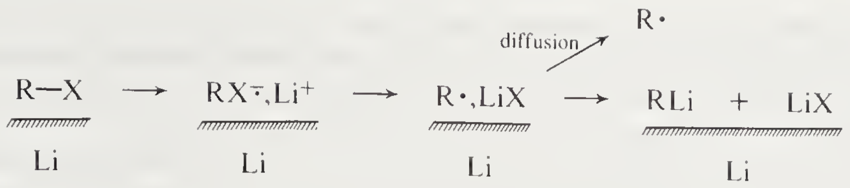
For lithium alkyl, vinyl and aryl compounds, both simple and functionally substituted compounds can be obtained from the organic chlorides and bromides using equation (14). Alkyl iodides, except MeI, are not normally used because of coupling products; however, the less reactive aryl iodides have found use. Coupled products so reduce the value of the reactions of lithium with benzyl and allyl halides that alternative routes have had to be devised.

As shown in Table 5, both ethers and hydrocarbons have been employed as solvents. Compared with organomagnesiums, the organolithiums have much greater solubility in hydrocarbons. Another advantage in the use of hydrocarbon solvents is that RLi can react with ethers.

Some preparations of organo-sodium and -potassium compounds are listed in Table 6.

2.3.1.1 Mechanism

By-products in the reaction of RX have included RR, RH and $(R - H)$, which are highly suggestive of a radical native to the mechanism. Scheme 7 indicates an electron transfer from the Li surface to RX to give the anion radical, $RX^{\overline{\cdot}}$, which decomposes on the metal surface (with the eventually formation of RLi with retention of configuration) or can provide free R, which can diffuse into the bulk of the solution. Thus in the reaction of the fused cyclic compounds 1-diamantyl, 1-twistyl, 1-triptypcyl and 2-adamantyl chlorides with 2% Na/Li alloy in pentane, some RR and RH with the hydrogen being abstracted from the solvent were produced; no alkene was obtained with these particular compounds.[55] The greater the stability of $R\cdot$, the more RH and RR is obtained.



Scheme 7

Table 5 Preparations of Aryl- and Alkyl-lithiums from Organic Halides

Compound	*Organic halides*	*Solvent*	*Conditions*	*Yield* (%)	*Ref.*
MeLi	MeX (X = Cl, Br or I)	Et_2O	Li chips	>80	1
BuLi	BuCl	pentane	Li wire/reflux	93–98	2
		Et_2O	Li chips/reflux	75–80	3
		THF	Li wire/−25 °C	74	4
Me_3CCH_2Li	Me_3CCH_2Cl	Et_2O	Li powder	85	5
Bu^sLi	Bu^sCl	pentane	Li wire/reflux	93–98	2
Bu^tLi	Bu^tCl	pentane	Li dispersion	89	6
Ph_3CLi	Ph_3CCl	THF	Li chips	95	7
Cyclopropyl-Li	cyclopropyl-Br	Et_2O	Li wire/0 °C	88	8
Cyclohexyl-Li	cyclohexyl-Cl	pet. ether	Li shot/reflux	>70	9
$CH_2{=}CHLi$	$CH_2{=}CHCl$	THF	argon 20% Na in Li dispersion	60–65	10
1-Li-cyclohexane	1-cyclohexanyl-Cl	Et_2O	Li chips	60	11
PhLi	PhCl	Et_2O	Li dispersion	>90	12
	PhBr	THF	Li wire/−60 °C	90	13
	PhI	Et_2O	Li chips/reflux	80	1
$Li(CH_2)_4Li$	$Br(CH_2)_4Br$	Et_2O	Li powder/−10 °C	63	14

1. H. Gilman, E. A. Zoellner and W. M. Selby, *J. Am. Chem. Soc.*, 1933, **55**, 1252; E. Müller and D. Ludsteck, *Chem. Ber.*, 1954, **87**, 1887; K. Ziegler, K. Nagel and M. Patheiger, *Z. Anorg. Allg. Chem.*, 1955, **282**, 345.
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4. H. M. Cohen, *J. Organomet. Chem.*, 1967, **9**, 375.
5. H. D. Zook, J. March and D. F. Smith, *J. Am. Chem. Soc.*, 1959, **81**, 1617.
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11. E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 1950, 2014.
12. D. L. Esmay, in 'Metal Organic Compounds', American Chemical Society, Washington, 1959.
13. H. Gilman and B. J. Caj, *J. Org. Chem.*, 1957, **22**, 1165.
14. R. West and E. G. Rochow, *J. Org. Chem.*, 1953, **18**, 1739.

Table 6 Preparations of Organo-sodium and -potassium Compounds from Organic Halides

Compound	*Organic halides*	*Solvent*	*Conditions*	*Yield* (%)	*Ref.*
n-$C_5H_{11}Na$	n-$C_5H_{11}Cl$	Heptane	Na dispersion	89	1
n-$C_5H_{11}K$	n-$C_5H_{11}Cl$	Pentane	finely divided K	35	2
$Ph_3CNa^{a,b}$	Ph_3CCl	Pet. ether	Na amalgam	90	3
$CH_2{=}CHNa$	$CH_2{=}CHBr$	Heptane	Na dispersion	65	4
$CH_2{=}CHK$	$CH_2{=}CHCl$	But_2O	Na/K alloy	90	5
PhNa	PhCl	PhH	Na dispersion	75	6
PhK	PhCl	Heptane/PhH	K	55	7

[a] Other solvents employed have been Et_2O, NH_3, Et_2O/PhH, PhH and PhMe. [b] Ph_3CK, Ph_3CRb and Ph_3CCs have been similarly prepared.

1. A. A. Morton and E. F. Cluff, *J. Am. Chem. Soc.*, 1953, **75**, 134.
2. Text ref. 5.
3. B. Renfrow and C. R. Hauser, *Org. Synth., Coll. Vol. 2*, 1943, 607.
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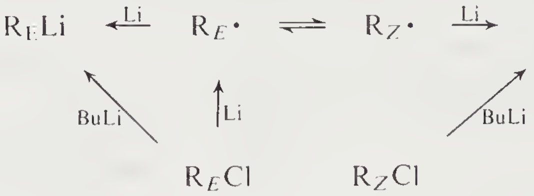
6. H. Rushig, R. Fugmann and W. Meixmer, *Angew. Chem.*, 1958, **70**, 71.
7. A. A. Morton and E. J. Lanpher, *J. Org. Chem.*, 1958, **23**, 1636, 1639; G. Gau, *J. Organomet. Chem.*, 1976, **121**, 1.

Partial racemization has been reported with some cyclopropyl halides.[56,57] Chiral 1-halo-1-methyl-2,2-diphenylcyclopropanes provide the corresponding lithium derivatives with partial retention; racemization increases as I > Br > Cl.[57] Other factors of importance are particle size and sodium content in the lithium.

Partial racemization has also been observed[58] with (*E*)- and (*Z*)-4-chlorohept-3-enes with Li (but not with BuLi); this is due to isomerization occurring between free $R_E\cdot$ and $R_Z\cdot$; however, other vinylic halides react with retention (Scheme 8).[4]



Scheme 8

Rigid cyclohexyl halides, *e.g.* 4-Bu^t-cyclohexyl chloride and menthyl chloride, gave epimeric lithium derivatives.[59] Other important factors, *e.g.* the purity, form, sodium content of the lithium sample, solvent, atmosphere and presence of lithium halide have been well discussed by Wakefield.[4]

As indicated elsewhere (Section 2.9.5.2), reactions of organic halides with aromatic radical-anion alkali metal compounds, *e.g.* $[p\text{-Bu}^tC_6H_4C_6H_4Bu^t\text{-}p]^{\overline{\cdot}},Li^+$ and $Naph^{\overline{\cdot}},Li^+$, can also lead to R—M compounds.[60]

2.3.2 Metallations[1,2,4,9]

Replacement of hydrogen by a metal is a regiospecific reaction; two examples are given by equations (15) and (16). In ideal and closed systems, these reactions are strictly equilibria, with the equilibrium constant depending on the relative acidities of the proton sources, with the more acidic hydrocarbon providing the greater amount of organometallic. In many cases the equilibrium

$$RH + R'M \rightleftharpoons RM + R'H \tag{15}$$

$$RH + MNR'_2 \rightleftharpoons RM + HNR'_2 \tag{16}$$

Solvents: ethers or amines

Table 7 pK_a Values for Hydrocarbons (at position)

Compound	pK_a
Me_3CH	47
Me_2CH_2	44
$Me—CH_3$	42
CH_4	40
Cyclopropane	39.5
PhH	39
$H_2C{=}CH_2$	38.5
$Ph—CH_3$	37
$H_2C{=}CH—CH_3$	36.5
Ph_2CH_2	33.5
Ph_3CH	32
$HC{\equiv}CH$	24
Fluorene (9-position)	23
Indene	18.5
Cyclopentadiene	15

lies far to one side or the reaction can be driven to one side so that the metallation becomes effectively complete, *e.g.* the metallations of Ph_3CH by ethyllithium, PhH by Bu^iNa and PhMe, xylenes or cumene by PhK.[61] A knowledge of K_a values for hydrocarbons is thus useful. Several compilations of pK_a values have been made[62] and a short listing of the more important hydrocarbons is offered in Table 7.

It has been reported that $LiNR_2$ are generally more effective metallating agents than the thermodynamically more basic aryl- and alkyl-lithiums, particularly for hydrocarbons having pK_a values <30. This increased kinetic basicity is a result of the use of the nitrogen lone pair in the four-centred transition state for the metallation.

While in principle many organometallics may be used as the metallating source, in practice a few have had really extensive use, *e.g.* BuLi, Bu^tLi and MeLi (all commercially available). For the other alkali metals, use of RNa ($R = n\text{-}C_5H_{11}$, Bu or Ph_3C), of RK ($R =$ Et, Bu or Me_3SiCH_2) and Me_3SiCH_2Cs have typically been made to metallate, among others,[2] ethylene, propene, benzene and methylbenzene. In addition, combination of an organometallic compound and an alkoxide has been employed, *e.g.* $BuLi/Bu^tOK$[63] and $n\text{-}C_5H_{11}Na/Bu^tOK$ (for kalliations) and BuLi/RORb.

Different metallating agents have been recommended for different systems, *e.g.* Schlosser *et al.*[64] recommended the use of Me_3SiCH_2K for allylic and benzylic deprotonations, while the combination of Bu^tLi/Bu^tOK is better for alkenes and cyclopropenes. Different metal amides have been employed; these include MNH_2 in liquid ammonia and a number of $LiNR_2$ compounds, such as $LiNPr^i_2$, in ethers.[1] Streitwieser has extensively studied metallations and equilibria using caesium cyclohexylamide in cyclohexylamine.[65]

The two equations (15) and (16) involving R′M and MNR'_2 are only two of a large number of reactions involving RH as a proton acid. The metals themselves can react with sufficiently acidic RH. Apart from the acidity of RH, other important factors are the electropositivity of M, the metal particle size and the solvent used. Some illustrative examples of the use of this method are (i) Li, Na and K with fluorene in THF, (ii) K with Ph_3CH in DME, (iii) K (in the presence of Na_2O) with PhMe and (iv) Cs with methyl aromatics, such as PhMe, in THF.[1,66] Caesium is indeed sufficiently reactive to metallate alkanes.

The metal hydrides can be used,[1] *e.g.* the combination of KH and 18-crown-6 in THF has been found successful for the preparation of benzylic potassium compounds from the following hydrocarbons: Ph_3CH, Ph_2CH_2 and $(p\text{-}MeC_6H_4)_2CH_2$ (with the reaction rate decreasing in the order given). However, $(2,4\text{-xylyl})_2CH_2$ was only partially metallated and $PhC_6H_4Me\text{-}p$ proved inert.[67]

Much more work has been done with lithium compounds; the reactivity of organolithium is higher in ethers than in hydrocarbons. The reactivity generally rises with the increasing Lewis basicity of the solvent, probably as a result of depolymerization of the organolithium aggregates increasing the carbanionic character and also probably due to the increasing stabilization of the transition state. Added donors, *e.g.* TMED[6] and DABCO, also dramatically enhance the metallating ability. The uses and advantages of TMED in metallations and also the disadvantages (one, for example, being metallation of TMED to give $Me_2NCH_2CH_2NMeCH_2Li$ by RLi of sufficient basicity) have been excellently reviewed.[6] Benzene can be readily metallated by BuLi/TMED and even more easily by Bu^sLi/TMED; the general effectiveness of BuLi/donor (1 : 1) combinations (*i.e.* towards PhH as well as PhMe and $CH_2{=}CHMe$) decrease in the donor sequence: TMED, $Me_2NCH_2CH_2CHMeNMe_2$, DABCO, $Me_2NCH_2CH_2CH_2CH_2NMe_2$. Despite there being a Δpk difference of >5 for PhH and BuH, metallation of PhH by BuLi in THF is extremely sluggish in the absence of TMED.[4] For the more reactive sodium and potassium compounds, *e.g* BuNa and $BuLi/Bu^tOK$, metallation (*e.g.* of PhH, PhR and alkenes) can proceed without the presence of TMED. The accompanying product, $LiOBu^t$, can be totally removed by washing with PhH or PhMe; in contrast, TMED tends to stick to the RM compound and cannot be readily removed.[68]

Equilibria, such as equation (15), are not so easy to follow for potassium and sodium derivatives due to the lack of solubility of the RNa and RK compounds. However, in the presence of a donor (equation 17; L = hexamethyltriethylenetetramine, $Me_2NCH_2CH_2NMeCH_2CH_2N\text{-}MeCH_2CH_2CH_2NMe_2$), values of the equilibrium constant K could be obtained: K for M = Na and K were 14 and 12 (for $R = m\text{-}Me_2C_6H_4$) and 0.3 and 0.5 (for $PhCHMe_2$), respectively.[61,69]

$$R'H \quad + \quad p\text{-}MeC_6H_4CH_2M,L \quad \overset{K}{\rightleftharpoons} \quad R'M,L \quad + \quad p\text{-}Me_2C_6H_4 \qquad (17)$$

Stabilized carbanionic compounds (*e.g.* benzyl- and allyl-metals) are very readily obtained using BuLi/TMED and the appropriate hydrocarbon.

In reaction of PhMe with BuLi/TMED in pure toluene, *ca.* 10% ring metallated product was initially obtained along with the $PhCH_2Li$. With time, these ring metallated products, richest in the *meta* isomer, rearranged to the more thermodynamically stable $PhCH_2Li$.[70] The rate of change was *ortho* > *para* > *meta*. Toluene may even be polylithiated by BuLi/TMED. Other aromatics have been polylithiated, including naphthalene, anthracene, fluorene, indene and ferrocene.[70] For *o*- and *m*-xylene (but not *p*-xylene), both methyl groups are lithiated to give $(LiCH_2)_2C_6H_4$. Some *gem*-dilithiated compound, *m*-$(Li_2CH)C_6H_4Me$, can also be obtained from *m*-xylene but can be suppressed if at least one equivalent of TMED is present. This suppression can be accounted for by the greater coordination of the initial product ($ArCH_2Li$) with TMED, thereby creating greater steric hindrance for further attack at the same site.[71] However, *p*-xylene, under forcing conditions, can give a *gem*-dilithio derivative, *p*-$MeC_6H_4CHLi_2$. The reactivity of the xylenes is *m*- > *o*- > *p*-.

The *n*-$C_5H_{11}Na$/TMED combination metallates[72] cumene ($PhCHMe_2$) to give eventually the thermodynamic product ($PhCMe_2Na{\cdot}TMED$), *via* the initial formation of the kinetic products (*o*-, *m*- and *p*-$Pr^iC_6H_4Na{\cdot}TMED$). Approximately the same relative amounts of ring metallated products are obtained from metallation using BuLi/TMED; however, the lithio compounds do not undergo subsequent rearrangements.[73]

Another metallation reaction producing kinetic and thermodynamic products[74] is $PhCH_2Me$ with *n*-$C_5H_{11}Na$/TMED in octane; the initial products (*o*-, *m*- and *p*-$MeCH_2C_6H_4Na$ as well as $PhCNa_2Me$) give way to the more stable PhCHNaMe. Additional evidence for complex rearrangements came from the isomerizations of *p*-EtC_6H_4Na (**6**), obtained from *p*-EtC_6H_4Br and sodium dispersion in octane. Initially (**6**) isomerized to a mixture of *o*- and *m*- (as well as some remaining *p*-) EtC_6H_4Na and the α,α'-disodio derivative, $PhCNa_2Me$, before providing PhCHNaMe. In the absence of TMED only slow metallation results.[74] These results should be compared with the stable reaction mixture (up to at least $6\frac{1}{2}$ hours) obtained from metallation of $PhCH_2Me$ (equation 18).

$$\mathrm{PhCH_2Me} \xrightarrow{\mathrm{BuLi/TMED}} \underset{38\%}{\mathrm{PhCHLiMe}} + \underset{9\%}{o\text{-},}\ \underset{36\%}{m\text{-}}\ \text{and}\ \underset{17\%}{p\text{-}\mathrm{MeCH_2C_6H_4Li}} \tag{18}$$

Arylsodium/TMED in hexane also dimetallates *o*- and *m*-xylene to give *o*- and *m*-$(NaCH_2)_2C_6H_4$, with no *gem* dimetallation. Only a monosodio derivative (*p*-$NaCH_2C_6H_4Me$) can be obtained from *p*-xylene.[75] The more powerful Bu^tOK/BuLi can dimetallate *p*-xylene, however, to give *p*-$(KCH_2)_2C_6H_4$ as well as the trikalliated species 1-KCH_2-4-$(K_2CH)C_6H_4$.[71] The reactivity sequence *m*- > *o*- > *p*-xylene towards *n*-$C_5H_{11}Na$/TMED is that also obtained for BuLi/TMED. It was suggested that the TMED, which is more effective than DABCO or $NaOBu^t$, has a dispersing rather than a solubilizing effect on pentylsodium.

The explanations for these findings with xylenes have been based on charge densities in a benzyl anion. The negative charge on a benzyl anion is delocalized into the ring in the order: *meta* < *ortho* < *para* and so parallels the observed order for dimetallation. An alternative way of explaining this is the preference for the second metallation to occur in such a manner as to introduce the new negative charges on the same set of carbon atoms as did the first.[71]

Another consideration is that lithium could bridge between the benzylic and an *ortho* ring site (see the structure of benzyllithium, Section 2.5.2) in the process leading to metallation. Hence the greater negative charge on the *ortho* site will result in stronger bridging and more stability. Additionally, the faster formation of *o*-$(MCH_2)_2C_6H_4$ than *p*-$(MCH_2)_2C_6H_4$ was considered to be due to lone pair attractive interactions between adjacent benzylic sites.

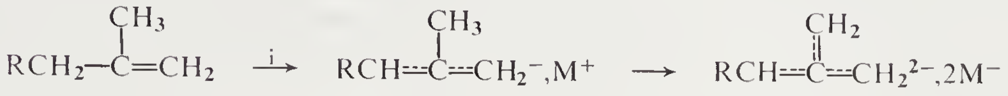
Abstraction of a proton by Bu^tOK/BuLi is much faster with the transition state closer to the reactant than the product and hence, for example, *para* dimetallation is not so prohibited. The higher methylated benzenes provided results[71] in keeping with the findings for the xylenes. The more powerful BuLi/Bu^tOK was able to provide more polymetallation than BuLi/TMED, *e.g.* it could tetrametallate 1,2,3,5-$Me_4C_6H_2$. The weaker BuLi/THF merely monometallated 1,2,3-trimethylbenzene. In none of these polymethylbenzene–(BuLi/TMED) reactions were ring metallated products found.

For naphthalenes, a similar but shorter story can be told. The 2-methyl group is more readily metallated[76] than 1-methyl, *e.g.* as found in 1,2,3,4-tetramethylnaphthalene. 1,8-Me_2-Naphthalene with excess BuLi is only monometallated, whereas with *n*-$C_5H_{11}Na$/TMED the di-

($NaCH_2$) derivative is quantitatively formed, as also happens with 1,2-, 1,3- and 1,6- but not 1,4-Me_2-naphthalene (the latter is only monometallated). The rates of dimetallation were 1,3- > 1,2- ≈ 1,6- ≈ 1,8- ≫ 1,4-Me_2-naphthalene.[75a] In the absence of TMED, poor yields of monometallated products are obtained.

Methyl heterocyclic compounds, *e.g.* pyridine, quinoline and isoquinoline derivatives, are also readily metallated at the benzylic position.[77]

As mentioned earlier, BuLi/TMED, effectively metallates propene to allyllithium and can dimetallate isobutene and methylallylbenzenes.[78] In parallel with the findings on methyl aromatics, BuLi/THF only provides monometallation, in contrast to dimetallation[79] using $Bu^tOK/BuLi$, *n*-$C_5H_{11}Na$ and BuLi/TMED (Scheme 9).



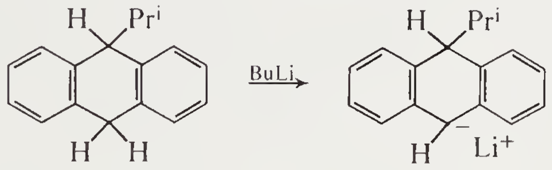
$$\mathrm{RCH_2{-}\overset{CH_3}{C}{=}CH_2} \xrightarrow{\mathrm{i}} \mathrm{RCH{\cdots}\overset{CH_3}{C}{\cdots}CH_2^-,M^+} \longrightarrow \mathrm{RCH{\cdots}\overset{CH_2}{\overset{\|}{C}}{\cdots}CH_2^{2-},2M^-}$$

i, BuLi; ii, $Bu^tOK/BuLi$ (M = K); *n*-$C_5H_{11}Na$; BuLi·TMED

Scheme 9

Metallation of (*Z*)-1-alkylpropenes at the allylic site occurs more readily than metallation of the (*E*)-isomers, no matter which configuration is thermodynamically the more stable;[80] for Et-CH=CHMe the reactivity factor is *ca.* 15 using Me_3SiCH_2K. For production of more conjugated anions, BuLi/THF may be sufficient,[4] *e.g.* equations (19) and (20). Acetylenic hydrogens, RC≡CH, are very acidic and are easily replaced by metals.[81] Propargylic and allenic compounds are also readily metallated by RLi, often in the presence of TMED, to mono-, di-, tri- and even tetra-lithio derivatives (equation 21).[82]

$$\mathrm{CH_2{=}CH{-}CH_2{-}CH{=}CH_2 \xrightarrow{BuLi} CH_2{\cdots}CH{\cdots}\bar{C}H{\cdots}CH{\cdots}CH_2,Li^+} \qquad (19)$$



(20)

$$\mathrm{PhC{\equiv}CCH_2R \longrightarrow PhC{\equiv}C\bar{C}HR,Li^+ \longrightarrow PhC{\equiv}C{-}CR^{2-},2Li^+} \qquad (21)$$

Propyne with one equivalent of BuLi provides MeC≡CLi, and with excess, C_3Li_4 is obtained. Similarly, 1-butyne with BuLi (3 equiv.) or MeC≡CMe with Bu^tLi/TMED (3 equiv.) can provide MeC_3Li_3 (formally $MeCLi_2{\equiv}CLi$; however, see Section 2.8.3 for discussion on structures, *etc.*).[70,92]

2.3.2.1 α-Heteroatom and ortho*-directing effects*[4,10,83]

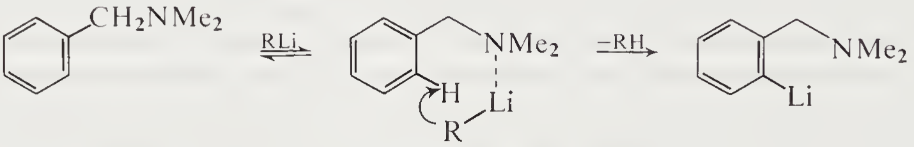
Apart from benzylic, allylic and propargylic groups, others containing heteroatoms have been found to enhance the acidity of α-protons in alkyl and alkenyl compounds and *ortho* protons in aromatic species sufficiently to react with organolithium compounds. This effect has been most thoroughly studied with lithium and a number of excellent reviews have dealt with the topic.[4,10,83] More and more groups are being used as time goes by: references to these are included in the annual reviews on organolithium chemistry.[17] Owing to the nature and reactivity of these groups, many of the metallations are carried out at extremely low temperatures and the organolithium compounds than used *in situ*.

Among the groups which enhance the acidity of an α-hydrogen are the following: R_2B—, —C(O)NR_2, —C(S)NR_2, —CO_2H, —CO_2R, R_2N—, cyanide, isocyanide, —NO_2, —N(R)NO, diazo group, =NOH, azines, hydrazones, oxazolinyl, $(R_2N)_2P(O)$—, $(RO)_2P(O)$—, $R_2P(O)$—, R_2M— (M = P, As or Sb), $R_2As(O)$—, R_3M— (M = Si, Ge and Sn), RO—, RS—, RS(O)—, $RS(O)_2$—, RSe— and halides.

2.3.2.2 ortho-*Directing groups*[4,10]

Among those groups able to direct lithium to the *ortho* site in lithiation reactions using RLi are NR_2, CH_2NR_2, $CH_2CH_2NR_2$, OR, $CONR_2$, SO_2R, SO_2NR_2, CF_3, 2-oxazolinyl and halides, especially F and Cl, as well as a number of groups which are metallated themselves prior to *ortho* substitution (and hence two equivalents of RLi are required), *e.g.* CH_2OH, NHR, CONHR, CONSR, SO_2NHR, —N≡C and SO_3H. Examples are known with potassium and sodium compounds,[5] e.g. *ortho* metallation occurs in reactions of anisole in diphenyl ether with phenylsodium and -potassium.

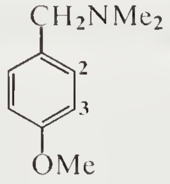
The listing includes groups which have electron releasing properties, and should thus decrease the acidity of the adjacent *ortho* site, as well as groups having electron withdrawing effects and groups having coordination sites. Two extreme or limiting mechanisms have been proposed.[10] These are (i) a coordination only mechanism and (ii) an acid–base mechanism, *i.e.* lithiation occurring at the most acidic *ortho* site, a site made acidic by the electron withdrawing effect of the *ortho* substituent. The former is exemplified by $PhCH_2NMe_2$. Despite the electron releasing effect of the CH_2NMe_2 group, lithiation of $PhCH_2NMe_2$ occurs at a faster rate than that of PhH and in the *ortho* position. Coordination of the lithiating agent with the NMe_2 unit initially occurs and this holds it in an ideal position for attack at the *ortho* site; a simplified mechanism is shown in Scheme 10.



Scheme 10

Many studies have been done with aryl alkyl ethers, such as PhOR′, in which both coordination and the ($-I$) inductive effect occur. Coordination to the ether oxygen by RLi (as has been shown by NMR spectroscopy)[84a] will enhance the $-I$ effect of the OR′ group and so render the *ortho* proton even more acidic. Further evidence for coordination comes from the enhanced reactivity of $PhOCH_2CH_2OMe$ compared with PhOMe (by a factor of 14 using BuLi),[84b] due to the chelating effect of the two oxygens. Of interest, $PhOBu^t$ and PhOMe are of equal reactivity for *ortho* lithiation, despite the steric differences; however, steric retardation for *ortho* (to OMe) substitution occurs[10] in *o*-$Bu^tC_6H_4OMe$.

An interesting situation is found with **(7)**. The acidity of the proton at position-3 should be the greater of the two different ring protons due to the $-I$ effect of the OMe group.[85] This is indeed the site of metallation by a monomeric BuLi/TMED (1 : 1) complex, but not by the butyllithium aggregate, which gives the 2-lithio product. The complex has a reduced Lewis acid character, caused by the coordination of the TMED, and attacks the most acidic site. On the other hand, $(BuLi)_6$, a stronger Lewis acid, becomes coordinated to the CH_2NMe_2 group and from that provides the 2-lithio product.



(7)

Sequences of *ortho* directing ability have been established from competition reactions, *e.g.* from an internal competition using *p*-substituted anisoles and BuLi in hexane at room temperature, the directing ability was found[85] to be $SO_2NMe > SO_2NHMe > CONHMe > CH_2NMe_2 > OMe > CH_2CH_2NMe_2$, NMe_2, CF_3, F. Other competition studies have involved $YC_6H_4CONEt_2$ with Bu^sLi in THF at − 100 °C in the presence[86] of TMED: Y = $CONEt_2$ was superior to Y = SO_2NR_2, oxazolinyl, OMe, CH_2NMe_2, Cl, CO_2H and Me and an intermolecular competition of phenyloxazoline and PhX for BuLi (1 equivalent) at low temperatures; here the sequence obtained[87] was $SO_2NMe_2 > SO_2NHMe$, $CONPr^i$, $CONEt_2 >$ oxazolinyl $>$ CONHMe $>$ CH_2NMe_2. Some anion crossover occurred in the latter systems.[87] Differences occur in the different studies and, as shown for the reactions of *p*-$Me_2NCH_2C_6H_4OMe$, the products may be dependent on the organolithium. However, it appears that the following sequence is the best one from all available data: R_2NSO_2, $ArSO_2 >$ CONR $>$ oxazolinyl $>$ CONHR, CSNHR, $CH_2NMe_2 > CR(O^-Li^+)CH_2NMe_2 >$ OMe $>$ OAr $>$ NHAr $>$ SR $>$ NRAr $>$ $NAr_2 >$ $CR_2O^-Li^+$.

Interesting differences have been found[88] between sodium and lithium derivatives of $PhCH_2NMe_2$. Reaction of BuNa with $PhCH_2NMe_2$ in hexane initially provides *o*-$NaC_6H_4CH_2NMe_2$ but this rearranges after 20 h to the benzylic $PhCHNaNMe_2$. The latter, on treatment with LiBr, provides $PhCHLiNMe_2$, which now undergoes a slow rearrangement (48 h at 45 °C) to *o*-$LiC_6H_4CH_2NMe_2$. These groups also activate *ortho*-methyl groups to metallation, *e.g.* as in *o*-$MeC_6H_4SO_2NHR$ and *o*-$MeC_6H_4NMe_2$.[10]

meta-Directing abilities have been found for the *t*-butyl group and the $Ph_2P(O)$ group.[10]

2.3.3 Metal–Halogen Exchange[1,4]

This reversible and rapid exchange (equation 22) has had particular use for lithium, although it has found some employment in sodium and potassium chemistry. Equation (22) is in reality an equilibrium. Some general findings are as follows. (i) The more RM is present at equilibrium, the more readily the R group can support a negative charge, *i.e.* the more acidic is RH. Hence it is possible to exchange an alkyllithium with aryl halides, cyclopropyl halides, vinyl halide (stereospecifically), heteroaryl halides, *e.g.* thiophenyl, pyridinyl, quinolinyl and isoquinolinyl, or polyhalogenoalkyl halides, but not generally for another alkyl halide. Some equilibrium constants have been obtained,[89,90] *e.g.* equations (23) and (24). (ii) The rate of reaction is I ≈ Br > Cl > F. For Cl and F the metal–halide exchange is sufficiently slow to allow other reactions to occur, such as *ortho*- or α-metallations (a consequence of the halogens making the *ortho*- or α-hydrogens more acidic). Polychloroorganics, however, can undergo chloride–lithium exchange reasonably readily. (iii) The exchange reaction is faster in Et_2O than in hydrocarbons. The presence of TMED, however, could promote a competitive metallation. Lithium halides also retard the metal–halide exchange. (iv) In competition with the rapid metal–halide exchanges are the already mentioned metallations and also alkylations (equation 25). Examples with halogenoanisoles indicate clearly the complexities that these three reaction types can bring.[4] Such competitions can be swung over to the metal–halide exchanges by a number of means, *e.g.* use of more basic solvents such as THF rather than Et_2O, insolubility of the product RM compound, use of short reaction times and very low temperatures. In addition, it has been found that BuLi favours metal–halide exchange, whereas MeLi or PhLi lead to more metallation.

$$\mathrm{RX} + \mathrm{R'M} \rightleftharpoons \mathrm{RM} + \mathrm{RX} \qquad (22)$$

$$\mathrm{RLi} + \mathrm{PhI} \xrightleftharpoons{K} \mathrm{RI} + \mathrm{PhLi} \qquad (23)$$

$$\mathrm{p}K(\mathrm{RLi}) = -2.4\ (\text{vinyllithium});\ 3.5\ (\mathrm{EtLi});\ 5.5\ (\mathrm{Bu^tCH_2Li})$$

$$\mathrm{PhLi} + \mathrm{YC_6H_4Br} \xrightleftharpoons{K} \mathrm{YC_6H_4Li} + \mathrm{PhBr} \qquad (24)$$

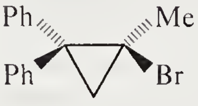
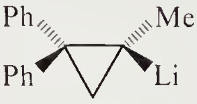
$$\mathrm{p}K(\mathrm{Y}) = 0.6\ (p\text{-Me});\ 0.8\ (m\text{-Me});\ 5.3\ (p\text{-Cl});\ 3.8\ (p\text{-Ph});\ 289\ (m\text{-CF}_3)$$

$$\mathrm{RX} + \mathrm{R'M} \longrightarrow \mathrm{RR'} + \mathrm{MX} \qquad (25)$$

Particularly well studied reactions are the aryl halide–aryllithium exchanges since these proceed at convenient rates. Such studies,[91] *e.g.* using PhLi and ^{14}C-labelled PhX (X = Cl, Br or I), have indicated second order reactions, probably involving a four-centred transition state. A radical component, *i.e.* some homolytic fission, has been detected in reactions of alkyllithiums and alkyl halides. The mechanism has been discussed by Wakefield. The following reactivity sequence towards BuLi at −100 °C has been established:[92] $ArCH_2Br > ArBr > ArCH_2CH_2Br >$

Ar(CH$_2$)$_n$Cl. After all these words on the problems which may be associated with metal–halide exchange, it is necessary to redress the balance by stating one big advantage — the complete regioselectivity, a most important factor for organolithiums to be used in synthesis. Examples are given in Table 8.

Table 8 Metal–Halide Exchange Reactions
$RX + R'M \rightleftharpoons RM + R'X$

Organic halide (*RX*)	*R'M* (*solvent*)	*Product* (*yield*; %)	*Ref.*
PhBr	BuLi (PhMe)	PhLi (95)	1
p-BrC$_6$H$_4$Cl	BuLi (Et$_2$O)	*p*-ClC$_6$H$_4$Li (90)	2
2,5-Br$_2$C$_6$H$_3$NMe$_2$	BuLi (THF) −100 °C	2-Me$_2$N-4-BrC$_6$H$_3$Li (95)	3
2,6-(O$_2$N)$_2$C$_6$H$_3$Br	BuLi (THF)	2,6-(NO$_2$)$_2$C$_6$H$_3$Li (58)	4
o-(CN)C$_6$H$_4$Br	BuLi (THF) −78 °C	*o*-(CN)C$_6$H$_4$Li (82)	5
p-HO$_2$CC$_6$H$_4$I	BuLi (Et$_2$O)	*p*-LiO$_2$CC$_6$H$_4$Li (62)	6
2,7-Br$_2$Naph[a]	BuLi (THF) −35 °C	2,7-Li$_2$Naph (72)	7
C$_6$F$_5$X (X = Cl or Br)	BuLi (Et$_2$O) −78 °C	C$_6$F$_5$Li (85)	8
3-Br-thiophene	PhCMe$_2$K	3-K-thiophene	9
2-Bromobenzo[*b*]furan	BuLi (Et$_2$O) −70 °C	RLi (86)	10
3-Br-selenophene	PhLi (Et$_2$O) reflux	3-Li-selenophene (65)	11
2,6-X$_2$-pyridine (X = Br or I)	BuLi (THF) −90 °C	2,6-Li$_2$-pyridine (52)	12
(X = Br)	BuLi (Et$_2$O) −80 °C	2-Li-6-Br-pyridine (60)	12
CCl$_4$	BuLi (THF) −100 °C	CCl$_3$Li (76)	13
	BuLi (Et$_2$O)[b] 29 °C	 (70)	14
2-I-Adamantane	Bu^{t}Li (Et$_2$O) −45 °C	2-Li-adamantane (77)	15
(*Z*)-PhCH=CBrPh	BuLi (Et$_2$O)	(*E*)-PhCH=CLiPh[c]	16
Ph$_2$C=CHBr	BuLi (THF)[d] −76 °C	Ph$_2$C=CHLi (73)	17
CH$_2$=CBrCF$_3$	BuLi (Et$_2$O) −78 °C	CH$_2$=CLiCF$_3$ (72)	18
Me$_2$C=C(Br)CO$_2$H	BuLi (THF) −100 °C	Me$_2$C=CLi(CO$_2$Li) (94)	19

[a] Naph = naphthalene. [b] Racemization occurs using Li (H. M. Walborsky and M. S. Aronoff, *J. Organomet. Chem.*, 1973, **8**, 55). [c] Retention of configuration. [d] Metallation results in Et$_2$O.

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2.3.4 Transmetallations[1,4,5,83]

These reactions, two types of which are given by equations (26) and (27), are general reactions for all alkali metals but have in fact only found use under specific circumstances, *e.g.* for the production of organoalkali metal derivatives difficult to prepare by more direct routes. These include substituted allyl, benzyl, certain functionally substituted organolithiums, configurationally pure vinyl species and, more recently, chiral organolithiums as well as preparations of organoalkali metal compounds uncontaminated by metal halides and thus more suitable for structural studies. Equation (27) has in fact been shown to be an equilibrium.[93]

$$\mathrm{R{-}m} + \mathrm{M} \longrightarrow \mathrm{R{-}M} + \mathrm{m} \tag{26}$$

$$\mathrm{R{-}m} + \mathrm{R'{-}M} \longrightarrow \mathrm{R{-}M} + \mathrm{R'{-}m} \tag{27}$$

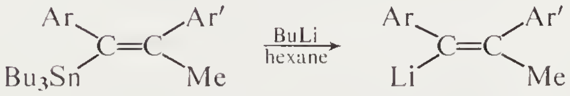
M = alkali metal; m = less electropositive metal, *e.g.* Hg, Si, Sn, Pb, Sb, Bi, Cd or Zn

Particular use has been made of organotin compounds. Equation (26) has more of a historical value but it has still found use in recent times. Included under equation (26) would be replacement of lithium by the heavier alkali metals. However, one of the better ways of carrying out such an exchange involves the alkoxide of the heavier alkali metal (equation 28). In an earlier section (2.3.2) it was mentioned that the combination $\mathrm{BuLi/Bu^tOK}$ is a useful kalliating agent; sodium and rubidium derivatives can be made in a similar manner. As routes have been designed to remove the alkoxide, highly pure organo-sodiums, -potassiums and -rubidiums with a low lithium content may be obtained, *e.g.* BuLi and $\mathrm{NaOBu^t}$ in heptane at 0 °C gave BuNa containing[94] just 0.07% Li.

$$\mathrm{R{-}Li} + \mathrm{R'OM} \longrightarrow \mathrm{R{-}M} + \mathrm{LiOR'} \tag{28}$$

The reaction in the reverse sense, *i.e.* organopotassium to organolithium, has been achieved by Schlosser[68] using LiBr.

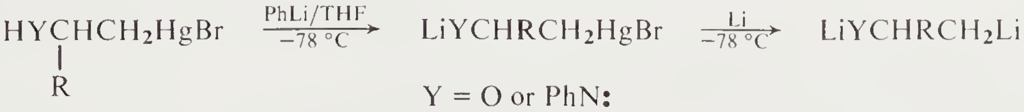
Transmetallations involving vinyl compounds proceed with retention of configuration, *e.g.*[95] equation (29).



(29)

Various unsymmetric allylic lithiums have been obtained by transmetallations (see examples in Table 9).

Transmetallations have proved useful means of obtaining functionally substituted compounds, *e.g.* alkoxy, hydroxy and amino substituted organolithiums; some examples[96,98] are given in equations (30)–(32).



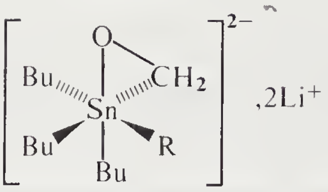
$$\mathrm{HY\underset{\displaystyle R}{\underset{|}{C}}HCH_2HgBr} \xrightarrow[-78\,^{\circ}\mathrm{C}]{\mathrm{PhLi/THF}} \mathrm{LiYCHRCH_2HgBr} \xrightarrow[-78\,^{\circ}\mathrm{C}]{\mathrm{Li}} \mathrm{LiYCHRCH_2Li} \tag{30}$$

Y = O or PhN:

$$\mathrm{Bu_3SnCH_2OH} \xrightarrow{\mathrm{2BuLi}} \underset{70\%}{\mathrm{LiCH_2OLi}} \tag{31}$$

$$\mathrm{Me_2NCH_2SnBu_3} \xrightarrow{\mathrm{BuLi}} \mathrm{LiCH_2NMe_2} \tag{32}$$

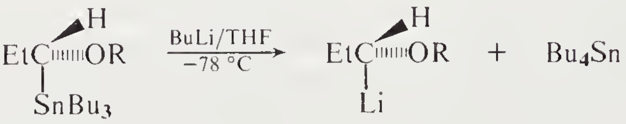
Of interest is the reaction of BuLi with $\mathrm{Bu_3SnCH_2OH}$, which was reported[97] to lead not to free $\mathrm{LiCH_2OH}$ but rather to a tin derivative, formulated as (**8**).



(8)

Exchange reactions of alkyllithiums with chiral *s*-butylmercury(II) chlorides[99] and chiral α-alkoxyorganotin compounds[100] proceed with retention of configuration. The tin reaction (equation 33) leads to enantomerically pure α-alkoxyorganolithiums.

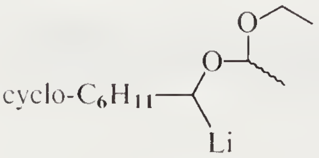
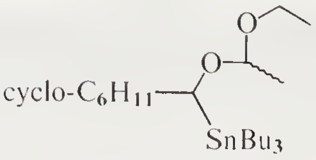
Further examples of the uses of transmetallations are given in Table 9.



$$\mathrm{EtC(H)(OR)SnBu_3} \xrightarrow[-78\ ^\circ\mathrm{C}]{\mathrm{BuLi/THF}} \mathrm{EtC(H)(OR)Li} + \mathrm{Bu_4Sn} \qquad (33)$$

$R = PhCH_2OCH_2$

Table 9 Formation of Organoalkali Metal Compounds by Transmetallation

Product	*Reagents and conditions*	*Yield* (%)	*Ref.*[a]
EtNa	Et_2Hg/Na/hexane/r.t.		[19]
PhLi	$Ph_2Hg/Li/Et_2O$	95	1
PhNa	$Ph_2Hg/BuNa$		[5]
$LiCH{=}CHCH_2OLi$ (Z:E = 5.1)	$Bu_3SnCH{=}CHCH_2OH/BuLi$ (Z:E = 5.1)	88	[97]
$CH_2\overset{\cdots}{-}\bar{C}H\overset{\cdots}{-}CH_2,M^+$ (M = Na, K, Rb or Cs)	$(CH_2{=}CHCH_2)_2Hg$/M film/ THF, −20 °C		[257]
$CH_2\overset{\cdots}{-}\bar{C}H\overset{\cdots}{-}CH_2,Li^+$	$Ph_3SnCH_2CH{=}CH_2/PhLi/Et_2O$	75	2
$CH_2\overset{\cdots}{-}\bar{C}H\overset{\cdots}{-}CF_2,Li^+$	$Me_3SnCH_2CH{=}CF_2$/THF/MeLi; −95 °C		3
$CH_2\overset{\cdots}{-}\bar{C}H\overset{\cdots}{-}CCl(SiMe_3),Li^+$	$Ph_3PbCH_2CH{=}CClSnMe_3$/BuLi/THF, −90 °C		[260(d)]
$MeSCH_2Li$	$MeSCH_2SnBu_3/BuLi$		[83]
$(PhCH_2)MeNCH_2Li$	$(PhCH_2)MeCH_2SnBu_3$/BuLi/THF, −65 °C	87	[83]
$MeN(CH_2Li)_2$	$MeN(CH_2SnBu_3)_2$/BuLi/THF/hexane, −65 °C	52	[83]
	 /BuLi	80	4

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[a] References in brackets refer to text references.

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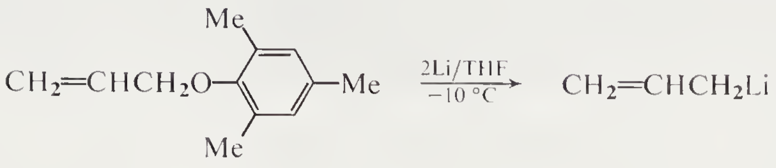
2.3.5 Cleavage of Ethers and Sulphides[1,4,5]

This is another method of limited use. For lithiums, it has been used mainly to prepare allyl and benzyl derivatives; however, for sodium and potassium, *etc.*, it has wider application. Cleavage of unsymmetric ethers and sulphides by an alkali metal provides the organometallic species best able to support the negative charge, *i.e.* equations (34)–(37).[101] Aromatic radical-anion alkali metal compounds,[102] such as $Naph^{\overline{\cdot}}, M^+$ can also cleave sulphides (equation 38).

$$Ph_3COPh \xrightarrow[Et_2O]{Na/K\ alloy} Ph_3CK + PhOK \qquad (34)$$

$$PhCH_2OPh \xrightarrow{2M} PhCH_2M \qquad (35)$$

$$PhOMe \xrightarrow[heptane]{2K/25\ °C} PhK \qquad (36)$$



(37)

$$Ph_2CMeSPh \xrightarrow{i} Ph_2CMe,M^+ \qquad (38)$$

i, Na dispersion, Li, K chips or Naph $^{\overset{-}{\cdot}}$,M$^+$

2.3.6 Addition to Carbon–Carbon Multiple Bonds[1,4]

Organoalkali metal compounds can add to carbon–carbon multiple bonds to give new organometallics. Whereas organolithiums add readily to conjugated polymers and styrenes and can produce polymers unless steric hindrance is excessive (equations 39[103] and 40[104]), forcing conditions may be required for alkyllithium additions to isolated carbon–carbon multiple bonds, *e.g.* primary alkyllithiums, such as ethyllithium or butyllithium, in hydrocarbons react with ethylene under pressure to give simple addition products and low molecular weight polymers. In the presence of ethers, *e.g.* DME, and amines, *e.g.* DABCO and TMED, addition to ethylene occurs more readily, *e.g.* with secondary and tertiary alkyllithiums, and can lead to polymerization, *e.g.* with BuLi. Unconjugated alkenes, other than ethylene, require quite severe conditions.[4] Organosodiums and organopotassiums also add to alkenes, *e.g.* equations (41)–(43); subsequent rearrangement of (**9**) to the thermodynamically more stable benzylic compounds results.

$$Bu^tLi + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow (Z)\text{- and }(E)\text{-}Bu^tCH_2CH{=}CHCH_2Li \qquad (39)$$

$$Bu^tLi + PhCMe{=}CH_2 \xrightarrow[TMED]{cyclopentane} Bu^tCH_2{-}\bar{C}MePh,Li^+ \qquad (40)$$

$$trans\text{-}PhCH{=}CHMe \xrightarrow{PhCMe_2K} PhCHKCHMe(CMe_2Ph) \qquad (41)$$

$$PhCH_2Na + H_2C{=}CH_2 \longrightarrow \underset{(\mathbf{9})}{PhCH_2CH_2CH_2Na} \longrightarrow PhCHNaEt \qquad (42)$$

$$Ph_2C{=}CH_2 + n\text{-}C_5H_{11}Na \longrightarrow Ph_2CNaCH_2C_5H_{11} \qquad (43)$$

Intramolecular additions also are known,[4] *e.g.* equation (44). Other additions which occur readily are to alkoxy- or hydroxy-alkenes, coordination to the oxygen apparently being a vital factor. Thus Pr^{i}Li adds to $CH_2{=}CH(CH_2)_nOR$ ($n = 2$ or 3) and TMED has been found to catalyze the addition of RLi to allylic alcohols. Additions to vinyl-silanes, -germanes,[93] phosphines and sulphides also occur (equations 45 and 46).[4]

(44)

$$Ph_3GeCH{=}CH_2 + PhLi \longrightarrow \underset{60\%}{Ph_3GeCHLiCH_2Ph} \qquad (45)$$

$$BuLi + PhSH{=}CH_2 \xrightarrow[0\ °C]{Et_2O} PhSCHLiCH_2Bu \qquad (46)$$

2.3.7 Use of Lithium Vapour

A direct synthesis of polylithium compounds has been achieved from lithium and carbon vapour, generated by an arc between graphite electrodes, in a Knudsen cell at 800 °C. The principal product was C_3Li_4, as shown by derivatization.[105] Lithium atom reactions with chlorocarbons (equations 47 and 48)[106] and with α,ω-dichloroalkanes (equations 49 and 50)[107] also lead to perlithio compounds. In the latter process, the abstraction of Cl from the chlorocarbon (RCl) by Li is an extremely exothermic reaction ($\sim$460 kJ mol^{-1}) and the subsequent Li reaction of the free radical (R·) forms a 234 kJ mol^{-1} bond. Hence the product is vibrationally excited and enables the reaction to proceed to substitution of the hydrogens by lithium.

$$\mathrm{Li(g)} + \mathrm{CCl_4} \xrightarrow{800\ ^\circ\mathrm{C}} \underset{14\%}{\mathrm{CLi_4}} + \underset{61\%}{\mathrm{C_2Li_4}} + \underset{20\%\ \text{(average yields)}}{\mathrm{C_2Li_2}} \tag{47}$$

$$\mathrm{Li(g)} + \mathrm{C_2Cl_6} \xrightarrow{800\ ^\circ\mathrm{C}} \underset{80\%}{\mathrm{C_2Li_6}} \tag{48}$$

$$\mathrm{Li(g)} + \mathrm{Cl(CH_2)_5Cl} \xrightarrow{800\ ^\circ\mathrm{C}} \underset{31\%}{\mathrm{Li(CH_2)_5Li}} + \underset{19\%}{\mathrm{C_3Li_4}} + \underset{11\%}{\mathrm{C_2Li_6}} + \underset{28\%}{\mathrm{C_2Li_2}} \tag{49}$$

$$\mathrm{Li(g)} + \mathrm{Cl(CH_2)_3Cl} \xrightarrow{800\ ^\circ\mathrm{C}} \underset{33\%}{\mathrm{CLi_3CLi_2CLi_3}} + \underset{39\%}{\mathrm{C_2Li_6}} + \underset{13\%}{\mathrm{Li_2C{=}CLiCLi_3}} \tag{50}$$

The polylithio compound C_2Li_6 was obtained in 99% purity at 800 °C from lithium vapour and diethylmercury.[108] In contrast, from Et_4Sn and Et_4Pb the major product was ethyllithium with only about 10% C_2Li_6. Lithium vapour reactions with compounds such as Me_2Hg, $(ICH_2)_2Hg$ and $(CH_2{=}CH)_4Sn$ led to perlithio-C_2 compounds (C_2Li_2, C_2Li_4 and C_2Li_6) in varying amounts.

Alkenes also react with lithium vapor (equation 51). Two types of reaction occur: (i) stepwise replacement of hydrogens by lithium and (ii) addition of lithium to the double bond. A small yield of *trans*-$CLi_3CLi{=}CLiCLi_3$ is obtained from *trans*-2-butene. The initial reaction of alkenes with lithium is the substitution of a vinylic hydrogen with subsequent replacement of both vinyl and alkyl hydrogens. The latter step is in competition with reactions in which lithium is added across the double bond. Under the reaction conditions,[109] fragmentation of the alkenes leads to C_3Li_6, C_2Li_4 and C_2Li_2, whose combined yields range from 25 to 80%.

$$\mathrm{Li(g)} + \mathrm{Me_2C{=}CH_2} \xrightarrow{800\ ^\circ\mathrm{C}} \underset{28\%}{\mathrm{Me_2C{=}CLiH}} + \mathrm{Me_2C{=}CLi_2} + \underset{3.5\%}{\mathrm{Me_2CLi{-}CLi_3}} +$$
$$\mathrm{C_2Li_4} + \mathrm{C_3Li_4} + \mathrm{C_2Li_6} + \mathrm{C_2Li_2} \tag{51}$$

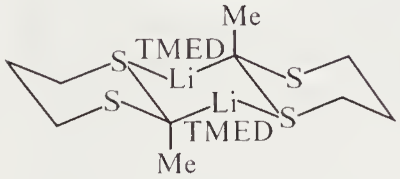
Lithiation of benzene with lithium vapour provides mainly C_2Li_2, C_2Li_4, C_2Li_6 and C_3Li_4 with less than 1% C_6 compounds.[110]

2.4 ALKYL- AND ARYL-ALKALI METAL COMPOUNDS

2.4.1 Structures in the Solid State

Several structures of simple alkyl and aryl alkali metal compounds have been determined (Table 10). There are problems in obtaining pure solvent-free and halide-free materials; preparation in hydrocarbon solvents and by transmetallation are thus favoured. Methyl- and ethyl-lithium exist in the solid state as tetramers with some interaggregation association. The arrangement in $(MeLi)_4$, deduced from powder diffraction data,[20] can be considered as interpenetrating tetrahedra of methyl groups and lithium atoms. Another descriptive view is that the methyl groups are above each of the triangular Li_3 faces of an Li_4 tetrahedron, *i.e.* methyl groups bridging lithium atoms (Figure 1). The normally adopted view is that these are electron deficient compounds, *i.e.* the number of bonds exceeds the number of valence electron pairs, although there are proponents for different (ionic) interpretations (see Section 2.4.4).

Table 10 Structure of Alkyl- and Aryl-alkali Metal Compounds

Compound	*Features*	*Ref.*
$(MeLi)_4$	Tetramer: bridging methyl groups; tetrahedra of lithium and methyl groups. Some interaggregate association (C—Li = 2.36 Å); Li···Li, 2.68 Å; ∠LiCLi, 68.3 ± 0.2°; Li—C, 2.31; C—H, 0.95 ± 0.05 Å	20
MeNa	Probably also a tetrameric molecule like $(MeLi)_4$	111
MeK MeRb MeCs	Ionic: hexagonal structure of an NiAs type with isolated Me^- and M^+ moieties; M—C for M = K, 3.22; M = Rb, 3.56; M = Cs, 3.53 Å	19
$(EtLi)_4$	Tetramers with bridging ethyl groups; Li···Li, 2.424 ± 0.009, 2.603 ± 0.010, 2.633 ± 0.008; Li—C, 2.188 ± 0.004, 2.252 ± 0.006, 2.468 ± 0.005 Å; ∠LiCLi, 66.1 ± 0.2, 66.7 ± 0.2; ∠LiLiLi, 63.1 ± 0.2°	112
EtNa	Rhombohedral structure, built up of double layers; Na—C, 2.6(8), 2.6(3) Å	113
(Cyclohexyl-Li)$_6$(PhH)$_2$	Hexamer with two solvate PhH molecules: bridging cyclohexyl groups above six faces; two PhH above the other two faces; Li···Li, 2.397(6), 2.969(9); Li—C, 2.184(3), 2.300(4) Å; ∠LiCLi, 64.6(2), 85.6(3)°	114a
$(Me_3SiLi)_6$	Six-membered Li ring; D_{3d} symmetry (folded chair); Me_3Si located above Li_3 faces; Li···Li, 2.70, 3.27; Li—Si, 2.68 Å	114b
$(MeLi)_4(TMED)_2$	TMED bridging $(MeLi)_4$ units; Li···Li, 2.56–2.57; Li—C, 2.23–2.27 Å; ∠LiLiLi, *ca.* 60; ∠LiCLi, 59.5(2), 68.5(2), 69.5(2)°	115
(Bicyclobutyl[1.1.0]Li·TMED)$_2$	Bridging bicyclobutyl groups; chelating TMED; Li···Li, 2.74(7) Å; ∠CLiC, 104(2)°; Li—C, 2.23(5) Å; ∠LiCLi, 76(2); ∠NLiN, 84(2)°	116
(PhLi·TMED)$_2$	Phenyl bridging groups; chelating TMED; Li—C, 2.208(6), 2.278(6) Å; ∠CLiC, 105.6; ∠LiCLi, 67.4; ∠NLiN, 84.3(1)°	117
(Ferrocenyl-Li)$_2$PMDT[a]	Li(2)—C(1), 2.146(10)–2.193(10); Li(1)—C(6), 2.123(10); Li(1)—C(6), 2.112(10) Å	118
(2-Li-2-Me-1,3-dithiane)$_2$ 	Chelating TMED; Li—C, 2.186; Li—S, 2.516 Å	167

[a] PMDT = Pentamethyldiethylenetriamine.

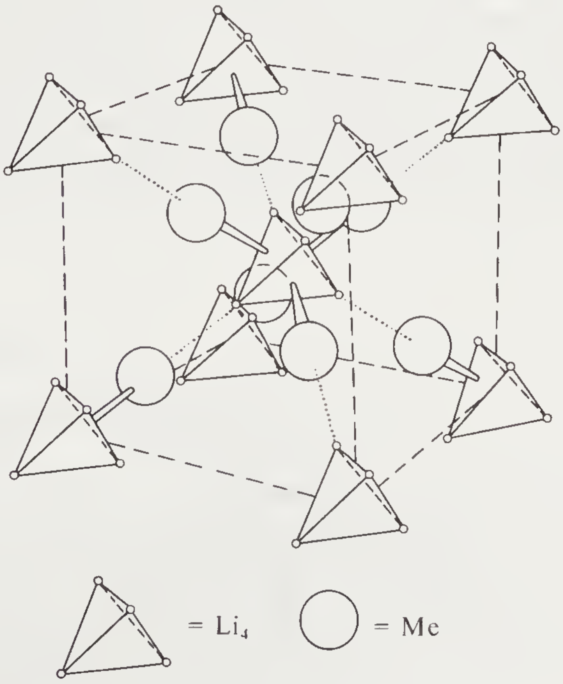


Figure 1 Structure of methyllithium[20]

Unfortunately no details have been published regarding the structure of methylsodium, although it was briefly reported[111] to be tetrameric and akin to methyllithium. In contrast to methyllithium, the structures of methyl-potassium (Figure 2), -rubidium and -caesium are clearly ionic, being hexagonal structures of the nickel arsenide type.[19]

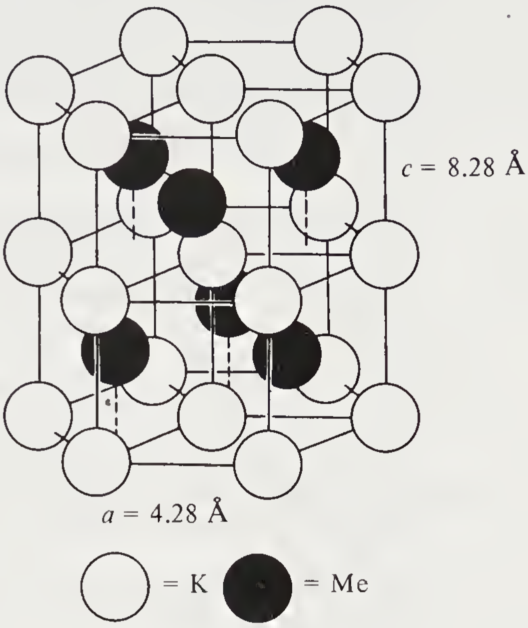


Figure 2 Structure of methylpotassium[19]

The strength of the methyllithium tetramer is clearly seen from its intact complexation with TMED, a ligand which normally leads to breakdown of oligomeric organolithium compounds (see Section 2.4.2.2). Better structural resolution was achieved with crystalline $(MeLi)_4(TMED)_2$, compared with powdered $(MeLi)_4$. In this complex the TMED acts as a bridging rather than a chelating ligand.

Differences have been found between the structures of ethyl-lithium[112] and -sodium.[113] The rhombohedral form of ethylsodium (there is also a cubic modification) is built up of double layers, the outer portions of each containing ethyl anions arranged perpendicular to the plane. The CH_2 groups are orientated towards the inner part of the layer and are surrounded by sodium ions in a trigonal pyramidal array.

The structure of (cyclohexyllithium)$_6$·2PhH is essentially[114a] a distorted octahedron of lithium atoms with cyclohexyl groups above six of the eight Li_3 faces, the remaining two transoid faces being associated with the benzene solvates. A simplified form of the hexamer is shown in Figure 3. The α-carbon of each cyclohexyl unit is most closely associated [C—Li, 2.184(3) Å] with the two lithiums which make the longer contact [Li···Li = 2.968(6) Å] in each Li_3 face. A vector from the α-carbon to the plane of the Li_3 face intersects the plane at the mid-point of the shortest Li—Li contact. It was also considered that Li···H interactions may play a role in determining the stereochemistry in cyclohexyllithium. There is no indication for inter-aggregate associations.

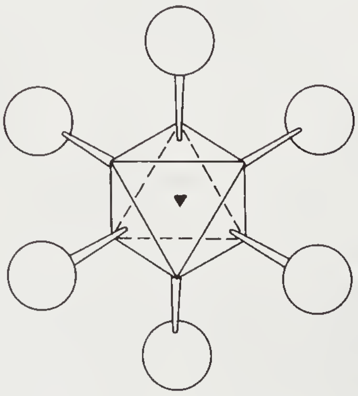


Figure 3 Structure of $(RLi)_6$

The description given[114b] to the lithium arrangement in $(LiSiMe_3)_6$ was that of a folded chair. In the dimeric bicyclobutyl[1.1.0]lithium·TMED[116] and phenyllithium·TMED[117] complexes, bridging by the organic groups and a chelating TMED renders each lithium tetracoordinate.

Two distinct lithium environments occur in the ferrocenyllithium·PMDT complex (Figure 4);[118] all three nitrogens of the PMDT ligand are coordinated to one of the unique lithium atoms while the second, unsolvated, lithium bridges between one carbon atom of a Cp ring from each ferrocene monomer to form the dimer. The Li···Fe distance is short [2.667(8) Å] and is ascribed to bonding between the ferrocene e_g MO and the unsolvated lithium.

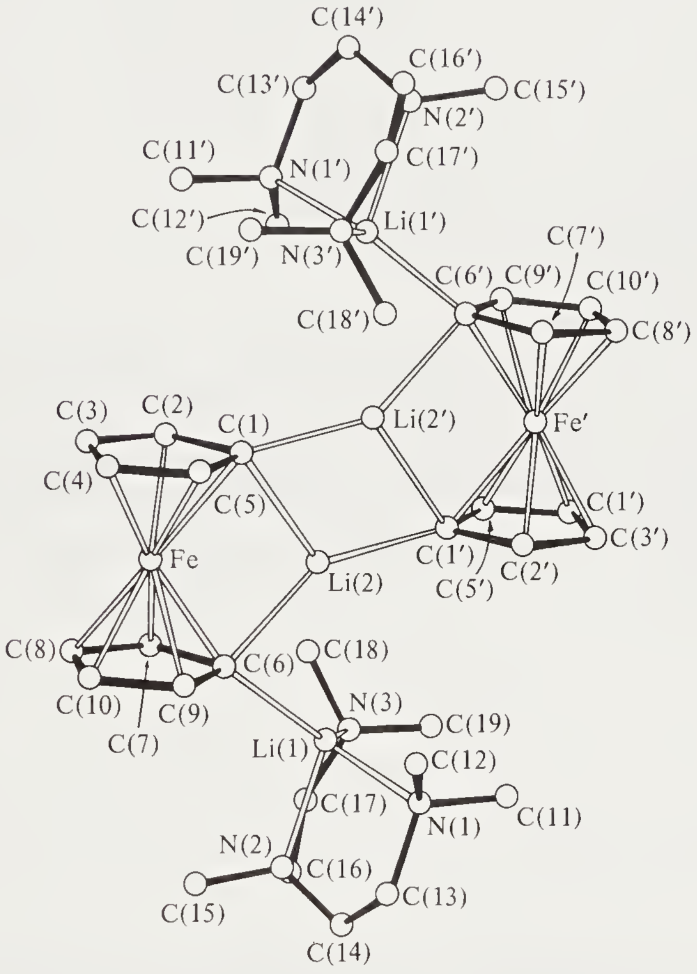


Figure 4 Structure of ferrocenyllithium·PMDT[118]

The Li···Li distance in these various compounds should be compared with the distance in Li_2 (2.67 Å). While these are short enough to be indicative of Li···Li bonding, some evidence points against this, *e.g.* from ESR and NMR spectroscopic data (see Section 2.4.2.1).

2.4.2 Structures in Solution

2.4.2.1 Aggregation in hydrocarbon solvents

As determined by such methods as cryoscopy, ebullioscopy and NMR spectroscopy, oligomers of organolithium persist in solution.[4] The extent of the aggregation of alkyllithiums depends upon the steric requirements of the alkyl group with more branching near the α-carbon resulting in smaller aggregation, *e.g.* ethyl- and butyl-lithiums are hexameric in cyclohexane and benzene whereas *t*-butyllithium is tetrameric in the same solvents. The even bulkier menthyllithium is dimeric and so continues the sequence. These findings clearly reflect the reduced steric hindrance in the smaller oligomers (Table 11).

Table 11 Aggregation of Organolithiums in Solution

		Solvent		
Compound	*Paraffins*, e.g. *cyclohexane*	*Aromatics* e.g. *PhH or PhMe*	Et_2O	*THF*
MeLi	—	—	4	4
EtLi	6	6	4	4
Pr^iLi	4–6	4	4	4
BuLi	4–6[a]	6	4	4
Bu^sLi	4	4	—	—
Bu^tLi	4	4	4	4
Octyl-Li	6[1]	6	—	—
Menthyl-Li	2	2	—	—
$CH_2{=}CHLi$	—	—	—	4[2]
PhLi	—	—	2	2
$CH_2{=}CHCH_2Li$	—	—	>10	1–2
$PhCH_2Li$	—	—	>1	>1
Polyisopropenyl-Li	2	2	1	1
o-FC_6H_4Li	$(RLi)_4(THF)_4$[3]	—	—	—
$R_2NCH_2CH_2CH_2Li$ (R = Me or Et)	—	4	—	1[b]
(5-Me-2-Me_2NCH_2-$C_6H_3Li)_4$[5]	—	4	—	—
CBr_3Li	—	—	1[6]	—

[a] 4 at concentrations between 0.2 and 1.0 M; 4 in *n*-heptane.[16] [b] In 1,4-dioxane.

1. Text ref. 12.
2. P. West, R. Waach and J. I. Purmot, *J. Am. Chem. Soc.*, 1970, **92**, 840.
3. O. M. Nefedov, A. I. Dyachemko and A. Ya. Shteinshneider, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1975, 256.
4. K. H. Thiele, E. Langguth and G. E. Müller, *Z. Anorg. Allg. Chem.*, 1980, **462**, 152.
5. Text ref. 141.
6. Text ref. 183.

Other factors having an influence on the degree of aggregation of alkyllithiums are the concentration and temperature. For instance, both isopropyl- and trimethylsilylmethyl-lithiums are reported to change from tetramers to hexamers as the concentration is increased.[119] Data were obtained for the hexamer–tetramer equilibrium[120] for isopropyllithium in isooctane; values of the equilibrium constant (at 226 K) and ΔH were found to be 3.4 l mol^{-1} and -20.5 ± 5.0 kJ mol^{-1}. At low concentrations of 2-methylbutyllithium (*ca.* 0.05 molar, based on the monomer) the degree of aggregation in pentane at 18 °C is as low as three. However, lowering the temperature results in an increase in the oligomer size beyond six, *e.g.* the average degree of association is 7.6 at −12 °C at 8.9 molar, based on monomer.

Fraenkel *et al.*[121] have established from ^{13}C and ^{6}Li NMR data for $CH_3CH_2{}^{13}CH_2{}^{6}Li$ that propyllithium in cyclopentane solution exists not only as hexamers but also as octamers and three different nonamers. While the hexamers predominate above 250 K, the other aggregates are present in appreciable amounts at lower temperatures. Equilibria are set up between the various aggregates: thermodynamic data for the hexamer–octamer equilibrium are $\Delta H = -7.1$ kJ mol^{-1} and $\Delta S = -34.3$ J K^{-1} mol^{-1}, with $K_{6,8} = 1.05$ and 0.36 l mol^{-1} at 197 and 253 K, respectively (equation 52).

$$4(PrLi)_6 \rightleftharpoons 3(PrLi)_8 \qquad (52)$$

$$K_{6,8} = [(PrLi)_8]^3/[(PrLi)_6]^4$$

2.4.2.2 Aggregation in donor solution and in the presence of donors

The solvent also plays an important role, as seen in Table 11. In a coordinating solvent such as THF or Et_2O, simple alkyllithiums and aryllithiums exist as coordinated tetramers and dimers.

The presence of a strong chelating donor, such as DABCO or TMED, also usually results in smaller coordinated oligomers. There is one notable exception: methyllithium. Tetrameric methyllithium complexes interact with TMED in solution as in the solid state. This is a clear indication of the strength of this unit. All types of organolithium apart from methyllithium form 1 : 1 complexes with TMED in solution; such complexes have been shown to be monomeric and dimeric,[6] *e.g.* both BuLi·TMED and $(BuLi{\cdot}TMED)_2$ have been identified.

The order of basicity of donors towards alkyllithiums has been established from enthalpy data. Heats of interaction of a series of donors with alkyllithium oligomers at 25 °C in hydrocarbon solvents, determined[119] at high dilutions and with low donor to lithium atom ratios, decreased in the sequence: THF > 2-Me-THF > 2,5-Me_2-THF > Et_2O > Et_3P > Et_3N > tetrahydrothiophene. It was also established that for a given donor the enthalpies decreased as $(Me_3SiCH_2Li)_6 > (Me_3SiCH_2Li)_4 > (Pr^iLi)_4 > (BuLi)_6 \approx (EtLi)_6 \gg (Bu^tLi)_4$. At the concentrations used, coordination of the donor occurs to an intact oligomeric unit, whether hexameric or tetrameric, with the sole exception of $(Me_3SiCH_2Li)_6$. This particular hexamer breaks down on interaction with the donor to give the base-solvated tetramer. Steric effects on coordination of the donors were more pronounced with hexamers than with tetramers. The effect of varying concentrations of NEt_3 on ethyllithium in benzene has been studied. At low ratios of NEt_3 to $(EtLi)_6$, coordination of the base occurs to the intact hexamer, but as the ratio is increased so formation of a coordinated dimer, $(EtLi)_2\ (NEt_3)_2$, occurs. At higher base concentration, further solvation results.[122]

Slightly different results have been indicated for butyllithium in isooctane solution. At high donor : lithium atom ratios, coordinated tetramers, $(RLi)_4{\cdot}nL$ ($n = 1$–4; L = ether, NEt_3 or Et_2S) are generally produced. These have been indicated in solution by spectral methods, *e.g.* butyllithium, hexameric in the absence of the ligands, can form 1 : 1 complexes, $(BuLi)_4{\cdot}4L$, on addition of sufficient ligand (L = THF, DME or Me_2O); other donors, *e.g.* Et_2O, Et_3N or Et_2S, bind less well and only produce $(BuLi)_4{\cdot}nL$ complexes, containing less than one equivalent of donor per lithium atom,[123] *i.e.* $n < 4$. From IR data [ν(C—Li) shifts on complexation] the following sequences of coordinating ability of bases (L) towards BuLi was established: L = THF > Me_2O > MeOEt and THF > Me_3N > Et_3N. These qualitative sequences, in the main, agree with that based on the quantitative calorimetric data of Quirk *et al.*,[119] despite the differences in the relative concentrations used in the two studies and the consequently different complex stoichiometries. In addition, $(Bu^sLi)_4$ was found to be a weaker acceptor than *n*-butyllithium.

Equilibria involving various solvated tetrameric *n*-butyllithiums were monitored at low temperatures (equations 53 and 54). An estimate of the dissociation equilibrium constant, $K_{1,4}$, for tetrameric *n*-butyllithium in Et_2O and THF at 25 °C was obtained (equation 55), in part from the kinetics[124] of reaction with PhCN in Et_2O and THF. Assuming that only the solvated monomers are reactive, values of K were calculated to be *ca.* $10^{-4}\ mol^3\ l^{-3}$ (THF) and *ca.* $10^{-16}\ mol^3\ l^{-3}$ (Et_3O). While not applying to this case, caution must be exercised in deciding aggregate numbers from kinetic data.

$$3(BuLi)_4(MeOEt)_2 \rightleftharpoons (BuLi)_4(MeOEt)_4 + 2(BuLi)_4MeOEt \qquad (53)$$

$$5(BuLi)_4(MeOEt)_2 \rightleftharpoons 2(BuLi)_4(MeOEt)_4 + (BuLi)_6{\cdot}MeOEt \qquad (54)$$

$$(BuLi)_4{\cdot}nL \rightleftharpoons 4BuLi{\cdot}mL + (n-4m)L \qquad (55)$$

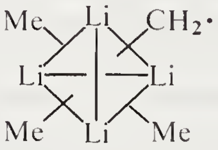
$$K_{1,4} = [BuLi{\cdot}mL]^4/[(BuLi)_4{\cdot}nL)]$$

2.4.2.3 Spectral studies

NMR spectroscopy has proved to be of particular value in elucidating structures.[11,12] For the tetrameric oligomers, a similar tetrahedral structure to that determined in the solid state is indicated from spectral studies. In ether, as in THF and triethylamine, ^{13}C enriched tetrameric methyllithium exhibits ^{13}C–^{7}Li scalar coupling in the ^{13}C and ^{7}Li NMR spectra at low temperatures; the $^{1}J(^{13}C–^{7}Li)$ value is 15 Hz in all three solvents.[125] Each lithium couples only with three carbons, the three neighbouring carbons, and not with the more distant carbon in the tetrahedron (the local environment hypothesis).

Thus one can rule out, for the solvated methyllithium tetramer, a rapid intra-aggregate exchange process which would have led to each Li coupling on average equally well with all four carbons (and *vice versa*). At higher temperatures, *e.g.* above −60 °C, inter-aggregate exchanges occur, however.[11,12] The absence of ^{6}Li–^{7}Li scalar coupling has been reported[126] and indicates a near-zero Li—Li bond in the tetramer despite a short Li· · ·Li distance of 2.6 Å $(MeLi)_4$ compared with 2.67 Å in Li_2. Hence the bonding electron density is concentrated in the region about the bridging alkyl groups and thus it is the multiple bridge bonding in the Li—C—Li framework, in contrast to Li—Li bonding, which holds the tetramer together.

Further insight into the structure of methyllithium in solution has been provided[127] by the ESR spectra of $Me_3Li_4CH\cdot$ (**10**) and $(CD_3)_3Li_4CD_2\cdot$, produced on proton abstraction from $(MeLi)_4$ in Et_2O solution by photochemically generated $Bu^tO\cdot$. The ESR spectrum of each radical indicates hyperfine splitting by three equivalent lithiums; the fourth, more distant, Li does not produce a significant hyperfine splitting. This fits the local environment hypothesis, as used with the ^{13}C NMR data and also in a normal mode analysis.[128] A rapid rotation ($>10^7$ s^{-1}) of the CH_2 group about a six-fold barrier was further suggested. There was no evidence for an intermolecular exchange of radical sites among clusters. The radical $Me_3Li_4CH_2\cdot$ was also probably produced during reaction of $TiCl_4$ with $(MeLi)_4$ by the two-step sequence shown in equations (56) and (57).[43]



(10)

$$(MeLi)_4 \quad + \quad TiCl_4 \quad \xrightarrow[Et_2O/C_6H_6]{fast} \quad Me\cdot \tag{56}$$

$$Me\cdot \quad + \quad (MeLi)_4 \quad \xrightarrow{slow} \quad MeH \quad + \quad \underset{\textbf{(10)}}{\cdot CH_2Li_4Me_3} \tag{57}$$

The small upfield displacement of the ^{13}C chemical shift of methyllithium, relative to methane, was interpreted as evidence for a predominantly sp^3 hybridized carbon, with little excess charge density on carbon. In addition, an estimated value for the charge separation in the C—Li bond of 0.1 electron was calculated from the ^{13}C chemical shift value (although this has been considered too low).[11] From another relationship, involving ^{13}C chemical shift values and substituent electronegativity, the lithium in the methyllithium tetramer is substantially more electronegative than atomic lithium. To account for the $^{1}J(^{13}C–^{1}H)$ values (*ca.* 98 Hz) being less than normally obtained for sp^3 hybridized carbon, an increased s character of the C—Li orbital (to about 40%) was considered.

The ^{13}C NMR spectrum of (*n*-butyllithium)$_4$ in ether also indicates coupling of ^{13}C with three equivalent lithiums;[129] the $^{1}J(^{13}C–^{7}Li)$ value is 14 Hz at −70 °C. In contrast, for $(Bu^tLi)_4$ in hydrocarbon solvents[130] the ^{13}C NMR spectrum indicates coupling of the α-carbon with four equivalent lithiums; $^{1}J(^{13}C–^{7}Li)$ values are between 10–11 Hz in toluene, benzene and cyclohexane solutions. Hence a rapid *intra*-aggregate exchange is occurring in $(Bu^tLi)_4$ in these hydrocarbon solvents with the $^{1}J(^{13}C–^{7}Li)$ values representing the average of the three nearest C–Li couplings with that of the distant lithium in the tetramer. If the latter coupling is assumed to be near zero, then the directly bonded $^{1}J(^{13}C–^{7}Li)$ value is *ca.* 14 Hz, comparable with values obtained for methyl- and *n*-butyl-lithium tetramers in ethers.

Only broad unresolved coupling[130] is observed in hydrocarbon solutions of Bu^sLi and Pr^iLi. For other organolithium oligomers, *e.g.* $(BuLi)_6$ in hydrocarbons, only broadening of the ^{13}C NMR spectrum occurs at low temperatures and no splitting due to ^{13}C–^7Li coupling results. This is assumed to arise from averaging of the ^{13}C–^7Li coupling by a combination of carbon–lithium bond exchanges and ^7Li quadrupole relaxation. The fact that ^6Li quadrupole relaxation is too slow to perturb the spectra, *i.e.* does not cause broadening, renders ^6Li a useful probe for studying alkyllithiums.

An illustration of ^6Li use is given by Fraenkel *et al.*[121] with enriched $CH_3CH_2{}^{13}CH_2{}^6Li$. High-field ^{13}C and ^6Li NMR spectra of $CH_3CH_2{}^{13}CH_2{}^6Li$ in cyclopentane show splittings due to ^{13}C–^6Li couplings and reveal the existence of hexamers, octamers and nonamers, as mentioned earlier. These oligomers undergo fast *intra*-aggregate carbon–lithium bond exchange, which are still fast on the NMR time scale at 180 K. In the symmetrical, octahedral propyllithium hexamer, for example, each α-carbon is coupled equally with all six lithiums, and not just the nearest three. Thus as with (t-butyllithium)$_4$, a fluxional process operates whereby each α-carbon becomes associated with all the lithiums. The 3.35 Hz splitting represents the average of the three nearest neighbour ^{13}C–^6Li couplings with the three couplings to the more distant lithiums in the octahedron. If the latter is near zero, then the directly bonded $^1J(^{13}C{-}^6Li)$ is *ca.* 6.7 Hz, which is equivalent to a $^1J(^{13}C{-}^7Li)$ value of 17.7 Hz. This is similar to the values of *ca.* 15 Hz obtained in tetrameric units.

As with other alkyllithiums, inter-aggregate carbon–lithium bond exchanges occur at higher temperatures, as shown by ^{13}C and ^7Li lineshape changes. The same mechanism is responsible for exchanging the propyl and lithium groups (for exchanges involving hexamers, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 180 kJ mol^{-1} and -150 J K^{-1} mol^{-1} from the ^{13}C NMR data and 184 kJ mol^{-1} and -155 J K^{-1} mol^{-1} from the ^6Li spectra). The large negative entropy of activation suggests a bi-aggregate exchange step but clearly not a dissociative–recombination process. The inter-aggregate exchange processes involving different species occur at different rates.

2.4.2.4 Vibrational and electronic spectra

(*i*) *Vibrational spectra*

The Raman line at 521 cm^{-1} in $(Bu^tLi)_4$ in benzene is IR inactive and suggests the symmetry class T_d for the tetramer. The IR spectra of organolithiums in vapour, solution and solid phases have been reported.[11a] The frequencies which exhibit mass effect upon substitution of ^6Li for ^7Li are below 600 cm^{-1}; these must be the carbon–lithium valence vibrations. The normal lithium–carbon modes of motion must be complex, involving the skeletal modes of the framework of the aggregate (Table 12).

Table 12 IR Spectra of Alkyl- and Phenyl-lithiums

Compound	*Medium*	ν(*C—Li*) (cm^{-1})	*Ref.*[b]
$(MeLi)_4$	mull	514, 417	[131]
$(CD_3Li)_4$	mull	436, 336	
(EtLi)	vapour	531	[11a]
	C_6H_6 solution	530, 576	[11a]
	hexane solution	532	[11a]
	Bu_2O solution	516	[11a]
	mull	565, 445, 318	[11a]
$(BuLi)_6$	isooctane solution	550 (370)	[123a]
$(BuLi)_4{\cdot}1D^a$	isooctane solution	547–535	[123a]
$(BuLi)_4{\cdot}2D^a$	isooctane solution	535–530	[123a]
$(BuLi)_4{\cdot}3D^a$	isooctane solution	525–520	[123a]
$(BuLi)_4{\cdot}4D^a$	isooctane solution	504	[123a]
$(Bu^sLi)_4$	isooctane solution	518, 445	[123a]
	benzene solution	512	[123a]
$(Pr^iLi)_6$	isooctane solution	508, 417	[123a]
$(Pr^iLi)_4$	isooctane solution	480, >400	[123a]
$(Pr^iLi)_4(THF)_2$	isooctane solution	470	[120]
$(Bu^tLi)_4$	benzene solution	480, 420 521 Raman	1
$(PhLi)_n$	mull	421, 378	[131]

[a] D = THF or Me_2O. [b] References in brackets refer to text references.

1. M. Weiner, G. Vogel and R. West, *Inorg. Chem.*, 1962, **1**, 656.

The ν(C—H) stretch in solid (cyclohexyllithium)$_6$·2PhH[114] are at 2800 (asym) and 2720 cm^{-1} (sym), compared with 2900 cm^{-1} in cyclohexane. The shift to lower frequency was considered in terms of H· · ·Li interactions. Reported frequencies for methyllithium tetramers are ν(C—H) stretch at 2840 and 2780 cm^{-1} for $(MeLi)_4$, as well as 2150 and 2027 cm^{-1} for $(CD_3Li)_4$; the ν(CH) bend (1480 and 1427 cm^{-1}) and ν(CH) rock (1001 and 1096 cm^{-1}) for $(MeLi)_4$ were also quoted.[131] Values of ν(C—H) stretch for ionic, solid methylpotassium[132] are 2805 and 2740 cm^{-1}.

(*ii*) *UV spectra*

The absorption maxima in the UV spectra of alkyllithiums are listed in Table 13. Calculations at the CNDO/2 level indicated that the lowest energy transition in the tetramer corresponds to an electron transfer from an orbital centred mainly on carbon to one centred on the lithium; see also the *ab initio* calculations of Streitwieser *et al.*[35]

Table 13 Absorption Maxima and Extinction Coefficients for Alkyllithiums in the Vapour Phase and in Solution

Compound	*Medium*	λ_{max} (nm)	ϵ	*Ref.*[a]
$(EtLi)_6$	vapour	215	10^3–10^4	1
$(EtLi)_4$	vapour	203	—	1
$(EtLi)_6$	hexane solution	210	2×10^3	[134]
$(BuLi)_6$	hexane solution	210	5.2×10^2	1
	benzene	278–282[b]	9.1×10^1	2
$(BuLi)_4$	Et_2O	240	—	3
	THF	270	—	3
$(Bu^sLi)_{4,6}$	vapour	206	10^3–10^4	1
$(Bu^tLi)_4$	vapour	190	10^3–10^4	1
$(PhLi)_2$	Et_2O	*ca.* 290	—	4
$(2,4,6\text{-}Me_3C_6H_2Li)_n$	Et_2O	*ca.* 300	—	4

[a] Reference in brackets refers to text reference. [b] Concentration dependent.

1. J. B. Smart, R. Hogan, P. A. Scherr, L. Ferrier and J. P. Oliver, *J. Am. Chem. Soc.*, 1972, **94**, 8371.
2. J. R. Urwin and P. J. Reed, *J. Organomet. Chem.*, 1968, **15**, 1.
3. T. Holm, *Acta Chem Scand., Ser. B*, 1978, **32**, 162.
4. K. L. Rogozhin, A. N. Rodionov, D. N. Shigorin, N. I. Sheverdina and K. A. Kocheshkov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1975, **24**, 1874.

Photolysis[133] of ethyllithium in solution provides ethylene predominantly as well as a little ethane, but only traces of butane; an elimination of LiH was suggested. For phenyllithium the major photolysis product was biphenyl.[134] Photochemical reactions of alkyllithiums occur primarily at high energy and involve formation of radicals by a charge transfer mechanism. An intra-aggregate disproportionation mechanism for the photodecomposition of ethyllithium[133] was proposed.

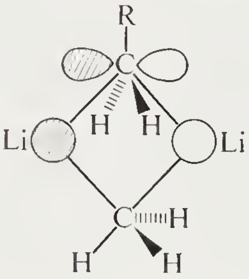
2.4.2.5 Inversion at carbon bonded to lithium and configurational stability of sp^3*-hybridized organoalkali metal compounds*

The compounds (*R*)-2-methylbutyllithium and the racemic (*RS*)-2-methylbutyllithium, hexameric in pentane solution under the conditions used, undergo exchange processes.[135] Two exchange processes at equilibrium occur in the racemate. These are (i) inversion at the α-carbon bonded to lithium in an *intra*-aggregate process (k at 281 K = 4.0 s) and (ii) a faster *inter*-aggregate exchange of carbon–lithium bonds (k at 281 K = 72 s). In the (*R*)-2-methylbutyllithium compound only the inversion was detected (k at 281 K = 6.4 s). The activation parameters for the inter-aggregate exchange process with the racemic species are $\Delta H^{\ddagger} = 13.8 \pm 2.1$ kJ mol^{-1} and $\Delta S^{\ddagger} = -163 \pm 4$ J K^{-1} mol^{-1} and are similar to those measured for (propyllithium)$_6$ in cyclopentane.

Inversion at carbon bonded to lithium has also been indicated for another primary alkyllithium, namely $Me_3CCH_2CH_2Li$ in Et_2O;[136] the enthalpy of activation for the *intra*-aggregate inversion in $Me_3CCH_2CH_2Li$ was quoted as 63 kJ mol^{-1}· The activation parameters for (*R*)- and (*RS*)-

2-methylbutyllithiums were calculated to be $\Delta H^{\neq} = 61.9 \pm 4.6$ and -65.2 ± 4.6 kJ mol^{-1}, $\Delta G^{\neq}$ (at 281 K) = 65.6 ± 4.2 and -66.0 ± 4.2 kJ mol^{-1}, and $\Delta S^{\neq} = -12.5 \pm 12.5$ and -2.5 ± 12.5 J K^{-1} mol^{-1}, respectively. The similarity in the enthalpies of activation for the inversion of $Me_3CCH_2CH_2Li$ and 2-methylbutyllithium, despite the difference in solvents and consequent differences in the extents of aggregation, is striking.

The inversion process has also been considered by an *ab initio* MO method.[137] This treatment, using STO-3G/4-31G basis sets and modelled on methyllithium dimers, indicated that RCH_2Li_2 fragments could be involved in the inversion mechanism. In these RCH_2Li_2 units, two lithium atoms stabilize a planar RCH_2 (C_s symmetry), *via* overlap of the carbon p_x-orbital with an antisymmetric combination of lithium *s*-orbitals (**11**). This contrasts with the pyramidal arrangement of alkyl groups above the Li_3 faces of the organolithium tetramers and hexamers, as shown by the crystal structure. It was argued[137] that the most important consequence for inversion is that the planar alkyl group should be preferentially stabilized by an Li—Li edge rather than an Li_3 triangular face. Inversion may take place in a hexamer during migration of a pyramidal alkyl group from an Li_3 face, *via* an Li—Li edge (at which stage the alkyl group becomes planar) to a vacant Li_3 face. This process appears to be less favourable in tetramers which contain no vacant Li_3 faces, although concerted centre to edge movements of three of the four alkyl groups, *via* a C_{3v} transition state, is possible. This mechanism is specific for primary alkyllithiums since at least two hydrogens are required at the α-carbon. Because of steric problems, secondary and tertiary alkyllithiums should have higher barriers to inversion.

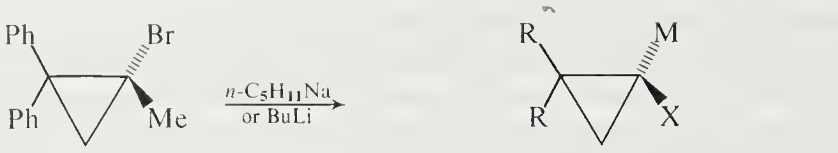


(**11**)

Menthyllithium and *trans-t*-butylcyclohexyllithium[59] are are two configurationally fixed compounds. Menthyllithium, prepared from either menthyl or neomenthyl chloride and lithium in refluxing pentane, is configurationally rigid to at least 50 °C in hydrocarbons but only to below 0 °C in Et_2O. The siting of the apparently small lithium in the equatorial position in the stable epimer was accounted for by the real (and larger) steric requirement of the remainder of the menthyllithium dimer. In 2-lithiodithianes there is also a thermodynamic preference for an equatorial lithium (see Section 2.4.5).

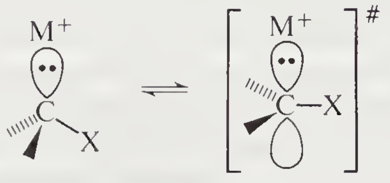
Early attempts to prepare pure optically active organo-lithiums and -sodiums by reaction of Li and Na with chiral alkyl halides failed due to extensive racemization.[138,139] This probably arises from the free radical nature of this preparative reaction. However, use of other preparative methods, *e.g. trans*-metallations and halogen–metal exchanges, has brought success. A sample of *s*-butyllithium with a high but not complete optical purity was produced from chiral di-*s*-butylmercury and 2-octyllithium in pentane. At −40 °C with a reaction time of 4 h, 83% retention was achieved. Longer reaction times, higher temperatures and the presence of ethers all lead to more racemization.[99]

Certain chiral cyclopropyl-lithiums, -sodiums and -potassiums, once formed,[140] are also stable, *e.g.* reaction of (*R*)-1-Br-1-Me-2,2′-Ph_2-cyclopropyl bromide and *n*-pentylsodium in pentane or BuLi in benzene provided the stable alkali metal cyclopropyl derivatives (**12**), with retention of configuration. The configurational stability of (**12**; R = Ph, X = Me, M = Li) was shown to be unaffected by the solvent, reaction time or even the temperature and hence is configurationally more stable than sp^3 hybridized alkyllithiums and stibenyllithiums and is of comparable stability to alkylvinyllithiums (see Section 2.7.3). There is considerable strain energy (*ca.* 109 kJ mol^{-1}) associated with cyclopropane; in the transition state leading to inversion the strain would be even greater and hence the inversion process is not normally favoured in cyclopropylalkali metal compounds. Other compounds (**12**) having appreciable configurational stability are those where X is a non-delocalizing substituent, such as methyl, halide, methoxyl and in particular isocyanide, but not for X = RC≡C or C≡N. Both these substituents are able to delocalize the negative charge and hence stabilize planar configurations. Thus lower inversion barriers result (Scheme 11).



(58)

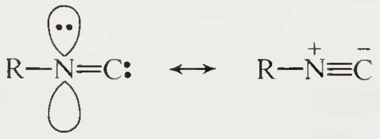
(**12**) R = Ph, X = Me, M = Li or Na



Scheme 11

Compound (**12**; R = H, X = C≡CH) is configurationally stable in benzene but addition of only a little THF results in its racemization. Thus inversion is easier in s.s.i.p., compared to t.i.p., organolithiums having delocalizing substituents, *e.g.* CN, COR, C≡CH and $CH{=}CH_2$ (see also Section 2.6.3). The contrast between (**12**; R = Ph, M = Li, X = CN) and the isocyanide derivative is considerable. The cyano derivative is configurationally unstable in ethers at −72 °C, unlike the Li, Na or K salts of the isocyanide species; these are also stable in the presence of crown ether, glymes, TMED or HMPT, *i.e.* even when s.s.i.p. or glyme separated ion-paired. However, racemization occurs in ether solutions on warming and becomes complete at −5 °C.

The isocyanide group has the resonance forms (**13a**) and (**13b**). In (**13a**), which is the more important, a lone pair of p-electrons resides on nitrogen. The increase in the inversion barriers, *i.e.* the destabilization of the planar transition state in Scheme 11, by a delocalizing group, arises from the repulsive interaction between the non-bonding pair of p-electrons of the α-heteroatom and the adjacent carbanionic p-orbital.



(**13a**) (**13b**)

Enantiomerically pure α-alkoxyalkyllithiums have been prepared from the corresponding tin compounds, with complete retention of configuration even in THF solution,[100] *e.g.* equation (59). The ease with which the α-alkoxyorganotin compounds can be resolved, and the mildness of the high-yielding *trans*-metallation reaction, renders this a most valuable reaction. In addition to the α-heteroatom effect, chelation of the α-alkoxy group to lithium, either of an intramolecular or *intra*-aggregate nature, could result in a more rigid system.

(59)

R = $PhCH_2OCH_2$

Of interest, the methylene protons and the NMe_2 groups in $(5\text{-Me-2-NMe}_2CH_2C_6H_3Li)_4$ in benzene solution are diastereotopic.[141] Coalescence of the Me_2N singlets does not occur below 90 °C, at which temperature the AB pattern of the methylene protons begins to broaden. These spectral effects are due to strong N → Li coordination in the tetramer. Addition of Et_2O to benzene solution breaks this coordination and results in coalescence of the methylene and the NMe_2 protons.

2.4.2.6 *Other exchange processes*

Primary alkyllithiums undergo inter-aggregate exchanges with other alkyllithium aggregates, *e.g.* $(MeLi)_4$ and $(EtLi)_4$, in ether to produce mixed aggregate compounds. At low temperatures, ^7Li NMR spectroscopy indicates distinct scrambled aggregates which at higher temperature undergo sufficiently fast exchange to give averaged ^7Li chemical shift values. Exchanges also occur with lithium halides,[142] alkoxides and with complex metal alkyls, such as $LiMR_4$ (M = B, Al or Ge),[143] Li_2MR_4 and Li_3MR_5 (M = Sn or Mg)[144] in ether.

Mixed associated complexes, $Li_4Me_nX_{4-n}$ (X = Br, n = 2, 3; X = I, n = 3), as well as $(MeLi)_4$ and $(LiX)_n$ are indicated by ^7Li NMR spectroscopy in solutions made up from $(MeLi)_4$ and $(LiX)_n$ in ether. The exchanges are slower in THF than in Et_2O. Two distinct ^7Li resonances are observed in Me_3Li_4I, obtained from excess $(MeLi)_4$ and LiI in Et_2O. These coalesce as the temperature is raised due to an increasingly rapid inter-aggregate exchange process.[142]

Dissociative mechanisms, *i.e.* $(RLi)_4 \rightarrow (RLi)_2$, were proposed for some of the exchange reactions including those involving the lithium halides and also $LiAlR_4$. A theoretical treatment has calculated, however, that the energy for the dissociation $(MeLi)_4 \rightleftharpoons 2(LiMe)_2$ is rather high, being about 180 kJ mol^{-1} (see also Fraenkel's findings, p. 71).

Exchanges also occur with organocuprates.[145]

2.4.3 Gas Phase Studies

Oligomers of alkyllithiums also persist in the gas phase, *e.g.* for ethyllithium,[146] *t*-butyllithium[147] and trimethylsilylmethyllithium.[148] The mass spectrum of ethyllithium at 75 eV contained peaks due to $[Li_nEt_{n-1}]^+$ (n = 1–6), with the base peak being $[Li_2Et]^+$. No peak due to $[Li_nEt_n]^+$ was observed. The appearance potentials for the formation of $[Li_6Et_5]^+$ and $[Li_4Et_3]^+$, at 7.7 and 8.0 eV, were significantly lower by 3–4 eV than for the other $[Li_nEt_{n-1}]^+$ ions (n = 2, 3 and 5).

With the assumption that the processes (equation 60) would yield ions of similar stabilities and that all Li_nEt_n would have similar ionization potentials, the results were interpreted as showing that only hexamers and tetramers of ethyllithium are present (in comparable amounts) in the gas phase. The ions $[Li_nEt_{n-1}]^+$ (n = 2, 3 and 5) were considered to arise by fragmentation of $[Li_6Et_5]^+$ and $[Li_4Et_3]^+$.

$$Li_nEt_n \quad + \quad e^- \quad \longrightarrow \quad Li_nEt^+_{n-1} \quad + \quad Et\cdot \quad + \quad 2e^- \tag{60}$$

A later semi-empirical MO treatment[149] (PRDDO, see Section 2.4.2), however, has indicated similar binding energies for $(MeLi)_n$ oligomers (n = 3–6) but with different ionization potentials for the clusters, calculated to have planar as well as condensed geometries (Figure 5). A different interpretation of the mass spectral data for ethyllithium was consequently provided, namely that the peaks for $[Li_nEt_{n-1}]^+$ do in fact correspond at low electron energies to the loss of Et from parent neutral Li_nEt_n clusters rather than from fragmentation of the tetramer and hexamer. The variation in appearance potentials of $[Li_nEt_{n-1}]^+$ is due both to the variation in ionization potentials and to different mechanisms by which Et is lost from a given cluster. The loss of an ethyl group is in agreement with the theoretical finding that the HOMO electrons are predominantly localized on carbon rather than on lithium.

The temperature required to obtain a suitable vapour pressure of ethyllithium is at least 85 °C. Unfortunately methyllithium has no significant vapour pressure below its decomposition point (150 °C). In contrast, *t*-butyllithium has a reasonable vapour pressure even at room temperature. The fragmentation spectrum in the photoionization of *t*-butyllithium was measured between 6 and 13 eV (Scheme 12). As with ethyllithium, the parent ion $[Li_4Bu^t_4]^+$ was not reported. The appearance potentials of the observed ions were 6.2 ± 0.25 eV for $[Li_4Bu^t_3]^+$ and *ca.* 8.1 ± 0.25 eV for $[Li_4Bu^t_2]^+$, $[Li_4Bu^t]^+$ as well as $[Li_2Bu^t]^+$. The relative populations of the fragments varied with the photon energy; up to 10.5 eV the amounts of the ions were in the sequence $[Li_4Bu^t_3]^+ > [Li_2Bu^t]^+ > [Li_4Bu^t]^+ > [Li_4Bu^t_2]^+$. Purely hydrocarbon fragments, such as $C_4H_9^+$, $C_3H_6^+$ and $C_2H_5^+$, did not appear until 11 eV. The stability of the four-atom lithium cluster is illustrated by the fact that three of the four fragment ions contain such a system, probably in a tetrahedral array. The methyllithium system, a much simpler one for *ab initio* computational purposes, has been used to model *t*-butyllithium. Comparisons, where possible, were reasonably good, *e.g.* the

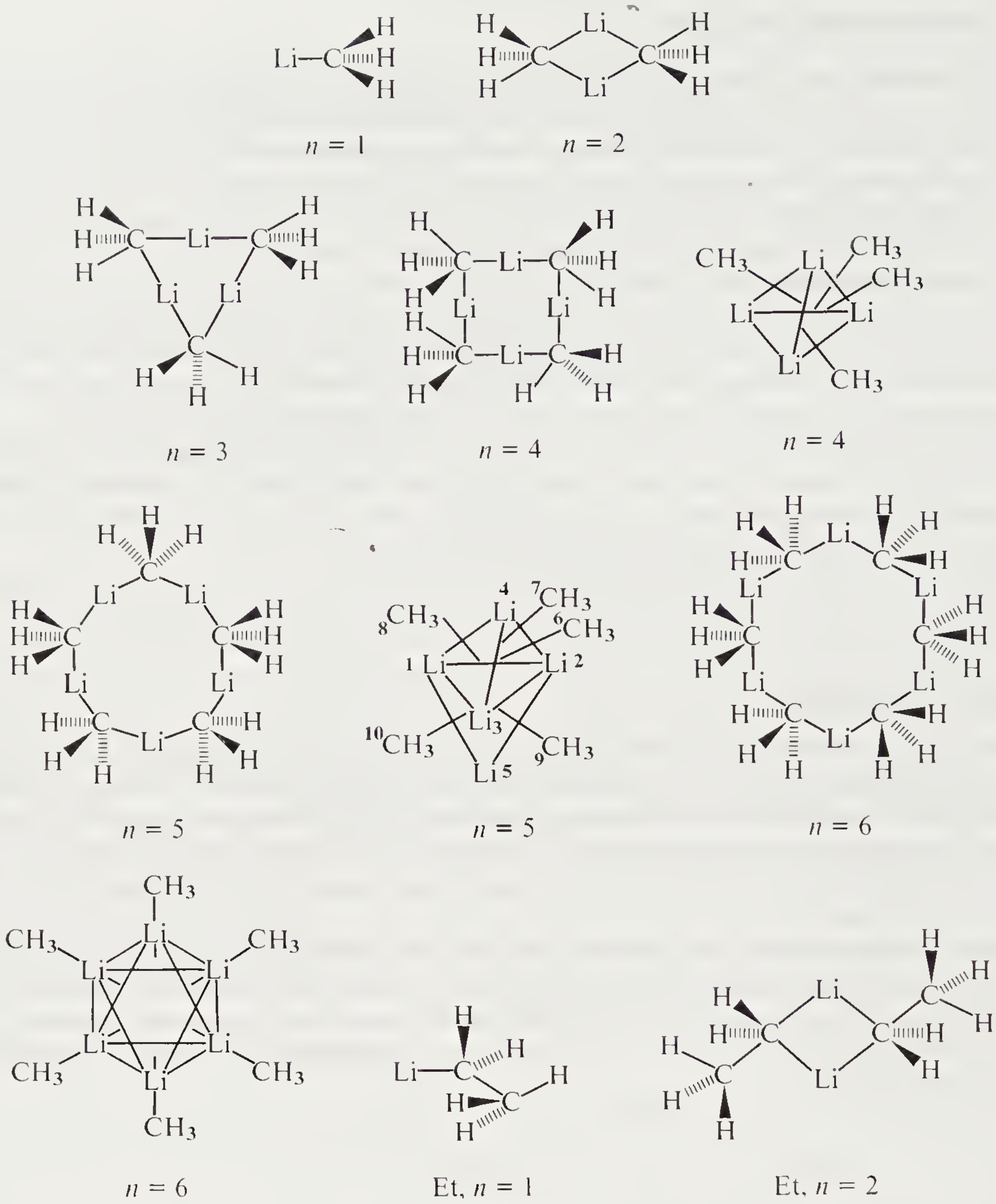


Figure 5 Structures of methyllithium oligomers and ethyllithium monomers and dimers, calculated by the PRDDO MO method[149]

measured vertical ionization potentials for $(LiBu^t)_4$ were at 6.7, 10.4, 11.1 and 12.7 eV, compared with calculated values (at the STO-3G level) for $(MeLi)_4$ of 6.9, 9.2, 12.9 and 13.2 eV. The energies of fragment methyllithium ions and molecules in their optimum geometries were used to determine the dissociation pathways available to the optically excited methyllithium tetramer at various photon energies. Processes calculated to be allowed for $(MeLi)_4$ are listed in Scheme 13; analogous ones are likely for $(LiBu^t)_4$. Each ion $[Li_4Me_n]^+$ is stable with respect to dissociation into $[Li_4Me_{n-1}]^+$ and Me·.

$$Li_4Bu^t_4 \longrightarrow [Li_4Bu^t_3]^+ + [Bu^t]\cdot + e^-$$

$$\Delta E_1 = 6.2 \text{ eV}$$

$$Li_4Bu^t_4 \longrightarrow [Li_4Bu^t_3]^+ + [Li_4Bu^t_2]^+ + [Li_4Bu^t]^+ + [Li_2Bu^t]^+ + [LiBu^t]^+ + [Bu^t]\cdot + e^-$$

$$\Delta E_2 = \Delta E_1 + 1.9 \text{ eV}$$

Scheme 12

At the first calculated I.P. (6.9 eV)

$$(\mathrm{LiMe})_4 \longrightarrow \mathrm{Li_4Me_3^+} + \mathrm{Me\cdot} + \mathrm{e^-} \quad \Delta E = 4.89\ \mathrm{eV}$$

At the second calculated I.P. (9.2 eV)

		ΔE (eV)
$(\mathrm{LiMe})_4$	$\rightarrow \mathrm{Li_4Me_2{}^+} + \mathrm{2Me\cdot} + \mathrm{e^-}$	6.7
	$\rightarrow \mathrm{Li_4Me^+} + \mathrm{3Me\cdot} + \mathrm{e^-}$	8.26
	$\rightarrow \mathrm{Li_2Me_2} + \mathrm{Li_2Me^+} + \mathrm{Me\cdot} + \mathrm{e^-}$	6.88
	$\rightarrow \mathrm{Li_4Me_2^+} + \mathrm{MeH} + \mathrm{CH_2} + \mathrm{e^-}$	6.49
	$\rightarrow \mathrm{Li_2Me} + \mathrm{Li_2Me^+} + \mathrm{2Me\cdot} + \mathrm{e^-}$	8.61
	$\rightarrow \mathrm{Li_2Me_2} + \mathrm{LiMe^+} + \mathrm{LiMe} + \mathrm{e^-}$	8.16

Scheme 13

The ion $\mathrm{MeLi_2^+}$ has also been the object of another *ab initio* study (STO-3G, 6-31G levels).[150] It is a known gas phase species, appearing as the abundant ion in the mass spectrum of $\mathrm{LiBMe_4}$. Related ions, $\mathrm{RLi_2^+}$, appear as the most abundant peaks in the mass spectra of alkyllithiums. The stability is due to all possible pathways of decomposition being highly endothermic. The bonding and geometry of $\mathrm{MeLi_2^+}$ is considered in Section 2.4.4.

2.4.4 Bonding in Alkyl- and Aryl-alkali Metal Compounds

A satisfactory bonding treatment of organolithium species has to account for the various, and potentially conflicting, features of organolithiums, *viz.* (i) lithium is a highly electropositive element and thus is expected to form highly ionic bonds with less electropositive elements, (ii) NMR studies indicate that the charge separation in typical organolithiums is substantially less than unity,[11,125] (iii) many organolithiums form oligomers whose structures are, as has been described, those of electron deficient compounds with bridging organic units, rather than ionic aggregates or crystals, (iv) polylithiation, *e.g.* of methane, occurs and (v) alkyllithiums can undergo radical reactions.

The IR spectral analysis of a matrix-isolated monomeric methyllithium yielded little structural information apart from the force constant for asymmetric deformations of the pyramidal methyl group and a rough estimate of the dipole moment (6 D), assuming $r(\mathrm{C{-}Li}) = 2.10$ Å. Theoretical studies have been carried out on monomeric and aggregate species at both semi-empirical[149,151] MO and *ab initio* levels; in addition, an electrostatic model[21] was used.

Ab initio calculations have been made on simple alkyl derivatives such as methyllithium,[35,152,153,154] ethyllithium[35] and lithium substituted carbanions,[155] carbonium ions[156] and carbenes.[157] Polylithio species, such as $\mathrm{CH_3Li_2^+}$,[150] $\mathrm{CH_2Li_2}$,[158,159] $\mathrm{CHLi_3}$[158] and $\mathrm{CLi_4}$,[158] have also been studied. Among the other organolithiums studied are vinyllithium,[35] ethynyllithium,[35] allyllithium,[160] lithiated allenes, propynes and cyclopropenes,[22] cyclopentadienyllithium[161] and lithium carbenoids.[162] Further discussions on the functionally substituted compounds will be left to the relevant sections. Fewer calculations have been made on compounds of the heavier alkali metals, although $\mathrm{CH_3Na}$,[159] $\mathrm{CH_2Na^+}$ [163] and $\mathrm{CH_3Na_2^+}$ have been studied.

The most studied organolithium is methyllithium and it is perhaps not too surprising that various conclusions have been made regarding the ionic or covalent character of the carbon–lithium bond in the monomer. The problem is possibly one of definition and the different parameters used for the basis of these conclusions. However, most workers have concluded that the bonding in monomeric methyllithium is covalent with a significant polar (ionic) character. An extreme view has been taken by Streitwieser *et al.*,[35,152] who declared methyllithium to be wholly or mainly ionic. They performed SCF calculations with a Gaussian split shell with carbon *d*-orbitals and hydrogen *p*-orbital basis sets with complete geometry optionization. They deduced from the electron density along the C—Li axis, and from projection plots as well as the integrated electron population, that the C—Li bond had essentially no shared-electron covalent character. Monomeric methyllithium was thereby described by Streitwieser as being largely ionic with about 0.8 electron transferred. Streitwieser argued that since the methyl radical has a low electron affinity the energy required to transfer an electron back from carbon to lithium should be relatively low. The calculated energy for σ(C—Li) (localized mainly on carbon) to σ (C—Li) (localized mainly on Li) is indeed low (2.8 eV). The dissociation energy for MeLi monomer (to Li· and CH_3·) is expected to be less than 188 kJ mol^{-1}. Experimental data gave a C—Li dissociation energy of 211.1 kJ mol^{-1} for gaseous $(ethyllithium)_n$ ($n = 4$ or 6). This latter value should be reduced by the amount of the oligomerization energy. Thus, either by electronic transition to a low-lying excited state or by the lower-energy process of direct C—Li homolysis, radical species can be readily formed.

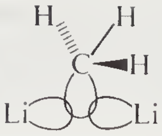
The conclusion from a subsequent and more elaborate *ab initio* treatment (near Hartree–Fock basis set with configurational interaction) was of a lower charge separation of 0.55 to 0.60 electrons. Graham *et al.*[153] cautioned against using the minimum electron density along the C—Li axis as a measure of charge separation and argued instead for the use of the integrated value of the charge density function over the full spatial extent of the chemical bond. In addition it was argued[153] that a charge separation of 0.55–0.60 electron, while being sufficient to make ionic mechanisms believable, was not so complete as to rule out occasional radical behaviour. The approximately half-covalent character of carbon–lithium bonding would not prohibit the existence of polylithiated species or organolithium oligomers with electron deficient bonding schemes. In fact, elaborate and unusual multicentre bond networks might be especially prevalent in such compounds, as both the presence of vacant *p*-orbitals and the partial positive charge contribute to the lithium atomic electron deficiency.

Another study to conclude against a wholly ionic bond was that of Clark *et al.*[154] These authors used an INDO-type calculation to determine coupling constants, $^1J(^7Li–^{13}C)$, in methyllithium and its oligomers at the levels STO-3G, 4-31G and MNDO. The coupling constant values of each oligomer are practically independent of the level used, the values being 116.0 for MeLi (C_{3v}), 22.7 for $(MeLi)_2$ (C_{2v}), 7.3 for $(MeLi)_4$ (T_d staggered), 7.2 for $(MeLi)_4$ (T_d eclipsed) and 123 Hz for MeLi–NH_3. Ionic bonding should provide only relatively small coupling constants and it was thus concluded that the monomer is a predominate covalent structure, especially as it appears that these INDO calculations underestimate the coupling constants by a factor of two. For example, $J(^7Li–^{13}C)$ values for alkyllithium tetramers have been found to be about 10–15 Hz.[121,125,129] Furthermore, if the factor of two is consistent, then a coupling constant of *ca.* 200 Hz is anticipated for the methyllithium monomer.

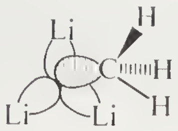
The decrease in coupling constants from the monomer to tetramer results from both the decrease in the C—Li overlap on going from two-centre to multi-centre bonding and the large decrease in *s*-character on lithium upon oligomerization.

The multi-centred electron deficient bonding in methyllithium oligomers has featured in many other theoretical studies. In the most extensive study[149] the optimized geometries and wave functions were determined for $(MeLi)_n$ ($n = 1$–6) and also for $(EtLi)_n$ ($n = 1$ or 2), using the PRDDO approximate MO method (PRDDO: partial retention of diatomic differential overlap). This approach provides results in good agreement with those from the more costly *ab initio* minimum basis-set calculations, using STO-3G expansion or Slater orbitals.

These PRDDO calculations[149] indicated interesting stable planar arrangements for $n = 2$–6 in addition to a stable condensed tetramer (T_d) and hexamer (D_{3d}) (Figure 5). The D_{4h} tetramer was calculated as having more stability than the T_d tetramer; the two hexamers had similar energies. There was, in addition, a condensed C_s pentamer of appreciable binding energy but of lesser stability than the planar D_{5h}. In the planar forms, significant metal–metal interactions were suggested from the overlap populations but there was little intermetallic bonding in the condensed aggregates, in particular in the T_d tetramer (the lithium orbitals are directed *exo* to the occupied triangular faces). The bonding in all of the methyllithium clusters was interpreted in terms of localized MOs. The planar forms are bound by a network of closed three-centre Li—C—Li bonds (see **14**). The hybridization on carbon is normal but that on lithium for $n > 1$ usually has significantly more Li(2*p*) than Li(2*s*). The heavy atoms of the T_d tetramer are connected by closed four-centre bonds (three lithiums and one carbon; see **15**). The bonding in the D_{3d} hexamer takes place about the two open faces. The lithium atoms around an open face are bound by three bridging methyls utilizing closed three-centre Li—C—Li bonds. However, the respective apical lithium on the adjacent triangle of lithiums from the other vacant face shows a significant interaction with the central methyl group (donating 0.16 electron). It is this donation from the apical lithium that holds the cluster together. In essence, the hexamer can be considered to be composed of weakly interacting distorted trimers.



(14)



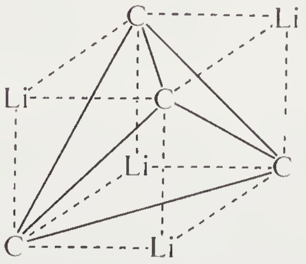
(15)

A different view of the methyllithium tetramer has been taken by Streitwieser,[21] who considered that the Li—Li and C—C distances obtained from the X-ray structure determination of the tetramer (namely 2.68 and 3.68 Å) are consistent with a wholly ionic model. This model consisted of a tetrahedron of four point charges (carbons) and an interpenetrating tetrahedron of the opposite charges (lithiums); the coulombic energy was calculated to be a minimum for (Li—Li)/(C—C) = 0.783, a ratio which compares well with the experimental value of 0.73.

Ab initio calculations showed that lithium substitution reduces the energy differences between planar and tetrahedral geometries of four coordinate carbon. Some multiply substituted lithio compounds, *e.g.* 1,1-dilithiocyclopropene and 3,3-dilithiocyclopropene, are calculated (RHF/STO-3G) to be more stable planar than tetrahedral.[158] The lithium aids the stabilization of planar carbon by (i) delocalizing the carbon lone pair by π-conjugation and (ii) providing electron density to carbon by σ-donation. An additional important factor with these small ring compounds is the reduction in the strain on lithiation.[158] A planar form of CH_2Li_2 was calculated to be *ca.* 42 kJ mol^{-1} less stable than the tetrahedral form.[155] It was also concluded that the singlet–triplet states of planar CH_2Li_2 should be close in energy.[158,159] A third lithium substituent has only a modest lowering of the tetrahedral–planar energy difference and evidently steric, repulsive σ, effects in CLi_4 dominate whatever favourable influences are produced by substitution of the fourth lithium atom since the planar–tetrahedral energy difference increases somewhat. Dimerization[159] of CH_2Li_2 was also studied; the most stable dimer was the head-to-head dimer, *i.e.* four lithium atoms bridging two perpendicular CH_2 units, and had a dimerization energy of 155 kJ mol^{-1} (at RHF/STO-3G–RHF/4-31G levels).

Sodium had a much smaller effect than lithium on stabilizing planar CH_3Na and CH_2Na_2, presumably because of the diffuseness of the 3*d*-orbitals.[159]

Lithium substitution was calculated (*ab initio*, STO-3G) to reduce the strain energies in cyclic and polycyclic systems, based on three- and four-membered rings,[164] a consequence of lithium's σ-donor and π-acceptor nature. Examples of the reductions in the strain energies by lithium monosubstitution are 81.5 in cyclopropane and 170.1 kJ mol^{-1} in bicyclobutane (bridgehead site). However, quite remarkable is the reduction (by *ca.* 585 kJ mol^{-1}) on replacing all four hydrogens in tetrahedrane to give a face-lithiated species (**16**). The structure (**16**) bears a striking (reverse) relationship to that of $(MeLi)_4$.



(16)

Compound (**16**) may have been prepared.[165] Photochemical reaction of LiC≡CLi [δ(^{13}C), 75.0] in liquid ammonia at −45 °C provided a product [δ(^{13}C), 57.2] which was shown to be C_4Li_4 according to field desorption mass spectrometry (peaks observed for $C_4{}^7Li_4$ and $C_4{}^7Li_3{}^6Li$ but not for C_2Li_2 or C_6Li_6). The C_4Li_4 product is stable to −20 °C as an isolated solid, reacts with water to give acetylene but, most interesting of all,[166] gives Me_4C_4 (tetramethyltetrahedrane?) on methylation. Considering the difficulties and efforts to acquire tetrahedrane and its derivatives, this organolithium route appears most promising.

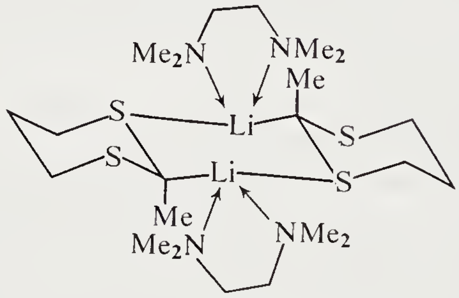
The structures of pentacoordinate carbonium ion species $CH_3M_2^+$ (M = Li or Na) were studied by *ab initio* calculations.[150] $CH_3Li_2^+$ is actually known in the gas phase and the related species

RLi_2^+ are seen in the mass spectra of all alkyllithiums. At the RHF/6- 31G$^+$ level the C_s–D_{3h} energy difference for $CH_3Li_2^+$ is 10.4 kJ mol^{-1}. Single point calculations, including all functions on sodium (STO-3G), have shown the C_s form of $CH_3Na_2^+$ to be favoured over the D_{3h} form by 36.8 kJ mol^{-1}.

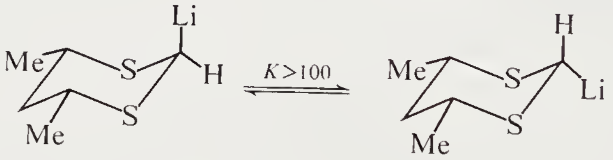
2.4.5 Functionally Substituted Alkylalkali Metal Species

The effects of certain α-functional groups, such as RO, cyano or isocyano, on the configurational stability of sp^3 hybridized organoalkali metal compounds have been mentioned (Section 2.4.2.5). In this section, consideration will be given to the effects of some selected substituents on the carbanionic centre.

The majority of the information regarding the structural effects of functional substituents has come from spectroscopy studies. However, the crystal structure of the 2-lithio-2-methyl-1,3-dithiane,TMED dimer (**17**) has been obtained.[167] One significant aspect of the structure is that the dimer is a tricyclic species in which the TMED chelated lithium apparently is bound equally strongly to the carbanoid centre of the one dithiane unit and to a sulphur of the other. It is to be noted that the complexed lithiums are in the equatorial positions while the methyls are axial. The equatorial preference for lithium in 1,2-dithianes also persists in solution,[168] *e.g.* in THF or DME solution there is a large thermodynamic preference (>25 kJ mol^{-1}) for equatorial lithium (equation 61) which is suggested to be due to the anomeric effect, *i.e.* an nC–σ^*(S—C) hyperconjugative interaction. However, steric effects of the complexed (or aggregated) lithium may be as important. There is a smaller kinetic preference for equatorial lithiation of the 2,4-Me$_2$-1,3-dithiane by BuLi. Metallation of the oxygen analogues, the 1,3-dioxanes, and related compounds also indicates an equatorial kinetic selectivity.[169]



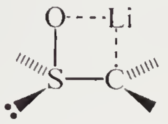
(**17**)



(61)

Ion pairing studies with the 1-lithium and 1-potassium derivatives of 2-phenyl-1,3-dithianes, essentially benzylic carbanions, indicate t.i.p. in THF and s.s.i.p. in HMPT; both types react stereoselectivity with electrophiles. As described more fully with simpler benzylic species, charge delocalization into the phenyl ring results in hindered phenyl rotations.[170] Ring inversion can also occur. Even in the s.s.i.p. forms these metallated dithianes were considered to be pyramidal. Other findings from ^{13}C spectral studies of α-sulphur substituted carbanionic species can be summarized thus:[171] (i) the carbanionic centre is nearly pyramidal in $PhSCH_2^-,M^+$ (M = Li or K, $\Delta J = -13$ to -20 Hz), (ii) the centre is nearly planar in $PhS(O)CH_2^-,M^+$ (M = Li or K) in simple α-lithiodialkyl or benzyl alkyl sulphoxides and in cyclic α-lithiosulphoxides, such as 2-lithio-4-*t*-butylthiacyclohexane *trans*- and *cis*-1-oxides (ΔJ = 10 to 20 Hz), and (iii) for $PhSO_2CH_2^-,M^+$ and $PhSONMeCH_2^-,M^+$ the geometry at the carbanionic centre depends on the metal and solvent. The ΔJ values quoted are for changes in the $^1J(^{13}C-^1H)$ values on metallation and can be compared with a ΔJ value of -27 Hz for methyllithium/methane, the decrease being due to an increase of the effective nuclear charge.

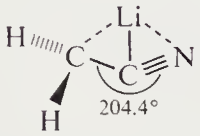
Four-centred chelate structures (**18**) are proposed for the sulphoxides. Strong external donors or cryptates can break this chelation. The carbanionic centres in $(EtO)_2P(O)\bar{C}HR,Li^+$ (R = Ph or CN) are also planar ($\Delta J = +23.5$ and $+26.0$ Hz) and carry a high charge.[172] A similar situation occurs for $(EtO)_2PO\bar{C}HCN,K^+$ ($\Delta J = +25$ to $+30$, depending on solvent). As well as the ΔJ criterion for the geometry about a carbanionic centre, others such as ΔJ_{PC} and the sign of $^2J_{PH}$ also pointed to planarity.



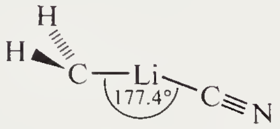
(18)

The influence of the cyano group on the configurational stability of cyclopropyl anions has been discussed (Section 2.4.1.5).

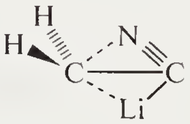
Interesting structures (**19**)–(**21**) have been calculated,[173] by *ab initio* STO-3G basis sets, for $LiCH_2CN$. Each of these structures appears as local minima in the singlet potential energy surface; stability was in the sequence (**21**) > (**19**) > (**20**).



(**19**) Ion pair $H_2\bar{C}{-}C{\equiv}N,Li^+$



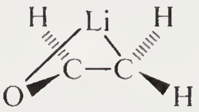
(**20**) Complex $CH_2{:}LiC{\equiv}N$



(**21**) H_2CLi^+,CN^-

IR spectra of $M^+,\bar{C}H_2CN$ (M = Li, Na or K) in THF and HMPT solutions were interpreted as being due to an s.s.i.p. (or free ions) of a planar anion, $CH_2C\overset{\cdots}{-}\bar{C}\overset{\cdots}{\equiv}N$, and the metal cation.[174] Criticism of earlier work on cyanomethyl anionic compounds was made in this paper.

The molecular structure of the lithium enolate of acetaldehyde, formally $LiCH_2CHO$, was also calculated at the restrictive Hartree–Fock levels. The lowest energy structure[175] (at the $3s2p1d/3s2p/2s$ level) is the chiral structure (**22**), which is akin to the allyllithium structure (a related situation was considered for a lithium salt of an imine).[176] Another stable structure (6.0 kJ mol^{-1} less stable than **22**) on a rather flat potential energy was a planar lithium enolate.



(22)

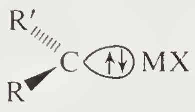
There have been several physicochemical studies of enolates in regard to aggregation,[177] ion-pairing and structure. The rotational barrier of the C—C bond in $PhCOLiCMe_2$ was high (113 kJ mol^{-1}) and indicated considerable location of charge on oxygen and that species involving a carbon–lithium bond, if present at all, are at a kinetically insignificant concentration.[178] Enolate structures have also been confirmed for Li, Na and K salts of aliphatic ketones,[179] *e.g.* Me_3C-$COCH_2M$ (M = Li, Na or K), in solvating media such as THF, by NMR and IR spectra, *e.g.* from a band at 1500–1550 cm^{-1} [ν(C=C)] and the absence of ν(C=O). In heptane, keto forms may be present. These salts have been isolated, as have α-lithio substituted carboxylic esters, *e.g.* Me_2CLiCO_2R (R = Me, Et, Pr^i, Bu^t, *etc.*). These aggregated compounds are stable[180] in the solid state and in benzene solution for days at room temperature, whereas self-condensation reactions take place in THF solution. Higher aggregates exist in PhH than in THF. Keto forms are suggested from the ν(CO) values in the range 1700–1650 cm^{-1}.

2.4.5.1 Carbenoids

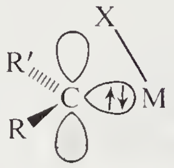
Carbenoids, RR′CXM (R, R′ = alkyl, hydrogen or halide; X = halide), have stability at low temperatures but thermally decompose to give carbene derived products CRR′ on α-elimination of MX.

Matrix isolation,[181] *e.g.* of Cl_3CM (M = Li, Na, K or Cs), the reactivity[182,183] and ^{13}C NMR evidence all suggest that equilibrium mixtures of more than one structure or isomer can exist.[184] While most of the solution work has been with lithium species, sodium and potassium carbenoids have been prepared and used. Of interest, these heavier alkali metal compounds are thermally more stable than the lithium analogues.[185]

Some unusual structures, quite distinct from conventional forms, have also been calculated by *ab initio* methods[162] for CH_2FLi, CHF_2Li and CCl_3Li. Three general structural types emerge from these calculations, namely (**23a**), (**23b**) and (**23c**). In (**23a**) the singlet carbene lone pair interacts with an empty metal orbital; in (**23b**) the carbene LUMO and a filled halogen orbital are involved in bonding, *i.e.* bridging halogens; while in (**23c**) both interactions are occurring. The most stable form for CH_2FLi is (**23c**) and for CCl_3Li a (**23b**) type interaction. For CF_2HLi the (**23c**) type and a (**23b**) type, with two 'bridging' halogens, are of comparable stability. For the (**23b**) type structures each halogen present is considered to act as a bridging group.



(**23a**) Carbene:MX complex



(**23c**) Metallocarbenium–halide ion pair

CRR′X⁻,M⁺ ion pair
R, R′ = alkyl or H; X = halogen

CX_3M; all halogens are bridging

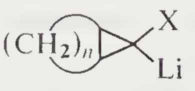
(**23b**)

The structure (C_{3v}) (**23b**) with triply bridging chlorines satisfies the IR data for one of the CCl_3Li species detected in the matrix isolation study; the other species was considered[181] to be the carbene–MX complex $CCl_2 \cdot LiCl$ (**23a**). However, the metallocarbenium–halide ion pair, CCl_2Li^+,Cl^- (**23c**), more stable according to von Schleyer *et al.*'s calculation,[162] also fits the data. In addition, structures (**23b**) and (**23c**) were considered to represent the two dissociation modes of CCl_3Li suggested by Köbrich.[183]

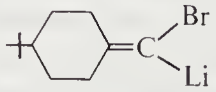
Thermal stabilities of carbenoids vary with substituents, the number of halogens, the metal and also with the solvent. Coordinating solvents, such as THF, enhance the stability of lithium carbenoids. Hence the order of stabilities calculated for isolated gas-phase species may be significantly changed by solvation in solution.

It is interesting to consider the calculated structures of von Schleyer *et al.*[162] along with the ^{13}C NMR results obtained by Seebach *et al.*[184] in THF at 100 °C for ^{13}C enriched lithium carbenoids, such as CX_3Li, CX_2HLi (X = Cl, Br or I), $MeCBr_2Li$, (**24**) and (**25**).

Invariably the exchange of hydrogen or halogen by lithium causes deshielding of the ^{13}C signal by up to 289 and 434 p.p.m. respectively. These are changes considerably larger than normally



(**24**) n = 4, X = I or Br
n = 6, X = Br



(**25**)

obtained for such replacements at an sp^3-hybridized carbon centre (*e.g. ca.* 2 p.p.m. for the hydrogen–lithium exchange in cyclopropyllithiums), even for sulphur and phosphorus substituted carbenoid centres (*ca.* −40 to +40 p.p.m.).[172] Values of $^1J(^1H-^{13}C)$ are also low, *e.g.* for CX_2HLi the values are 110, 102 or 95 Hz for X = Cl, Br or I, compared with $^1J(^1H-^{13}C)$ values for CX_2H_2 of 178 and 173 Hz for X = Cl or I respectively.

For $^{13}CBr_3Li$ in THF solution at −100 °C there were, in addition to the signal for CBr_2 (δ 144.1), two signals for distinct lithium carbenoid species, both shown to be monomeric by the 1 : 1 : 1 : 1 $^7Li-^{13}C$ coupling. The structures assigned were a solvated tetrahedral molecule [δ 101.5, $^1J(^{13}C-^7Li) \approx 43$ Hz], containing strongly polarized C—Br bonds, and a more stable solvated metallocarbenium ion pair, Br_2CLi^+,Br^- (δ 152.2) [*i.e.* type (**23c**)] or a $LiBr{\cdot}CBr_2$ complex [type (**23a**)] but not a type (**23b**) structure. As calculated by von Schleyer *et al.*[162] for CCl_3Li, the stable structure in the gas phase is a triply bridged (**23b**) form, but the high $^1J(^{13}C-^7Li)$ value (43 Hz) eliminates this species as a contender in solution.

Only one structure of CH_3CBr_2Li prevails in THF solution from the ^{13}C NMR spectrum, and this is probably a (**23c**) type. von Schleyer calculated both stable (**23b**) or (**23c**) types for CHF_2Li but again the high $^7Li-^{13}C$ coupling constant (45 Hz) excludes (**23b**).

The $^1J(^7Li-^{13}C)$ values of 40–45 Hz for these and other lithium carbenoids, no matter what the substitution pattern or the halogen, are much larger than those observed for alkyllithium aggregates (10–15 Hz) but lower than those calculated by the INDO method for the methyllithium monomer. In contrast the $^1J(^{13}C-^{13}C)$ coupling constants are much lower than normal for *ethane* derivatives. On warming above −100 °C there is loss of the fine structure in the ^{13}C spectra, which indicates some exchange (and reversible) process. The finding that CBr_3Li and related carbenoids are monomeric in THF contrasts with the tetrasolvated tetramers indicated for trichloromethyllithium in mixed hydrocarbon–ether media.[27,185] The effect of aggregation on the reactivity of such carbenoids has been studied, as have other features of the stability and modes of decomposition of carbenoids and arynoids.[27]

2.5 BENZYLIC, INDENYL- AND FLUORENYL-ALKALI METAL COMPOUNDS

2.5.1 Preparation

There are several routes used for the preparation of benzylic compounds, especially for the study of properties. As already outlined, the direct route from benzylic halides and alkali metals is not too useful owing to coupling reactions and other procedures have been adopted. These include (i) addition of RM to alkenes (equation 62;[186] see Section 2.3.6); (ii) cleavage of benzylic ethers by alkali metal (equation 63;[187] see Section 2.3.5); (iii) cleavage of benzylic tin and mercury compounds by organoalkali metals or alkali metals (equation 64;[188] see Section 2.3.4); (iv) formation of benzylic sodium, potassium, *etc.* compounds from benzylic lithiums using metal alkoxides (equation 65);[189] (v) metallations of methyl aromatics (see Section 2.3.2).

$$Bu^tLi \quad + \quad PhCH{=}CH_2 \xrightarrow[\text{isooctane}]{\text{TMED}} Ph\bar{C}HCH_2Bu^t,Li^+ \qquad (62)$$

$$PhCR^1R^2OMe \xrightarrow{K} Ph\bar{C}R^1R^2,K^+ \qquad (63)$$

$$R^1, R^2 = Me, Me; Me, CH_2CMe_3$$

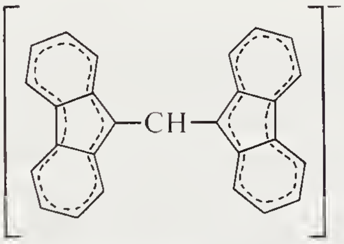
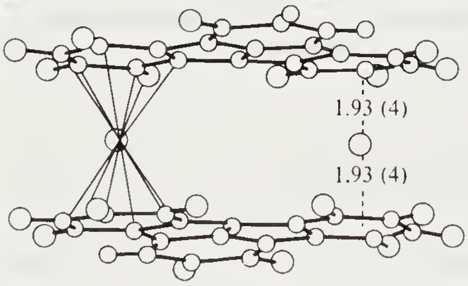
$$ArCH_2SnBu_3 \quad + \quad BuLi/Bu^tOM \longrightarrow ArCH_2^-,M^+ \qquad (64)$$

$$(PhCH_2)_2Hg \quad + \quad 2Li \longrightarrow PhCH_2Li \qquad (65)$$

2.5.2 Structures in the Solid State

The crystal structures of various delocalized carbanionic complexes have been determined.[190-200] Some features are given in Table 14. With one exception (that of lithium 7b*H*-indeno[1,2,3-*j*,*k*]fluorenide$\cdot\frac{1}{2}C_6H_4$), all compounds contain a stabilizing donor ligand. The situation regarding bonding has been expertly discussed by Stucky.[201]

Table 14 Features of the X-ray Crystal Structures of Delocalized Carbanion Alkali Metal Compounds

Compound	*Features*	*Ref.*
Benzyllithium·triethylenediamine $PhCH_2Li{\cdot}N(CH_2CH_2)_3N$	Infinite chains of $PhCH_2$—, bridged by $N(CH_2CH_2)_3N{\cdot}Li^+$ units; each lithium is coordinated to two half $N(CH_2CH_2)_3N$ molecules; ∠NLiN, 118.6°; Li—C, 2.21(2), 2.39(2), 2.59(2) Å	190
Triphenylmethyllithium·TMED $Ph_3CLi{\cdot}TMED$	Twisted (propellor shaped) phenyl rings; Li—C, 2.227(8) (C_1), 2.511(13) of one Ph group, 2.488(10) and 2.541(9) Å of another Ph group; ∠NLiN, 88.5°	191
Triphenylmethylsodium·TMED $Ph_3CNa{\cdot}TMED$	Twisted phenyl rings; Na—C, 2.643(3) (C_1), 2.88(1) and 3.044(1) of one Ph group, 3.052(1) and 3.088(1) of another Ph group, 2.960(1) Å to carbon of another carbanion unit; ∠NLiN, 76.6(1)°	192
Cyclopentadienylsodium·TMED $C_5H_5Na{\cdot}TMED$	Puckered chains; Cp rings bridging NaTMED units; chelating TMED; Na—C, 2.856(15)–2.909(13) Å; ∠NNaN, 70.5°	193
Indenyllithium·TMED $C_9H_7Li{\cdot}TMED$	(TMED)Li above five-membered ring; approximate η^3 coordination of Li to the indemyl (C_5 ring); 3C—Li, 2.298 ± 0.019, 2C—Li, 2.377 ± 0.002 Å; ∠NLiN, 86.4°	194
Fluorenyllithium bisquinuclidiene $C_{13}H_9Li{\cdot}[N(CH_2CH_2)_3CH]_2$	Allylic coordination of Li; C—Li, 2.333(10) (C_9), 2.471(11) and 2.794(13) Å; ∠NLiN, 123.7°	195
Fluorenylpotassium·TMED $C_{13}H_9K{\cdot}TMED$	TMED bridging K; each K is associated with two N and two fluorenyl carbanions; K—ring plane, 3.052(1) and 2.972(1) Å; ∠NKN, 90.4(1)°	196
Bifluorenyl(Li·TMED)$_2$	Two (Li·TMED) units closely associated to the central C—C bond; Li—C, 2.287(5) and 2.287(5), 2.5439(6) (to C_{13})Å; ∠NLiN, 88.0(2)°	197
Acenaphthylenide(Li·TMED)$_2$	(Li·TMED) units are coordinated (approx. η^3) to each side of the five-membered ring; Li—C, 2.18(3), 2.24(2), 2.27(2), 2.42(1), 2.52(1) Å; ∠NLiN, 85.9(3)°	198
 $Li^+(Et_2O)$	Coordination sphere of Li consists of two rings from different carbanions and oxygen; Li—ring, 2.42, Li—O, 1.91 Å; approximately planar trigonal	199
	Li over six-membered rings; Li—ring, 1.93; Li—C, 2.694–2.974 Å	200

For the benzylic carbanionic complexes, an allylic type interaction of the alkali metal with the carbanion moiety occurs. This is shown simplistically in Figure 6, and is illustrated more fully in Figures 7 and 8 with the structures of $Ph_3CLi{\cdot}TMED$ and benzyllithium·triethylenediamine, respectively.

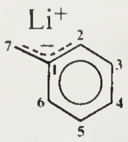


Figure 6 Allylic-type interactions in benzylic lithium compounds

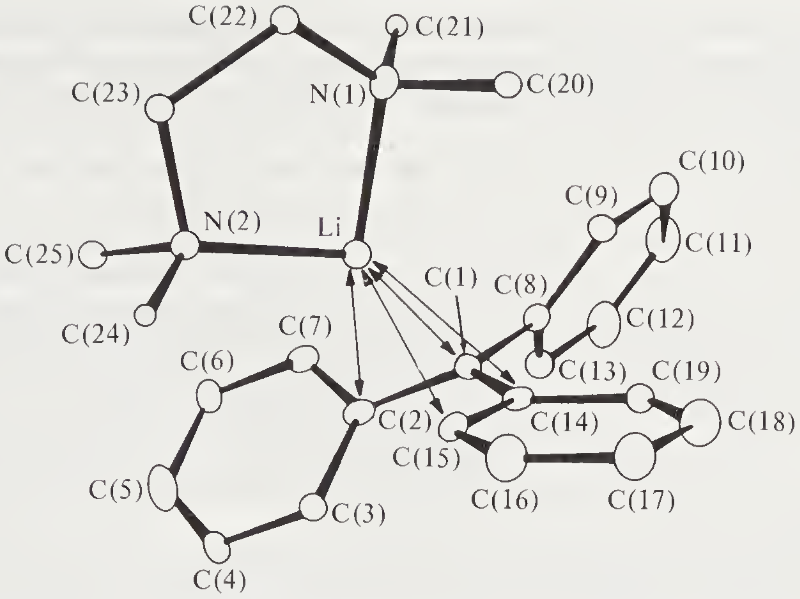


Figure 7 Structure of $Ph_3CLi{\cdot}TMED$[191,201]

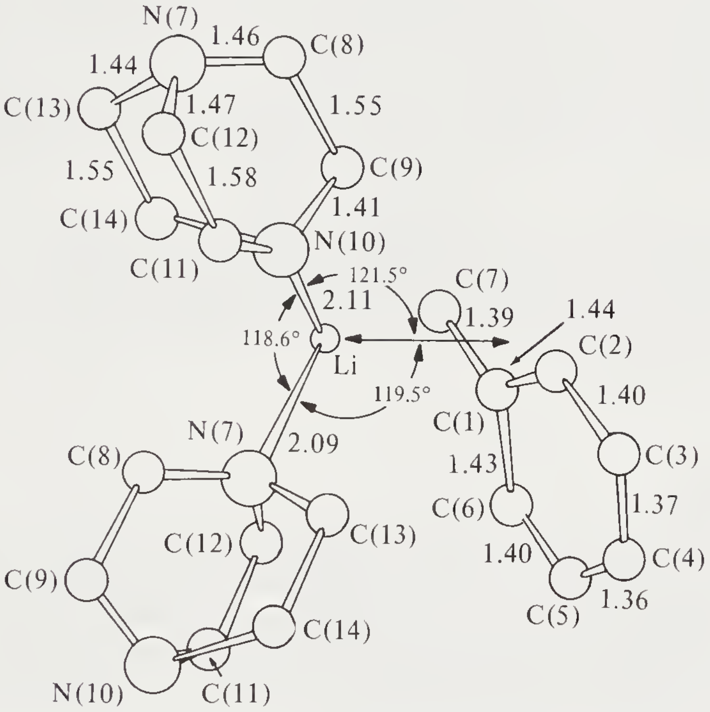


Figure 8 Structure of benzyllithium·triethylenediamine[190,201]

The allylic configuration in the benzylic lithium complexes, the orientation of the NLiN plane, the INDO overlap integrals, MO coefficient and charge densities, calculated for model compounds, are all compatible with a three-centre bonding model that requires the use of lithium 2*s* and 2*p* orbitals. In a simple valence bond picture the lithium is sp^2 hybridized with two sp^2 bonds to the nitrogens and one sp^2 orbital coordinated to the carbanion. The unhybridized *p*-orbital, parallel to the plane of the carbanion, is then able to form a bond with the π-cloud of the carbanion. The NLiN group has to be so orientated to allow the most favourable overlap of the Li *p*-orbital and the π-ligand orbital.[201]

INDO and CNDO/2 calculations have been performed on model compounds, *e.g.* $PhCH_2Li{\cdot}(NH_3)_2$ and fluorenyllithium$\cdot(NH_3)_2$. The findings for benzyllithium are typical. With the NLiN group positioned on or close to a model surface in the HOMO of the carbanion, the symmetry of the benzyl carbanion HOMO was found appropriate for overlap of the C(2) and C(7)p_z orbitals and a combination of lithium p_x and p_y orbitals. The contribution of the C(1)p_z orbital to the HOMO is relatively small. The INDO results further indicate that a σ interaction involving the sp^2 lithium orbital directed towards the unsaturated ring and the combination of ring carbon *s* and p_z orbitals that make up lower energy carbanion molecular orbitals is important. It is this interaction which is responsible for positioning the lithium atom close to the carbon atom(s) with the largest atomic charge.

The three-centre bonding model provides a convenient mechanism for transfer of charge density back to the lithium atom so that the charge on lithium in $PhCH_2Li{\cdot}(NH_3)_2$, as calculated by CNDO, is slightly negative (−0.05e) compared with the value of +0.35e expected for the isolated disolvated cation.[201]

An electrostatic model predicts correctly that the closest approach of the metal will be to the most highly charged carbon atom in the carbanion and that the geometry of the organic group will approximate to that of the carbanion. However, it does not correctly predict the allylic geometry. The overlap of sodium and potassium 3*p* and 4*p* orbitals with the carbon 2*p* orbitals should not be nearly as effective as that of the lithium 2*p* orbital. Hence these metals should form complexes that fit the electrostatic model better. This is realized with fluorenylpotassium·TMED.[196] The projection of one potassium on to the fluorenyl plane is at a point within the periphery of the five-membered ring and 0.2 Å off the position predicted for the electrostatic model.

As the ability of the organic group to accept an electron increases, so the metal–donor distance decreases. This reduction allows more electron donation to the metal to compensate for the electron transfer to the organic group.

The NLiN angle in the monodentate complexes $PhCH_2Li{\cdot}N(CH_2CH_2)_3N$ and fluorenyllithium·bisquinuclidine is close to 120°. In the TMED chelates a smaller angle must result; the values given in Table 14 range from 85.9 to 88.5°. The N· · ·N distances for ethylenediamine compounds are fairly consistently *ca.* 2.9 ± 0.1 Å, *i.e.* the lone pair orbitals of the two nitrogen atoms make an angle of 85 ± 3° with each other. This is clearly close to ideal for chelation to lithium but obviously not to the larger alkali metals; for these, smaller NMN bond angles are required to accommodate the longer M—N bond lengths. Chelation of TMED to sodium, as in $Ph_3CNa{\cdot}TMED$[192] and CpNa·TMED,[193] still results (∠NMN, 76.6 and 70.5°), but in fluorenylpotassium·TMED[196] the TMED cannot chelate potassium; instead the potassium is disolvated by two bridging TMED units. The consequence is a polymeric system in the solid state with each fluorenyl carbanion coordinated to two potassium atoms.

If a trisolvated lithium ion were to be formed, the empty Li *p*-orbital is no longer available and the bond would probably be that predicted by the electrostatic model.

The positions of the lithiums in the dicarbanion $(Li{\cdot}TMED)_2$ also cannot be predicted from electrostatic considerations alone but are consonant with some direct covalent bonding involving the HOMO of the dicarbanion.

2.5.3 Solution Studies

These delocalized carbanionic alkali metal compounds have been investigated by a range of spectroscopic methods, including ^7Li, ^1H, ^{13}C NMR and UV in a variety of solvents at a different temperatures.[14,15] Monomeric as well as aggregated species, polar covalently bonded compounds in addition to ion pairs (both s.s.i.p. and c.i.p.) and ion aggregates have all been recognized. Dissociation into free ions has also been considered;[202,203] however, in the solvents usually employed, small amounts of free ions are formed at the most.

2.5.3.1 Aggregation

Benzyllithium[4] itself is dimeric in benzene solution, as are for example $Ph\bar{C}HCH_2R,Li^+$ and $Ph\bar{C}MeCH_2Bu^t,Li^+$, whereas in the presence of amines or ethers, monomeric compounds can be obtained, *e.g.* as shown with benzyllithium in THF and 1- and 2-naphthylmethyllithium in ether.[188] Association of more readily delocalized carbanionic compounds, *e.g.* fluorenyllithiums, occurs *via* dipole–dipole interaction of ion pairs, especially in hydrocarbons.[203] This is illustrated with 9-(2-hexyl)fluorenyllithium, which is dimeric in cyclohexane at 25 °C (λ_{max} 370 nm) throughout the concentration range 0.01–0.1M. Dimers, albeit in equilibrium with monomers, still apparently persist in THF solution.[204] 9-Propylfluorenyllithium also exists[205] as monomers (λ_{max} 353 nm) and dimers (λ_{max} 370 nm) (in toluene solution) with a dimerization constant at 25 °C of 2.9×10^{-6} mol l^{-1}. The dimer structure was visualized as containing two lithium atoms sandwiched between two fluorenyl rings. Addition of small quantities of THP or THF to the hydrocarbon solutions results in the formation of externally disolvated light ion pairs (λ_{max} 359 nm) and, in the presence of excess ethers, s.s.i.p. forms (λ_{max} 386 nm) are obtained. These ether solvated species are also probably aggregated.

The ^1H NMR spectra of benzylic lithiums, *e.g.* 1- and 2-naphthylmethyllithiums in Et_2O solution, have also been interpreted in terms of the allylic interaction found in the solid structures of benzylic lithiums(Section 2.5.2), *i.e.* in Et_2O solution the lithium also interacts with an *ortho* ring carbon as well as the methylene anionic centre to complete its coordination, while in the better solvating THF this additional interaction does not occur[188] and a largely ionic, monomeric, delocalized ion pair results.

2.5.3.2 Structures in solution

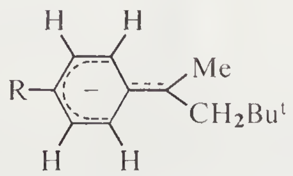
Significant differences are found in the NMR spectra of benzyllithium in benzene and in THF solution.[189,206] In addition, there are UV–visible absorption differences, namely λ_{max} at 292 nm in benzene and 330 nm in THF. These cannot just arise from the change in the aggregation state since smaller spectral differences are experienced for $Ph\bar{C}HCH_2Bu,Li^+$ and $Ph\bar{C}MeCH_2Bu^t,Li^+$, both of which are also dimeric in benzene and monomeric in THF.

The ^{13}C chemical shift and $J(^{13}C–^1H)$ values indicate appreciable sp^3 character at the α-carbon in $PhCH_2Li$ in PhH solution but less in THF, with the situation in Et_2O being intermediate.[206] It was argued that the ^7Li chemical shifts also indicate an appreciable increase in the anion–cation interaction (with transfer of electron density from the benzyl group to lithium as the solvent polarity decreases).

The considerable shielding of the ring hydrogens of benzyllithium is indicative of extensive conjugation: calculations based on the chemical shifts of the C(2)–C(6) ring protons point to more delocalization in the THF solution (*ca.* 0.6 electron) compared with that in benzene solution (0.3 electron).[189,206] Similar calculations show increased delocalization into the phenyl ring of $PhCH_2K$ in THF solution (*ca.* 0.75 electron), and even more with $Ph\bar{C}MeCH_2Bu^t,Li^+$ (0.80 electron in THF, 0.74 electron in PhH), PhCHMeK (0.88 electron in THF) and $PhCMe_2K$ (0.85–0.90 electron in THF).[189,207]

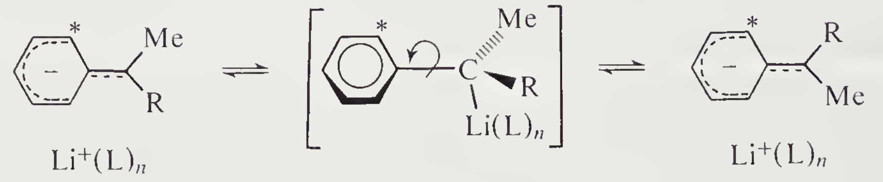
Further deductions from the proton chemical shifts are that more charge density resides in the anion of the s.s.i.p. fluorenyllithium (FlLi) in DME or THF (*ca.* 0.72 electron) compared with that in the c.i.p. FlLi·DME in PhH (0.22 electron). It was argued that charge density has been passed back to lithium in the c.i.p. using the three-centre bonding mechanism, described on p. 84 for the crystal structures.[201]

Extensive charge delocalization into the aromatic ring renders the benzylic system planar with a large degree of double bond character in the aryl–methylene bond. This leads to all the ring hydrogens (and carbons) being non-equivalent for unsymmetric compounds, such as $Ph\bar{C}RR',M^+$ and $Ar\bar{C}HAr',M^+$ and a high barrier to aryl rotation results.[186,187,189,208] If rotation can proceed on increasing the temperature, then equivalence of both *ortho* positions and of both *meta* ring sites occurs. Examples of this effect have been provided by Fraenkel *et al.*[186,187] Below 300 K the non-equivalence of the ring hydrogens and carbon of (**26**) in isooctane solution, containing one equivalent of a donor such as TMED, confirms the planarity of the structure. Above 300 K, ring rotation results and can be analyzed by NMR line shapes. Complexed compounds (**26**) in isooctane solution are probably monomeric and are separated ion-paired species. The NMR parameters of (**26**; R = H) are essentially constant below 300 K (*i.e.* before the onset of rotation), and independent of the complexing ligand (L) and the concentration. In addition, the ^{13}C and ^1H chemical shifts of the ring atoms are similar to those for cumylpotassium ($Ph\bar{C}Me_2,K^+$) in THF, Et_2O or TMED. Indeed, the chemical shifts of tertiary benzylic compounds are essentially unperturbed by the counterion. Thus the benzyl carbon in these tertiary compounds is part of the π-system and does not undergo changes in hybridization, as proposed for the parent benzylalkali metal compounds ($PhCH_2Li$). This simpler behaviour of the tertiary benzylic lithiums such as (**26**) is linked to the bulkiness about the benzyl carbon preventing tight ion-pairing or any carbon–lithium covalent interaction in the ground state.



(**26**) $Li(L)_n^+$; L_n = TMED or $(THF)_n$

The rates of aryl ring rotations depend on the counterion, the complexing ligand, the ring substituents and on the steric effects about the benzylic carbon. The mechanism for the first-order process involves formation of a bond between an sp^3 hybridized carbon and the metal in a transition state or reaction intermediate. This is accompanied by some decrease in the metal–ligand interaction (equation 66). In contrast to the spectrum for (**26**; R = H), that of the potassium salt did not change up to 94 °C, *i.e.* rotation is slow on the NMR time scale up to 94 °C. Higher temperatures were prohibited by reaction with the solvent.



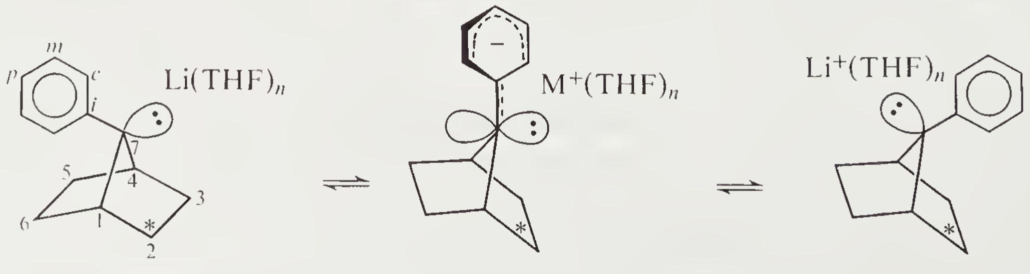
(66)

$R = CH_2Bu^t$; L_n = TMED or $(THF)_n$

The effect of the ligand on the barrier to rotation in (**26**; R = H) can be seen in the reduction from 75 to 59 kJ mol^{-1} on changing the ligand from TMED to THF. Ring substitution effects are quite significant with electron acceptor groups, especially Me_3Si, increasing the rotation barrier by increasing the stability of the benzylic anion; values of $\Delta H^{\ddagger}$ (kJ mol^{-1}), $\Delta S^{\ddagger}$ (J K^{-1} mol^{-1}) and k (at 300 K, s^{-1}) for the process in isooctane containing TMED are, for R = cyclopropyl, 49.3, − 64.8 and 7.1; for R = Pr^i, 77.3, 19.2 and 2.1; for R = H, 78.2, 1.3 and 0.11; and for R = Me_3Si, 92.0, 14.2 and 8×10^{-5}. Clearly the cyclopropyl group reduces the conjugation and destabilizes the anions. For other R groups (PhS, $PhSiMe_2$ and Ph) the rates are too slow to measure by NMR line shape methods.

Similar relative effects of *para* substituents (Me_3Si, Me and H) on ring rotations were observed in the unsymmetric diarylmethyllithiums $[(p\text{-}MeC_6H_4)(p\text{-}DC_6H_4)\bar{C}H,Li^+]$ and $[(p\text{-}Me_3SiC_6H_4)(p\text{-}MeC_6H_4)\bar{C}H,Li^+]$: the $p\text{-}Me_3SiC_6H_4$ ring rotates at 255 K about 200 times faster than the p-tolyl ring. Rotation of naphthyl–methyl bonds of c.i.p. $1\text{-}NaphCH_2M$ are also dependent on the metal and solvent,[188] with rotations being faster in Et_2O than in THF. In THF the ΔH values are 55.6, 63.5 and 76.1 kJ mol^{-1} for M = Li, Na or K. However, unlike the spectra of tertiary benzylic compounds such as (**26**), which are independent of the cation, those of the 1- and 2-naphthylmethylmetals show significant dependence on the metal. The partial localization of the methylene–metal bonds is calculated to be 50, 71 and 79% for Li, Na and K respectively.

The NMR spectra of the bicyclic and tertiary benzylic carbanion compounds 7-phenylnorbornylalkali metal[209] indicate ground state differences in THF between the lithium salt on the one hand (pyramidal), *i.e.* (**27**), and the potassium and caesium compounds on the other (planar), *e.g.* (**28**; M = K or Cs). The lithium salt undergoes inversion, as shown by the temperature effects on the C(2) and C(6) chemical shifts; at −90 °C, δ (C_2) and $\delta(C_6)$ are different but they coalesce on warming. The extrapolated barrier to inversion at 25 °C is 46 ± 4 kJ mol^{-1}; the activation parameters are $\Delta G^{\ddagger}_{205} = 39.3 \pm 0.8$ kJ mol^{-1}, $\Delta H^{\ddagger} = 28.0 \pm 8$ kJ mol^{-1} and $\Delta S^{\ddagger} = -59 \pm 42$ J K^{-1} mol^{-1}. The ^{13}C NMR spectrum of the lithium salt is quite different from those of the potassium and caesium salts, especially in regards to $\delta(C_7)$ and $\delta(C_p)$ as well as to $\delta(C_1)$ and $\delta(C_i)$ [designations as in (**27**)]. The spectra of the caesium and potassium salts are similar in THF as well as in DME, with the aryl chemical shifts typically those for delocalized benzylic anions,[210] *e.g.* those of cumylpotassium. Throughout the working temperature range, C(2) and C(6) were equivalent and a planar structure was proposed for the potassium and caesium salts, probably s.s.i.p. The conclusions regarding the lithium salt were that it was pyramidal in shape and undergoes inversion *via* a planar transition state (**28**; M = Li) (Scheme 14).



(**27**)

(**28**) M = Li

Scheme 14

2.5.3.3 Ion pairing effects

The nature of the ion pairing in solution,[14,15] including c.i.p. $\rightleftharpoons$ s.s.i.p. equilibria, can be investigated[211] for benzylic metal compounds (RM) by UV–visible[212] [*e.g.* for R = fluorenyl,[213] indenyl,[214] triphenylmethyl,[215] diphenylmethyl,[216] 9,10-dihydroanthracenyl[217] and (diphenylalkyl)methyl[218]], ^1H NMR [*e.g.* R = fluorenyl,[219] indenyl,[219] cyclopentadienyl,[219] triphenylmethyl[219] and (phenyl)(alkyl)methyl[187] as well as 1- and 2-naphthylmethyl[188]) and ^{13}C NMR spectroscopy[211] [*e.g.* R = fluorenyl, triphenylmethyl, diphenylmethyl, α-(trimethylsilyl)benzyl and benzyl]. In the main, reasonable agreement has been found between the techniques, although it is clearly an advantage to use more than one for each system. Each method has particular disadvantages and advantages. Severe band overlapping of the two ion pairs prevents the general application of UV–visible spectroscopy, and the small chemical shifts in ^1H NMR spectra (relative to ^{13}C shift changes) are major drawbacks. The problems with ^{13}C NMR spectroscopy are mainly the lack of suitable solubility and prolonged solution stability of the carbanions, and possibly a lack of sensitivity to solvation of the larger cations.

An advantage of UV–visible spectroscopy has been shown, for certain compounds, by the recognition of ion pairs intermediate between c.i.p. and s.s.i.p., namely partially or externally solvated species, species not detectable by the NMR methods. Each type of ion pair has a different absorption maximum, *e.g.* for the $PhCH_2Li$ c.i.p. the partially solvated ion pair and s.s.i.p. have λ_{max} at 407 (in ether solution), 418 (in THF solution) and 448 nm (in DME solution).[216] The NMR methods provide information on charge delocalization, not available from the UV–visible spectral studies.

The general findings from the UV–visible spectra regarding the s.s.i.p. and c.i.p. forms are as follows: (i) the s.s.i.p. exhibits a bathochromic shift relative to the c.i.p. form for the same RM; (ii) for the s.s.i.p. of RM, λ_{max} only varies slightly with M^+ and solvent; and (iii) the c.i.p. of RM exhibit bathochromic shifts as M^+ increases from lithium to caesium. Some data[220] for fluorenylalkali metal compounds are given in Table 15. In the c.i.p. form the cation is close to the most electron rich carbon (C_α) and the π-density is strongly polarized towards it. In the s.s.i.p. species the cation is wrapped with solvent and the carbanion responds by spreading the π-electron density over the carbanion. Hence, for example, the ^{13}C chemical shifts of the α-carbon in the s.s.i.p. are deshielded and are essentially independent of the cation whereas those of the c.i.p. are shielded (upfield) and are proportional to the reciprocal of the interionic distance. The largest chemical shift changes occur at the α-carbon.

Table 15 λ_{max} Values in the UV–Visible Spectra of Fluorenylmetals in Ethereal Solvents[220]

FlM	*Solvent*	λ_{max}	*Ion pair type*
Fl^-,Li^+	Dioxane	346	c.i.p.
	THP	349, 373 (7:3)	c.i.p.:s.s.i.p.
	THF	349, 373 (1:4)	c.i.p.:s.s.i.p.
	DME	373	s.s.i.p.
Fl^-,Na^+	THP	356	c.i.p.
	THF	356, 373 (19:1)	c.i.p.:s.s.i.p.
	THF (below 10^{-7} M)	373	free ions
	DME	356, 373 (1:4)	c.i.p.:s.s.i.p.
	THF/crown ether	373	s.s.i.p.
Fl^-,K^+	THF	362	c.i.p.
Fl^-,Rb^+	THP	363	c.i.p.
Fl^-,Cs^+	THP	364	c.i.p.
	THF	364	c.i.p.
	DME	364	c.i.p.

The energy required to convert c.i.p. → s.s.i.p. is the balance between the coulombic energy needed to separate oppositely charged ions and the energy gained from ion–dipole interaction between the cation and the solvent. Such conversions are exothermic due to the gain in the solvation energy in forming the s.s.i.p. with a negative entropy due to the ordering of the solvent molecules in the s.s.i.p.

The s.s.i.p. form of RM is favoured by the following factors. (i) Decreasing size of M^+: the enthalpy change becomes more negative as the distance between the ions in the c.i.p. and s.s.i.p.

Table 16 Ion Pairing of Benzylic Alkali Metal Compounds in Ethereal Solutions[a]
K = [s.s.i.p.]/[c.i.p.] at 25 °C; ΔH (kJ mol^{-1}) and ΔS (J K^{-1} mol^{-1})

		Ion pairing				
R	*Solvent*	*RLi*	*RNa*	*RK*	*RRb*	*RCs*
$PhCH_2$	THF	c.i.p.[b,1]	c.i.p.[b,1]	c.i.p.[b,1]	c.i.p.[b,1]	c.i.p.[b,1]
	DME	c.i.p.[b,1]	—	—	—	—
$Ph(Me_3Si)CH$	THF	c.i.p.[b,1]	—	—	—	—
	DME	K, 0.1 ΔH, −22.2; ΔS, −96[b,1]	K, 0.1 ΔH, −14.6; ΔS, −67[b,1]	c.i.p.	c.i.p.	c.i.p.
Ph_2CH	Et_2O	mainly c.i.p.[b,1]	c.i.p.[b,1]	c.i.p.	c.i.p.	c.i.p.
	2-Me-THF	K, 1.31 ΔH, 29.7; ΔS, −96[b,1]	c.i.p. $\rightleftharpoons$ s.s.i.p.	—	c.i.p.	c.i.p.
	THF	[e]	[e] K, 0.1 ΔH, −31.8; ΔS, −130[d,1]	c.i.p.	c.i.p.	c.i.p.
	DME	K, 6.33 ΔH, −30.1; ΔS, −84[b,1]	ΔH, −27.6; ΔS, −84[b,1]	—	—	—
Indenyl	DME	ΔH, −20.9; ΔS, −84	ΔH, −14.6; ΔS, −63	—	—	—
	cyclohexylamine	ΔH, −33.4; ΔS, −109[d,2]				
Fl	2-Me-THF	K, 1.01 ΔH, −32.2; ΔS, −109[b,1]		c.i.p.[b,1]	c.i.p.[b,1]	c.i.p.[b,1]
	THF	K, 3.36 ΔH, −20.5; ΔS, −59[b,1]	K <0.1 ΔH, −33.0; ΔS, −134[b,1]			
	cyclohexylamine	ΔH, −35.5; ΔS, −96[d,2]				
	DME	ΔH, −23.4; ΔS, −63	ΔH, −22.6; ΔS, −71	ΔH, 17.1; ΔS, −67		
Ph_3C	Et_2O	K, 0.1 ΔH, −49.7; ΔS, −192[d,3]	—	—	—	—
	2-Me-THF	K large ΔH, −64.8; ΔS, −184[b,1]	—	—	—	—
	THF	K, 39 ΔH, −38.5; ΔS, −100[d,3]	K <0.1 ΔH, −48.9; ΔS, −184[b,1]	K, 2 ΔH, −28.0; ΔS, −88[d,3]	—	—
	DME	s.s.i.p.	ΔH, −34.3; ΔS, −117[c,4]	K, 5.7 ΔH, −49.3; ΔS, −150[d,3]	ΔH, −14.2; ΔS, −54[c,3]	—

[a] K = [s.s.i.p.]/[c.i.p.] at 25 °C; ΔH in kJ mol^{-1}; ΔS in J K^{-1} mol^{-1}. [b] From ^{13}C NMR data. [c] From ^1H NMR data. [d] From UV data. [e] Externally solvated c.i.p. present, as shown by UV data.

1. Ref. 211.
2. Ref. 214.
3. Ref. 215.
4. Ref. 219.

increases; there is less solvation of the larger cation. (ii) Decreasing temperature: since ΔS is negative, lower temperatures reduce the entropy term. (iii) Increasing anion delocalization or increasing size of the π-system; this reduces the energy required to separate the ions as the charge in the carbanion is more dispersed. (iv) Increasing dielectric constant. (v) Increasing coordinating ability of the solvent; the more coordination by the solvent, the more reduction in the entropy term. (vi) The presence of crown ethers (and glymes) which lead to crown ether separated ion pairs. (vii) Increasing pressure.[15,221] There is a volume contraction on binding solvent molecules to the cation (M^+) of the separated ion pair. ΔV° values for formation of the s.s.i.p. of FlLi and FlNa in THF are -16 ml mol^{-1} and -10 ml mol^{-1} respectively, which compare with the formation of the s.s.i.p. FlNa in DME of -21 ml mol^{-1}. The larger value in DME is due to the tighter binding of the bidentate molecule to sodium. Table 16 gives some data for the ion pairing of various delocalized systems in ethereal solvents. Also included are some thermodynamic parameters where equilibria are set up.

2.5.3.4 Cyclopentadienyl compounds

The crystal structure of the cyclopentadienylsodium·TMED complex has been determined.[193] It consists of puckered chains of cyclopentadienyl rings bridged by Na·TMED; see Table 14.

Various calculations have been carried out on cyclopentadienyllithium.[161] The most extensive *ab initio* treatment was by Streitwieser *et al.*[161] and involved both STO-3G and double basis sets. The most stable arrangement contained the lithium cation over the middle of the cyclopentadienyl ring with the hydrogen atom folded back (by 3.56°) out of the plane of the C_5 ring; optimum distances were $r(CC) = 1.422$, $r(CH) = 1.070$ and $r(\text{ring—Li}) = 1.820$ Å.

In solution in ethereal solvents, cyclopentadienyllithium was indicated by ^1H NMR spectroscopy to exist as a c.i.p. (as do the other alkali metal derivatives), with the lithium cation (as shown by ^7Li NMR spectroscopy[222]) above the π-cloud of the ring. The single proton chemical shifts from each of the cyclopentadienyl groups in CpLi and CpNa in THF are dependent on the temperature and concentration,[223] reflecting structural and/or aggregation changes. The ^1H chemical shift of the ring protons in CpNaL complexes also vary with the solvents used (THF, PhH, MeCN and DMSO) and on the ligand L. In THF solution, increasing anionic character is in the sequence L = TMED < py < Et_3N < THF.[193] The ^{13}C NMR spectra of cyclopentadienylalkali metal compounds, including MeC_5H_4Li and $Me_4C_5H_4K$ in monoglyme, also indicate the pentahapto nature of the ligand–metal interaction.[224]

No absorption peaks have maxima in the UV region[223,225] above 200 nm in ethereal solution; only shoulders to shorter wavelength absorptions are seen, *e.g.* the shoulders are at 208 nm for CpLi and 220 nm for CpK in Et_2O. IR spectra of CpM both in solution and in the solid state have been variously recorded.[193,223]

2.6 VINYLMETAL COMPOUNDS

2.6.1 Preparation

Several routes to vinylmetal compounds have been used. Particularly important routes are those which have regio- and stereo-selective or -specific control. The most typical routes used are described below.

(i) Halide–metal exchange (see Section 2.3.1 for general reports on this mode of preparation). Illustrations of this method, which normally proceed at low temperatures with retention of configuration, are shown in equations (67)[226] and (68).[227] Normally the bromide or iodide is taken, since the chloride can promote α-hydrogen metallation.

$$(E)\text{-RCH=CHBr} \quad + \quad 2\text{Bu}^t\text{Li} \quad \xrightarrow[\text{Et}_2\text{O/THF/C}_5\text{H}_{12}]{-120\ ^\circ\text{C}} \quad (E)\text{-RCH=CHLi} \quad + \quad \text{Bu}^t\text{H} \quad + \quad \text{Me}_2\text{C=CH}_2 \qquad (67)$$

(stereospecific)

$$\text{RCH=CXSiMe}_3 \quad + \quad \text{BuLi} \quad \longrightarrow \quad \text{RCH=CLiSiMe}_3 \qquad (68)$$

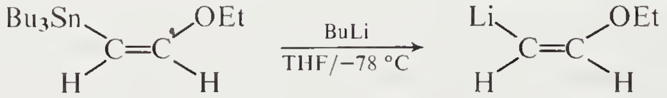
X = Br or I (stereoselective)

Reactions of the metal with vinyl halides also can give vinylmetal compounds, *e.g.* reaction of vinyl chloride with potassium and vinyl bromide with sodium.

(ii) *trans*-Metallation (see Section 2.3.4). This has been used frequently with tin derivatives, (*e.g.* equations 69–71),[95,228–230] although mercury compounds have also been employed.[99] The reaction occurs with retention of configuration at low temperatures. Both simple and functionally substituted derivatives can be prepared.

(69)

$$(E)\text{-}Bu_3SnCH{=}CHSNBu_3 \quad + \quad BuLi \xrightarrow{\text{(1 or 2 equiv)}} Bu_3SnCH{=}CHLi \qquad (70)$$



(71)

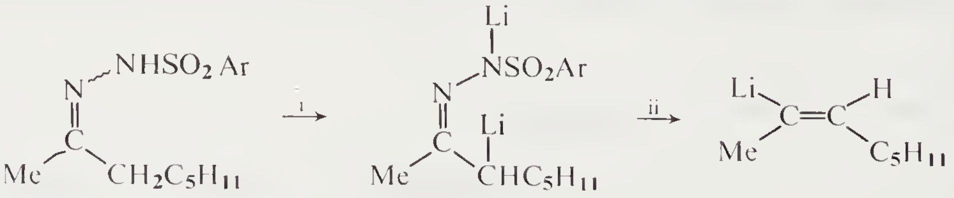
(iii) Metallation: metal–hydrogen exchange. In general there are replacements of vinylic hydrogens rendered acidic by α-substituents such as RO, RS, RSe, RSO, RSO_2,[231] CN,[232] *etc.* (equations 72 and 73;[231,232] see also Section 2.3.2.1). Differences between kinetic and thermodynamic effects have been seen in metallations of α-substituted alkenes (see p. 95).

$$RCH{=}C(SO_2Ph)H \xrightarrow{MeLi} RCH{=}CLiSO_2Ph \qquad (72)$$

$$(E)\text{-}PhCH{=}CHCN \xrightarrow{LiNPr^i_2} (E)\text{-}PhCH{=}CLiCN \qquad (73)$$

Terminal alkenes such as 1-heptene can be metallated by the n-$C_5H_{11}Na{\cdot}Et_3N$ complex in octane;[233] the product mixture was treated with CO_2/H_2O and was thereby shown to contain vinyl ($BuCH_2CH{=}CHNa$ and $BuCH_2CNa{=}CH_2$) as well as allylic sodium compounds ($BuCHNaCH{=}CH_2$ and $BuCH{=}CHCH_2Na$).

(iv) From arenesulphonylhydrazones. This reaction exhibits[234] extensive regioselective control, especially in hexane/TMED as the solvent, *e.g.* Scheme 15.



i, $2Bu^sLi$, −78 °C, TMED, hexane; ii, 0 °C

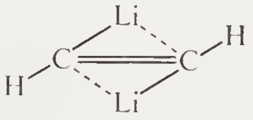
$Ar = 2,4,6\text{-}Pr^i_3C_6H_2$

Scheme 15

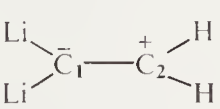
2.6.2 Theoretical Treatment

Several theoretical treatments have been made on vinyllithium, including *ab initio* calculations (using a split shell with *d*-orbitals on carbon,[35] a large Gaussian basis set[235] and at 4-31G/6-31G levels[236]). A classical geometry has been deduced for the monomer from these *ab initio* calculations; from one study[236] it was concluded that the C—Li bond is composed of a weak σ-interaction between a carbanion sp^2 hybrid orbital and the lithium cation with a negligible contribution from the Li *p*-orbitals to the C—Li overlap population.

Also considered by *ab initio* methods were dilithioethylenes.[236] Singlet *trans*-LiCH=CHLi was the most stable dilithioethylene isomer; it has a highly distorted partially bridged structure (**29**) with ∠CCLi = 87°. Structures and rotational barriers in singlet and triplet 1,1-dilithioethylenes were also discussed.[237] Some of the interesting findings were: (i) the rotational barrier of the double bond was calculated to be small; (ii) perpendicular forms may be more stable than the planar form; and (iii) triplet states were more stable than the corresponding singlet state. The carbon–carbon bond length is essentially that of a double bond and does not change significantly during the rotation in $Li_2C{=}CH_2$, in contrast to the finding from a calculation on ethylene itself. The reasonably high stability of the single perpendicular form is due to the combination of the σ-donor and π-acceptor characters of lithium. This can be readily seen with the zwitterionic representation (**30**) of the single perpendicular species. The carbanion centre (C_1) is stabilized by delocalization of the two π-electrons on C_1 in a three-centre orbital with the lithium *p*-orbitals, while at the cationic centre (C_2) hyperconjugation of the C p_x-orbital with the two Li—C_1 σ-orbitals occurs. In the perpendicular triplet a p_y electron has been transferred from C_1 into a σ-orbital ($7a_1$) which binds the two lithiums. In the planar triplet the electron transfer is from the singlet HOMO (a $3b_2$ σ-orbital, bonding the two lithiums to C_1 but having an antibonding character between the two lithiums) to another σ-bonding orbital ($7a_1$) which does have a bonding character between two lithiums. As the authors[237] state, it would be most interesting to see if their theoretical predictions are borne out by experiment.



(**29**)

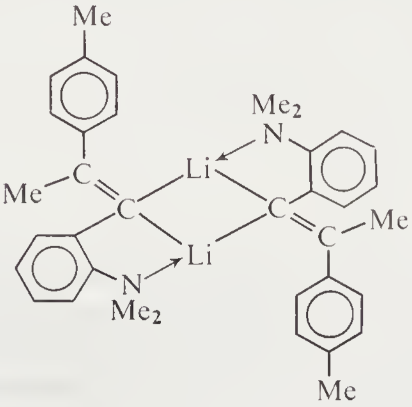


(**30**)

2.6.3 Properties

Crystal structures of vinylmetal compounds have not, as yet, been determined.

Vinyllithium, insoluble in hydrocarbons, has been reported to be tetrameric in THF solution, while *trans*-1-propenyllithium is tetrameric in Et_2O.[238] The alkyllithium (*E*)-(*o*-$Me_2NC_6H_4$)-CLi=CMe(C_6H_4Me-*p*) (*E*-**31**), which has the 'in-built' donor NMe_2 group,[95] however, has been shown to be dimeric in benzene by cryoscopy; the structure (**31**) proposed contains bridging propenyl groups. Addition of diethyl ether to (**31**) in benzene results in coordination to lithium with breakage of the NMe_2 lithium coordination. A complex, [(*o*-$Me_2NC_6H_4$)CLi=C-Me(C_6H_4Me-*p*)]$_2$·Et_2O, can be isolated from diethyl ether solution.

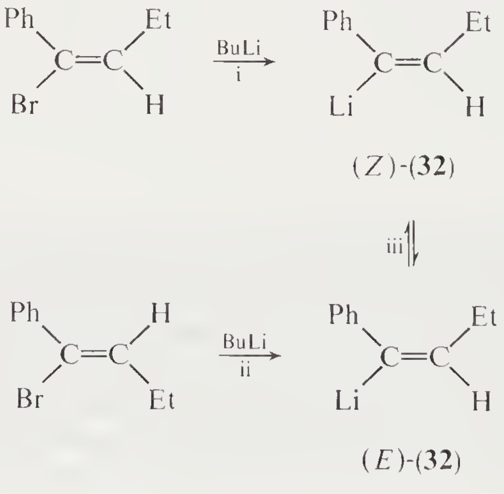


(**31**)

2.6.4 Configurational Stability

The configurational stability of vinyllithiums is highly dependent on the substituents, the solvent and temperature.[95,99,239,240] Those substituted in the α-position with alkyl groups or hydrogens are reported not to undergo isomerization, typical examples being *cis*- and *trans*-1-propenyllithium.[241] On the other hand, α-aryl substituted vinyllithiums have been shown to isomerize, examples being (*Z*)- and (*E*)-PhCLi=CHD,[240] (*Z*)- and (*E*)-1-lithio-1-phenyl-1-butene,[239] and (*Z*)- and (*E*)-1,2-diphenyl-2-(*p*-chlorophenyl)vinyllithium[99] (potentially to equilibrium mixtures of (*Z*)/(*E*)-isomers), as well as (*Z*)-stibenyllithium[99] and (*Z*)-1,2-diaryl-1-propenyllithium,[95] all of which isomerize practically completely to the (*E*)-isomers.[95] The configurational stability is markedly greater in hydrocarbons than in ethereal solutions or in solutions containing a donor molecule. In pentane/hexane solution, (*Z*)-(o-$Me_2NCH_2C_6H_4$)LiC=C(C_6H_4Me-*p*)Me and (*Z*)-PhCLi=CPhMe, prepared by transmetallation from the triphenyltin analogues, isomerized totally to the insoluble (*E*)-isomers even in this hydrocarbon medium within 4 h.[95]

The different solvent effects are seen with the (*Z*)- and (*E*)-1-lithio-1-phenyl-1-butene isomers (**32**), formed by lithium–halogen exchange reactions (Scheme 16). These lithio derivatives are configurationally stable in THF at −78 °C and in hexane at room temperature containing up to one equivalent of THF. Raising the temperature of the THF solutions or increasing the amount of THF in the hexane solutions results in isomerization to equilibrium distributions at increasing rates. Effects on the isomerization rate of added donors to hexane solutions are in the sequence: TMED > DME > THF > Et_2O. The position of equilibrium depends on the hexane–donor solvent system, *e.g.* at 22 °C and with a mole ratio of donor : vinyllithium equal to 10 : 1, the equilibrium proportions of (*Z*)-(**32**) varied from 31% in Et_2O to 55% in TMED. Discrete ^1H NMR spectra are obtained for each isomer during and after the attainment of equilibrium at 35 °C. Thus the isomerization is slow on the NMR time scale. The ^1H NMR spectral changes in the aromatic region on addition of THF to hexane solution of (*Z*-**32**) at −30 °C indicates that the C—Li bond becomes more ionic and a limiting spectrum is obtained[239] at a THF/(*Z*-**32**) ratio of 3.

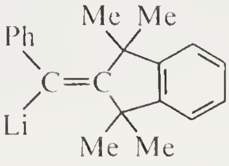


i, THF at −78 °C, or hexane at room temperature; ii, THF at −78 °C, or hexane + 0.5 equiv. THF at room temperature; iii, TMED, DME or THF (>1 equiv.)

Scheme 16

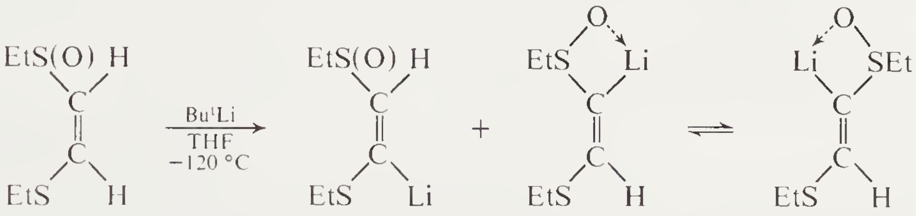
Even small quantities of ether dramatically alter the configurational stability of stibenyllithium.[99] The isomerization of PhCLi=CHD was followed using a ^1H NMR line-shape analysis of the alkenic signals (with deuterium decoupling). The order in the vinyllithium was found to be *ca.* 0.5 in THF solution, and Knorr *et al.*,[240] while recognizing the hazards associated with deducing aggregate numbers from kinetic data, put forward a mechanism in which a dimer of PhCLi=CHD dissociates to an ion-paired monomer. The activation parameters were $\Delta H^{\ddagger}$ =

-32.6 ± 2.5 kJ mol^{-1} and $\Delta S^{\ddagger} = -150 \pm 8$ J K^{-1} mol^{-1}. The large negative entropy term is indicative of extensive solvent ordering, as anticipated for a dissociation into s.s.i.p. species. The solvent and donor effects and the ease of isomerization with α-aryl substituents also support an ion-pair mechanism. Bulky groups at the vinyl centre tend to make the isomerization easier. Thus the (*Z*)/(*E*) topomerization of PhCLi=C(C$_6$H$_4$Me-*o*)$_2$ (**33**) is rapid in THF, even at −25 °C, and the ^{13}C coalescences in the even-bulkier compound (**34**) occur at −45 °C. The relative rates of PhCLi=CH$_2$:(**33**):(**34**) are 1:820:24 200. The comparison between the reactivities of PhCLi=CH$_2$ and (**34**) indicates a vast steric acceleration to isomerization which could arise from smaller aggregates, *i.e.* monomers, of (**34**) in the ground state.



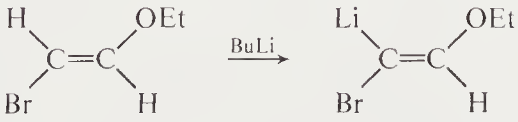
(**34**)

The functionally substituted vinylic lithium[242] (*Z*)-EtSCH=CLi(SOEt) (**35**) undergoes isomerization at −100 to −80 °C. One driving force is the increase in the intramolecular coordination. The compound (*Z*)-EtSCLi=CH(SOEt) (**36**), prepared along with (**35**) in the non-regiospecific metallation of (*Z*)-EtSCH=CH(SOEt) by Bu^{t}Li in THF, does not undergo (*Z*)/(*E*) isomerization at −80 °C. A related finding was that *both* the (*Z*)- and (*E*)-alkenyl sulphoxides RCH$_2$CH=C(H)SOAr are metallated at −78 °C in THF by LiNPr$^i_2$ to (*E*)-RCH$_2$-CH=C(Li)SOAr.[243]

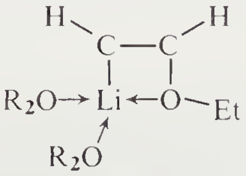


(**36**) (**35**) (74)

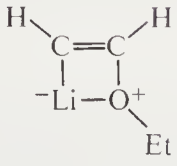
There are appreciable differences[244] in the thermal stabilities and ease of formation of (*Z*)- and (*E*)-2-ethoxyvinyllithiums. The (*Z*)-CHLi=CHOEt is obtained by halide-metal exchange using BuLi and (*Z*)-CHBr=CHOEt at −80 °C in Et$_2$O [in contrast, a metallation reaction occurs between (*E*)-CHBr=CHOEt and BuLi to give (*E*)-BrCLi=CHOEt (**37**)]. The (*Z*)-isomer is stable to −50 °C in Et$_2$O and to −30 °C in THF or DME, whereas the (*E*)- isomer decomposes on its formation [from (*E*)-BrCH=CHOEt and PhPh$^{\overline{\cdot}}$,Li$^+$] at −80 °C to HC≡COEt. The relative stability of (*Z*)-CHLi=CHOEt arises from two factors: (i) the lack of a facile, *i.e. trans*, elimination mode and (ii) intramolecular solvation which can be formally written as (**38**) or (**39**). Such intramolecular solvation of lithium by oxygen occurs also in (**37**) and in EtOCLi=CH$_2$, (*E*)-MeOCLi=C(OMe)Cl, MeOCLi=CHOMe, 3-Cl-2-Li-5,6-dihydro-4*H*-pyran, 1,2-(tetrahydropyranyloxy)vinyllithium and in the allylic compound (*Z*)-3-phenoxyallyllithium.[244]



(**37**) (75)

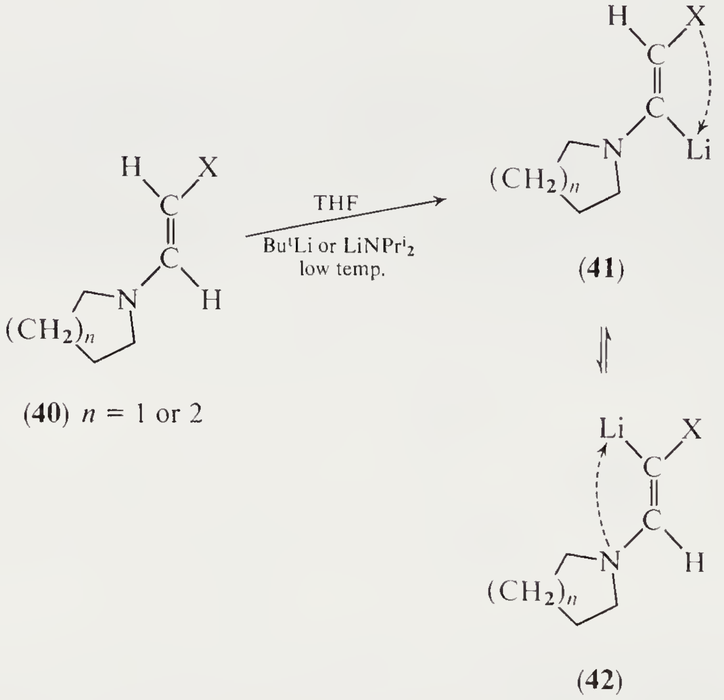


(**38**)



(**39**)

Interesting differences in the stability of functionally substituted vinyllithiums have been found. These differences illustrate the importance of electronic effects, intramolecular complexation and solvation (Scheme 17).[245] Metallation of (**40**) occurs at low temperatures to give compounds (**41**), the kinetic product. The compounds (**41**), having X groups such as $CONEt_2$, CO_2Et and COPh which are able to coordinate to Li, are stable up to 20 °C, in contrast to (**41**; X = CN). At −80 °C, (**41**; X = CN) isomerizes completely to the thermodynamically more stable (**42**; X = CN). The cyano group is a poorer complexing agent than the tertiary amine group and in (**42**; X = CN) coordination of Li to the amine becomes significant (see Scheme 18). For (*E*)-$MeOCH_\beta{=}CH_\alpha CO_2Et$, kinetic lithiation occurs at H_β, in keeping with the relative inductive effects of MeO and CO_2Et; however, with prolonged contact time at −90 °C, partial isomerization to (*E*)-$MeOCH_\beta{=}CLiCO_2Et$ results. *Ab initio* (STO-3G and STO-4-31G) and MNDO/3 calculations indicated the importance of *intra*-molecular association and solvation to the thermodynamically more stable isomer; see, for example, the calculations for (*E*)-$H_2N{-}CH{=}CHLi$.

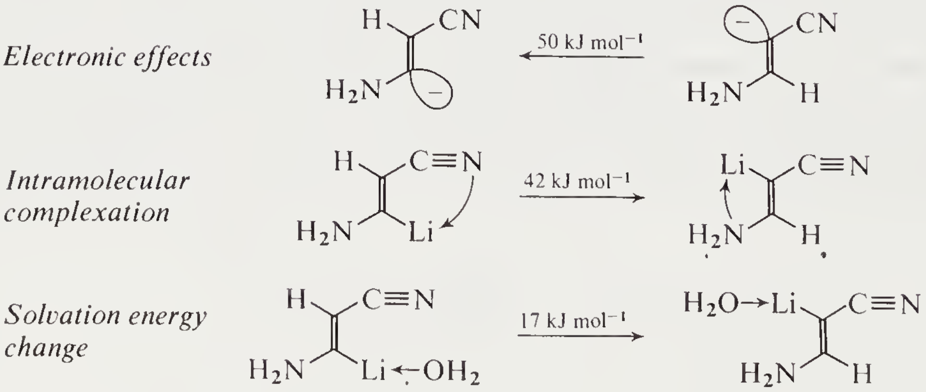


(**40**) *n* = 1 or 2

(**41**)

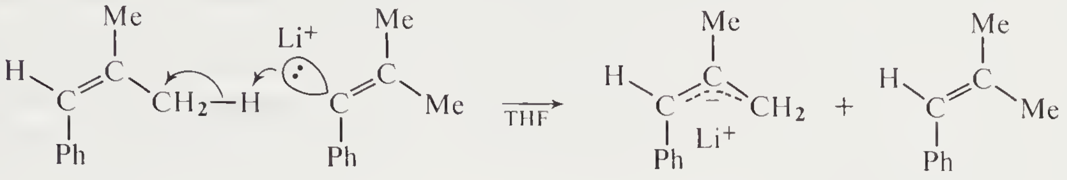
(**42**)

Scheme 17



Scheme 18

Another mode of isomerism was indicated by the change of $PhCLi{=}CMe_2$ above 0 °C to the allylic species $PhCH\text{---}CHMe\text{---}CH_2,Li^+$ in THF solution. This occurs in the presence of small amounts of $PhCH{=}CMe_2$, the hydrolysis product of $PhCLi{=}CMe_2$, and is essentially a deprotonation reaction. This is not a general reaction since (*Z*)-1-lithiopropene and 2-lithiopropene in THF do not undergo rearrangement in the presence of propene.[246] Other vinyllithiums deprotonated $PhCH{=}CMe_2$ to give $PhCH\overset{\cdots}{-}CMe\overset{\cdots}{-}CH_2,Li^+$ with a reactivity sequence of $H_2C{=}CHLi:PhCLi{=}CH_2:Me_2C{=}CPhLi$ (**43**) = 0.006 : 1 : 10 : 110. The reactivities were argued to be due to changes in aggregation in the ground state and in the basicity of the carbanions.


(**43**) (76)

2.7 ALLYLIC ALKALI METAL COMPOUNDS

2.7.1 Preparation

As pointed out in the general preparation section (Section 2.3), direct routes from the allyl halide and alkali metal are not used due to extensive coupling of allylic fragments. However, there are many general routes available to these most important species. Methods which have been used to prepare allylic alkali metal compounds, expecially for spectral studies, include the following.

2.7.1.1 Metallation of alkenes

There is certainly no lack of choice in metallating agent one can use. These include, for lithiation, lithium amides,[247] alkyllithiums, in particular BuLi,[248,249] alkyllithium–TMED and related complexes;[250] for kalliation, Me_3SiCH_2K[250–252] and $BuLi/Bu^tOK$;[251] and Me_3SiCH_2Cs.[250] All the alkali metals have also been employed with alkenes, especially with 1,3-diarylpropenes.[248,253,254] In addition to the 1,3-diarylallylmetal product, some $(ArCH_2)_2CH{-}CH(CH_2Ar)_2$ is also formed. See also Section 2.3.2.

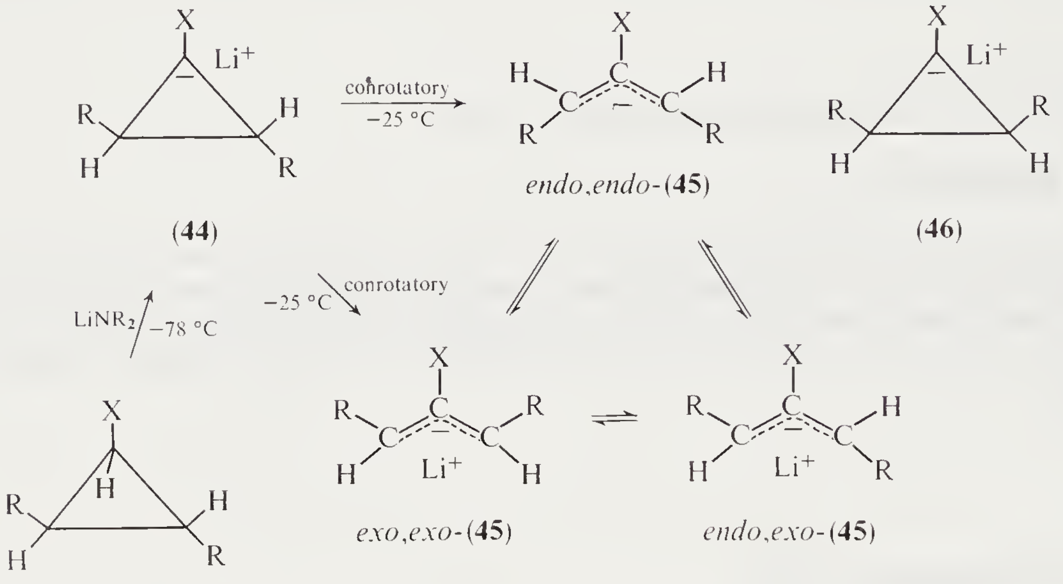
2.7.1.2 Transmetallation

Variations of this method are (a) replacement of lithium by a heavier alkali metal, *e.g.* potassium using potassium menthoxide (equation 77);[250] (b) replacement of potassium or a heavier alkali metal by lithium using lithium bromide;[255] (c) cleavage of allyl–mercury in $(CH_2{=}CHCH_2)_2Hg$ by alkali metal M (M = Li → Cs);[256,257] (d) cleavage of tetraallyl–tin bonds by lithium;[258] (e) cleavage of allyl–tin bonds[250,259] (in $allylSnR_3$) or allyl–lead bonds[260] by alkyllithiums. This method has proved particularly useful for obtaining unsymmetric and halo-substituted ambident allylic species[134] (see Table 9). Cleavage of silicon–allyl bonds by alkyllithiums does not occur and reaction will occur elsewhere in the molecule, *e.g.* $Ph_2(CH_2{=}CH)Si{-}CH_2{-}CH{=}CH_2$ and MeLi·TMED provided[261] $Ph_2(CH_2{=}CH)Si{-}CH\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2,Li^+$.

$$CH_2\overset{\cdots}{-}\bar{C}H\overset{\cdots}{-}CH_2,Li^+ \underset{LiBr}{\overset{K^+,{}^-OMenth}{\rightleftarrows}} CH_2\overset{\cdots}{-}\bar{C}H\overset{\cdots}{-}CH_2,K^+ \qquad (77)$$

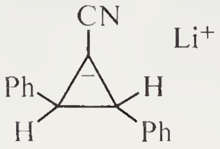
2.7.1.3 Ring opening of cyclopropylalkali metal compounds[263,264]

Thermal ring openings of cyclopropylalkali metal compounds are conrotatory processes, as predicted on theoretical grounds. Thus *trans*-cyclopropyllithium compounds (**44**) open directly to *exo,exo*-allyllithiums (*exo,exo*-**45**) [and/or *endo,endo*-(**45**)], whereas *cis*-cyclopropyllithium (**46**) initially produces the *exo,endo*-(**45**) isomer (Scheme 19).[264] However, kinetics have shown that isomerization of allylic anions (*e.g.* **45**; R = Ph, X = CN) is faster than the opening process and so the most thermodynamically stable *exo,endo*-isomer results from both (**44**) and (**46**) (R = Ph, X = CN). Table 17 lists the activation parameters. MO calculations (MINDO/3 and *ab initio* STO-3G/4-31G levels) also indicate the higher barrier to the conrotating opening relative to the allylic isomerization.

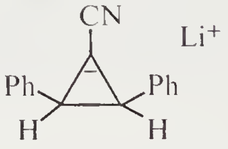


Scheme 19

Table 17 Activation Parameters for Conrotatory Ring Opening



(**44**)

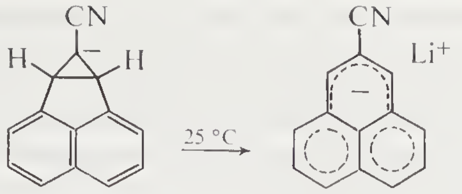


(**46**)

Process	E_a (kJ mol^{-1})	log *A*	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})
k_{conrot} (**44**; R = Ph, X = CN)	77.3 ± 6.3	13.0 ± 1.4	75.2 ± 6.3	−4 ± 25
k_{conrot} (**46**; R = Ph, X = CN)	86.5 ± 5.9	13.6 ± 1.2	84.4 ± 5.9	8 ± 21
$k_{endo\text{-}exo}$[a]	75.7 ± 4.6	14.0 ± 1.0	72.7 ± 8.4	13 ± 29

[a] For process *endo,exo* → *endo,endo*.

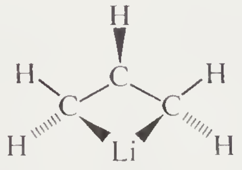
It is necessary to have at least one anion stabilizing substituent, such as phenyl, at each terminus of the allylic system for reasonable reactivity. In addition, ring opening proceeds[263,264] for (**44**) and (**46**) in which X = cyanide, PhSO, $PhSO_2$, CO_2H and CO_2Me but not for X = isocyanide, H or SPh. A partial reactivity sequence for ring opening of (**44**; R = Ph) was in the order X = CO_2Li > CO_2Me > CN. When the geometry prevents a conrotating ring opening, as with the polycyclic anion (**47**), produced from 7a,7b-dihydrocycloprop[*a*]acenaphthylenecarbonitrile on treatment with $LiNPr^i_2$ at −78 °C in THF, only slow reactions result; anion (**47**) ring opens 5500 and 740 times slower than (**44**; R = Ph, X = CN) and (**46**; R = Ph, X = CN), respectively.



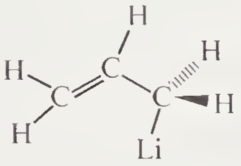
(47) (78)

2.7.2 Theoretical Treatment

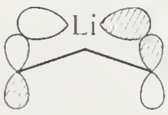
The structure of allyllithium has been calculated at *ab initio*[156,265] levels as well as at INDO and CNDO/2 levels[266] of approximation. The most stable arrangement (at RHF/STO-3G, 4-31G and 6-31G levels) is symmetric and delocalized with lithium centred over the plane of the allyl anion (**48**) and with significant bonding between the allyl anion and lithium involving donation from the filled non-bonding allyl orbital (π_{nb}) into the empty lithium $2p$-orbital of the appropriate symmetry, rather than the classical structures (**49**) and (**50**). The allyl fragment of the C_s structure is distorted from a planar arrangement in order to enhance this bonding. Relative energies at the RHF/6-31G level were (**48**):(**49**):(**50**) = 0:67:75 kJ mol^{-1}.

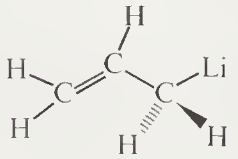


(**48**) C_s



(**49**) *syn*





(**50**) *anti*

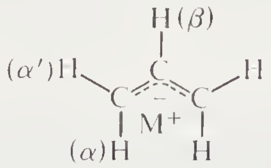
2.7.3 Solution Studies

The aggregation of allyllithium in THF is predominately monomeric with some dimers also present;[238] in Et_2O, allyllithium is highly aggregated (greater than 10 units per aggregate).[33]

2.7.3.1 *Allyl and alkylallyl compounds*

The ^1H NMR spectrum of allyllithium changes from an AB_4 to an A′BB′X type spectrum (*ca.* −87 °C) in THF solution on lowering the temperature. Those of the other allylalkali metal derivatives are AA′BB′X type at ambient temperatures[257] (Table 18). The hindered rotations in

Table 18 ^1H Resonance Parameters[b] for Allylalkali Metal Derivatives in THF Solution[257]



	Li	*Na*	*K*	*Rb*	*Cs*
$\delta_{\alpha'}$	1.79	1.75	1.94	2.01	2.18
δ_{α}	2.23	2.53	2.32	2.26	2.04
δ_{β}	6.22	6.46	6.28	6.14	5.84
$J_{\alpha,\alpha'}$	1.6	2.6	2.6	2.4	2.6
$J_{\alpha,\beta}$	14.6	14.5	14.7	14.7	14.7
$J_{\alpha',\beta}$	8.3	8.4	8.2	9.6	8.8
$J_{C_\alpha,H}{}^a$	146	148	148	148.5	145
$J_{C_\beta,H}{}^a$	133	132	131.8	131	132

[a] Mean values; for Rb, individual values of 154 and 143 were measured. [b] δ values in p.p.m.; J values in Hz.

these compounds rule out covalent structures for allyllithium and the heavier alkali metal compounds.

The ^{13}C NMR spectrum of $Bu^tCH_2CH{=}CRCH_2M$ (R = H or Me; M = Li → Cs) in ether was interpreted in terms of a delocalized ionic model involving increased charge equalization at the α- and γ-positions as the size of the alkali metal increased.[186b,267]

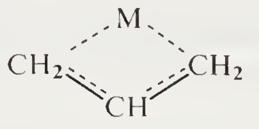
In the ^{13}C NMR spectrum of each allylalkali metal, C_1 and C_3 are equivalent (Table 19). Of interest, the ^{13}C NMR spectrum of allyllithium in THF was shown to be remarkedly independent of concentration (from 0.2 to 2 M), of temperature (−84 to +63 °C), of the presence of TMED, and of changes[250] from THF to Et_2O. The magnetic equivalence of the terminal sites is compatible with a ground state bridged (**48**) or ion-pair formation (**51**) as well as with a fast, reversible transition between two identical and asymmetric structures, *e.g.* equation (79). Arguments[258] against (**51**) for allyllithium included the low rotational barriers, compared with the higher values for allyl-potassium and -caesium[250] and the values calculated for the free allyl anion, as well as the observed ^{13}C–^{13}C coupling constants for alkylallyl compounds.[267]

Table 19 ^{13}C Chemical Shifts for Allylalkali Metal Compounds in THF Solution[e]

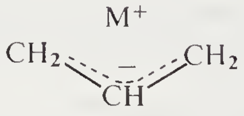
$$\underset{(3)}{H_2C}{=}\underset{(2)}{\bar{C}H}{=}\underset{(1)}{CH_2},M^+$$

	$\delta(C_3)$	$\delta(C_2)$	$\delta(C_1)$	*Ref.*
Allyllithium	51.1	147.0	51.1	255
1-D-Allyllithium[a,d]	51.1	147.0	51.2	255
Allylsodium[b]	48.7	145.1	48.7	257
Allylpotassium	52.9	144.1	52.9	255
1-D-Allylpotassium[c]	52.9	144.1	52.7	255
Allylrubidium	54.5	143.9	54.5	257
Allylcaesium	58.7	143.8	58.7	257
$CH_3CH{=}CH_2$	115	—	—	—

[a] $\delta(C_3) - \delta(C_1)$ for 1,1-D_2-allyllithium, 1.12 p.p.m. [b] $\delta(C_3) - \delta(C_1)$ for 1,1-D_2-allylsodium, 0.88 p.p.m. [c] $\delta(C_3) - \delta(C_1)$ for 1,1-D_2-allylpotassium, <0.5 p.p.m. [d] $J(^{13}C-^{1}D)$ = 21–23 Hz; 1 : 1 : 1 triplet. [e] Relative to TMS.



(**48**) C_s bridged species



(**51**)

(79)

The use of the Saunders isotopic perturbation method,[268] in three separate studies,[257,258,255] has led to the conclusion of C_s bridged species in THF solution for allyl-lithium, -sodium and -potassium (see Table 19) and probably for the rubidium and caesium compounds too. The basis of the method is that deuterium labelling at C(1) of the allylmetal species should perturb an equilibrium such as equation (79) so that two well separated ^{13}C signals should be observed for C(1) and C(3), while the C_s bridged structure should exhibit only a slight perturbation of symmetry and a very small separation of C(2) and C(3) (*ca.* 0.2 to 0.4 p.p.m.) would result. The latter in fact occurred.

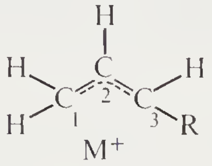
Schlosser and Stable[255] argued for a slightly asymmetric C_s structure for allyllithium with slight differences in the Li—C(1) and Li—C(3) distances. Allylpotassium, on the other hand, they adjudged to be a symmetric bridged species in both THF and Et_2O,[255] as were its derivatives 2-isopropyl-, 2-*t*-butylallyl-, crotyl- and prenyl-potassium from their ^{13}C NMR spectra.

Crotyllithium and prenyllithium were considered to be unequally distorted π-complexes, *i.e.*

between η_1 and η_3, with the bond to the secondary or tertiary carbon atom becoming longer on increasing substitution. The differences between potassium and lithium are associated with the larger size of potassium, making bridging easier, and also with the reduced tendency of potassium for solvation.[255] An interesting feature of allyl–M compounds (M = Na, K, Rb or Cs) is that when freshly prepared (from diallylmercury and M) and maintained below −20 °C, they are in a freely rotating metastable state but irreversible changes to more hindered species occur on raising the temperature.[257]

The barriers to rotation in the parent allylalkali metal compounds are dependent on the metal (Table 20). For allyllithium the barrier was the same in THF, in Et_2O and in the presence of TMED,[250] despite the differences in the states of aggregation,[33,238] *i.e.* monomers and some dimers in THF, with aggregation of more than 10 monomer units in diethyl ether. For the allylalkali metal compounds in THF (as well as simple alkylallyl compounds) the c.i.p. forms (or higher ion-aggregates) are indicated by UV and NMR spectra, and chemical evidence over a considerable range of temperatures[250] suggests that s.s.i.p. forms and free ions can be discarded. The rotational processes occur by separate rotations about the two carbon–carbon bonds[257] and a concerted mechanism can be ruled out.

Table 20 Rotation Barriers for Allyl Alkali Metal Compounds in THF



Compound[a]	*Bond*	ΔG (kJ mol^{-1})	T(°C)	*Ref.*
Allyllithium		44.7 ± 0.8	(−51)	250
Allylsodium		48.1	(5)	257
Allylpotassium		69.8 ± 0.8	(68)	250
		71.5	(68)	257
Allylrubidium[b]				
Allylcaesium		75.2 ± 1.3	(68)	250
2-Me-allyl-K		66.5 ± 1.3	(51)	250
(Z)-1-Me-allyl-K	C_1—C_2	est. 75–92	(68)	250
	C_2—C_3	71.1 ± 1.3	·	
(Z)-1-Pr^i-allyl-K[c]	C_1—C_2	>80.7	(68)	250
	C_2—C_3	71.1 ± 1.3	(47)	
(E)-1-Pr^i-allyl-K	C_2—C_3	⩽58.5	(28)	250
1-Ph-allyl-Li	C_2—C_3	71.1	(60)	272
	C_2—C_3	[65.6][d]	[25][d]	272
	Ph—C_1	49.7	(−31)	272
1-Ph-allyl-Na	C_2—C_3	>74.4	(>95)	272
	Ph—C_1	53.9	(−15)	272
1-Ph-allyl-K	C_2—C_3	>84	(>115)	272
	Ph—C_1	53.9	(−15)	272
1,3-Ph_2-allyl-Li (s.s.i.p.)	C_1—C_2	71.1		280
(Z)-1-Ph-3-Me-allyl-K (s.s.i.p.) in liquid NH_3		79.0		273
1,3-Ph-2-Me-allyl-M (s.s.i.p.), M = Li, Na or K	Ph—C_1	45.6	(−40)	278

[a] T.i.p. species. [b] Allylrubidium has same lifetime at 70 °C as allylpotassium at 50 °C. [c] Determined at 220 MHz (^1H); no broadening[32] of ^{13}C spectrum up to 50 °C. [d] In Et_2O.

(*i*) *Carbon–carbon bond rotations*

The transition state for the rotation is considered to be similar to the classical structure (**49**) or the slightly less stable (**50**). Thus the theoretically calculated barrier in allyllithium is *ca.* 67 kJ mol^{-1}, *i.e.* the difference between the bridged structure and the *syn* classical structure. Calculations at the same level indicate a higher barrier for sodium.[156] If the metal and the allyl fragments are bound to the same extent in the ground and transition states, the barrier to rotation would be independent of the metal and should be approximated by that of the allyl anion itself, (calculated to be 121 kJ mol^{-1} at RHF 4-31G). If the metal is bound to a greater extent in the rotational transition state than in the ground state, a reduced barrier and a dependency on the metal would result. The larger and more electropositive metals are not expected to stabilize a localized transition state such as the *syn* classical structure, or its ion pair, as well as the delocalized ground state, the bridged ion (C_s). The lithium–carbon bonding, because of partial covalent character in the transition state, reduces the rotational barrier appreciably.

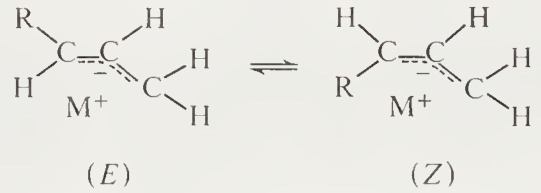
Rotational barriers are also quoted in Table 20 for alkylallylpotassiums, also c.i.p. in THF solution. To account for the similarity of the barriers for rotation about C(1)—C(2) in (*Z*)-1-R-allylpotassiums, it was suggested that the cation follows the electron density through the *anti* face of the allyl plane away from the (*Z*)-alkyl group, rather than through the *syn* face which would result in crowding in the transition state and a significant dependence on the alkyl group. On the other hand, the (*E*)-1-propyl substituent on allylpotassium lowers the C(2)—C(3) rotational barrier by 12.5 kJ mol^{-1}, by pushing electron density towards C(3), still permitting the more stable *syn* location of the cation in the transition state.

(*ii*) (Z) *Configurational preference in alkylallyl compounds*

There is a thermodynamic preference for the (*Z*) configuration of 1-alkylallylalkali metals in solution (equation 80; see Table 21).[251,252] This has also been shown by calculations at CNDO/2[269a] and *ab initio* SCF[269b] levels for 1-methylallyl carbanionic systems.[270] The conversion of the pure isomers of alkylallyl potassium to equilibrium mixtures occurs only slowly: half lives are of the order of hours at room temperature. At equilibrium, the (*Z*)- and (*E*)-allylpotassium isomers have separate ^{13}C spectra, as do crotyllithium isomers indicating a slow exchange on the NMR time scale. In contrast, for crotylmagnesium bromide derivatives, rapid exchanges occur even at −80 °C as shown by the averaged resonances; anionic hyperconjugation has been proposed.[270]

(80)

Table 21 (*Z*)/(*E*) Ratios of 1-Alkylallylalkali Metal Compounds at Equilibrium

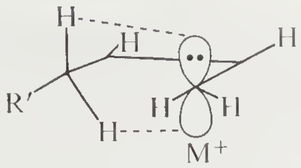


	R = *Me*	*Et*	*Pr*	*Pr^i^*	*Bu^t^*
M = Li					
Et_2O[a] at 0 °C	67:33	—	24:76	14:86	3:97
THF[a]	85:15	—	80:20	—	—
M = Na					
Hexane[a] at −48 °C	93:7	—	61:39	38:62	7:93
THF[a]	—	—	85:15	—	8:92
M = K					
Hexane[a] at −48 °C	96:4	—	94:6	56:44	8:92
THF at 26 °C[b]	100:0	86:14	—	65:35	0:100
M = Cs					
Hexane[a] at −48 °C	99.9:0.1	—	90:10	66:34	9:91
THF[a]	—	—	—	—	12:88
M = H[c]	23:77	29:71	—	26:74	0.1:99.9

[a] Ref. 25. [b] Ref. 252. [c] Calculated from thermochemical data.

Schlosser *et al.*[251] prefer an explanation based on hydrogen bonding (**52**) to account for the greater stability of the (*Z*)-isomers and the (*Z*):(*E*) ratios in hexane, which increase from lithium to caesium, *i.e.* in the sequence of increasing negative charge on the anion. The greater solvation by THF also leads to 'freer' carbanions and larger (*Z*):(*E*) ratios. The (*Z*):(*E*) ratios in 1-R-allyl-M increase in the sequence R = $Bu^t < Pr^i < Pr$ (Et) < Me for each metal. Of interest, the (*Z*):(*E*) ratios for 1-Me_3Si-allylpotassium are similar to those for 1-Bu^t-allylpotassium, an indication that hyperconjugation may not be the complete answer. It is also of interest to compare these (*Z*):(*E*) ratios with those calculated for the alkenes.

The (*E*)-1-alkyl group has a larger electron repelling effect than a (*Z*)-1-alkyl group in 1-alkylallylpotassiums, as shown by the relative downfield shift of *ca.* 1.5 p.p.m. at the terminal site on changing from the (*Z*)-isomer to the (*E*)-isomer. This suggests a through bond effect rather than a through space effect.[252]



(52)

2.7.3.2 Arylallyl compounds

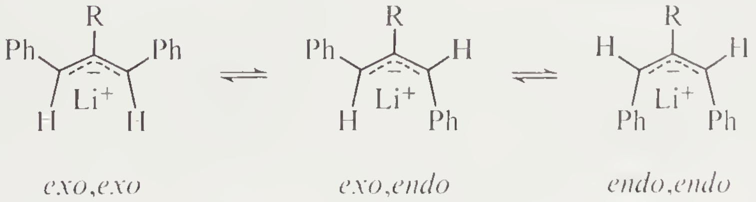
In mono- and di-phenylallyllithiums, the extra delocalization of charge relative to the situation in alkylallyl compounds renders these compounds s.s.i.p. in solvents[253,271] such as THF.

Rotational barriers for phenylallyl compounds are given in Table 20.[272,273] Ion pairing of 1,3-diphenylallylalkali metal compounds, *e.g.* $\mathrm{PhCH{\cdots}\bar{C}H{\cdots}CHPh,M^+}$ and $\mathrm{PhCH{\cdots}\bar{C}H{\cdots}CMePh,M^+}$ have been studied by UV, ^{1}H and ^{13}C NMR spectroscopies in ethers[253,254] and in liquid NH_3:[275] the advantages and disadvantages of these methods have been indicated on p. 89. As well as c.i.p. and s.s.i.p., intermediate partially or externally solvated ion pairs have been recognized[274–277] from the UV spectra of some 1,3-diarylallyl compounds, such as p-$\mathrm{Bu^tC_6H_4CH{\cdots}CH{\cdots}CHPh,M^+}$ (M = Li, Na or K).[276] The factors influencing ion pairing have been mentioned in Section 2.5.3.4. Suffice here to state that 1,3-diphenylallyllithium (RLi) and the sodium salt (RNa) in DME are predominantly s.s.i.p., while all other RM [M = Na (except in DME), K, Rb or Cs] are predominately c.i.p. at 30 °C in solvents such as THF, 2-MeTHF, THP or DME. In liquid ammonia the species are s.s.i.p. (λ_{max} 550 nm). On lowering the temperature in the ethereal solution, some ^{1}H NMR spectral indication was observed for s.s.i.p. for R^-,Na^+ in THF and 2-MeTHF and for R^-,K^+ in THF; some thermodynamic data for s.s.i.p./c.i.p. equilibria are ΔH (kJ mol^{-1}) and $\Delta S°$ (kJ K^{-1} mol^{-1}) = 25.4 and 93.4 for Na (THF), 11.5 and 63.2 for Na (2-MeTHF) and 17.0 and 68.6 for K (THF). Related data for 1-Me-1,3-Ph_2-allyl-M have been obtained by UV–visible spectroscopy.[277] In benzene solution, 1,3-Ph_2-allyllithium is shown to interact with ethers (*e.g.* THF or 2,5-Me_2THF) to give the partially solvated c.i.p. species, containing four ether molecules.[253]

The conformational distribution and rotational barriers have been obtained for a number of 1,3-diphenyl-2-R-allylalkali metal compounds, especially lithium compounds[249] (*e.g.* see Table 22).

The *exo,exo*-conformer is the major conformer only for 1,3-diphenylallyllithium; values of K = [*exo,exo*] : [*endo,exo*] are 17 at −30 °C, 9 at 0 °C and 8 at 17 °C. Increasing size of the R group leads successively to more *exo,endo*- and *endo,endo*-conformers at the expense of the *exo,exo*-isomers. This trend is associated with decreasing free energies of rotations. The decreasing $\Delta G^\ddagger$ values, in the sequence R = H, Me, Et and Pr^i, indicate an increasing destabilization of the

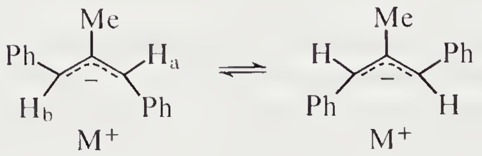
Table 22 Conformation[a] and Free Energies of Activation for Rotation of C—C Bonds ($\Delta G^\ddagger$, 273 °C) in 1,3-Diphenyl-2-Allyllithium in THF Solution[280]



R	% *exo,exo*	$\Delta G^\ddagger$	% *exo,endo*	$\Delta G^\ddagger$	% *endo,endo*
H[b,c]	92	← 71.1	8	—	—
Me	8	← 59.4	92	—	—
CN	4.5	← 68.6	91	68.6 →	4.5
Et	15	← 57.7	68	57.7 →	17
Ph	—	—	56	59.8 →	44
Pr^i	—	—	38	52.3 →	62
Bu^t	—	—	—	—	100

[a] Populations between −46 and 20 °C: little change (±4%) in this temperature range. [b] 93% *exo,exo* and 7% *exo,endo* in liquid ammonia/MeOBu^t solution for the lithium, sodium and potassium salts.[37] [c] $\Delta H^\ddagger$ for *exo,endo* → *exo,endo* = −9.1 ± 17 kJ mol^{-1} in THF at −30 °C;[44] for the sodium salt in liquid ammonia, $\Delta H^\ddagger$ = −6.9 ± 1.0 kJ mol^{-1}.[43]

ground state conformation with the transition states being all less hindered and of comparable stability. Ion pairing effects on $\Delta G^{\ddagger}$ values are limited *e.g.* addition of HMPT (4.5 equivalents) to 1,3-diphenylallyllithium in THF only increases $\Delta G^{\ddagger}$ by 3.8 kJ mol^{-1} and has no effect on 1,3-diphenyl-2-methyllithium. For the exchange process (equation 81) the coalescence temperature for the allylic protons (H_a and H_b) of the lithium salt in THF is at 30 ± 2 °C compared with the value for the potassium salt (15 ± 4 °C), *i.e.* the free energy change is greater for M = Li than for M = K. This is due[248] to 1,3-diphenyl-2-methylallylpotassium being t.i.p. in THF (λ_{max}, 505 nm) and thus there is more localization of charge between the allyl group and potassium than in the lithium salt, which is s.s.i.p. (λ_{max}, 536 nm).[248]



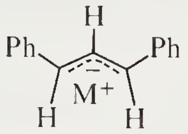
(81)

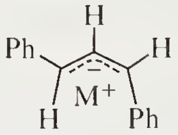
Of interest, phenyl ring rotation[248] occurs in 1,3-diphenylallyllithium in THF with a coalescence temperature of −30 °C by ^{1}H NMR, while the rotational barriers in MeOBu^t–liquid NH_3 solution are the same by ^{13}C NMR ($\Delta G^{\ddagger}_{rot}$ = 45.6 kJ mol^{-1}; coalescence temperature *ca.* −40°C) for the lithium, sodium and potassium salts, all s.s.i.p.[278] In addition, the free energies of rotation in 1,3-diphenyl-2-cyanoallyllithium in THF are the same as those for the lithium, sodium and potassium salts[264] in DMSO. The independence of the gegenion of the rotation probably arises from the classical benzylic anion-like transition states, *i.e.* $[\mathrm{PhCH{=}\bar{C}RCHPh,M^+}]$, being s.s.i.p., as are the ground states.

It has been recognized that the conformational equilibria are highly photosensitive in THF solution[254] but *not* in liquid ammonia.[279] On removal of the light source the species relax back to the dark equilibrium position with t.i.p. reacting faster than the s.s.i.p. form. In Table 23 are given the absorption maxima of 1,3-diphenylallylalkali metal species.

As shown in Table 22, 1,3-diphenyl-2-CN-allyllithium is preferentially in the *endo,exo* conformation at equilibrium. Above −50 °C, topomerization of the *endo,exo*-isomer occurs; the free energy of activation, $\Delta G^{\ddagger}$(62 °C), is 69.0 kJ mol^{-1}. The similar value for $\Delta G^{\ddagger}$(62 °C) of 63 ± 4 kJ mol^{-1} for the single C—C rotation of *endo,exo*- to give *endo,endo*-1,3-diphenylallyllithium gives support to the view that the mechanism of the topomerization is due to two consecutive single rotations, with *exo,exo*-1,3-phenyl-2-cyano-allyllithium as the intermediate.

Table 23 Visible Absorption Maxima for Conformers of 1,3-Diphenylallylalkali Metal Compounds in THF Solution[254]





	exo,exo		*exo,endo*		*Allyl-M*[b]	
	t.i.p.	*s.s.i.p.*	*t.i.p.*	*s.s.i.p.*	*t.i.p.*	*s.s.i.p.*
Li	—	565 (550)[a]	—	536 (525)[a]	318	—
Na	534	565	*ca.* 510	536	—	—
K	537	—	*ca.* 515	—	346	—
Rb	540	—	*ca.* 517	—	—	—
Cs	545	—	*ca.* 522	—	344	—

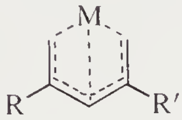
[a] λ_{max} in 15% MeOBu^t/85% NH_3 solution: independent of M. [b] Ref. 257.

2.7.4 Pentadienylalkali Metal Compounds

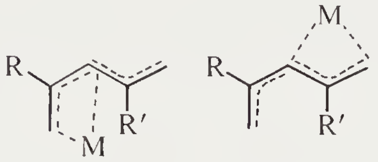
These compounds, related to allyl compounds, have also been studied with regard to bonding, ion-pairing and conformations in solution.

Pentadienylalkali metal compounds, $C_5H_7M{\cdot}THF$ (M = Li → Cs), as well as various acyclic and cyclic derivatives, have been isolated as crystalline materials from the reaction of 1,3- or 1,4-pentadienes with the alkali metals in THF solution in the presence of a base, such as NMe_3

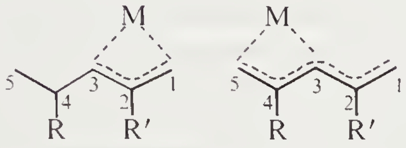
or TMED. The THF solvate molecule can be removed on evacuation. Different hydrolysis products have been obtained, an indication of different solution structures, *e.g.* from $C_5H_7Li{\cdot}THF$ a 70:20:10 mixture of *trans*- and *cis*-1,3-pentadiene and 1,4-pentadiene, from $C_5H_7Na{\cdot}THF$ a 62:38 mixture of *trans*- and *cis*-1,3-pentadiene, and from C_5H_7M (M = K, Rb or Cs) in THF essentially *trans*-1,3-pentadiene, but in isooctane, *cis*-1,3-pentadiene was exclusively obtained.[280] Several theoretical calculations have been made,[281–283] including some using the CNDO/2 method,[281,282] for pentadienyllithium, the bis(dimethyl ether) solvate and the 1-methyl isomer. Possible conformations and binding sites for pentadienyllithium have been calculated at the CNDO/2 level (**53–57**; R, R′ = H, M = Li), the most stable conformer being the W-shape for pentadienyllithium. The bonding is both of a σ- and π-type and involves the HOMO of the pentadienyl anion and the Li $2p$ orbital, with lithium above the plane of the pentadienyl chain.



(**53**) U-shaped (η^5)

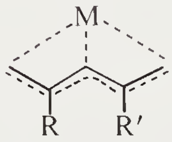


(**54**) S-sickle shaped (η^3)



(**55**) W-shaped (η^3)

(**56**) W-shaped (η^3)



(**57**) W-shaped (η^5)

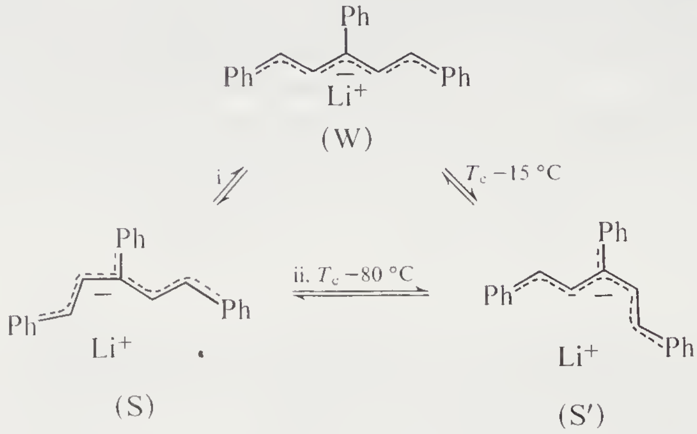
For consistency of the calculated structures of pentadienyllithium with its ^{13}C NMR spectrum,[284,285] which shows C(1) and C(5) to be equivalent, the internally coordinated (**56**) or rapidly equilibrating forms (**55**) are required. (The species in solution will of course be solvated.)

The CNDO/2 calculations suggest that the central carbon should be the most reactive site, since this has the highest negative charge; however this is in contrast to the experimental findings.[281] Conformations in solution have been generally studied by NMR spectroscopy as well as by quenching equilibrium mixtures. As found for pentadienyllithium in THF,[285,286] W-forms also predominate for pentadienylpotassium in liquid ammonia,[273] the 1-methyl[273,285] and 3-methyl isomers and also for 1,5-diphenylpentadienyllithium;[287] other forms may be present in small amounts. Whereas these may escape detection by NMR spectroscopy, quenching experiments can indicate their presence in the equilibrium mixtures.

In contrast to the above situation, 2-methyl- and 2,4-dimethyl-pentadienylmetal can have appreciable if not predominant U-shaped conformations in solution.[286,288] These conformational conclusions come particularly[288] from quenching experiments, using a dimethoxyboration–oxidation sequence, a sequence which provides alcohols with extreme regioselectivity by hydroxylation of terminal allylic sites. Thus 2,4-dimethylpentadienyl-potassium and -lithium at −78 °C were found to be exclusively U-shaped, 2-methylpentadienylpotassium predominantly U-shaped, while 2-methylpentadienyllithium exists as a 3:7:5 mixture of (**54**; R = H, R′ = Me):(**54**; R = Me, R′ = H):(**55**).

Schlosser[288] argues that the sequence of stabilities of the conformers of the anions will change on substitution. 2,4-Dimethyl substitution, for example, will have less steric effect on the U-shaped (**53**) than on the S-shaped (**54**) and in particular on the W-shaped (**55**) conformers. This results in the U-shaped conformer of the anion being only slightly disfavoured relative to the others. In the salts, the extra gain from η^5-coordination in the U-conformation for *both* Li and K will render this form relatively more stable than the η^3 W- and S-conformers. (For the larger potassium, an η^5 coordination could also occur in the W-conformers.) The energy difference between the U-form on the one hand and the S- and W-forms on the other for the 2-methyl derivatives is still large and here the effects of the metal are significant; coordination by potassium is sufficient to stabilize the U-conformation. Conformation differences apparently arise in the lithium and potassium salts of the 1-pentylpentadienyl anion.[288b]

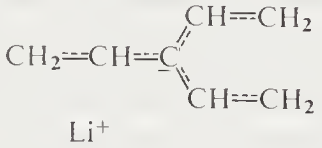
1,3,5-Triphenylpentadienyllithium in THF adopts[289] a W- and two S-shaped conformations (Scheme 20). However, barriers to rotation have been found for path (ii) rather than for (i) in Scheme 20. In the former process, 1,3-hydrogen/phenyl interactions involving the central ring are relieved. The conversion of S → S′ in Scheme 20 probably proceeds *via* a twisted U-conformation.



Scheme 20

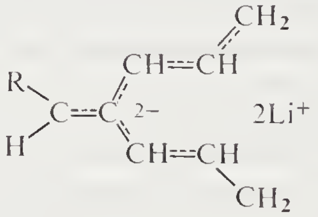
Barriers to rotation of C—C bonds, both terminal and internal, in other pentadienyl compounds have also been measured; rotation of phenyl groups have also been detected.[278,286,290] The gegenion influences the rotation rates for the parent pentadienylalkali metal compounds; thus the coalescence temperatures of the methylene protons of the lithium salt in THF is at 30 °C, indicating an approximate barrier of 63 kJ mol^{-1}, while for the potassium salt, no exchange was detected[286] up to 50 °C. A larger but qualitative sequence of barrier heights was established[290] as Li < Na < K < Rb < Cs.

Rotational barriers have been determined for the more extensively delocalized systems (**58**)[291] and (**59**)[292] in THF. The barriers for (**59**; R = Ph) are 60.6 kJ mol^{-1} (C_4—C_5) and 48.1 kJ mol^{-1} (C_1—C_2); a W-W conformation was assumed.



$CH_2{=}CH{=}\overset{-}{C}(CH{=}CH_2)_2\;Li^+$

(58)



$RHC{=}C(CH{=}CH{-}CH_2)_2^{2-}\;2Li^+$

(59)

Several related delocalized carbanionic systems have been obtained, in particular by Bates.[293]

2.7.4.1 Ion pairing

For the parent pentadienylalkali metal compounds and for the simple alkyl substituted ones, c.i.p. forms are anticipated. A study of the more delocalized 1,5-diarylpentadienyl (and also α,ω-diphenylheptatrienylnonatetraenyl) compounds revealed the presence of s.s.i.p. forms.[294] The trends were as expected from other ion-pair studies; for example, values of K (= [s.s.i.p.]/[c.i.p.]) for 1,5-diphenylpentadienyllithium were >50 (in THF) and 1.81 (in 2-MeTHF) at 20 °C compared with values for the sodium salt of 1.74 and 0.02 respectively in the two solvents. Increasing the electron releasing ability of groups in the aromatic rings and the length of the polyenylic chain led to more s.s.i.p.

2.8 ALKYNYLALKALI METAL COMPOUNDS

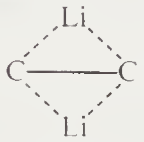
2.8.1 General

The acetylenic hydrogen is acidic and may be readily replaced by an alkali metal,[4] including Cs.[295] In addition to monometallated acetylene, MC≡CM can also be obtained.[4] However, CsC≡CCs was considered to be considerably unstable relative to the elements. The standard enthalpies of formation of NaC≡CNa, NaC≡CH, and CsC≡CH were calculated to be 20.0 ± 1.7, 96.6 ± 1.1 and 78.8 ± 1.1 kJ mol^{-1} at 25 °C.[296] Structures of HC≡CM (M = Na, K or Rb) and MeC≡CM (M = Na or K) have been determined.[297]

2.8.2 Theory

Ethynyllithium, HC≡CLi, has been considered at several levels, including several *ab initio* methods [STO-3G,[298] (STO-4G, SS and SS + d basis sets),[35] SCF-MO, large Gaussian basis set];[235] MeC≡CLi has also been considered at the STO-3G/4-31G/5-21d level.[22] Classical structures were deduced. As with calculations on other organolithiums, Streitwieser concludes[35] that there was little covalent character to the carbon–lithium bond. Hinchliffe calculated that the C—Li bond was weak, with only a weak electrostatic interaction between a carbon *sp* hybrid orbital and the lithium cation.[235] In addition there were negligible contributions from the lithium $2p$ orbitals to the C—Li overlap population. A variety of C—Li bond lengths have been calculated for HC≡CLi, *e.g.* 1.93 Å at the (SS + d) level,[35] 1.83 Å (STO-3G)[298] and 1.90 Å (4-31G),[235] while in MeC≡CLi the value calculated[22] is 1.83 Å. The C—Li homolysis energies increase from EtLi to CH_2=CHLi to CH≡CLi. The more stable the anion the more energy, it was argued,[22] would be required for back transfer of charge from the carbanion to lithium during the C—Li homolysis. The relative stabilization of organolithiums was calculated at the (4-31G/STO-3G) level.[22] In addition, LiC≡CLi, LiC≡C—C≡CX (X = H or Li) and $Li(C{\equiv}C)_nCN$ (n = 1 or 2) were also investigated by *ab initio* methods.[298]

A cyclic bridged D_{2h} structure (**60**) has been indicated (*ab initio*: STO-3G/4-31G/6-31G levels) to be *ca.* 29 kJ mol^{-1} more stable than linear $D_{\infty h}$ form (**61**). The cyclic nature of (**60**) and the use of Li $2p$ orbitals enables the $1b_{2u}$ orbital to benefit from 2π-electron aromaticity and allows increased C—Li bonding in the $2b_{3u}$ orbital. However, σ-bonding is also important.[298]



(**60**) C—Li = 2.06 A
C—C = 1.26 A

Li—C≡C—Li

(**61**)

2.8.3 Polylithiated Compounds

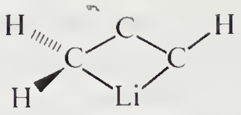
Metallation of propargylic compounds[299] has been reviewed by Klein and was considered in Section 2.3.2. All propargylic hydrogens can be successively replaced by lithium,[70,82] in addition to the acetylenic hydrogen. Thus propyne (C_3H_4) provides successively $CH_3C{\equiv}CLi$ (ν_{CC} 2050 cm^{-1}, acetylidic), $C_3H_2Li_2$ (ν_{CC} 1870 cm^{-1}), C_3HLi_3 (ν_{CC} 1770 cm^{-1}) and C_3Li_4 (ν_{CC} 1675 cm^{-1}, allenic). While 1-butyne can be lithiated by BuLi (3 equivalents) in hydrocarbons to MeC_3Li_3 (ν_{CC} 1750 cm^{-1}), an internal alkyne requires a more reactive lithiating agent, *e.g.* MeC≡CMe forms the same MeC_3Li_3 compound only from BuLi/TMED (3 equivalents). 1,3-Pentadiyne can be completely perlithiated to C_5Li_4 (ν_{CC} 1800 cm^{-1}, cumulene). A further example is the reaction of BuLi/TMED with 1-phenylpropyne, which leads to PhC_3Li_3 (ν_{CC} 1780 cm^{-1}, allenic) and *o*- and *p*-$LiC_6H_4C_3Li_3$; more forcing conditions, *i.e.* a 50-fold excess of BuLi at 75–85 °C for 48 h, provides penta- and hexa-lithio compounds as major products in addition to some C_9HLi_7 and C_9Li_8 (1%), as shown by derivatization using D_2O.

The IR spectra of the lithiated products were used to identify the type of multiple carbon bonding present, *i.e.* allenic or acetylidic. In addition, the structures of the $C_3Li_nH_{4-n}$ compounds derived from allenes and cyclopropenes as well as from propyne were studied by *ab initio* methods.[22]

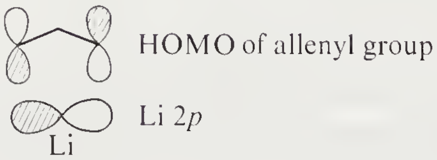
Two basically distinct bonding arrangements were calculated for the open-chain compounds derived from allene and propyne. The most stable arrangement is the conventional acetylidic bonding with one lithium attached to or associated with one of the terminal carbons (*e.g.* **62**, propynyllithium). The other bonding type consists of lithium bridging between C_1 and C_3 (as in allyllithium), with a bent C—C—C chain (*e.g.* **63**, allenyllithium). As in allyllithium, the lithium lies closest to C_2 but its bonding overlap with C_2 is nearly zero. The lithium is closer to C_1 due to preferential overlap.[22] The structure (**62**) is 50 kJ mol^{-1} more stable than (**63**).

$Li{-}C{\equiv}C{-}CH_3$

(62)



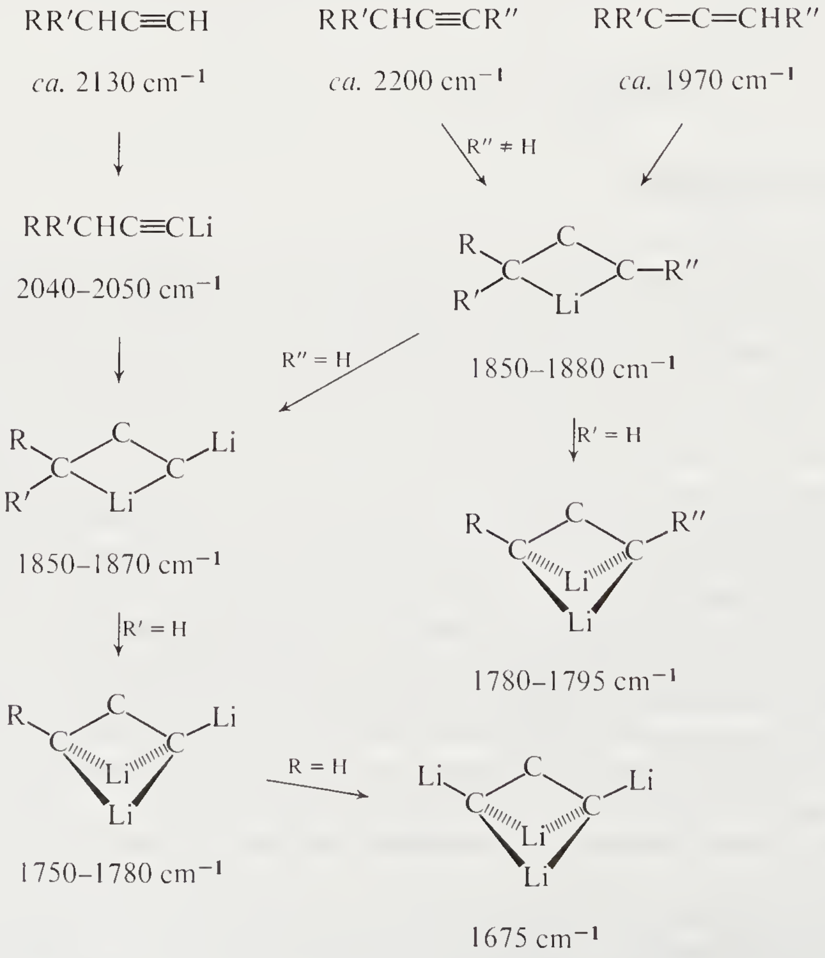
(63) ∠CCC = 157.6°



Allene is monolithiated to a species which is different from monolithiated propyne and which provides both 3-propynyl and allenyl products.[8] A bridging structure (**63**) thus does account for its ambident nature. Of further interest is the fact that the lithium derivative of $Me_2C{=}C{=}CH_2$ in the presence of excess $Me_2C{=}C{=}CH_2$ is completely isomerized to the $Me_3CHC{\equiv}CLi$ complex in Et_2O solution after 10 days at room temperature. Classical cyclopropenyllithium isomers were calculated to be less stable than (**62**) by *ca.* 169.3 and 298.9 kJ mol^{-1} for the 1- and 3-isomers.

The most stable structures for the other $C_3H_{4-n}Li_n$ (n = 2–4) compounds are shown in Scheme 21; $C_3H_{4-n}Li_n$ (n = 2–4) can be obtained from either allene or propyne. The IR frequencies in Scheme 21 give some backing to the calculated structures. Allenic and propargylic products from reactions of $C_3H_2Li_2$, for example, also indicate the significance of a bridged structure. These structures consist of at least one classical acetylidic C—Li bonding with additional lithium bridging. Other structures were considered for each $C_3H_{4-n}Li_n$ formula and although found to have lower stabilities, they may still have some importance in solution, where solvation could change the relative stabilities, as may appropriate substitutions.

An alternative view of the structures in terms of an ionic model was also considered,[22] *i.e.* the lithium cation associating electrostatically with the carbon centre(s) bearing the highest negative charge. This gave the same general structures.



Scheme 21 Sequences of lithiation and IR frequencies for lithiated propynes and allenes

2.9 HYDROCARBON RADICAL ANION AND DIANION ALKALI METAL COMPOUNDS

2.9.1 Introduction

Aromatic hydrocarbons, ArH, can undergo electron-transfer reactions with alkali metals to give paramagnetic aromatic radical anion compounds, ArH^{-},M^{+}, and/or diamagnetic aromatic dianion species, $ArH^{2-},2M^{+}$. In these highly coloured species the additional electrons reside in the lowest unoccupied MO of the aromatic hydrocarbon. Usually ethers are used as solvents, but in the presence of a crown ether it is possible to obtain salts of the radical anions in hydrocarbons.[300] Radical anions of the simplest aromatic, benzene,[301] its derivatives, *e.g.* p-$Me_3M'C_6H_4M'Me_3$ (M′ = C, Si, Ge or Sn),[302] arylalkenes, *e.g.* stilbenes, and polycyclic aromatics have all been prepared, as have dianions of the arylalkenes and polycyclic aromatics.[303]

Several reviews and articles have been concerned with alkali metal radical anions and dianions; the main interest in these reviews has been with the radical anionic species.[14,15,303,304]

The general terms hydrocarbon radical anion and dianion will be most frequently used here, *e.g.* naphthalene radical anion ($Naph^{\cdot-}$) and naphthalene dianion ($Naph^{2-}$) for the naphthalene derivatives. Alternative names for $Naph^{\cdot-}$ are naphthalenide, naphthalide and dihydronaphthylide, while for $Naph^{2-}$, dihydronaphthalendiide has found use.

2.9.2 Preparation

Matters of paramount importance in the formation of these species are the ionization potentials of the metal (see listing in Table 1) and the electron affinities (a listing of relatives values is given in Table 24; for others, including gas phase values, see ref. 303).

Table 24 Relative Electron Affinities of ArH Values[1] obtained by Potentiometric Titration with Sodium Biphenylide in THF at 25 °C

$$PhPh^{\cdot-},Na + ArH \rightleftarrows PhPh + ArH^{\cdot-},Na^{+} \qquad \epsilon_1$$
$$PhPh^{\cdot-},Na^{+} + ArH \rightleftharpoons PhPh + ArH^{2-},2Na^{+} \qquad \epsilon_2$$

ArH	ϵ_1 (V)	ϵ_2 (V)
Biphenyl	0	—
Naphthalene	0.043 ± 0.02	—
Triphenylene	0.132 ± 0.01	—
Phenanthrene	0.142 ± 0.01	—
Pyrene	0.529 ± 0.02	—
Anthracene	0.642 ± 0.01	0.33 ± 0.1
Perylene	0.965 ± 0.01	0.56 ± 0.01

1. R. V. Slates and M. Szwarc, *J. Phys. Chem.*, 1965, **69**, 4124.

The formation of ArH^{-},M^{+} and $ArH^{2-},2M^{+}$ is in fact governed by equilibria (82) and (83). Values of K_{form} are usually too large for accurate measurement; those for ArH = Ph—Ph and Naph have however been obtained. These values reflect the importance of specific solvent–solute interactions, *e.g.* the equilibrium yields of $Ph{-}Ph^{\cdot-},M^{+}$ at 25 °C are (i) 45% $Ph{-}Ph^{\cdot-},Li^{+}$ and 15% $Ph{-}Ph^{\cdot-},Na^{+}$ in diethoxyethane, (ii) 0% $Ph{-}Ph^{\cdot-},Li^{+}$ and 4% $Ph{-}Ph^{\cdot-},Na^{+}$ in dioxane, and (iii) 100% $Ph{-}Ph^{\cdot-},Na^{+}$ in DME. In addition, sodium is a more effective reducing agent than potassium in THF and in THP but the reverse is true[305] in DME.

$$ArH \quad + \quad M_{solid} \quad \rightleftharpoons \quad ArH^{\cdot-},M^{+} \tag{82}$$

$$K_{form} = [ArH^{\cdot-},M^{+}]/[ArH]$$

$$2ArH^{\cdot-},M^{+} \quad \rightleftharpoons \quad ArH^{2-},2M^{+} \quad + \quad ArH \tag{83}$$

$$K_{disp} = [ArH^{2-},2M^{+}][ArH]/[ArH^{\cdot-},M^{+}]^{2}$$

Values of K_{disp} are listed in Tables 25 and 26. As can be seen, there are significant solvent (K_{disp} decreases in $Et_2O \gg THF > DME$) and metal ion effects. Compared to free ions the free energy of $ArH^{2-},2M^+$ is more strongly decreased than that of $ArH^{\cdot-},M^+$ due to cation–anion interactions. This effect should become more important with smaller ArH and M^+, provided that M^+ is not significantly solvated, and so shift the equilibrium towards the $ArH^{2-},2M^+$ side. However, stronger cation solvation, as with smaller M^+, will shift the equilibrium towards $ArH^{\cdot-},M^+$, since M^+ can be more readily solvated when paired with $ArH^{\cdot-}$ compared to ArH^{2-}. Hence complex trends in K_{disp} can be expected.[14]

Table 25 Values of the Disproportionation Equilibrium Constants, K_{disp}

$$2ArH^{\cdot-},M^+ \rightleftharpoons ArH^{2-},2M^+ + ArH$$

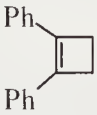
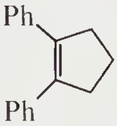
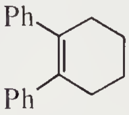
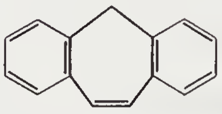
$$K_{disp} = [ArH^{2-},2M^+][ArH]/[ArH^{\cdot-},M^+]^2$$

ArH	*M*	K_{disp} Et_2O[1]	*THF*[2]	*DME*[2]
Naphthalene	Li	1270	—	—
Anthracene	Li	42	—	—
Tetracene	Li	16	9.4×10^{-10}	2.7×10^{-10}
Perylene	Li	0.76	5.6×10^{-10}	2.5×10^{-10}
Perylene	Na	—	2.9×10^{-6}	2.2×10^{-9}
Perylene	K	—	2.8×10^{-6}	9.4×10^{-8}
Perylene	Cs	—	1.6×10^{-5}	0.67×10^{-6}

1. At ambient temperature: G. Levin, B. E. Holloway and M. Szwarc, *J. Am. Chem. Soc.*, 1976, **98**, 5706.
2. At 25 °C: F. Jachimowicz, H. C. Wang, G. Levin and M. Szwarc, *J. Phys. Chem.*, 1978, **82**, 137.

Table 26 Values of K_{disp} for *cis*-Diphenylalkenides in THF at Ambient Temperature[15,308]

$$2PhCR{=}CRPh^{\cdot-},Na^+ \rightleftarrows PhCRCRPh^{2-},2Na^+ + PhCR{=}CRPh$$

Alkene	K_{disp}
trans-PhCH=CHPh	0.03
cis-PhCH=CHPh	>2
	0.15
	110
	3000
	0.10
$Ph_2C{=}CPh_2$	400

It has been reported that in THF only $\mathrm{Naph}^{\cdot-},\mathrm{Na}^+$ can be obtained, whereas dianions, $\mathrm{Naph}^{2-},2\mathrm{M}^+$ can also be produced for lithium and potassium. For potassium at low temperatures (*e.g.* at −80 °C), $\mathrm{Naph}^{\cdot-},\mathrm{K}^+$ is favoured, while at 25 °C, especially at low concentration of naphthalene and excess potassium, $\mathrm{Naph}^{2-},2\mathrm{K}^+$ predominates.[306]

Thermodynamic parameters for the disproportionation of alkali metal perylene radical anions ($\mathrm{Pe}^{\cdot-}$, M^+) in THF indicate different solvation effects (Table 27); of particular note is the very high entropy value for the sodium system. This is due to the sodium cation being strongly solvated only when associated with $\mathrm{Pe}^{\cdot-}$. In contrast, Li^+ is well solvated either with $\mathrm{Pe}^{\cdot-}$ or Pe^{2-}, and the potassium and caesium cations are always poorly solvated.[307]

Table 27 Thermodynamic Data[307] for the Disproportionation of $\mathrm{Perylene}^{\cdot-},\mathrm{M}^+$ in THF

$$2\mathrm{Pe}^{\cdot-},\mathrm{M}^+ \rightleftharpoons \mathrm{Pe}^{2-},2\mathrm{M}^+ + \mathrm{Pe}$$

M	*Temp. range* (°*C*)	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})	K_{disp} (25 °C)
Li	−55 to −40	55.2	0	
Li	0 to +25	67.3	49.7	5.6×10^{-10}
Na	−55 to +25	112.4	275.0	2.9×10^{-6}
K	−55 to +25	58.9	92.8	2.8×10^{-6}
Cs	−55 to +25	46.0	62.7	1.6×10^{-5}

The K_{disp} value for $\mathrm{Ph_2C{=}CPh_2}^{\cdot-},\mathrm{Na}^+$ is 400 (Table 26) at ambient temperature and is at least partly due to the destruction of the carbon–carbon double bond on addition of two electrons in forming the dianion. This leads to a less hindered skewed conformation for the dianion and one which enables the cation to approach more closely compared with the situation in the radical anion, which still retains the hindered framework of the alkene. The K_{disp} values for stilbenes and the cycloalkenides (Table 26) are governed by the reduction in steric crowding and strain on forming the less rigid dianionic species.[308]

A large K_{disp} value is obtained[15,299] for cyclooctatetraene (cot), even in HMPT where free ions may exist. Both $\mathrm{cot}^{\cdot-}$ (from ESR spectral evidence) and cot^{2-} are planar [as shown by the crystal structures[310] of $(\mathrm{cot})\mathrm{M}_2$, M = K and Rb], in contrast to tub-shaped cot. Moreover, cot^{2-} is a 10-electron aromatic species and this is the reason for the very large K_{disp} value.

2.9.3 Ion Pairing and Structure in Solution

The radical anion species $\mathrm{ArH}^{\cdot-},\mathrm{M}^+$ at the concentrations used for their study have been shown to exist in solution as free ions (*e.g.* in HMPT) or ion pairs (s.s.i.p. and t.i.p.) as well as aggregates. The dianions $\mathrm{ArH}^{2-},2\mathrm{M}^+$ are normally expected to form relatively tight ion aggregates.

Ion pairing in the radical anion compounds has been investigated by such techniques as conductivity,[15,311] ESR and NMR[15] spectroscopies. UV–visible spectra can be used but the differences in the absorption maxima for t.i.p. and s.s.i.p. are usually small, with the s.s.i.p. absorbing at the longer wavelengths, *e.g.* the values for $\mathrm{Ph{-}Ph}^{\cdot-},\mathrm{Na}^+$ are 400 and 406 nm.[312] Table 28 lists the details of the electronic spectra and colours of radical anions and dianions.

From ESR work, many fine details of ion pair structure and dynamic processes, undetected by other means, have been indicated, *e.g.* the ESR data for $\mathrm{PhH}^{\cdot-},\mathrm{M}^+$ (M = K, Rb or Cs) in solvents such as THF, DME or HMPT were interpreted as being due to M^+ oscillating parallel to the benzene plane with an average position on the six-fold axis of the benzene ring.[301a] The existence of different types of ion pairs can be shown by differing line widths or hyperfine coupling constant (a), *e.g.* a_{Na} values at 20 °C in THF for $\mathrm{Naph}^{\cdot-},\mathrm{Na}^+$ are 1.23 G (t.i.p.) and 0.38 G (glyme separated ion pairs).[313] As well as the broad distinction between t.i.p. and s.s.i.p., subtle subdivisions have been recognized by ESR, *e.g.* in combination with UV spectral data, four differently solvated ion-paired species of triphenylenide–M (M = Na, K, Rb or Cs)[314] have been recognized.

The t.i.p. $\rightleftharpoons$ s.s.i.p. equilibria for the radical anions are similarly affected by the factors[14,15] which influence ion pair equilibria for delocalized carbanions (benzyl and allyl, *etc.*), *e.g.* solvent, temperature, cation size, size of the ArH (*i.e.* extent of the delocalization), presence of glymes and crown ethers.

Table 28 Maxima in the Visible Absorption Spectra[b]

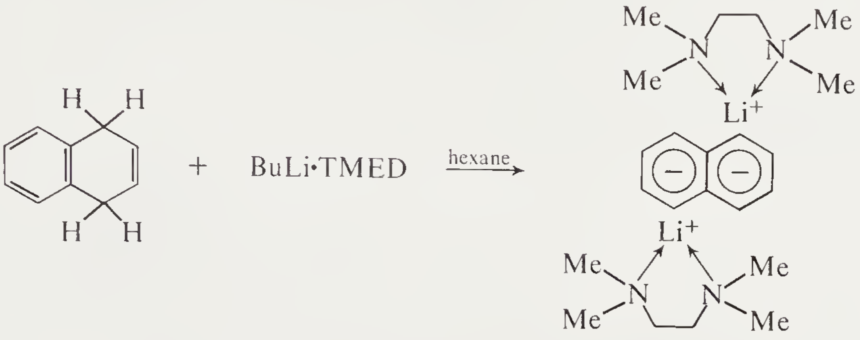
	ArH^-,M^+			$ArH^{2-},2M^+$			
	M = K[1] *in* THF	M = Na[2] *in* THF	*Reported colour*[a]	M = K[1] *in* THF	M = Na[2] *in* THF	M = Li[3] *in* Et_2O	*Reported colour*[a]
Biphenyl	402 (ϵ = 49 000),[4] 605	405, 617, 637	blue	—	—	—	—
Naphthalene	366, 433, 463, 820 (ϵ = 2460)[4]	366, 437, 465, 735	green	—	—	530	red-brown
Anthracene	403, 546, 595, 637, 654, 694, 725 (ϵ = 10 000)[4]	369, 401, 549, 599, 662, 714	blue	621	613	554	blue
Pyrene	364, 383, 450, 490 (ϵ = 49 500),[4] 735	366, 385, 455, 493, 719	orange-red	351, 455, 602	—	569	—
Perylene	574 (ϵ = 59 000),[4] 676, 730, 769	581, 676, 724, 758	blue	446, 559, 649, 690	463, 559, 649, 694	552	violet
Tetracene	353, 377, 398, 640, 710 (ϵ = 14 500)[4]	360, 383, 403, 645, 704	green	352, 398, 629, 709	353, 398, 498, 617	580	blue
Terphenylene	345, 410 (ϵ = 13 200),[4] 535, 676, 741	347, 413, 535, 671, 709	lavender	—	—	—	—

[a] The colour most frequently reported. [b] In nm.

1. E. de Boer and S. I. Weissmann, *Recl. Trav. Chim. Pays-Bas*, 1957, **76**, 824.
2. P. Balk, G. J. Hoyjtink and J. W. H. Schrews, *Recl. Trav. Chim. Pays-Bas*, 1957, **76**, 813; see also A. G. Evans and B. J. Tabner, *J. Chem. Soc.*, 1963, 5560.
3. G. Levin, B. E. Holloway and M. Szwarc, *J. Am. Chem. Soc.*, 1976, **98**, 5706.
4. Ref. 15.

2.9.4 Solid State Structures of Radical Anion and Dianion Species

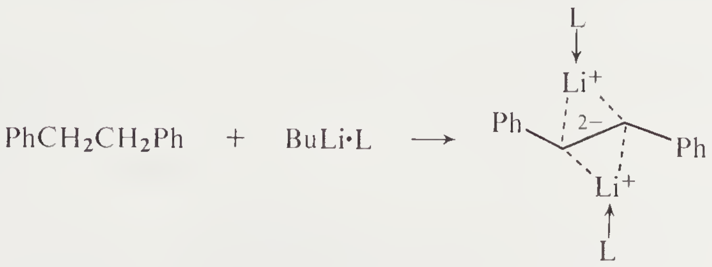
Crystal structures of $\mathrm{PhPh}^{\overline{\cdot}},\mathrm{Na}^+(\text{triglyme})_2$ and $\mathrm{PhPh}^{\overline{\cdot}},\mathrm{M}^+(\text{tetraglyme})$ ($\mathrm{M} = \mathrm{K}$ or Rb) have been determined. The cation in each case is surrounded by the oxygens of the glyme ligands, *i.e.* glyme separated ion pairs,[315] with a dihedral angle between the two phenyl groups (*ca.* 9.4 ° for the Rb salt). Stucky and coworkers have obtained[201,316] the crystal structure of the dianion compounds $\mathrm{Naph}^{2-}(\mathrm{Li{\cdot}TMED})_2$ and $\mathrm{Anth}^{2-}(\mathrm{Li{\cdot}TMED})_2$. These compounds can be considered as externally complexed t.i.p. species. In $\mathrm{Naph}^{2-}(\mathrm{Li{\cdot}TMED})_2$, prepared as shown in equation (84), each TMED chelated lithium is located over a six-membered ring and this can form multicentre bonds involving the Li $2p$ orbitals and a combination of carbon $2p$ orbitals which is derived from the HOMO of the isolated dianion. The aromatic unit is not planar: four atoms are 0.15 Å off the mean plane of the naphthalene framework. Detail discussion is given in the review by Stucky.



(84)

Of interest, an INDO calculation on $\mathrm{Naph}^{\overline{\cdot}}$ using a similar non-planar geometry gave an improved fit to the experimental ESR hyperfine coupling constants. The complex $\mathrm{Anth}^{2-}(2\mathrm{Li{\cdot}TMED})^+$ similarly contains a non-planar dianion fragment; the two $(\mathrm{Li{\cdot}TMED})_2$ units are located over the central six-membered ring and one of the outside six-membered rings.

Stucky *et al.*[201,317] have also determined structures of complexed alkali metal arylalkene dianion compounds, including $(\mathrm{TMED{\cdot}Li})_2$bisfluorenylidene, acenaphthalene$(\mathrm{TMED{\cdot}Li})_2$ (cited in Table 14) and the complexes *trans*-stilbene$(\mathrm{Li{\cdot}L})_2$ (L = TMED or PMTD). The structures of the stilbene complexes, prepared as shown in equation (85), are essentially t.i.p. species of amine solvated lithium cations above and below the central carbon–carbon bond of a planar stilbene dianion. A considerable interaction between the cations and the ethylenic carbon atoms was indicated. This planar configuration of the stilbene dianion contrasts with the conclusions from solution studies. As was indicated in Section 2.9.2, a twisted structure was proposed to account for the high K_{disp} values.



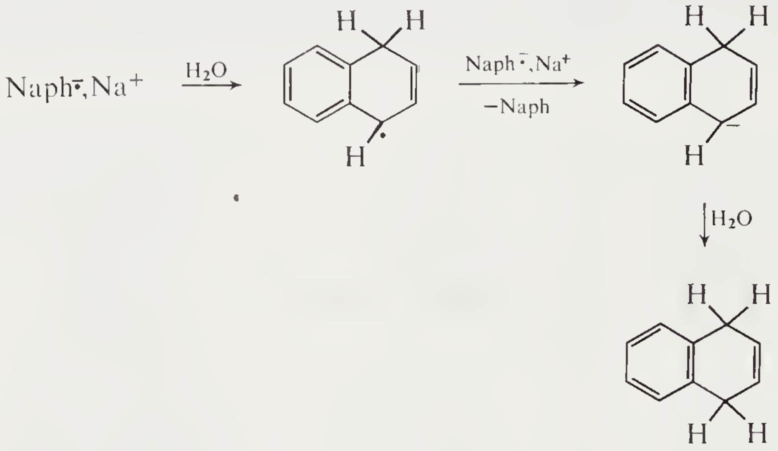
(85)

2.9.5 Reactions[304]

The different radical anion species (free ion, c.i.p., t.i.p., *etc.*) and the dianion for a given ArH and M have different reactivities. Indeed, different reactivity sequences are obtained for alkylation and electron transfer to Ar′H [*e.g.* $\mathrm{ArH}^{\overline{\cdot}} > \mathrm{ArH}^{\overline{\cdot}},\mathrm{M}^+$ (s.s.i.p.) $> \mathrm{ArH}^-,\mathrm{M}^+$ (t.i.p.) $> \mathrm{ArH}^{2-},2\mathrm{M}^+$] on the one hand and for protonation [*e.g.* $\mathrm{ArH}^{2-},2\mathrm{M}^+ > (\mathrm{ArH}^{\overline{\cdot}},\mathrm{M}^+)_2\mathrm{ArH}^{\overline{\cdot}}$ (t.i.p.) $> \mathrm{ArH}^{\overline{\cdot}},\mathrm{M}^+$ (s.s.i.p.)] on the other. The latter sequence is the order of increasing delocalization of the charge in the aromatic unit.

2.9.5.1 *Protonation*

The considerably increased reactivities of $ArH^{2-},2M^+$ towards protonation (approaching the diffusion limit), even at the low concentrations allowed by the disproportionation equilibria, can render it an important kinetic entity in solutions essentially containing $ArH^{\bar{\cdot}},M^+$. A consequence of this is that the order in $ArH^{\bar{\cdot}},M^+$ in protonation reactions with H_2O or alcohols can approach two,[318] *e.g.* with ArH^-,M^+ (M = Na or K) in THF and DME, whereas a first order dependence on $Naph^{\bar{\cdot}},Na^+$ in THF (see Scheme 22) was found.[319] The overall stoichiometries in the protonation reactions are given by equations (86) and (87).



Scheme 22 Protonation of $Naph^{\bar{\cdot}},Na^+$ by H_2O

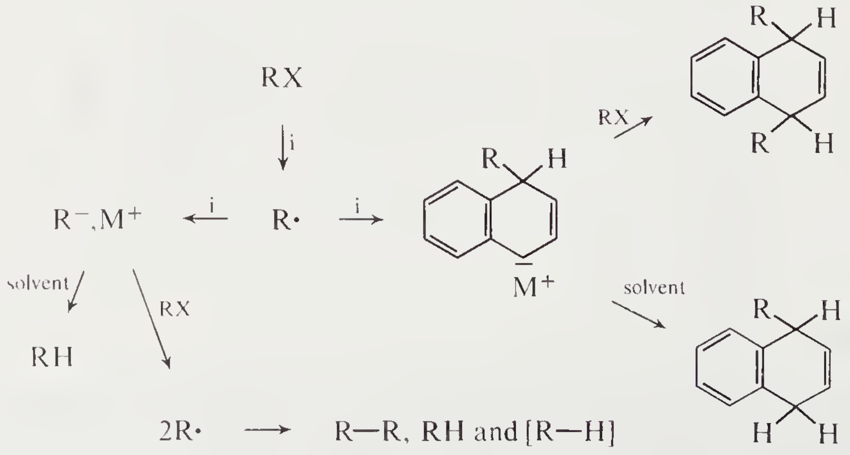
$$2ArH^{\bar{\cdot}},M^+ \; + \; 2ROH \longrightarrow [ArH{\cdot}H_2] \; + \; ArH \; + \; 2RO^-,M^+ \qquad (86)$$

$$ArH^{2-},2M^+ \; + \; 2ROH \longrightarrow [ArH{\cdot}H_2] \; + \; 2RO^-,M^+ \qquad (87)$$

$ArH{\cdot}H_2 \equiv$ 9,10-dihydroanthracene, 1,4-dihydronaphthalene, *etc.*

2.9.5.2 *Alkylation*[304b]

The mechanistic scheme is exemplified in Scheme 23 with $Naph^{\bar{\cdot}},M^+$. The kernal of the scheme is the initial step, involving electron transfer to RX and formation of the alkyl radical, $R\cdot$. Evidence for radicals as intermediates is extensive, *e.g.* ESR detection[320b] of $(3,5\text{-}Bu^t_2C_6H_3)_2CH\cdot$ in the reaction of $(3,5\text{-}Bu^t_2C_6H_3)_2CHBr$ with $Naph^{\bar{\cdot}},Na^+$, lack of configuration integrity in cyclopropyl halide reactions,[320b] and general observations of CIDNP.[320c] In contrast, despite vigorous efforts,



i, $Naph^{\bar{\cdot}},M^+$

Scheme 23 Reaction of RX with $Naph^{\bar{\cdot}},M^+$

no direct evidence for alkyl halide radical anion species, $RX^{\bar{\cdot}}$, in reactions with $ArH^{\bar{\cdot}},M^{+}$, potential precursors to the radical R·, has yet been obtained. However, some indications for a finite lifetime have come from reactions of hexenyl halide with $Ph_2C{=}CPh_2^{2-},2Na^{+}$.

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3

Beryllium

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3.1 INTRODUCTION

Beryllium having the electronic configuration $1s^22s^2$ almost exclusively forms covalent compounds due to its high ionisation potentials and the small size and therefore high polarising power of the dipositive cation. Compounds of beryllium have covalencies of two, three or four for the metal atom. There are no known compounds with a coordination number greater than four, since the atomic orbitals of principal quantum number three are of too high an energy to participate in bond formation. The coordination number of two arises from the use of *sp* hybrid orbitals by beryllium to give a linear molecule as found for Bu^t_2Be[1] while the rather unusual coordination number of three is found, for example, in Me_2BeNMe_3,[2] in which the metal must make use of sp^2 hybrid orbitals. Beryllium however, has a strong tendency to form tetravalent compounds using sp^3 hybrid orbitals to give tetrahedral bonding. The chemistry of organoberyllium compounds is intermediate between that of magnesium and the subgroup; zinc, cadmium and mercury. The covalent radius of magnesium (140 pm) is somewhat larger than that of beryllium (93 pm) and therefore allows a greater volume of ligand to be bonded to the metal, so that magnesium compounds tend to be more associated than beryllium compounds and have higher coordination numbers. As beryllium is less electropositive than magnesium, the Be—C bond is less polar than the Mg—C bond and so beryllium alkyls are less reactive than their magnesium counterparts. Nevertheless, the Be—C bond is still very polar and this is largely responsible for its reactivity, for example in its reactions with protic acids, except when steric obstruction of the attacking reagent prevents reaction, as is the case with $(PhBeOCPh_3)_2$ which dissolves in neither sulphuric ($1\ mol\ dm^{-3}$) nor nitric ($6\ mol\ dm^{-3}$) acids at room temperature.[3]

The high toxicity of beryllium compounds,[4–6] together with the air sensitive nature of organometallic derivatives, have limited study in this promising area of chemistry. Much of the experimental development of an understanding of this area is due to work by Coates and co-workers between 1964 and 1974 at Durham and Wyoming. Since 1974, publications on experimental work have diminished considerably and there has been a much greater emphasis on molecular orbital studies, so that there are now many theoretical studies of both real and fanciful organoberyllium systems.[7–33] Review articles particularly recommended are those by Coates and Morgan[34] and by Fetter.[35] Two books[36,37] contain sections devoted to organoberyllium chemistry, and two Russian[38,39] and one French reviews[40] have also appeared as well as a review devoted to organoberyllium–nitrogen and –oxygen systems[41] and another to the alkyl derivatives of the Group II metals.[42] A survey of structural aspects of electron-deficient organometallic compounds of Li, Be, Mg and Al has been published recently.[43]

As the cyclopentadienyl compounds of beryllium are somewhat different from other organoberyllium compounds, these are discussed in this chapter as a separate section.

3.2 SYNTHESIS OF R_2Be AND RBeR′

A number of routes are available for the preparation of organoberyllium reagents of the type R_2Be. The major preparative routes are those involving the use of Grignard or organolithium reagents, usually in ether, or the sometimes unpleasant organomercurials. Due to the coordinative unsaturation of beryllium in R_2Be, these compounds are Lewis acids and retain ether. Separation from ether, if necessary, may be difficult, particularly for the aryl series which are stronger acceptors than beryllium dialkyls, such that Ph_2Be forms a 1 : 2 complex[44] whereas Me_2Be forms no isolable complex with Me_2S.[2] For example, Et_2Be still retains *ca.* 2% ether after a long time under reduced pressure at 85 °C.[45] However, prolonged boiling of the ether complexes at low pressure before distillation yields ether-free R_2Be ($R = Et, Pr^n, Pr^i, Bu^n, Bu^i$).[46,47] Separation of Me_2Be from ether is more difficult and requires repeated sublimation under reduced pressure, no doubt due to ether being occluded in the crystalline material.[46,48] This approach cannot be used for Bu^s_2Be[49] and Bu^t_2Be,[50] both of which readily lose alkene on warming, but a novel method has been used for obtaining ether-free Bu^t_2Be from its etherate. Addition of $BeCl_2$, which is a stronger Lewis acid than Bu^t_2Be, results in the ether being preferentially complexed by the halide so that the volatile Bu^t_2Be can be distilled out,[51] but some of the Bu^t groups are lost as $(Bu^tBeCl{\cdot}OEt_2)_2$.[46] This method has not been applied to other systems.

The organomercury method is more applicable to small scale preparations and does not require the separation of R_2Be from base. More recently, boron–beryllium exchange reactions have been useful since these also produce base-free products readily and have advantages over the organomercury method which is experimentally difficult in the case of aryls and fails when the organomercurial is thermally unstable. Surprisingly, no heteroaryl compounds of beryllium have been prepared.

3.2.1 Grignard Method

The addition of a Grignard reagent to a beryllium halide (usually the chloride, as $MgCl_2$ is less soluble than the bromide and iodide) in ether results in the precipitation of magnesium halide, which is removed by filtration (equation 1). The resulting solution is evaporated and R_2Be (R = Me,[52–56] Et,[45,52–54,57] Pr^n,[46] Pr^i,[47,52,58] Bu^n,[53,54] Bu^i,[46] Bu^t,[50,52,58] n-C_5H_{11},[49] Me_3CCH_2,[59] Ph,[44,57] Bz,[60] $MeO(CH_2)_4$,[61] $EtS(CH_2)_3$[61]), normally complexed with ether, is separated from dissolved magnesium halide by distillation or crystallisation; Me_2Be is separated by codistillation with ether and the ether recycled.[53,62,63] When R = Ph, magnesium halide is precipitated from solution by addition of 2 mol dioxane per atom of magnesium. A deficiency of PhMgX is needed otherwise the product contains Ph_2Mg and care is needed with the dioxane as both an excess and a deficiency result in halide contamination.[44,57]

$$2RMgX \quad + \quad BeX_2 \quad \longrightarrow \quad R_2Be \quad + \quad 2MgX_2 \tag{1}$$

Although Grignard reagents in hydrocarbon solvents have been employed to prepare base-free R_2Be (R = Et, Bu^n, n-C_5H_{11}, Ph, p-Tol),[64] this method may be more useful for aryl rather than alkyl derivatives as the former bind ether more strongly.

3.2.2 Organolithium Method

Organolithium reagents in ether or hydrocarbon solvents deposit lithium halide and this separates out more readily than the precipitate from the Grignard reaction (equation 2). Isolation of R_2Be (R = Bu^n,[65] Bu^i,[65] Bu^s,[49] (R)-2-methylbutyl,[66] Ph,[57,62,67] C_6F_5,[60] $MeC{\equiv}C$, $Bu^tC{\equiv}C$,[68] $PhC{\equiv}C$[69]) is achieved as from the Grignard reaction or in the form of complexes.

$$2RLi \quad + \quad BeX_2 \quad \longrightarrow \quad R_2Be \quad + \quad 2LiX \tag{2}$$

3.2.3 Organomercury Method

Heating beryllium (preferably powder), activated with a trace of I_2, $HgCl_2$ or Et_2Be, with R_2Hg in the presence or absence of solvent results in the transfer of the organic group to the more electropositive metal (equation 3). Sublimation, distillation or dissolution processes are used to separate R_2Be (R = Me,[54,56,57,70–72] Et,[57,67,73] Pr^n,[74] Ph,[44,53,54,60,62,67,75–77] p-Tol[53,54]) from mercury and excess beryllium. Traces of mercury in the product (particularly with Me_2Be) can be removed with gold foil. This method has been used in the microsynthesis of $Me_2{}^7Be$.[78] As the method requires relatively high temperatures, it is not applicable to branched chain alkyl derivatives (*e.g.* Pr^i_2Be[56]) which are thermally unstable. Exchange of organic groups between Ph_2Hg and Et_2Be produces Ph_2Be[60] but this method has not been studied as a route to other organoberyllium compounds.

$$R_2Hg \quad + \quad Be \quad \longrightarrow \quad R_2Be \quad + \quad Hg \tag{3}$$

3.2.4 Organoborane Method

Exchange reactions between R_3B and Et_2Be produce R_2Be (R = Pr^n, Bu^i, Me_3CCH_2, Me_3SiCH_2,[79] $CH_2{=}CHCH_2$,[80] Ph, *o*-Tol, *m*-Tol, *p*-ClC_6H_4, *p*-$Me_2C_6H_3$, 1-naphthyl[60]) after several days at room temperature. Dimethylberyllium does not react with organoboranes, presumably due to its polymeric nature[79] nor does Et_2Be react with R_3B (R = Pr^i, C_5H_9, Bz, $Me_3C_6H_2$, C_6F_5[60]). Diethylberyllium yields the hydride Et_3Be_2H with Bu^s_3B[79] and reacts rapidly with $(allyl)_3B$, the product being characterised as the bis(THF) complex, since in the absence of strong donors oligomeric products are formed by secondary reactions.[80]

3.2.5 Redistribution Reactions

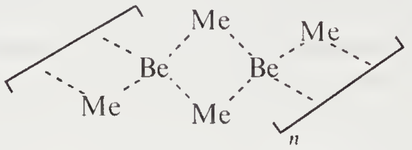
A series of mixed organoberyllium compounds of type RBeR′ (R = Bu^t, R′ = Me, Et, *o*-Tol, *p*-$Me_2C_6H_3$, Cp; R = C_6F_5, R′ = Cp) has been obtained by redistribution reactions between R_2Be and R'_2Be. In certain cases (R = Bu^t, R′ = Ph, 1-naphthyl; R = Cp, R′ = Me_3CCH_2,Me_3SiCH_2), the desired products were not obtained.[69]

3.2.6 Miscellaneous Methods

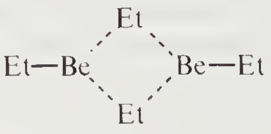
Beryllium chloride has been stated to react with chloroform to yield CCl_3BeCl at 20 °C and $(CCl_3)_2Be$ at higher temperatures but neither compound was isolated[81] and no further studies appear to have been made of this reaction. Claims have been made for the preparation of R_2Be from $BeCl_2$ and R_3Al at 100 °C, R_2Be being isolated after complexing the aluminium with, for example, quinoline.[82] Additionally $NaAlMe_4$ and $BeCl_2{\cdot}(Et_2O)_2$ produce Me_2Be[83] and methyl and ethyl radicals react with the metal to form Me_2Be and Et_2Be respectively.[84] Diethylberyllium adds across the double bond of $Pr(Me)C{=}CH_2$ on prolonged heating to form Pr(Me)(Et)-CH_2BeEt and addition of alkenes to BeH_2 is claimed to yield R_2Be.[85] Thermal decomposition of the complex salt $KF(BeEt_2)_2$ yields Et_2Be and this has been suggested as a useful route for obtaining the ether-free material.[86-88]

3.3 PROPERTIES OF R_2Be AND RBeR′

Many of the chemical properties of organoberyllium reagents, *e.g.* reactions with Lewis bases, protic acids, *etc.*, are considered under other sections. Beryllium alkyls, for which some enthalpies of formation have been derived,[89] have been much more extensively studied than the aryls. All are either solids or liquids and are very sensitive to air. Dimethylberyllium and Ar_2Be are solids whereas the higher alkyls are liquids. The extent of association of such compounds is determined mainly by the steric requirement of the organic group attached to beryllium, for example Me_2Be (**1**) is polymeric,[48,90] Et_2Be (**2**) dimeric[46,91] and Bu^t_2Be (**3**) monomeric.[92,93] The degrees of association of these compounds are listed in Table 1. Electron impact studies on a variety of compounds R_2Be (R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, Ph) have been studied in depth and fragmentation patterns, ionisation potentials and bond dissociation energies detailed.[94-97] The ion abundance of associated species is profoundly affected by source temperature, the most pronounced effect being with Et_2Be. The Be—C bond energy for beryllium alkyls in the parent monomer ion, *i.e.* $D(RBe^+{-}R)$, is in the range 180–192 kJ mol^{-1} and since ionisation probably removes a Be—C bonding electron, these bond energies are likely to be less than for a neutral molecule.[94,95]



(**1**)



(**2**)

$Me_3C{-}Be{-}CMe_3$

(**3**)

Table 1 Degree of Association (n) of R_2Be and $RBeR'$

Compound	n	*Compound*	n
Me_2Be	$\infty^{a,1,2}$	$(p\text{-}MeC_6H_3)_2Be$	$2^{b,12}$
Et_2Be	$2^{b,3,4}$	Bu^tBeMe	$3^{b,13}$
Pr^n_2Be	$2^{b,3}$	Bu^tBeEt	$2^{b,13}$
Pr^i_2Be	$2^{b,5}$	$Bu^tBe(o\text{-}Tol)$	$2^{b,13}$
Bu^n_2Be	$2^{b,3,6}$	$Bu^tBe(p\text{-}Me_2C_6H_3)$	$2^{b,13}$
Bu^i_2Be	$2^{b,3}$	Bu^tBeCp	$1^{b,13}$
Bu^t_2Be	$1^{b,c,7-9}$	C_6F_5BeCp	$1^{b,13}$
$(Me_3CCH_2)_2Be$	$1\text{-}2^{b,10}$	$MeBeCp$	$1^{b,14}$
$(Me_3SiCH_2)_2Be$	$2^{b,10}$	$HC{\equiv}CBeCp$	$1^{c,15}$
$[(R)\text{-}EtCH(Me)CH_2]_2Be$	$2^{b,11}$	Cp_2Be	$1^{a,b,c,14,16,17}$
$(o\text{-}Tol)_2Be$	$2^{b,12}$	$[MeO(CH_2)_4]_2Be$	$1^{b,18}$
$(m\text{-}Tol)_2Be$	$2^{b,12}$	$[EtS(CH_2)_3]_2Be$	$1^{b,18}$

[a] Solid phase. [b] Benzene solution. [c] Vapour phase.

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3.3.1 Beryllium Dialkyls

3.3.1.1 Dimethylberyllium

Me_2Be forms colourless needles when condensed from the vapour phase but has not been observed to melt.[54] It undergoes thermal decomposition beginning at 202 °C, forming $[Be(CH_2)]_n$ as intermediate and Be_2C as end product.[55] Solid dimethylberyllium has a polymeric structure (**1**), having an approximately tetrahedral distribution of methyl groups round each beryllium atom, with all the Be—C bonds equivalent and of length 192(3) pm. The larger than tetrahedral CBeC bond angle (114°) may be explained by some degree of Be—Be bonding, the internuclear distance being only 209(1) pm and also by the need for a sharp BeCBe angle.[48,90] The enthalpy of sublimation (46.3 kJ mol^{-1}), the extrapolated sublimation temperature (217–220 °C)[55,71] and the interchain distance in the polymer (410 pm,[48,90] the normal Van der Waals distance) exclude an ionic formulation. Both beryllium and carbon make use of four tetrahedral sp^3 atomic orbitals and it is probable that three-centre molecular orbitals are formed from these, so that each Be· · ·C bond can be considered as a one electron or half bond.[98] Owing to its polymeric nature, Me_2Be is only soluble in solvents which are sufficiently strong donors to break down the polymeric structure, for example, it is insoluble in benzene but monomeric in ether.[67,99]

Vapour density measurements between 160 and 200 °C show that the vapour consists of monomer, dimer and trimer molecules with structures doubtless similar to (**1**)–(**3**), together with high polymers which only become important at near saturation conditions. Heat and entropy terms have been obtained for the monomer–dimer and monomer–trimer equilibria and the energy difference between two half bonds and one whole bond is 38–50 kJ mol^{-1}, depending on the degree of polymerisation.[71]

Mass spectral studies of the vapour show the presence of ions containing one, two, five, six, seven or eight beryllium atoms under saturation conditions but the monomer is the major constituent in both this and the unsaturated vapour.[94,95,97] IR spectroscopic data for the unsaturated vapour at 125–180 °C have been interpreted in terms of a monomeric species of symmetry $D_{3h'}$ and band

Table 2 Beryllium–Carbon Distances in σ-Bonded Organoberyllium Compounds

Compound	Be—C (pm)	Coordination no. of carbon	Coordination no. of beryllium
Me_2Be[a,1]	169.8(5)	4	2
$(Me_2Be)_n$[b,2]	193(2)	5	4
Bu^t_2Be[a,3]	169.9(3)	4	2
$Me_2Be(quinuclidine)_2$[b,4]	183(3)	4	4
$(MeBe(C{\equiv}CMe)\text{-}NMe_3)_2$[b,5]	189.0(6)	5	4
	185.2(6)	5	4
	174.8(7)	4	4
$MeBeOSiMe_3$[b,6]	171(2)	4	4
Li_2BeMe_4[b,7]	184(10)	4	4
$Na(OEt_2)Et_2BeH$[b,8]	176.6(8)	4	4
	181.0(8)	4	4

[a] Electron diffraction. [b] X-ray diffraction.

1. A. Almenningen, A. Haaland and G. L. Morgan, *Acta Chem. Scand.*, 1969, **23**, 2921.
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assignments were confirmed by analysis of the spectrum of the deuterio analogue. Additional bands in the saturated vapour have been attributed to polymeric species.[97] The C—Be—C stretching frequency is much higher (1081 cm^{-1}) than that for Bu^t_2Be (450 cm^{-1}).[93] Although it was suggested[97] that the Be—C bond in Me_2Be might be significantly strengthened and therefore shorter due to hyperconjugation, electron diffraction studies of gaseous, linear Me_2Be[100] and Bu^t_2Be[1] show similar Be—C distances (Table 2) both somewhat shorter than the electron-deficient Be· · ·C distance in solid polymeric Me_2Be.[48,90] The vibrational spectrum of solid Me_2Be has been rationalised in terms of a polymeric structure with D_{2h} symmetry, having six IR and six Raman active absorptions.[55]

3.3.1.2 Diethylberyllium

Diethylberyllium is a colourless liquid boiling at 93–95 °C/4 mmHg and melting at −13 to −11 °C.[53,54] It is less thermally stable than Me_2Be, decomposing slowly at 85 °C and rapidly at 190–200 °C resulting in the formation of C_2H_6, C_2H_4 and C_4H_8 in the ratio 2 : 1 : 1.5 together with small amounts of other hydrocarbons. The residue is a distillable oil of approximate formula $[(HBeCH_2)_2]_n$ and a crystalline solid approximating to $[Be_2(CH_2)_3]_n$ or $[HBe(CH_2)_3]_n$ but these compounds have not been clearly characterised.[45,56] The Raman spectrum of Et_2Be (containing *ca.* 2% ether) indicates association *via* four- or six-membered rings.[45] It is dimeric in benzene solution but monomeric in dioxane[46,91] in which it doubtless exists as a coordination complex as it has a dipole moment of 1.0 D in heptane, 1.69 D in benzene but 4.3 D in dioxane.[101] The conductance of Et_2Be in organic solvents is low[102] but electrolysis of Et_2Be in pyridine in a 1 : 1 ratio over a long time at 60 °C with Cu electrodes yields a dark blue liquid from the cathode compartment corresponding to $EtBeNC_5H_5$.[103]

Electron impact studies of Et_2Be are profoundly affected by source temperature. Trimeric fragments $Et_5Be_3^+$ and $Et_4Be_3^+$ decrease rapidly in abundance as the source temperature is raised from 45 °C to 80 °C, providing unambiguous evidence that trimeric species are present in the vapour phase. Similarly eight diberyllium ions including the parent ion $Et_4Be_2^{+\cdot}$ are present in considerable abundance at 70 °C but barely detectable at 200 °C, a behaviour consistent with increased thermal dissociation of associated molecules at higher temperatures before ionisation. The greater abundance of hydrocarbon ions at higher temperatures is due to thermal decomposition.[94,95]

3.3.1.3 *Dipropylberyllium*

Both Pr^n_2Be[46] and Pr^i_2Be[47] are dimeric in benzene solution and electron impact studies indicate dimeric but not trimeric species in the vapour phase, and the increase in abundance of hydrocarbon ions as the source temperature is raised is consistent with thermal decomposition preceding ionisation.[94,95] Decomposition of Pr^i_2Be commences at 40–50 °C and is rapid at 200 °C producing $(Pr^iBeH)_n$ and propene (equation 4),[47] though in view of the behaviour of Bu^t_2Be it would be surprising if some isomerization of the Pr^i groups bound to beryllium had not occurred.

$$Pr^i{}_2Be \xrightarrow{200\ °C} Pr^iBeH + C_3H_6 \tag{4}$$

3.3.1.4 *Dibutylberyllium*

The three isolated isomeric dibutylberyllium compounds (Bu^n_2Be, Bu^i_2Be, Bu^t_2Be) are liquids which, except for the very sterically crowded and therefore monomeric Bu^t_2Be, are dimeric in benzene solution.[46,64,93] The multiplet for the α-methylene protons in the ^1H NMR spectrum of Bu^n_2Be is either due to the non-equivalence of the α-methylene groups in the bridged and terminal positions of a dimeric structure or to the non-equivalence of the α-methylene protons,[64] as seen in certain hindered alkylmagnesium compounds.[104,105] Pyrolysis of Bu^i_2Be complexed with ether beyond the Bu^iBeH stage yields a product which with TMEDA produces $(BeH_2)_2{\cdot}TMEDA$ showing terminal Be—H vibrations as a strong sharp doublet at 1787 and 1807 cm^{-1} [106] and probably having a similar structure to that suggested for $(RBeH)_2{\cdot}TMEDA$ (Section 3.8.2). Pyrolysis of both Bu^n_2Be and Bu^i_2Be is claimed to yield BeH_2.[65] In marked contrast to the lower members of the series, electron impact studies of Bu^i_2Be and also Bu^t_2Be produce only monomeric ions and again as the source temperature is raised, the abundance of hydrocarbon ions increases and that of the monomer decreases due to thermal decomposition.[94,95]

Bu^t_2Be is monomeric both in the vapour phase and in benzene solution.[92,93] The vibrational spectra of liquid and gaseous species are consistent with a monomer belonging to the D_{3d} symmetry point group. On crystallisation there is a loss of symmetry and a D_3 point group is assigned, though a lower symmetry group could not be excluded. IR frequencies at 458 and 545 cm^{-1}, attributable to vibrations of the Be—C bonds are extraordinarily low, suggesting that the Be—C bonds have an unusually small stretching force constant.[93,107] Electron diffraction data of gaseous Bu^t_2Be have been interpreted in terms of a linear structure (**3**) with a short Be—C bond (169.9(3) pm). The butyl groups undergo non-hindered rotation, the barrier to internal rotation being in the range 0–25 kJ mol^{-1}.[1]

Ether-free Bu^t_2Be has a vapour pressure of 35 mmHg at 25 °C[51] and slowly isomerises to Bu^i_2Be at room temperature: after 24 days the ratio $Bu^i : Bu^t$ is 4.2 : 1, after 13 weeks, 12 : 1 and after 40 weeks, $\infty : 1$.[106] Though BeH_2 cannot be obtained by direct combination of the elements[108] and reaction between LAH and R_2Be in ether produces BeH_2 contaminated with lithium, aluminium and ether,[51,56,109] pyrolysis of Bu^t_2Be or its etherate produces a purer, less reactive form of BeH_2 with no evidence for the intermediate formation of a half-hydride, RBeH.[50] Because of its potential use as a rocket propellant, many attempts have been made to obtain a denser and purer form of BeH_2.[51,110–121] Owing to the low molecular mass of BeH_2, almost any contaminant has an unusually large effect on purity and the best method is by the controlled pyrolysis of $Bu^t_2Be{\cdot}OEt_2$ in hot oil at 200 ± 5 °C, producing a remarkably thermally stable product which is 90–98% pure and resistant to attack by water and common organic solvents. The residual impurities have been shown by deuterium labelling to be derived largely from incomplete pyrolysis and ether cleavage. The butyl groups present after pyrolysis are Bu^i rather than Bu^t groups.[111]

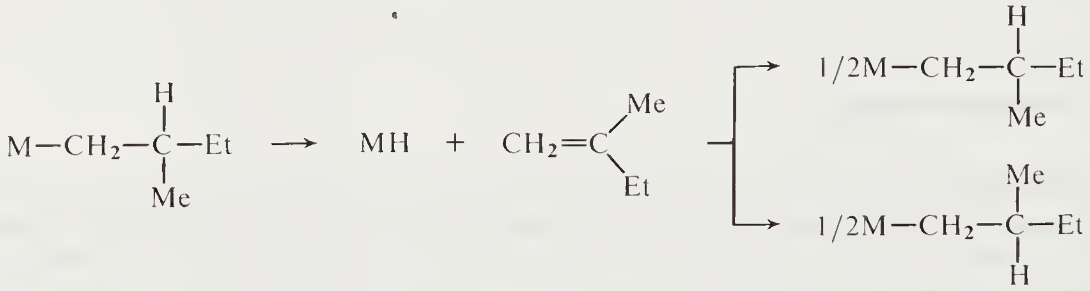
Vapour plating of beryllium on metallic and non-metallic surfaces is based on the decomposition of Bu^t_2Be by substrates heated at 280–305 °C under vacuum, producing dense, continuous and adherent coatings.[122]

3.3.1.5 Dineopentylberyllium

$(Neopentyl)_2Be$ is the only beryllium alkyl existing in a monomer–dimer equilibrium in solution. It is prepared from the organoborane by an exchange reaction[79] as separation from ether does not occur even after refluxing for 29 h under reduced pressure.[59]

3.3.1.6 (+)-Bis[(R)-2-methylbutyl]beryllium

This compound is dimeric in benzene solution and readily undergoes thermal decomposition to the organoberyllium hydride. Like the corresponding B and Al but not Zn, Cd and Li analogues, it racemises at an appreciable rate below 105 °C because the metal is readily able to form hydride and alkene reversibly according to Scheme 1. The specific rate constants decrease in the order Be > Al > B and the racemisation is not catalysed by nickel salts.[66,123]



Scheme 1

3.3.2 Beryllium Diaryls

No structural information is available for beryllium diaryls. Diphenylberyllium, melting at 244–8 °C,[76] whose sparing solubility in non-coordinating solvents,[60] lack of volatility[96] and low conductance in a variety of solvents[102] may be due to a covalent polymeric constitution or to good crystal packing, has a dipole moment of zero in heptane, 1.64 D in benzene and 4.33 D in dioxane.[101] It may form a weak interaction with solvent in benzene solution and a much stronger complex with dioxane as it most certainly does with ether in which it is monomeric.[67] Di-*p*-chlorophenylberyllium and the 1-naphthyl compound are also sparingly soluble in benzene but with bulkier groups attached to beryllium, such as *o*-Tol, *m*-Tol and *p*-xylyl, dimeric species are formed.[60] Electron impact studies on Ph_2Be at 200–240 °C produce parent trimer molecules $Ph_6Be_3^{+\cdot}$. No beryllium-containing ions appear below 200 °C nor above 250 °C. The main product from thermal decomposition at 240–250 °C in a vacuum is benzene. Acid hydrolysis of Ph_2Be leads to $\Delta H_f^\circ(Ph_2Be(s)) = 153.1 \pm 2.5$ kJ mol^{-1}.[96] The stronger acceptor character of beryllium diaryls as compared to the dialkyls is well illustrated by dibenzylberyllium which retains 1 mol ether even after several distillations[60] under reduced pressure, in marked contrast to the behaviour of the dialkyls under similar conditions.

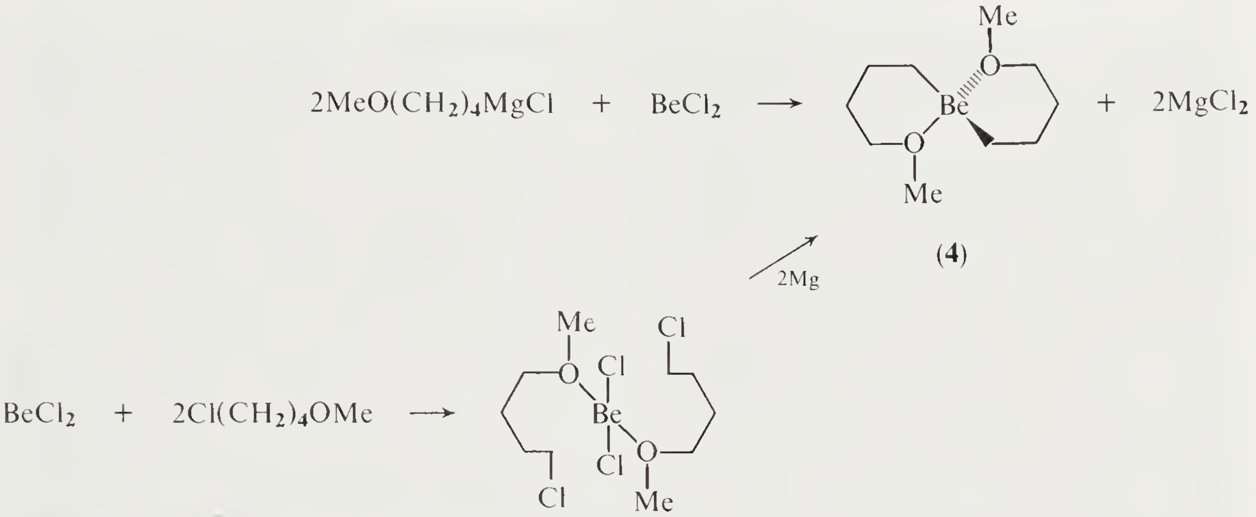
3.3.3 Beryllium Alkynyls

The compounds $(RC\equiv C)_2Be$ (R = Me, Bu^t) are prepared by the organolithium method and separated as ether complexes but once the ether is removed, benzene insoluble products are formed, and these are likely to be electron deficient polymers with bridging alkynyl groups[68] analogous to $(Me_2Be)_n$ (**1**). Alkynyl bridges are so strong that they are not depolymerised by Me_2S, whereas $(Me_2Be)_n$ dissolves in Me_2S giving solutions in which equilibria exist between mono-, di- and poly-nuclear complexes containing methyl bridges.[2,124] Additionally, the stronger bridging nature of alkynyl groups as compared to methyl groups is exemplified by the structure of the dimer $(MeBe(C\equiv CMe)\cdot NMe_3)_2$ in which alkynyl rather than alkyl groups bridge the metal atoms.[125] $(PhC\equiv C)_2Be$ has only been obtained complexed with ether or other donors.[69]

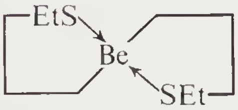
3.3.4 Miscellaneous Compounds

A series of mixed *t*-butylberyllium compounds ($(Bu^tBeR)_n$), in which R rather than Bu^t groups act as bridges between metal atoms, has been prepared by redistribution of Bu^t_2Be and R_2Be. Steric effects determine the extent of association (Table 1) of such compounds so that the methyl derivative is trimeric to minimise valency angle strain about beryllium, and as the size of R increases so *n* decreases. For $(Bu^tBeMe)_3$, both methyl and butyl groups were equally reactive to Bu^tOH.[126] Pyrolysis of these compounds to form organoberyllium hydrides and their complexes is discussed in Section 3.8.1.

Two spiran type organoberyllium compounds, $(MeO(CH_2)_4)_2Be$ (**4**) and $(EtS(CH_2)_3)_2Be$ (**5**), both monomeric in benzene solution, have been obtained from the corresponding Grignard reagents and beryllium chloride but nothing else is known about them. The former may also be prepared by reaction of the 2:1 complex of $Cl(CH_2)_4OMe$ and $BeCl_2$ with magnesium (Scheme 2).[61]



Scheme 2



(**5**)

3.4 COORDINATION COMPLEXES OF R_2Be AND RBeR′

A range of coordination complexes has been prepared particularly with oxygen and nitrogenous bases. Coates has examined the degree of association of such complexes and shown that steric effects are of paramount importance, so that only three-coordinate complexes are formed with bulky ligands, instead of the coordinative unsaturation of beryllium being satisfied by the formation of four-coordinate pseudotetrahedral complexes. Of course, the inductive effect of the organic group bonded to beryllium and the donor strength of the ligand are also important. Studies of Me_2Be with a variety of ligands have shown that the order of stability of complexes is $N > O > P \approx S > As$. In fact, arsenic as a donor atom has only been studied with Me_2Be and complex formation was not obtained, but this example is in any case special; owing to the polymeric nature of Me_2Be, ligands will only complex if the enthalpy of coordination exceeds the enthalpy required to depolymerise Me_2Be.[2] The Be—C bond is somewhat polar and prone to undergo protolysis so that complexes have largely only been isolated for ligands devoid of acidic hydrogen. Though ligands such as R_2NH, RNH_2, ROH, *etc.* doubtless form complexes at low temperature, elimination of hydrocarbon takes place at or below room temperature or on gentle warming (Section 3.5). The chemical shift in the ^1H NMR of organoberyllium compounds are at high field of tetramethylsilane, as for organic groups bonded to other electropositive elements.[124,127–129] The proton chemical shifts of methyl groups bonded to beryllium depend only on local diamagnetic shielding, so that the replacement of a group bonded to beryllium by a relatively electronegative group shifts the resonance of Me—Be group to lower frequency; bases of increasing strength shift the resonance to successively higher field and 2 : 1 adducts exhibit Me—Be resonances at higher field than corresponding 1 : 1 adducts. ^{9}Be chemical shifts are found to be sensitive to the environment and dependent only on local diamagnetic factors, *cf.* ^{11}B and ^{19}F, the chemical shift being determined by changes in inductive effect of the groups bonded to Be. The ^{9}Be chemical shifts of four-coordinate beryllium are to higher field than those of three-coordinate beryllium atoms.[128] Detailed vibrational spectroscopic assignments of 1 : 1 complexes of Bu^t_2Be with N, P, O and S donors have been made[130–133] and spectral assignments made for some methylberyllium compounds such as $Me_2Be{\cdot}NMe_3$, $Me_2Be{\cdot}$TMEDA and $(MeBeNMe_2)_3$.[129]

3.4.1 Monodentate Ligands

3.4.1.1 Oxygen and sulphur donors

Though definite complexes cannot be isolated, dimethylberyllium is monomeric in boiling ether, 1 : 1 adducts being present in solution between 40 and 13 °C and 2 : 1 adducts at lower temperatures.[128] Though Ph_2Be,[134] Pr^n_2Be[46] and Bu^t_2Be[92] form bis(diethyl etherate) complexes, these are unstable due to steric crowding around the metal, but the 1 : 1 complexes $R_2Be{\cdot}OEt_2$ (R = Bu^t,[51,92,133] Me_3CCH_2*,[59] PhC≡C,[69] Bz*[60]) are quite stable. The Bu^t complex is monomeric in the vapour phase,[92] while the neopentyl complex like the benzyl compound, does not lose ether on heating[59] as do other dialkylberyllium etherates.[46,47] The alkynyl complex exists in a monomer–dimer equilibrium, the average degree of association in benzene solution being 1.6–1.7.[69]

Dimethylberyllium forms a range of complexes with dimethyl ether of the type $(Me_2Be)_x(OMe_2)_y$, the values of x and y depending on the temperature and pressure of ether. Since the affinity of Me_2Be molecules for each other must be similar to the affinity of Me_2Be molecules for oxygen, these complexes probably consist of oligomeric Me_2Be units with the ether molecules as chain ending groups.[2] For steric reasons, Bu^t_2Be forms only a 1 : 1 dimethyl ether complex[133] whereas Ph_2Be forms $Ph_2Be{\cdot}(OMe_2)_2$ having a negligible dissociation pressure of the ether at 0 °C in contrast to the more sterically crowded $Ph_2Be{\cdot}(OEt_2)_n$, which has a dissociation pressure of 16 mmHg in most of the range n = 1–2.[44]

The stronger base THF has a small steric requirement and forms more stable complexes than either dimethyl or diethyl ethers, so that compounds $R_2Be{\cdot}(THF)_2$ (R = $CH_2{=}CHCH_2$,[80] MeC≡C*,[68] PhC≡C*,[69] C_6F_5[126]) have been readily obtained, the allyl complex being the only allylberyllium compound known. Bu^t_2 Be again only forms a 1 : 1 complex[126] but $(MeC{\equiv}C)_2Be$ forms a 1 : 1 as well as a 2 : 1 complex, the former being dimeric and therefore formulated with both terminal and electron-deficient bridging alkynyl groups,[68] analogous to those found for the corresponding trimethylamine complex.[125]

Reactions of aldehydes and ketones with R_2Be are complicated by reduction and by addition of Be—C across the double bond (Section 3.10) so that only $Ph_2Be{\cdot}OCBu^t_2$ and $(Me_3SiCH_2)_2Be{\cdot}OCBu^t_2$ have been isolated.[3]

Sulphur is a much weaker donor to beryllium than is oxygen. Dimethylberyllium dissolves in dimethyl sulphide from which Me_2Be can only be obtained free from Me_2S after about six sublimations. Two equilibria are present in solution (equations 5 and 6): the polymeric species are presumably similar to those which exist in the Me_2O–Me_2Be system in which oligomeric dimethylberyllium units have S (or O) as chain terminating atoms (**6**).[124] In contrast MeBeCl exists only as $MeBeCl{\cdot}(SMe_2)_2$ in Me_2S solution.[124,128] The failure to isolate a complex of Me_2Be with Me_2S [2] contrasts with that of the stronger acceptor Ph_2Be for which a bis(dimethylsulphide) complex can be isolated, having a negligible dissociation pressure but being partially dissociated in benzene solution.[44] Vibrational spectroscopic studies have been made of 1 : 1 complexes of Me_2S and Et_2S with Bu^t_2Be.[132]

$$Me_2BeSMe_2 \;+\; SMe_2 \;\rightleftharpoons\; Me_2Be(SMe_2)_2 \quad > -65\ ^\circ C \qquad (5)$$

$$n[Me_2Be(SMe_2)_2] \;\rightleftharpoons\; (Me_2Be)_n(SMe_2)_2 \;+\; (2n-2)Me_2S \qquad (6)$$

$$< -65\ ^\circ C$$

$$n = 2, 3, 4 \ldots 9$$

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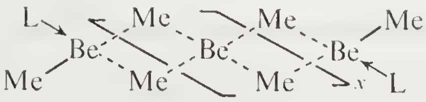
* Indicates monomeric in benzene solution.



(6)

3.4.1.2 Nitrogen and phosphorus donors

Trimethylamine forms complexes with a wide range of organoberyllium reagents. As the NMe_3 group is sterically similar to the Bu^t group, not surprisingly only stable 1:1 complexes $R_2Be{\cdot}NMe_3$ (R = Me,[2,68] Et,[135,136] Pr^i *,[47] Bu^t,[46,131] Me_3CCH_2*,[59] *o*-Tol*,[60] $Me_3C_6H_2$*,[60] $MeC{\equiv}C$,[68] $Bu^tC{\equiv}C$[68]) have been isolated except for the alkynyl derivatives, for which there is less steric congestion close to beryllium so that stable $R_2Be{\cdot}(NMe_3)_2$ have been obtained.[68] Though compounds R_2Be (R = Me,[128,137] Et,[136] Ph[44]) do form 2:1 complexes, the second amine molecule is only weakly held. The equilibrium for $Me_2Be{\cdot}NMe_3/R_2Be{\cdot}NMe_3$ (R = Me_3CCH_2, $MeC{\equiv}C$, $Bu^tC{\equiv}C$) favours the formation of the mixed complexes $MeBeR{\cdot}NMe_3$.[59,68] A structural examination of $Me_2Be{\cdot}NMe_3$ would be useful as its degree of association in benzene solution is greater than unity[68] and ^1H NMR of the melt shows evidence for dimerisation,[128] also indicated by the increased magnitude of the measured heat of vaporization as the temperature is lowered.[2] The greater bridging capabilities of alkynyl compared to alkyl bridges is indicated from the crystal structures of $(MeC{\equiv}C)_2Be{\cdot}NMe_3$[138] and $(MeC{\equiv}C)Be(Me){\cdot}NMe_3$,[125] both dimeric in the solid state and in solution, with the two beryllium atoms joined by two propynyl groups to form a planar four-membered ring (Figure 1). In the latter complex, the propynyl groups are almost in a plane defined by the beryllium and bridging carbon atoms with the amine and methyl groups disposed in another plane perpendicular to the first. The propynyl group is tilted towards one of the beryllium atoms of the ring, the Be—C(5)—C(6) angle being 136° as compared with 147° for the Be′—C(5)—C(6) angle and this may result from a bonding interaction between the π-bonding electrons of C≡C and the Be atom, an explanation further supported by the fact that the length of the Be—C bond nearest the C≡C (Be—C(5)) exceeds that of the further Be′—C(5) by 3.8 pm, or it could simply arise from packing considerations.[125]

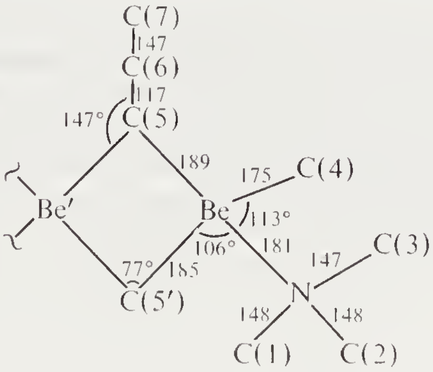


Figure 1 Structure of $[MeBe(C{\equiv}CMe)NMe_3]_2$. Only one half of the centrosymmetric molecule is shown (reproduced with permission)

The greater bulk of Et_3N prevents dimerisation and there are no instances known of more than one Et_3N molecule bonding to beryllium so that only complexes $R_2Be{\cdot}NEt_3$ (R = Bu^t,[131] $MeC{\equiv}C$*,[68] $PhC{\equiv}C$* [69]) are known.

Ligands containing acidic hydrogen atoms tend to react with the Be—C bond eliminating alkane under mild conditions. For example, Me_2Be and Et_2Be form 1:1 complexes, formulated as dimers, with NH_3 at −80 °C,[139] piperidine and morpholine form 1:1 complexes with Me_2Be[140] and Bu^t_2Be forms complexes with NH_3, $MeNH_2$ and Me_2NH at low temperature[141] but at higher temperature, hydrocarbon is evolved but the products have not been clearly characterised. The decrease in nucleophilic character of alkynyl beryllium relative to alkyl beryllium is so marked that the complexes $(PhC{\equiv}C)_2Be{\cdot}L_2$ (L = $MeNH_2$, Me_2NH, $PhNH_2$) are easily obtained even in a 1:1

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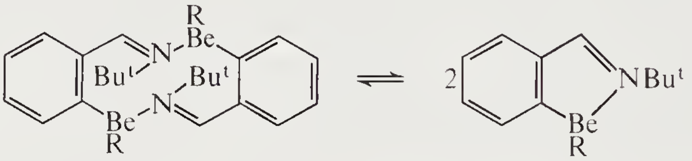
* Indicates monomeric in benzene solution.

ratio of reactants, and alkyne elimination from the methylamine complex requires temperatures of 60–80 °C.[69]

In general, the compounds R_2Be (R = Me,[142] Et*,[142] Pr^i *,[143] Bu^i *,[144] MeC≡C,[68] PhC≡C,[69] C_6F_5*, *o*-Tol*, *m*-Tol*, 1-naphthyl[60]), form 2:1 complexes with pyridine as it is less bulky than the tertiary amines and Me_2Be forms a 1:1 complex* with 2-methylpyridine[68] when mixed in that ratio. Quinuclidine forms 1:1 complexes with Ph_2Be, Bu^t_2Be[3] and $(o\text{-Tol})_2Be$,[126] the former being a dissociating dimer in benzene solution, presumably with phenyl bridges between the metal atoms, and the Bu^t complex for steric reasons is monomeric. The CBeC angle (118.3°) in $Me_2Be\cdot(quinuclidine)_2$, which has a pseudotetrahedral monomeric structure in the solid state, is larger than the NBeN angle (110.8°) and this is most readily explained in terms of the relatively short Be—C distance and the resulting demand placed on the Me–Me approach.[145]

Reactions of R_2Be with nitriles and Schiff's bases are complicated by addition of Be—C to the multiple bond or by reduction[3] (Section 3.10). However, in some cases complexes $R_2Be\cdot(R'N{=}CHR'')$ (R = Me, R′ = Me, R″ = Ph; R = Bu^t, R′ = Ph, R″ = Ph; R = Bu^t, R′ = Me, R″ = Pr^i; R = Ph, R′ = Me, R″ = Ph; R = Ph, R′ = *p*-Tol, R″ = Ph), all monomeric,[3] $Bu^t_2Be\cdot(NCPh)_2$[146] and $Bu^t_2Be\cdot NCBu^t$ [3] have been obtained and there is evidence for the existence of a weak complex in toluene solution between Me_2Be and Bu^tCN.[146] The benzonitrile complex is one of the few examples of four-coordinate beryllium in a Bu^t_2Be complex because the phenyl groups are distant from the Bu^t groups. When the pathway to reduction or alkylation of $ArCH{=}NR''$ by R_2Be is blocked, abstraction of hydrogen from the aromatic nucleus becomes the preferred route so that diethylberyllium reacts with the highly hindered *N*-benzylidene-*t*-butylamine evolving ethane to form the *ortho* metallation product (7) (R = Et) containing the cyclic $C_6Be_2N_2$ ten-membered ring. Bu^t_2Be reacts similarly but the degree of association suggests the monomer–dimer equilibrium shown in Scheme 3 (R = Bu^t).[3]



(7)

Scheme 3

Few phosphine complexes are known. Trimethylphosphine has a similar coordination affinity to the magnitude of the affinity of Me_2Be molecules for each other and therefore a number of complexes have been obtained with various Be:P ratios, doubtless similar to the dimethyl ether complexes mentioned earlier.[2] The more electron withdrawing aryl groups allow ready formation of $Ph_2Be\cdot(PMe_3)_2$ which is more stable than the Me_3N analogue. Models show that steric interference between methyl groups and the *ortho* hydrogen atoms of phenyl groups is greatly reduced when nitrogen is replaced by phosphorus.[44,69] Bu^t_2Be forms 1:1 complexes with Me_3P and Et_3P, the monomeric Me_3P complex being less stable than the Me_3N complex.[46,131]

3.4.2 Bidentate Ligands

Many organoberyllium compounds of type R_2Be and $RBeR'$ form 1:1 chelate complexes $R_2Be\cdot TMEDA$ (R = Me*,[142] Pr^i *, Bu^t *,[46] Me_3SiCH_2*,[126] MeC≡C,[68] PhC≡C*,[69] Ph*,[44] C_6F_5*, *o*-Tol*, *m*-Tol*, *p*-$Me_2C_6H_3$* [60]) and $RBeR'\cdot TMEDA$ (R = Bu^t, R′ = Me, C_6F_5*, *o*-Tol*, *p*-$Me_2C_6H_3$*;[69] R = Me, R′ = Me_3CCH_2* [59]). The di-propynyl complex crystallises with one molecule of benzene but the solvent-free complex is obtained by vacuum sublimation.[68] The ^1H NMR spectra of the complexes of $(Me_3CCH_2)_2Be$[59] and Pr^i_2Be[46] do not change with temperature and thus it appears that both nitrogen atoms are coordinated to beryllium. In contrast, ^1H NMR evidence supports only one nitrogen atom being coordinated to beryllium in the Bu^t_2Be complex.[46] Both Me_2Be[137] and Ph_2Be[44] form chelate complexes with *N*,*N*,*N*′,*N*′-tetramethyl-*o*-phenylenediamine.

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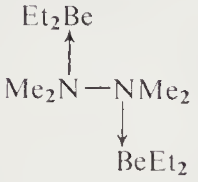
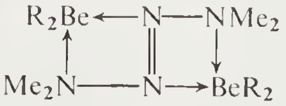
* Indicates monomeric in benzene solution.

Hydrazine is sterically less flexible than ethylenediamine type ligands and it is therefore unlikely to form chelate complexes. Diethylberyllium forms the complex $(Et_2Be)_2{\cdot}Me_2NNMe_2$ (**8**) with tetramethylhydrazine. The related ligand tetramethyltetrazene forms both 1 : 1 complexes with R_2Be (R = Et, Pr^i, Bu^t) and also complexes (**9**) containing two beryllium alkyls per ligand. The latter are the more stable and are obtained by heating the 1 : 1 complexes, though heating the Bu^t_2Be complex results in some thermal decomposition of Bu^t groups. Pyrolysis of the 2 : 1 complexes at 200 °C results in the formation of low mass polymers, containing approximately ten monomer units, which are glasses at room temperature but sufficiently thermoplastic to be fluid at 200 °C and contain both Be—H and Be—R groups with the ligand apparently serving as a linking agent for the beryllium atoms.[147,148]



(**8**)



(**9**)

2,2′-Bipyridyl forms complexes $R_2Be{\cdot}bipy$ (R = Me(yellow), Et(red),[142] Pr^n *(red),[46] Ph(yellow),[142] Me_3SiCH_2* (orange-red),[79] $Bu^tC{\equiv}C$(white),[68] $PhC{\equiv}C$(colourless)[69]), the colour being ascribed to a charge transfer transition from a Be—C bond to the LUMO of bipyridyl. With branched chain organoberyllium compounds as with organoberyllium hydrides, tarry products result due to attack on the azomethine bond.[142] 1,2-Dimethoxyethane forms 1 : 1 complexes with R_2Be (R = Me*,[142] Ph,[44] *m*-Tol*,[60] $PhC{\equiv}C$[69]) and diphenylberyllium forms a monomeric 1 : 1 complex with 1,2-dimethylthioethane,[44] all of which are doubtless chelated like the TMEDA complexes.

3.5 OXY-, THIO-, SELENO- AND AMINO-BERYLLIUM ALKYLS AND ARYLS

The polarity of the Be—C bond allows protolysis to occur with NH, OH, SH and SeH under moderate conditions. When the reaction is carried out using a 1 : 1 ratio of reactants, 1 mol of hydrocarbon is eliminated (equation 7) and the beryllium product (**10**) so formed would, if monomeric, contain both coordinatively unsaturated metal and electronegative atoms. This unsaturation is relieved by association and Coates has shown that the dominant factors affecting the extent of association are the steric bulk of the groups attached to beryllium, entropy factors and valency angle strain. Such compounds and their complexes may also be prepared by addition of Be—C or Be—H across C=O, C=N and C≡N multiple bonds.

$$R_2Be \quad + \quad R'EH \quad \longrightarrow \quad \underset{(\mathbf{10})}{RBeER'} \quad + \quad RH \tag{7}$$

$$E = O, S, Se, NR'$$

3.5.1 RBeOR′

A wide range of alkyl- and aryl-beryllium alkoxides has been prepared by alcoholysis of R_2Be or by addition of Be—C or Be—H across the double bond in ketones and aldehydes. The extent of association of such compounds, together with their method of preparation is indicated in Table 3. As hydrocarbon was not evolved, side reactions resulting from enolisation do not complicate the addition reactions of Me_2Be with MeCHO and Me_2CO or those of Et_2Be with Et_2CO. The butoxide, $(MeBeOBu^t)_4$ which forms $[Be(OBu^t)_2]_3$ on reaction with acetone, may also be formed from Me_2Be and either $[Be(OBu^t)_2]_3$ or di-*t*-butyl peroxide (Scheme 4).[149] Similarly (Me-

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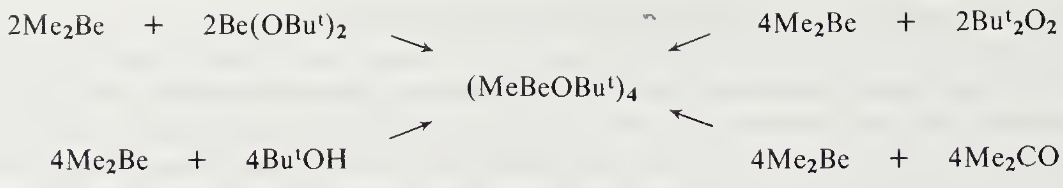
* Indicates monomeric in benzene solution.



Scheme 4

Table 3 Degree of Association (n) of Organoberyllium Alkoxides RBeOR′ in Benzene

R	R′	n	R	R′	n
Me	Me	$4^{a,1}$	Pr^i	Me	$4^{a,1,6}$
Me	Et	$4^{a,1}$	Bu^i	CH_2Bu^t	$3^{b,2}$
Me	Pr^n	$4^{a,1}$	Bu^i	$CHBu^t_2$	$2^{b,2}$
Me	Pr^i	$4^{a,b,1}$	Bu^t	Me	$4^{a,1}$
Me	Bu^t	$4^{a,b,1}$	Bu^t	Pr^i	$2^{b,2}$
Me	$CMeBu^t_2$	$2^{b,2}$	Bu^t	Bu^t	$2^{a,1}$
Me	Bz	$4^{a,d,3}$	Bu^t	CH_2Bu^t	$2^{b,2}$
Me	$CHPh_2$	$2^{a,d,1}$	Bu^t	$CHBu^t_2$	$2^{b,2}$
Me	CPh_3	$2^{a,1}$	Bu^t	$CHPh_2$	$2^{a,b,2}$
Me	$SiMe_3$	$4^{a,4}$	Bu^t	CPh_3	$2^{a,2}$
Et	Bu^t	$2–4^{c,5}$	Ph	Me	$4^{a,7}$
Et	$CHBu^t_2$	$2^{b,2}$	Ph	CPh_3	$2^{b,2}$
Et	CEt_3	$3^{a,b,1}$	PhC≡C	Bu^t	$\infty^{a,8}$
			Me_3SiCH_2	$C(CH_2SiMe_3)Ph_2$	$2^{b,2}$

Preparation: [a] $R_2Be + R'OH$. [b] $R_2Be + R'CHO$ or R'_2CO. [c] $Et_2Be + LiOBu^t$. [d] $RBeH + R'CHO$ or R'_2CO.

1. G. E. Coates and A. H. Fishwick, *J. Chem. Soc.* (*A*), 1968, 477.
2. R. A. Andersen and G. E. Coates, *J. Chem. Soc., Dalton Trans.*, 1974, 1171.
3. N. A. Bell and G. E. Coates, *J. Chem. Soc.* (*A*), 1966, 1069.
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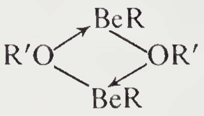
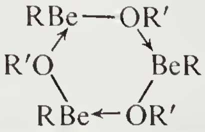
8. G. E. Coates and B. R. Francis, *J. Chem. Soc.* (*A*), 1971, 160.

$BeOMe)_4$, which is only dimeric in benzene solution by ebullioscopy,[150] may also be obtained by dissolving $Be(OMe)_2$ in a solution of Me_2Be, whilst $(MeBeOPr^n)_4$ results from Me_2Be with ethylene oxide[149] and $(MeBeOSiMe_3)_4$ from Me_2Be with $(Me_2SiO)_4$.[151]

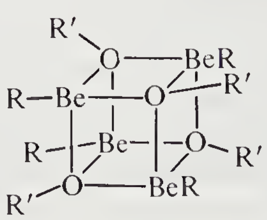
Dimers (**11**) would be favoured relative to trimers (**12**) or more associated species on entropy grounds but are disfavoured by the coordinative unsaturation of the metal. Tetramers (**13**) or polymers can be formulated with four-coordinate metal and oxygen atoms, the former being favoured on entropy grounds but disfavoured by valency angle strain.[149] Many of the compounds are tetrameric but to minimise steric repulsion, lower degrees of association result when the organic groups are large. The solid state tetrameric cubane structure of $(MeBeOSiMe_3)_4$ (**13**) (R = Me, R′ = $SiMe_3$) is confirmed by X-ray diffraction studies. Oxygen and beryllium are situated at alternate corners of an only slightly distorted cube with the O—Si and Be—C bonds lying on outward prelongations of the diagonals of the cube.[152] Though $(PhC{\equiv}C)_2Be$ is not reactive to OH and SH, both Bu^tOH and PhOH liberate PhC≡CH in THF solution forming $(PhC{\equiv}CBe(OR){\cdot}THF)_n$ (R = Bu^t, Ph) existing in a monomer–dimer equilibrium in benzene solution. Uncomplexed $(PhC{\equiv}CBeOBu^t)_n$ may be obtained from $(PhC{\equiv}C)_2Be{\cdot}L$ (L = OEt_2, NEt_3) as an insoluble solid, unreactive to acids, suggesting that it is polymeric, particularly as both alkyne and oxygen are good bridging groups.[69]



(**11**)



(**12**)

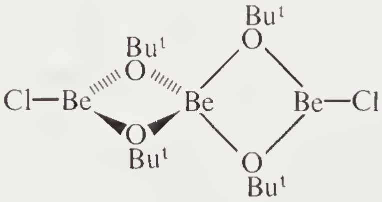


(**13**)

Reactions of the alkoxides with donors have not been systematically studied. Sometimes disproportionation occurs, as with $(MeBeOCH_2Ph)_4$ and bipy forming $Me_2Be{\cdot}bipy$[153] and with $(MeBeOMe)_4$ and 1 mol py/Be, or complex formation results as with $(MeBeOMe)_4$ and 2 mols py/Be forming a monomeric bis(pyridine) adduct.[149] Other complexes which have been isolated include $[MeBe(OCHPh_2){\cdot}L]_2$ ($L = Et_2O$, THF*),[153] $MeBe(OCPh_3){\cdot}OEt_2$*, $PhBe(OMe){\cdot}OEt_2$*, $MeBe(OPh){\cdot}OEt_2$[149] and $Bu^tBe(OCHBu^t_2){\cdot}L$* (L = quinuclidine, 4-dimethylaminopyridine).[3] Evidently the ligand is a stronger donor to beryllium than the alkoxy oxygen in an associated species, resulting in the formation of either a four-coordinate complex or a three-coordinate monomer in which steric effects impede association. Though $(MeBeOBu^t)_4$ crystallises solvent-free from ether and is tetrameric (isopiestically) in that solvent as well as in benzene (cryoscopically), both it and $MeBeOR'$ ($R' = Me, Et, Pr^n, Pr^i$) are dimeric (ebullioscopically) in very dilute ether solution and may contain three-coordinate beryllium (**11**) or ether may attach itself to the fourth coordination position of beryllium.[149] A series of *t*-butoxides, $R_2Be_3(OBu^t)_4$, ($R = Me$,[154] $PhC{\equiv}C$[69]) has been obtained by reaction of an ether or amine complex of R_2Be with Bu^tOH or with $[Be(OBu^t)_2]_3$ in ratios shown in Scheme 5.[69,154] The Bu^t compound obtained from Bu^tLi and $Cl_2Be_3(OBu^t)_4$ is essentially monomeric in benzene solution but the phenyl compound could not be obtained. The methyl compound is unreactive to NH_3 and Me_2NH and can be recovered unchanged from a solution of TMEDA. However it is sensitive to H_2O and reacts with Bu^tOH and MeOH forming $[Be(OBu^t)_2]_3$ and a mixture of $[Be(OBu^t)_2]_3$ and $Be(OMe)_2$, respectively, and with HCN and HNO_3 forming $X_2Be_3(OBu^t)_4$ ($X = CN, NO_3$).[154] The linear structure (**14**) with terminal chlorine atoms has been confirmed for $Cl_2Be_3(OBu^t)_4$ by X-ray analysis[155] and the other analogues doubtless have similar structures. Another interesting *t*-butoxide is the crystalline monomer $Me_3Al{\cdot}Be_3(OBu^t)_6$ obtained from Me_3Al and $[Be(OBu^t)_2]_3$ but as Me—Be and Me—Al resonances occur in the same region of the NMR spectrum, a structural analysis is desirable as exchange of methyl and *t*-butoxide groups may have taken place.[156]

$$3R_2Be \quad + \quad 4Bu^tOH \quad \xrightarrow{-4RH} \quad R_2Be_3(OBu^t)_4 \quad \longleftarrow \quad R_2Be \quad + \quad 2Be(OBu^t)_2$$

Scheme 5



(**14**)

3.5.2 RBeSR′ and RBeSeR′

All the solvent-free compounds $(RBeSR')_4$ ($R = Me, R' = Bu^t$; $R = Et, R' = Et, Pr^i, Bu^t$) are tetrameric in benzene solution and are prepared from R_2Be and the thiol except for $R = R' = Et$ which is obtained from Et_2Be and either $Be(SEt)_2$ or Et_2S_2. The compounds, which are believed to contain the Be_4S_4 cube like the oxygen analogues (**13**), have a higher tendency to disproportionate than the latter due to the weaker donor capability of S compared to O, and vary greatly in their reactions with bases. Whereas $(EtBeSR')_4$ ($R' = Et, Pr^i$) crystallise solvent-free from ether, Pr^iBeSR' ($R' = Et, Pr^i$) could only be obtained in the form of complexes such as $(Pr^iBe(SEt){\cdot}L)_2$ ($L = Et_2O$, py) and $Pr^iBe(SPr^i)py_2$: the first two are four-coordinate dimers *via* sulphur bridges while for the latter, there is less steric crowding in a monomeric bis(pyridine) complex than in a dimeric monopyridine complex. Other complexes obtained include $EtBe(SBu^t){\cdot}L$ (L = THF*, py, py_2*, bipy), the monopyridine complex being dimeric, and $(PhC{\equiv}CBe(SBu^t){\cdot}THF)_2$.

No uncomplexed seleno derivatives are known. Et_2Be reacts with EtSeH to form $Be(SeEt)_2$ but in the presence of the strong donor pyridine, $EtBe(SeEt)py_2$ is obtained, whereas Et_2O is not a sufficiently strong donor to break up the bridges in a dimeric structure so that complexes $(RBe(SePh){\cdot}OEt_2)_2$ ($R = Me, Et$) are formed.[143]

---

* Indicates monomeric in benzene solution.

3.5.3 RBeNR′R″

Reactions of R_2Be with secondary amines in equimolar proportions result in general in the liberation of 1 mol hydrocarbon (equation 7) and the formation of RBeNR′R″. As hydrogen bound to nitrogen is not as acidic as hydrogen bound to oxygen, sometimes gentle heating is necessary for complete reaction. For example, $(PhC{\equiv}C)_2Be{\cdot}(HNMe_2)_2$ requires temperatures in the range 60–80 °C for elimination of $PhC{\equiv}CH$.[69] The steric congestion about the NH group in $Bu^t_2Be{\cdot}HNMe_2$ results in much greater thermal stability than is found for other similar complexes and elimination of alkene could not be taken to completion.[157] With a 1 : 1 mixture of Me_2Be and $MeNH_2$, only 1.47 mol CH_4/Be are evolved on warming due to the formation of polymeric products.[150] The compounds RBeNR′R″ are also obtained from the addition of Be—C or Be—H to C=N in a Schiff's base.[3,153]

Monomeric RBeNR′R″ would contain coordinatively unsaturated beryllium and nitrogen and such unsaturation is relieved by association (Table 4). Dimers and trimers are preferred relative to higher oligomers on entropy grounds; tetrameric species, analogous to those found for the alkoxides (**13**), are of course not possible, as this would necessitate five-coordinate nitrogen. Dimers, analogous to (**11**), are preferred on both entropy and steric grounds but trimers, analogous to (**12**), are favoured because of the minimum valency angle strain. Consequently trimers are found for small substituents and dimers for large substituents, particularly at nitrogen.[157] The ^1H NMR spectrum (−90 to 25 °C) of $(MeBeNMe_2)_3$ is consistent with a six-membered Be_3N_3 ring structure undergoing rapid interconversion in the ring.[129]

Table 4 Degree of Association (n) of Organoberyllium Amides RBeNR′R″ in Benzene

R	R′	R″	n	R	R′	R″	n
Me	Me	Me	$3^{a,1,2}$	Et	Ph	Ph	$2^{a,1}$
Me	Et	Et	$3^{a,1}$	Et	Me	CHEtPh	$2^{b,4}$
Me	Pr^n	Pr^n	$2^{a,1}$	Et	Ph	CHEtPh	$2^{b,4}$
Me	Ph	Ph	$2^{a,1}$	Pr^i	Me	Me	$3^{a,1,5}$
Me	Ph	Bz	$2^{b,3}$	Bu^t	Me	Bz	$2^{b,4}$
Me	*p*-Tol	CHMePh	$2^{b,4}$	Bu^t	Ph	$PhCH{=}CHCH_2$	$2^{b,4}$
Et	Me	Me	$3^{a,1}$	Ph	Me	Me	$3^{a,6}$
Et	Et	Et	$2^{a,1}$	Ph	Ph	Ph	$2^{a,6}$

Preparation: [a] $R_2Be + R'R''NH$. [b] $R'N{=}CHR'' + R_2Be$ or RBeH.

1. G. E. Coates and A. H. Fishwick, *J. Chem. Soc.* (*A*), 1967, 1199.
2. G. E. Coates, F. Glockling and N. D. Huck, *J. Chem. Soc.*, 1952, 4512.
3. N. A. Bell and G. E. Coates, *J. Chem. Soc.* (*A*), 1966, 1069.
4. R. A. Andersen and G. E. Coates, *J. Chem. Soc., Dalton Trans.*, 1974, 1171.
5. G. E. Coates and F. Glockling, *J. Chem. Soc.*, 1954, 22.
6. G. E. Coates and M. Tranah, *J. Chem. Soc.* (*A*), 1967, 236.

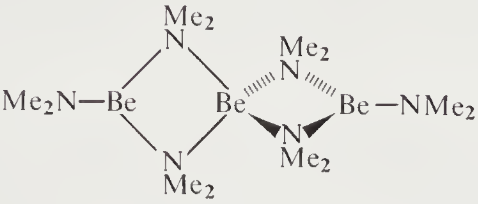
As these dimers and trimers contain three-coordinate beryllium, they would be expected to react with donor molecules. Reactions between such compounds and pyridine bases are complicated by disproportionation. With 1 mol equivalent of pyridine, $(MeBeNR'_2)_n$ ($R' = Me$, $n = 3$; $R' = Ph$, $n = 2$) yields $(MeBe(NR'_2)py)_2$, the change in ring size from trimer to dimer being due to increased steric congestion about the metal. With excess pyridine monomeric $MeBe(NR'_2)py_2$ and $EtBe(NPh_2)py_2$ are formed. In contrast, $(MeBeNPr^n_2)_2$ with 1 mol py/Be yields the disproportionation product Me_2Bepy_2.[157] 2,2′-Bipyridyl will also displace the amino lone pair to form monomeric coloured bipy complexes such as red $RBe(NPh_2){\cdot}bipy$ (R = Me, Et)[157] and orange $MeBeN(Ph)(CH_2Ph){\cdot}bipy$,[153] although $(PhBeNPh_2)_2$ and $(MeBeNMe_2)_3$ disproportionate to $Ph_2Be{\cdot}bipy$[44] and $Me_2Be{\cdot}bipy$[157] respectively. Similar dimeric complexes are formed by the reactions of RBeH with R′CN in the presence of pyridine or trimethylamine (equation 8).[146]

Though Me_2Be reacts with Me_2PH evolving methane, phosphine compounds $(RBePR'_2)_n$ have not been obtained.[151]

$$2RBeH \;+\; 2R'CN \;+\; 2L \longrightarrow [R(R'CH{=}N)Be{\cdot}L]_2 \qquad (8)$$

($R = Me$, $R' = Bu^t$, Ph, *o*-Tol, *m*-Tol, $L = Me_3N$; $R = Bu^t$, $R' = Bu^t$, Ph, L = py;
R = Me, R′ = Ph, L = py)

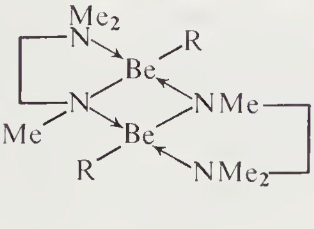
$Me_2Be_3(NMe_2)_4$, essentially monomeric in benzene solution, is obtained from Me_2Be and $[Be(NMe_2)_2]_3$ and possibly has a structure similar to that found for $Cl_2Be_3(OBu^t)_4$ (**14**)[155] and $[Be(NMe_2)_2]_3$ (**15**)[158] though the NMR spectrum cannot be rationalised in terms of such a structure.[154]



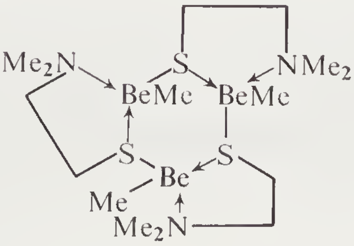
(**15**)

3.5.4 Reactions of R_2Be with Bidentate Ligands containing Acidic Hydrogen Atoms

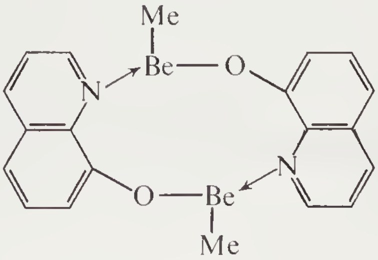
Bidentate ligands containing acidic hydrogen atoms also react with R_2Be liberating hydrocarbon to form associated products to satisfy the coordinative unsaturation unless prevented by steric hindrance. *N,N,N′*-Trimethylethylenediamine reacts with R_2Be to form compounds $(RBeN(Me)C_2H_4NMe_2)_2$ (R = Me,[142] Pr^n, Pr^i,[46] Ph[44]) which are assigned structure (**16**) like that found for the corresponding methylmagnesium[159] and hydridozinc compounds:[155] the product from Me_2Be and 2-(β-dimethylaminoethyl)pyridine is probably similar.[151] There is restricted rotation of the Pr^i group[46] and steric factors do not allow association in the Bu^t analogue[157] though $(Bu^tBeOC_2H_4NMe_2)_2$ is a dimer as O occupies less space than NMe.[46] Reaction between Me_2Be and *N*-methylethylenediamines containing two or more acidic hydrogen atoms leads to condensed polymeric products, though the dimethylethylenediamines give isolable intermediates similar to (**16**) which polymerise as they liberate further methane.[142] Dimethylberyllium and 2-dimethylaminoethanol form oligomeric $(MeBeOC_2H_4NMe_2)_n$ ($n \approx 7$) though it is not clear whether the nitrogen is coordinated. In contrast the thio analogue is trimeric (**17**) due to lower valency angle strain and sulphur being less bulky than NMe in trimethylethylenediamine,[160] while the Bu^t compound is dimeric due to larger steric effects.[46] Both $(RBeOC_2H_4OMe)_4$ (R = Me, Et) are tetrameric having the conventional cubane structure (**13**) suggested for other organoberyllium alkoxides, without coordination by the ether oxygen atom as the donor strength of oxygen bonded to an electropositive metal is greater than that of an ether oxygen.[160] Methylberyllium dimethylketoximate is also tetrameric like the zinc analogue which has a cage structure made up of fused five- and six-membered Zn—O—N rings with all the zinc atoms four-coordinate and the oxygen and nitrogen atoms three-coordinate (ref. 36, p. 139). The structure of tetrameric methylberyllium 8-hydroxyquinolinate is believed to consist of two non-planar dimeric units (**18**) parallel to each other with coordination between each oxygen atom in one dimer and beryllium atoms in another. An objection to a more conventional cubane arrangement is that it would necessitate coordination by a second lone pair on oxygen while the more strongly basic nitrogen would not be involved in internal coordination.[160]



(**16**)



(**17**)



(**18**)

Reactions of the methylhydrazines with diethylberyllium tend to give what are probably polymeric products. The presence of a methyl group on a nitrogen atom, due to its inductive effect, makes that the more basic nitrogen and seems to limit the substitution of ethyl groups to one, perhaps due to steric crowding round beryllium, preventing a second molecule attaching itself to beryllium before hydrocarbon elimination.[161]

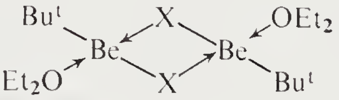
3.6 ORGANOBERYLLIUM HALIDES AND PSEUDOHALIDES

3.6.1 Alkyl- and Aryl-beryllium Halides and Pseudohalides

Detailed studies of organoberyllium halides are somewhat limited. Organic halides, particularly iodides as these have the weakest C—halogen bond, react with beryllium activated with traces of $BeCl_2$ or $HgCl_2$, on heating to form what are believed to be organoberyllium halides.[54,162,163]

Zakharkin *et al.* have found that powdered beryllium reacts with haloalkanes on prolonged boiling to precipitate RBeX.[164] Little is known about the extent of association of such compounds. The vibrational spectrum of EtBeCl has been rationalised in terms of a polymeric structure[165] and as Bu^tBeCl, formed from Bu^t_2Be and a benzene suspension of $BeCl_2$, is insoluble in benzene,[126] a polymeric constitution does not seem unreasonable. Redistribution in the R_2Be–BeX_2 system (R = Me, X = Cl, Br; R = Et, Ph, X = Br) occurs in ether solution so that equilibrium (9) lies predominantly if not entirely on the right. Equimolar mixtures of R_2Be and BeX_2 (R = Me, X = Cl, Br; R = Ph, X = Br) are approximately monomeric ebullioscopically in ether, RBeX doubtless being solvated and MeBeX (X = Cl, Br) can be identified in solution as the protons resonate at slightly lower field than do those in Me_2Be, due to the electron withdrawing effect of the halogen atoms.[67,99] Further support for their formulation as RBeX comes from selective precipitation reactions of Me_2Be–$BeBr_2$ mixtures with dioxane[99] and from reactions of 1 : 1 R_2Be–BeX_2 mixtures to form RBeH and their complexes (Section 3.8). In Me_2S solution, MeBeCl exists as $MeBeCl(SMe_2)_2$ in contrast to Me_2Be which exists in a monomer–oligomer equilibrium.[124,128] Only a few complexes of RBeX have been isolated. 2,2′-Bipyridyl and EtBeCl form an orange complex, disproportionating in boiling benzene[166] and Bu^tBeCl forms a 1 : 1 quinuclidine complex.[126] Dioxane is reported to form a 1 : 1 complex with EtBeBr but analytical data have not been cited[67] though with PhBeBr disproportionation occurs.[75] Trimethylamine and TMEDA cause disproportionation of Me_3CCH_2BeX (X = Cl, Br) and EtBeCl respectively, whereas RBeBr·TMEDA (R = Et, Me_3CCH_2)[59] and $Bu^tBeClNCBu^t$ [3] are the only monomeric alkylberyllium halide complexes known. Both $Bu^tBeX{\cdot}OEt_2$ (X = Cl, Br), the former being monomeric in ether and formed when $BeCl_2$ is added to $Bu^t_2Be{\cdot}OEt_2$[46] in order to prepare the ether-free dialkyl,[51] are dimers (**19**) in benzene solution.

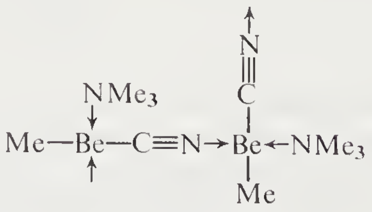
$$R_2Be + BeX_2 \rightleftharpoons 2RBeX \qquad (9)$$



(**19**)

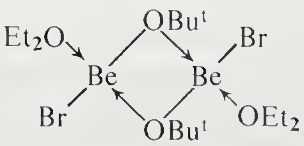
Methylberyllium cyanide, obtained from an equimolar mixture of Me_2Be and HCN in ether, probably has a polymeric constitution as does its trimethylamine complex for which a polymeric *trans* structure (**20**) is favoured.[167]

Aldehydes and ketones undergo either addition or reduction reactions with organoberyllium halides. Acetone reacts with MeBeBr in ether, in similar fashion to its reaction with Grignard reagents, forming $(Bu^tOBeBr{\cdot}OEt_2)_2$,[154] the *trans* structure (**21**) being confirmed by X-ray analysis.[155] Both Bu^t_2CO and Bu^tCHO are reduced by Bu^tBeCl forming $(ClBeOCHBu^t_2)_2$ and $ClBe(OCH_2Bu^t)OEt_2$, respectively, the latter existing in a monomer–dimer equilibrium in benzene.[3]



$$\mathrm{Me{-}\underset{\uparrow}{\overset{\overset{NMe_3}{\downarrow}}{Be}}{-}C{\equiv}N{\rightarrow}\underset{\underset{Me}{|}}{\overset{\overset{\overset{\uparrow}{N}}{\overset{|||}{C}}}{|}}{Be}}\!\!\leftarrow NMe_3}$$

(**20**)

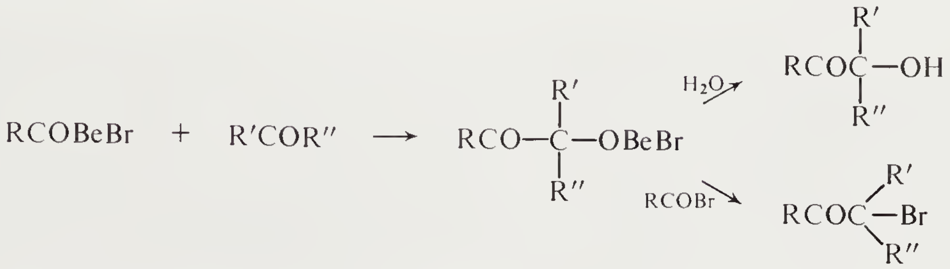


(**21**)

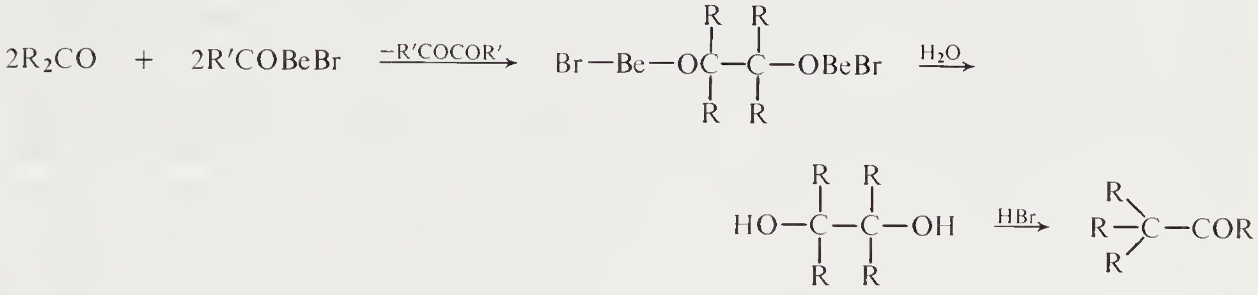
3.6.2 Acylberyllium Halides

In contrast to reactions of haloalkanes with beryllium, reactions of the powdered metal with acyl halides are relatively fast. The products which react vigorously with water and alcohols have unfortunately not been isolated in the pure state, but their formulation as acylberyllium halides RC(=O)BeX (R = Me, Et, Pr^n, X = Cl, Br, I) has been established by the nature of their chemical reactions.[168] The reactivity of the acid bromides increases with the complexity of the acid radical and consequently with decrease in the dissociation constant of the acid. The reaction proceeds readily in anhydrous ethyl ethanoate but only slowly in solvents such as ether and dioxane.

Acylberyllium bromides undergo some interesting chemical transformations, reacting vigorously with aliphatic ketones forming on hydrolysis a hydroxyketone and a bromoketone, the latter produced by reaction of excess acid bromide (Scheme 6). As the radicals R′ and R″ become more complex, the products of a crotonic type condensation are formed in addition to the hydroxyketones. Aromatic ketones react differently producing pinacols on hydrolysis. Under the catalytic influence of small amounts of acyl bromide which remain in the reaction mixture, upon hydrolysis the pinacols are converted into pinacolones (Scheme 7).[169,170]



Scheme 6



Scheme 7

Aromatic aldehydes react in extremely peculiar fashion forming *trans*-stilbenes (equation 10). Aldehydes of cinnamaldehyde type react to form diarylhexatrienes (equation 11),[171,172] while aromatic nitro compounds are converted into acid amides in high yield (equation 12) except when *o*-dinitro compounds are used.[173]

$$8RCHO + 8MeCOBeBr \longrightarrow 4RCH{=}CHR + 4BeBr_2 + Be_4O(OAc)_6 + Ac_2O \quad (10)$$

$$2PhCH{=}CHCHO + 2RCOBeBr \longrightarrow Ph(CH{=}CH)_3Ph + 2RCO_2BeBr \quad (11)$$

$$3RCOBeBr + R'NO_2 \longrightarrow R'NHCOR + 2RCO_2BeBr \quad (12)$$

3.7 ANIONIC COMPLEXES

3.7.1 Alkyl and Aryl Complexes

In the $MeLi$–Me_2Be system in ether, 1:1, 2:1 and 3:1 complexes exist in equilibrium over a wide temperature range and there is a rapid exchange of methyl groups between MeLi and the complexes formed. Solutions containing $LiBeMe_3$ and Li_2BeMe_4 react with LAH to form Li_2BeH_4 whereas Li_3BeMe_5 yields Li_3BeH_5, and $LiBeH_3$ can be formed from AlH_3 and $LiBeMe_3$ in a 1:1 ratio in ether.[174] The only structural study of this type of compound is for Li_2BeMe_4 which contains a distorted tetrahedral arrangement of methyl groups round beryllium. The Be—C distance is shorter than the electron-deficient bond in $(Me_2Be)_n$ and similar to other bond lengths involving four-coordinate carbon (Table 2). The shortest Li—C distance is 252 pm,[175] somewhat longer than the Li—C distance (231(5)pm)[176] in $(MeLi)_4$. Other complexes of this type include $Li_2Be(C{\equiv}CPh)_4$,[69] $LiBeR_3$ (R=Ph,[77,177] o-Tol[60]) and $NaBe(CPh_3)Ph_2{\cdot}2Et_2O$,[77] all obtained from R_2Be and the organoalkali metal and $NaBeEt_3$, formed as a product of the reaction of sodium with diethylberyllium.[178] The reactions of ketones with $LiBePh_3$, which crystallises containing 4 mol of solvent from dioxane solution, have been studied.[77]

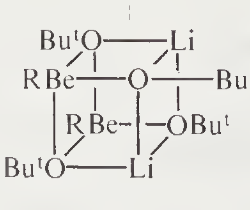
3.7.2 Halide Complexes

Strohmeier and co-workers have prepared a series of alkali metal salts of diethylberyllium of the type $MX(BeEt_2)_n$ (n = 2, X = F, M = K, Rb, Cs; n = 4, X = CN, M = K) as well as tetraalkylammonium salts $R_3NR'(BeEt_2)_2X$ (X = Cl, F). Complexes are more readily formed when the anion of the reacting salt is small and the cation large, so that chloride complexes have only been formed with the relatively large quaternary ammonium cations and the tendency for complex formation with fluorides is in the order $Cs > Rb > K > Na$, paralleling the increasing lattice energy of the metal halide.[86–88,179,180] The crystalline salt $KF(BeEt_2)_2$, probably having a structure similar to $KF(AlEt_3)_2$ with a single fluorine bridge between two metal atoms,[181] decomposes on heating to 100–130 °C or in hot benzene solution to pure ether-free Et_2Be and $KF(BeEt_2)$.[86–88] Both KF salts have been claimed as alkylating agents and polymerisation catalysts.[182] In boiling benzene $RbF(BeEt_2)_2$ disproportionates to $RbF(BeEt_2)$ and $RbF(BeEt_2)_3$, the latter evolving Et_2Be at 120 °C.[179] The vibrational spectra of $Me_4NCN(BeEt_2)_4$ have been interpreted in terms of diethylberyllium dimers bridged by CN^- [183] and it is likely that the potassium analogue which also evolves Et_2Be on heating[86,179] will have a similar structure. Spectral data for $Me_4NSCN(Et_2Be)_2$ indicate sulphur bridging the metal atoms[184] while for $CsN_3(BeEt_2)$ the complex anion is believed to exist as a cyclic trimer.[165] Electrochemical data for some of these anionic beryllium complexes have been measured.[179,185] Electrolysis of salts of the type $KF(BeEt_2)_2$ with Cu or Ag electrodes deposits a coating containing Be_2C as well as Be and polycrystalline K. The electrolysis initially collects K^+ at the cathode which then chemically precipitates beryllium. If a Be anode is used then quantitative formation of Et_2Be occurs and with the tetraalkylammonium salts a lower content of Be_2C and foreign elements results.[178,180,186]

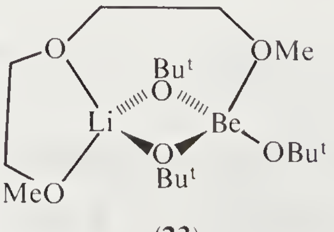
3.7.3 Alkylberyllium *t*-Butoxides

Two series of alkali metal alkylberyllium *t*-butoxides have been prepared. Diffraction studies to confirm their structures would be advantageous.

(*A*) The compounds $[MRBe(OBu^t)_2]_2$ (M = Li, R = Et, Bu^t; M = Na, R = Et), prepared from RLi and $[Be(OBu^t)_2]_3$ or from $NaOBu^t$ and $EtBeOBu^t$, are formulated as (**22**). The butylberyllium compound forms a monomeric complex with bis(2-methoxyethyl) ether (**23**). From $LiBe(OBu^t)_3$ and Bu^tLi, the dilithium salt $Li_2Bu^tBe(OBu^t)_3$ is formed. A similar nitrogen compound $LiBu^tBe(NMe_2)_2$ has been obtained from Bu^tLi and $[Be(NMe_2)_2]_3$ and this may have a salt-like constitution.

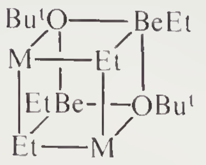


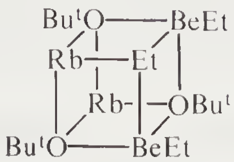
(**22**)



(**23**)

(*B*) The compounds $[MEt_2BeOBu^t]_2$ (M = Na, K), formulated as (**24**), are prepared from $MOBu^t$ and Et_2Be in equimolar amounts in ether. With $RbOBu^t$, the more unusual $Rb_2Et_3Be_2(OBu^t)_3$ (**25**) is formed. These salts undergo some unusual reactions with aromatic hydrocarbons; $[KEt_2BeOBu^t]_2$ is a protophile metallating the side chain of toluene and the nucleus of 1,3,5-trimethylbenzene giving red $K_5Et_2Be_3(OBu^t)_4(PhCH_2)_4$ in low yield and orange diamagnetic $K_3Et_2Be_2(OBu^t)_2(Me_3C_6H_2)_2$, respectively. The rubidium salt also metallates the nucleus of 1,3,5-trimethylbenzene forming red $Rb_5Et_3Be_3(OBu^t)_2(Me_3C_6H_2)_4$.[187]


(**24**)


(**25**)

3.7.4 Hydride Complexes

Sodium and lithium hydride react with beryllium dialkyls in boiling ether forming crystalline salts MR_2BeH (M = Li, R = Et;[188] M = Na, R = Me,[135] Et,[189] Pr^n, Pr^i, Bu^i [144]). The salt $LiBu^i_2BeH$ is readily prepared by metathesis from the sodium salt and lithium bromide in ether.[144] In some cases crystalline ether complexes have been isolated, *e.g.* $NaEt_2BeH{\cdot}(OR_2)$ (R = Me, Et), but the ether can be readily removed *in vacuo*.[144,190] Ether is evolved from $LiEt_2BeH{\cdot}(OEt_2)$ at 35–40 °C forming benzene insoluble $LiEt_2BeH$ which evolves Et_2Be on heating *in vacuo* at 80 °C.[188] Hydride ion will not only displace ether from R_2Be etherates but will also displace amine from Et_2BeNMe_3 to form $NaEt_2BeH$ which adds Be—H to ethylene in the presence of ether but only slowly in its absence.[153] X-ray diffraction studies have shown that $Na(OEt_2){\cdot}Et_2BeH$ (Figure 2) consists of $[Et_4Be_2H_2]^{2-}$ ions with pairs of sodium ions each coordinated to one disordered ether molecule. Each beryllium atom is surrounded by a pseudotetrahedral arrangement of two H and two C atoms (Table 2), while the bridging H atoms are surrounded by an approximately tetrahedral arrangement of two Na and two Be atoms.[190] Sodium hydride and Bu^t_2Be react in ether to form crystalline $Na(OEt_2)_4Bu^t_4Be_2H$ in low yield. The bulky butyl groups probably inhibit the formation of four-coordinate beryllium by virtue of BeH_2Be bridges as in Figure 2 so that

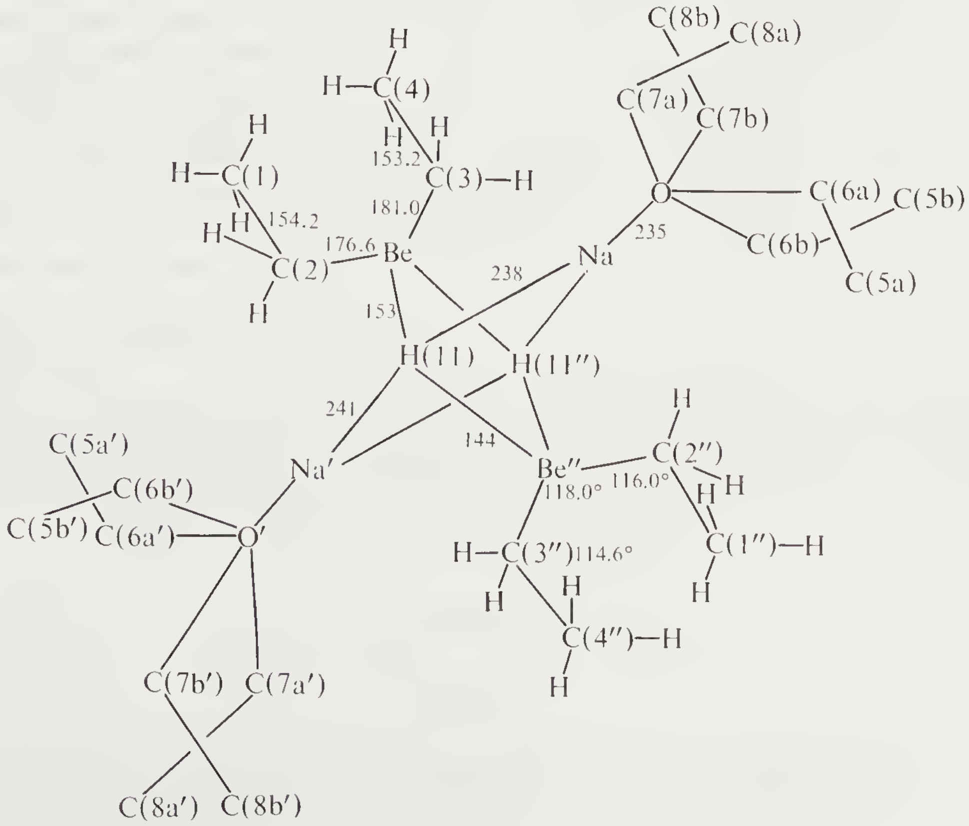


Figure 2 Perspective view of $[Na(OEt_2)]_2[Be_2Et_4H_2]$ (reproduced with permission)

only a single hydrogen atom bridges two Be atoms. Removal of ether results in the formation of a liquid which was not further studied. The salts NaR$_2$BeH (R = Et, Bu^i) combine with further R$_2$Be in hexane. The former results in the formation of insoluble NaEt$_6$Be$_3$H which reforms NaEt$_2$BeH on pyrolysis. The latter dissolves in solutions of Bu$^i_2$Be up to a limit corresponding to Na$_2$Bu$^i_6$Be$_3$H$_2$ and on concentration of the solution NaBu$^i_2$BeH is deposited. Pyrolysis of NaR$_2$BeH (R = Pr^i, Bu^i) at 60–200 °C eliminates alkene and some R$_2$Be leaving a residue of sodium beryllium hydride, the composition of which depends on the pyrolysis conditions, and LiBu$^i_2$BeH behaves similarly.[144] Only one member of the aromatic series is known, Li(OEt$_2$)-Ph$_2$BeH, obtained from LiH and Ph$_2$Be·OEt$_2$ at 160–165 °C and this reduces the 9-Ph-(CH=CH)$_4$CO derivative of carbazole to Ph(CH=CH)$_4$CHO.[134]

3.8 ORGANOBERYLLIUM HYDRIDES

3.8.1 Preparation and Properties

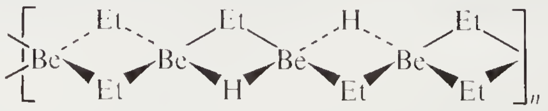
Organoberyllium hydrides have been obtained by a number of routes, though only in very few cases have solvent-free compounds been obtained and generally they have been characterised by the formation of coordination complexes.

(*A*) Reaction of NaR$_2$BeH (R = Me, Et) with one half molecule of BeCl$_2$ in ether results in precipitation of NaCl leaving solutions containing '$R_4Be_3H_2$'. There is little evidence about the constitution of such species which are viscous oils, retain ether and behave as mixtures of RBeH and R$_2$Be with donor molecules. Reaction of '$Me_4Be_3H_2$' with Me$_3$N results in the formation of Me$_2$BeNMe$_3$ and the less volatile (MeBeHNMe$_3$)$_2$.[135] Thermal decomposition of '$Me_4Be_3H_2$' at 170–210 °C results in the evolution of Me$_2$Be leaving species rich in hydride. Diethylberyllium separates more readily from '$Et_4Be_3H_2$' leaving predominantly EtBeH at 60–70 °C but the course of the reaction at higher temperature is affected by composition. If sodium is left in solution, then pyrolysis at 180 °C produces BeH$_2$ containing sodium beryllium hydride.[135,188]

(*B*) Solutions of RBeH (R = Me, Et, Bu^t, *n*-C$_5$H$_{11}$, Ph, *o*-Tol, *m*-Tol) or their ether complexes are more readily prepared from R$_2$Be, BeX$_2$ (X = Cl, Br) and LiH in boiling ether, the driving force being the formation of soluble LiX.[49,126,153]

(*C*) Alkyl–hydrogen exchange reactions have not been particularly useful for the formation of RBeH. Exchange takes place between R$_2$Be (R = Me, Et) and Et$_3$SnH in ether and the compounds RBeH so formed have been characterised by conversion to their trimethylamine complexes.[135,191] Reaction of ether-free Et$_2$Be and Et$_3$SnH in hexane results in precipitation of hydride-rich material, in which tin compounds are held.[191] Claims have been made for the formation of EtBeH from Et$_3$Al and Be(BH$_4$)$_2$, and for that of MeBeH from Me$_2$Be and BeH$_2$.[192]

(*D*) Branched chain organoberyllium compounds eliminate alkene at moderate temperatures to form Be—H bonds. 2-Methylprop-2-ene is eliminated from Bu$^t_2$Be at 105–110 °C yielding a mixture of Bu^{i}BeH and Bu^{t}BeH[106] and Pr$^i_2$Be forms Pr^{i}BeH.[47] Pyrolysis of Bu$^i_2$Be or its etherate produces extensively associated (*n* = 10–30) benzene soluble glassy Bu^{i}BeH[106] and refluxing Bu$^s_2$Be etherate under reduced pressure produces Bu^{s}BeH·0.1Et$_2$O.[49] Pyrolysis of (RBeBu^t)$_2$ (R = *o*-Tol, *m*-Tol) in boiling xylene results in the formation of white insoluble compounds RBeH which were converted into soluble amine complexes.[126] In the absence of solvent, (MeBeBu^t)$_3$ yields MeBeH, characterised as its trimethylamine complex while heating (EtBeBu^t)$_2$ with Et$_2$Be yields Et$_3$Be$_2$H (m.p. 132–134 °C), also obtained from Et$_2$Be and Bu$^s_3$B. Formulation of Et$_3$Be$_2$H (**26**) is supported by a strong IR absorption at 1565 cm^{-1} which may be associated with a single hydrogen bridge between two beryllium atoms[79] as vibrations associated with BeH$_2$Be occur in the 1310–1350 cm^{-1} region[129,135,191] and those with terminal Be—H at *ca.* 1800 cm^{-1},[106] and also steric factors prevent more than three ethyl groups bonding to beryllium.[193]



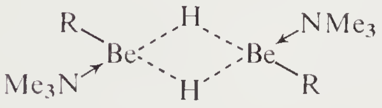
(**26**)

(*E*) Reactions of RBeCl (R = Et, Ph,[191] Me$_3$CCH$_2$[59]) with NaEt$_3$BH in ether result in the immediate precipitation of salt and, after filtration, ether and some Et$_3$B are evaporated. Though purification of the resulting hydride was not achieved, the hydrides were characterised by the formation of amine complexes.

3.8.2 Complexes

Ether cannot be completely removed from ethereal solutions of RBeH. For MeBeH, approximately one sixth mole of ether is retained after gentle heating under reduced pressure, and the residue shows broad IR absorptions similar to those in $(BeH_2)_n$, where there is probably a 3-dimensional Be···H···Be arrangement. The liquid $(MeBeH{\cdot}OEt_2)_2$, obtained by evaporation of ether from such a solution, is dimeric in benzene solution like the crystalline pyridine and 4-dimethylaminopyridine analogues[153] and $(Bu^iBeH{\cdot}THF)_2$.[106] Reaction with excess of these pyridines results in reduction of the pyridine nucleus.[151,153]

Trimethylamine complexes $(RBeH{\cdot}NMe_3)_2$ (R = Me,[126,135,191] Et,[79,135] Ph,[191] n-C_5H_{11},[49] *o*-Tol, *m*-Tol[126]) are dimeric in benzene and are formulated (**27**) with hydrogen rather than bridging R groups as the methyl compound is not decomposed by excess amine[135] whereas the bridges in $(Me_2Be)_n$ are cleaved by amine.[2] Most of the complexes are prepared from solutions of RBeH and amine but (**27**) (R = Et) is also obtained from Et_3Be_2H and the amine[79] and (**27**) (R = n-C_5H_{11}) from $(BeH_2{\cdot}NMe_3)_2$ and pent-1-ene.[49] The only phosphine complex known, $(PhBeH{\cdot}PMe_3)_2$, dissociates in benzene.[191] The bridging hydrogen resonance appears in the NMR spectra of $(RBeHL)_2$ (R = Me, L = Et_2O, py; R = Et, L = Me_3N) as a single broad resonance but is absent in (**27**) (R = Me). Splitting of the Me—N resonance in the latter is attributed to *cis–trans* isomerism about the BeH_2Be bridge in solution, the *cis* form being the more stable at low temperature and having a large entropy change (ΔS = 55(10) J K^{-1} mol^{-1}) associated with the isomerisation.[194] The strength of the BeH_2Be bridge is indicated by reaction with bidentate ligands which do not form mononuclear tetrahedral complexes like R_2Be. Though bipy complexes have not been isolated due to the ease with which Be—H adds across the azomethine bond,[135] complexes of stoichiometry $(RBeH)_2{\cdot}$TMEDA (R = Me,[135] Et,[49] Bu^i,[106] Bu^s, Bu^t, n-C_5H_{11},[49] Me_3CCH_2,[59] Ph,[49,153] *o*-Tol, *m*-Tol[126]) are readily obtained. Complexes (R = Me, Ph) were originally formulated as coordination polymers $\leftarrow(Me_2NC_2H_4NMe_2\rightarrow(Me)BeH_2Be(Me)\leftarrow)_n$ because of their involatility and insolubility in non-polar solvents.[135] However, more recent work has shown that (R = Me, Ph) can be recrystallised from chlorinated hydrocarbon solvents[49] and that the other TMEDA complexes mentioned above and $(RBeH)_2{\cdot}L$ (R = Me, Bu^i; L = *N,N,N′,N′*-tetraethylethylenediamine) are monomeric in benzene solution[49,106,126] so that they should be formulated, at least in solution, with the four- and seven-membered ring structure (**28**). A similar complex $(MeBeH)_2{\cdot}$DME has also been obtained as an oil.[135]



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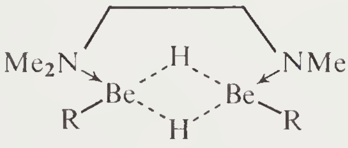


(28)

3.8.3 Reactions of the Be—H bond

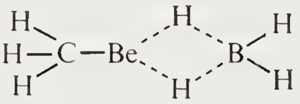
Addition reactions of Be—H to alkenes have been fairly widely studied though mechanistic studies have not been reported and the reduction of functional groups has not been studied in depth to any significant extent. Reduction of iodomethane by MeBeH in the presence of ether only takes place slowly[153] and $(EtBeH{\cdot}NMe_3)_2$ reduces Et_2Hg to mercury (equation 13).[191] Reduction of both C=O and C=N occurs rapidly as exemplified by the reaction of MeBeH with benzylideneaniline and benzaldehyde forming $(PhCH_2(Ph)NBeMe)_2$ and $(PhCH_2OBeMe)_4$, respectively. Benzophenone reacts similarly but produces monomeric complexes $(Ph_2CHOBeMe){\cdot}L$ (L = Et_2O, THF), steric constraints preventing beryllium from expanding its coordination number by association.[153] Slow addition of MeBeH in ether to benzonitrile at low temperature results in $(MeBeN{=}CPh)_4$ but it was not possible to add more than one Be—H to each C≡N moiety.[146,151] More readily isolable products were obtained if the reactions were carried out in the presence of py or Me_3N forming $[(R'CH{=}N)BeR{\cdot}L]_2$[146] (Section 3.4.1.2).

$$2Et_2Hg + (EtBeHNMe_3)_2 \longrightarrow 2Et_2BeNMe_3 + 2Hg + 2C_2H_6 \qquad (13)$$

Addition of Be—H to alkenes occurs readily but addition to alkynes gives a mixture of products.[69] Ethylberyllium hydride reacts rapidly with terminal alkenes in the presence of ether at 80 °C but only slowly with pent-2-ene whereas no reaction was observed with 2-methylbut-2-ene[153] although Bu^iBeH reacts very slowly, $t_{1/2}$ being 50 h at 110 °C.[106] Organoberyllium hydrides therefore react, as does $NaEt_2BeH$, in the presence of ether and, like hydroboration reactions, the metal tends to migrate to the end of the carbon chain. Complex formation with amines does not appear to inhibit completely these reactions since $(EtBeH{\cdot}NMe_3)_2$ also adds to C_2H_4[153] and $(BeH_2{\cdot}NMe_3)_2$ reacts with pent-1-ene to form $(n\text{-}C_5H_{11}BeH{\cdot}NMe_3)_2$, $t_{1/2}$ being 25 h at 33 °C,[49] similar to that for $(Bu^iBeH{\cdot}NMe_3)_2$ and pent-1-ene. The relative rates of reaction of Bu^iBeH, $Bu^iBeH{\cdot}OEt_2$ and $(Bu^iBeH{\cdot}NMe_3)_2$ with pent-1-ene at 33 °C are in the ratio 1:40:110.[106]

3.8.4 Organoberyllium Hydridoboronates

Reaction of Me_2Be and B_2H_6 yields a white solid of empirical formula $MeBeBH_4$ which is dimeric in benzene solution, with the vapour consisting of monomer and dimer species, the latter being the major component. The IR spectrum of the annealed solid agrees with the vapour phase spectrum implying that the solid contains dimer units. Sufficient spectroscopic data are available to conclude that the monomer has a linear C—Be—B skeleton (**29**) and the dimer a double methyl bridge between Be atoms in a linear B—Be—Be—B skeleton (**30**), both monomer and dimer containing double hydrogen bridges between beryllium and boron and also terminal BH_2 groups.[195,196]



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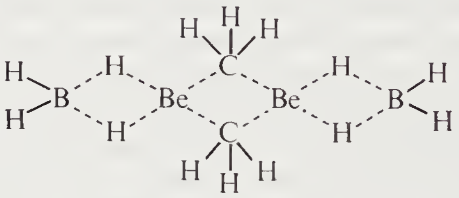

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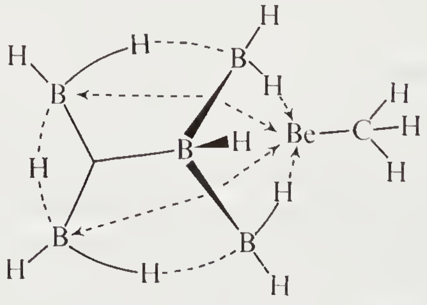
A beryllahexaborane of the *nido* series, $MeBeB_5H_{10}$ is prepared as a volatile liquid from $B_5H_{10}BeBr$ and Me_6Al_2. Like the corresponding η^5-cyclopentadienyl derivative, beryllium occupies a basal position in the pentagonal pyramidal boron cage and the $B_5H_{10}Be$ series is dominated by substitution at the Be atom. The nature of electron-deficient bonding is particularly acute when beryllium is incorporated into a *closo* or *nido* framework of the boranes because Be supplies one less electron than does each B atom.[197-200] The bonding in $MeBeB_5H_{10}$ is schematically represented in (**31**).[199]



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3.9 CYCLOPENTADIENYLBERYLLIUM COMPOUNDS

3.9.1 Dicyclopentadienylberyllium

Dicyclopentadienylberyllium, prepared as colourless, sublimable crystals from $BeCl_2$ and CpNa,[201-203] decomposes above 70 °C to cyclopentadiene.[204] It is unstable in air, reacts violently with water and it has a surprisingly large dipole moment (2.46(6) D in C_6H_6 and 2.24(9) D in C_6H_{12}).[201] Its structure, like that of $Be(BH_4)_2$, has a long and controversial history. In 1964, electron diffraction data of the gaseous species at 70 °C were interpreted in terms of a molecule having C_{5v} symmetry with beryllium situated unsymmetrically between the two parallel, staggered rings on the five-fold rotation axis, the perpendicular Be—ring distances being 1.472(6) and 1.903(8) Å.[205,206] The average lifetime of beryllium ions between the two energy minima was estimated to be of the order of 10^{-12} to 10^{-13} s.[207]

Though early spectroscopic data had supported one σ- and one π-bonded ring,[208,209] subsequent data on the solid and solutions in benzene and cyclohexane were interpreted as indicating that the gas phase structure was retained in the condensed phase.[210] However, the gas phase spectrum was also interpreted in terms of an ionic model,[204] supported by NMR studies,[202] and for the solid, two distinct ring environments were found, with the model $(CpBe)^+Cp^-$ claimed to be consistent with the data.[204] Because these data were neither consistent nor conclusive, the structure of the solid was examined by X-ray diffraction methods at −120 °C[211] because the atoms have large temperature factors at room temperature.[212] The structure is disordered but the two rings are related by a centre to form a slip-sandwich (Figure 3) with the normal distance between the rings being 3.33 Å. Beryllium is 1.53(3) Å from the plane of one ring on the five-fold symmetric axis with all Be—C distances equal (1.94(4) Å) and is therefore considered to be π-bonded. The second ring is essentially parallel to the first and is lying at a perpendicular distance of 1.81(5) Å from beryllium but has slipped *ca.* 1.20 Å sideways with the result that the shortest Be—C distance (Be—C(5′)) is perpendicular to the plane of the ring which is therefore considered to be σ-bonded to beryllium.[211] Beryllium moves freely between these two positions at room temperature[212] but at −120 °C it is frozen in one of these two positions. Because the Be—C(5′) distance is longer than the single Be—Me distance (1.706 Å) in CpBeMe and the angle between the planes of the rings is significantly different from the angle expected if Be is σ-bonded to C(5′),[215] an alternative bonding description considers the structure as a pentahapto–trihapto model in which one of the two π-bonded rings has slipped sideways,[213] and this is supported by Raman spectral data for the solid and liquid[214] and He(I) photoelectron spectroscopy.[27] A recent reinvestigation of the electron diffraction data[215] obtained on the vapour above 100 °C indicates that a slip-sandwich model with a sideways slip of 0.8(1) Å is compatible with the data and this structure is therefore more similar to the crystal structure. Only one single sharp peak is observed in the ^1H NMR spectrum between −100 and 50 °C indicating that the rings rotate relative to each other with the beryllium going back and forth from its two alternative positions at such a frequency that all the hydrogen atoms appear to be equivalent.[212] The ionic radius of Be^{2+} (0.3–0.4 Å)[216] is the smallest of any known metal cation and this is undoubtedly responsible for the less symmetrical structure of Cp_2Be compared to other π-metallocenes so that the metal has a different structural relationship to the two rings to minimise interplanar repulsion. Bonding between beryllium and the nearest Cp ring is effected mainly through molecular orbitals formed by the ring $e_1\pi$ orbitals and the $2p_x$ and $2p_y$ orbitals on beryllium.[16,217] Molecular orbital calculations using semi-empirical and *ab initio* procedures[29–33] indicate that the most stable form of Cp_2Be can be described either by a model of D_{5d} symmetry (like Cp_2Fe) or by one σ- and one π-bonded ring.

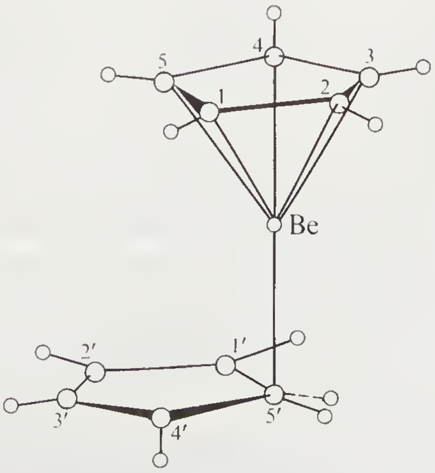

Figure 3 Slip-sandwich structure of Cp_2Be at −120 °C (reproduced with permission)

A 2:1 molecular complex (Figure 4) is formed between Cp_2Be and both benzene and toluene. Though these cannot be isolated, interactions in solution are strong enough to induce paramagnetism, causing large shifts in the aromatic ^1H NMR signals and observed directly by ESR spectroscopy.[202] Reaction of Cp_2Be with $FeCl_2$ produces ferrocene[201] and similar reactions may be used to prepare cyclopentadienyls of the actinoids (Cp_3NpCl, Cp_2BkCl, Cp_3Am, Cp_3Pu).[218–221]

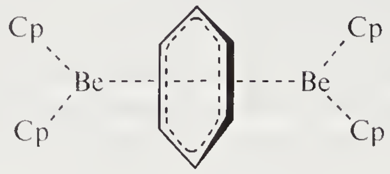

Figure 4 Proposed structure of $(Cp_2Be)_2C_6H_6$ (reproduced with permission)

3.9.2 Miscellaneous Beryllium Cyclopentadienyls

Reactions of Cp_2Be with BeX_2 (X = Me, H, Cl, Br, I) in the absence of solvent and of Cp_2Be with BeX_2 (X = Bu^t, C_6F_5) in benzene produce air sensitive compounds CpBeX which are monomeric in benzene solution.[126,203,222–224] IR studies show that, except for the hydride, there are no structural differences between species present in solution and in the vapour phase.[203] Important structural parameters are available, mainly from electron diffraction studies of gaseous species (Table 5). In all cases, the molecules are monomeric with C_{5v} symmetry, Be and X lying on the five-fold axis of the ring. Structurally the interaction between beryllium and the ring is the same in all cases (pentahapto) and to the closest ring in Cp_2Be.[211] Bonding between Be and X involves one *sp* hybrid orbital on the metal while the other *sp* hybrid interacts with the $a_1\pi$ orbital of the ring. The remaining 2*p* orbitals on beryllium overlap with filled $e_1\pi$ orbitals to form degenerate bonding orbitals. Beryllium is therefore surrounded by an octet of electrons and since these compounds are not electron deficient, there is relatively little tendency for association or complex formation,[225–228] indeed C_6F_5BeCp is obtained from Cp_2Be and $(C_6F_5)_2Be{\cdot}(THF)_2$.[126] The Be—X distances (X = Cl, Br) are longer than those in monomeric BeX_2 where there is probably some shortening due to dative π-bonding, not possible in CpBeX as the *p*-orbitals are already involved in bonding to the ring. This effect is not as marked with the bromide where there is less tendency for π-bonding due to the greater disparity in size of the pertinent *p*-orbitals.[225,226] The vibrational spectra of solid and liquid CpBeCl indicate C_{5v} symmetry but mass spectral data indicate that solid CpBeCl is not monomeric.[227]

Table 5 Structural Parameters (pm) of CpBeX

X	Be—C(Cp)	C—C	Be—X	h^e
$Cl^{a,1}$	191.6(6)	142.4(1)	183.7(6)	148.4(7)
$Br^{a,2}$	195.0(12)	142.4(2)	194.3(15)	152.8(16)
$H^{b,3}$	—	142.3(1)	132(1)	149^d
$Me^{a,4}$	192.3(3)	142.0(1)	170.6(3)	149.7(3)
$C{\equiv}CH^{a,2}$	191.9(5)	142.8(2)	163.4(8)	148.7(5)
$Cp^{c,5}$	194(4) 181(5)	137–145(3)	—	153(5)
$BH_4^{c,6}$	191.5(5)	142.2(1)	275.8(9)	148.4(7)
$B_5H_8^{c,7}$	187.7–189.4(3)	139.1–140.1(3)	—	—

[a] Electron diffraction. [b] Microwave spectroscopy. [c] X-ray diffraction. [d] Assumed.
[e] Normal distance from Be ring.

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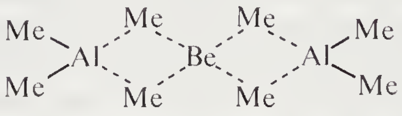
The Cp multiplet fine structure found in the NMR spectrum of CpBePh is consistent with a π-complex structure or with very rapid migration of the PhBe moiety round the C_5H_5 ring. Though ^{13}C–^9Be coupling was not observed for CpBePh, it was for CpBeBr.[229] The microwave spectrum of CpBeH shows the molecule is a symmetric top,[230] also supported by molecular orbital calculations,[32] and leads to a Be—H bond length of 1.32(1) Å,[230] considerably shorter than the bridging distance (1.49(2) Å) in $Na(OEt_2)Et_2BeH$,[190] and a dipole moment of 2.08 D,[230] considerably smaller than that of CpBeCl.[231] In contrast to Cp_2Be,[202] CpBeMe does not complex with aromatic solvents and its IR spectrum has been assigned on the basis of C_{5v} symmetry. The mass spectrum is dominated by a peak corresponding to $CpBe^+$, consistent with strong covalent interaction between metal and ring and the $Be—CH_3$ bond dissociation energy has been determined as 213 kJ mol^{-1} (*cf.* Me_2Be, 192.7 kJ mol^{-1} [94]). First ionisation energies obtained from the photoelectron spectra of CpBeX (X = Me, $C\equiv CH$, $C\equiv CCH_3$, Cl, Br) have been compared with orbital energies obtained from CNDO type calculations. In contrast to Cp_2Be where the split of the first band is 96 kJ mol^{-1},[27] these compounds show a small Jahn–Teller splitting of only 9–19 kJ mol^{-1}, supporting ionisation occurring from a weakly bonding molecular orbital.[26] The Cp ring in $CpBeB_3H_8$ and $CpBeBH_4$ exhibits an unusual electronic effect in that the ^{11}B resonance occurs at unusually low field in the former and unusually high field in the latter.[232] Both are colourless liquids, the former prepared from CpNa and $Be(B_3H_8)_2$ and the latter, the first reported example for which ^9Be–^1H coupling occurs, from CpBeCl and $LiBH_4$. Coupling of Be to B is also observed in $CpBeBH_4$ and though hydrogen exchange takes place within the BH_4 group so that all four hydrogen atoms are equivalent at room temperature, intermolecular exchange of BH_4 groups does not. In the gas phase and in benzene solution, $CpBeBH_4$ is monomeric and its IR spectrum can be rationalised in terms of a pentahapto ring system.[222] Electron diffraction data can be brought into satisfactory agreement with both a double and a triple hydrogen bridged structure between Be and B.[233] However, vibrational spectral data support the double hydrogen bridged structure in all three phases[222] and MNDO calculations show that this is favoured by *ca.* 2 kJ mol^{-1}.[30]

Reaction of CpBeCl and KB_5H_8 produces $CpBeB_5H_8$ as a colourless solid which decomposes in benzene at elevated temperatures and reacts with Brønsted acids forming B_5H_9 and with B_2H_6 on heating to produce mainly $B_{10}H_{14}$. Beryllium resides in a non-vertex bonding position in a *nido* framework between two adjacent basal boron atoms in a square pyramidal arrangement with the Cp moiety tilted up towards the apical hydrogen atom.[234] In contrast CpBe-2-BeB_5H_{10} and the methyl analogue (**31**) have beryllium incorporated at the vertex in a six atom *nido* framework that is structurally and electrically similar to the pentagonal pyramid of B_6H_{10}.[199,235]

3.10 MISCELLANEOUS REACTIONS

Reactions of R_2Be with more than 1 mol of ligand containing an acidic hydrogen atom per beryllium liberate 2 mol of RH[3,35,47,143,149,156,158,160,236–238] but as the products are not organometallic, they are not discussed herein. Alkyl–hydrogen exchange reactions have been used for the preparation of beryllium–hydride compounds. Formation of M_2BeH_4 (M = Li, Na, K, Rb, Cs) is claimed from $MAlR_3H$ or $MAlR_2H_2$ and BeR_2[239] whereas $NaEt_3AlH$ and Et_2Be or EtBeH form products of indefinite composition.[188] Reaction of R_2Be ($R = Bu^n, Bu^i$) with LAH is claimed to yield Li_2BeH_4,[65] though reaction of LAH with Me_2Be in ether yields BeH_2, inseparably contaminated with Li, Al and ether.[109] Beryllium hydride is also obtained from Et_2Be and $Et_4B_2H_2$[240,241] though Me_2Be and B_2H_6 form $Be(BH_4)_2$.[72]

Dimeric amine complexes $(R_3N{\cdot}BeH_2)_2$ are obtained by exchange reactions of R'_2Be and R''_2AlH in tertiary amine solvents.[242–244] Reactions of R_2Be (R = Me, Et) with B_4H_{10} produce a non-volatile liquid, suitable as a mobile liquid Be—B fuel[245,246] and Et_2Be and vinyloxybenzene form a solid polymer, claimed to be a useful rocket propellant.[247] Low temperature NMR studies on the Me_2Be–Me_3Al system can be interpreted in terms of the formation of a complex of empirical formula $Be(AlMe_4)_2$ but only $(Me_2Be)_n$ could actually be isolated. The suggested structure (**32**) is analogous to that found for the corresponding magnesium complex.[248] Electrodeposition from organoberyllium compounds in organic solvents produces 60–96% beryllium.[62,249] Controlled oxidation of ethereal solutions of Me_2Be produces methylberyllium peroxides as intermediate and $Be(OMe)_2$ containing variable amounts (2.6–6.9%) peroxidic oxygen as end product. The mechanism for the oxidation is described by a four-centre transition state with nucleophilic 1,3 rearrangement of the alkyl group and an intermolecular redox reaction.[250] Reaction of beryllium alkyls with 1,2-$B_7C_2H_{13}$ leads to insertion of beryllium and the attached donor solvent into the open face of the (3)-1,2-dicarbollide ion,[197] whereas alkylberyllium etherates with (3)-1,2-$B_9C_2H_{13}$ produce 3-Be(L)-1,2-$B_9C_2H_{11}$ (L = NMe_3, OEt_2), an analogue of $B_{11}CH_{12}^-$ (Figure 5).[198]



(**32**)

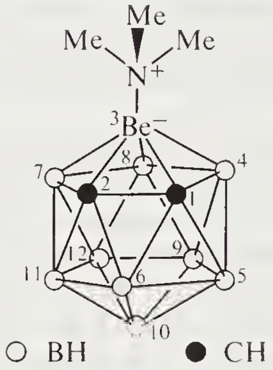


Figure 5 Proposed structure of (3)-$BeN(Me)_3$-1,2-$B_9C_2H_{11}$ (reproduced with permission)

Organoberyllium reagents such as Et_2Be, Ph_2Be and $NaBeEt_3$ are effective as catalysts for the dimerisation and polymerisation of alkenes.[251–255] However, due to the toxicity of beryllium, these are unlikely to be commercially important. The nickel catalysed displacement reaction between optically active organometallic compounds of Be, Zn, B and Al and 1-alkenes only shows small stereospecificity[123] whereas the reaction of bis((*R*)-2-methylbutyl)beryllium with CO_2, followed by hydrolysis to form the acid, is stereospecific with inversion of configuration.[66] In the asymmetric reduction of some alkyl phenyl ketones by the above organoberyllium reagent, the prevalent enantiomer produced is of the (*S*) absolute configuration.[256]

Dimethylberyllium reacts with CO_2 in ether solution to give acetic acid after acid hydrolysis and undergoes several other reactions similar to Grignard reagents: thus it yields, after hydrolysis, Ph_2MeCOH with Ph_2CO, $PhMe_2COH$ with benzoyl chloride and PhNHCOMe with phenyl isocyanate.[53,54] It also adds to azobenzene to give a hydrazine derivative $(PhMeN{-}NPh)_2Be$[257] which has not been completely characterised. Diphenylberyllium reacts with benzophenone forming Ph_3COH on hydrolysis[77] and undergoes 1,4 addition with both PhCH=CHC(O)Ph and $Me_2NC_6H_4CH{=}CHC(O)Ph$;[258] it also reacts in the presence of Ph_3CNa with butadiene, isoprene and styrene forming a mixture of products.[76]

Some reactions of R_2Be with carbonyls, azomethines and nitriles have previously been mentioned (Sections 3.4.1.1, 3.4.1.2, 3.5.1 and 3.5.3) in which the initial compounds formed before hydrolysis were described. Studies with Me_2Be have shown that product development control, a concept used to explain the stereochemistry of many reactions in which the isomer ratio reflects the stability of product, in the alkylation of ketones is not important compared to the steric approach control.[259] With carbonyls, addition, reduction or complex formation occurs. With Ph_2Be and $(Me_3SiCH_2)_2Be$, there is no possibility of reduction due to the absence of hydrogen atoms on the β-carbon atom and only complex formation occurs with Bu^t_2CO but addition of Be—C across the double bond occurs with Ph_2CO whereas Me_2Be adds to Bu^t_2CO. Thus it seems that with bulky groups present, complex formation is preferred to addition. With Et_2Be, Bu^i_2Be and Bu^t_2Be, the larger the alkyl group, the easier is alkene elimination and only in two cases ($Et_2Be + Ph_2CO$ and Bu^t-CHO) did alkylation proceed competitively with reduction, and reduction accounted for 42 and 78% of the overall reaction, respectively. In all other cases, reduction was the only reaction observed.

With azomethines and nitriles, there is less tendency for addition and reduction due to the lower polarity of the carbon–nitrogen bond compared to the carbon–oxygen bond. The dearth of reduction compounds and preponderance of addition compounds found for azomethines and bulky organoberyllium reagents, a situation opposite to that found for reactions with carbonyls, has been explained by steric effects.[3] Both reduction and addition products are formed from Bu^i_2Be and PhCN above 47 °C but below this temperature, addition occurs predominantly, the yields of reduction product increasing as temperature increases and becoming predominant at 67 °C. When an optically active beryllium compound is used, no racemisation has occurred in the addition product after hydrolysis, even though the beryllium compound undergoes thermal racemisation itself under the same conditions.[66,260] A more comprehensive study of reactions of organoberyllium compounds with nitriles is desirable.

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4

Magnesium, Calcium, Strontium and Barium

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Although organometallic compounds of magnesium had been synthesized earlier,[1] the observation in 1900 by Grignard[2] that such derivatives could be readily formed and used as intermediates in organic reactions led to considerable research activity in the field of organomagnesium chemistry. It has been estimated that by 1975 over 40 000 papers concerning this subject had appeared[3] although many of these relate to synthetic applications in organic chemistry (see Chapter 44, Volume 7) and not to fundamental studies of the organomagnesium compounds. In contrast, although the first organocalcium compounds were reported in 1905,[4] to date little more than 300 papers concern aspects of the organometallic chemistry of the heavier alkaline earth metals. The greater understanding of the organic chemistry of magnesium and proven differences in reactivity of the derivatives of this element justify a separate discussion of its organometallic chemistry. For all the metals, there is no convincing evidence for organometallic species with a formal oxidation state other than two, except possibly as transient intermediates in redox processes. Derivatives of basic formulae MR_2 and M(R)X exist (R and X being formally uninegative groups) but these have a tendency to achieve coordinative saturation and to increase the number of electrons in the valence shell so that complexation by donor ligands or association *via* bridging groups occurs (*cf.* Chapter 1).

4.1 MAGNESIUM

4.1.1 Halogenoorganomagnesium Derivatives

The most commonly prepared organomagnesium compounds are the solvated halogen-containing Grignard reagents having the simplest formula Mg(R)X* (X = halogen).[5–7] These are usually synthesized by the now classical technique of direct reaction between metallic magnesium and an organic halide (RX),[2] although there are many cases when alternative methods are more appropriate. Since these reagents are often used directly as intermediates in synthetic organic or organometallic chemistry the preparations of compounds incorporating a wide variety of organic groups R are of particular importance.

4.1.1.1 Preparation

(i) Direct reaction

(*a*) *General procedure.* The direct oxidative addition of organic halide to metallic magnesium to form Mg(R)X is normally carried out in an aprotic, polar solvent, usually diethyl ether or THF. Full details of the standard reaction procedure have been reported in many texts (*e.g.* refs. 5–7) so that only a brief account of the practical points will be made here.

A solution of the halide (RX) is normally added slowly to a stirred suspension of a slight excess of magnesium (as turnings) in the appropriate solvent. The reagents, solvent and apparatus must be dry and moisture and oxygen should be excluded. The utilization of an inert atmosphere of dry, oxygen-free nitrogen or argon is recommended, although in early work moisture and air were excluded only by the agency of drying tubes and the barrier effect of boiling ethereal solvent. The final product must be protected from air unless immediately used in a further reaction and in more sophisticated experiments vacuum techniques can be employed. The reaction generally shows an induction period and may be difficult to initiate, but when established in ethereal solvents it is exothermic and rapid so that care must be taken during the preliminary stage to avoid the addition of too much organic halide before the reaction sets in. After initiation, organic halide is added at a rate necessary to maintain a suitable temperature (often the boiling point of solvent) and the reaction will normally need continuation for a duration after the final addition of organic halide. Less reactive halides may require prolonged heating. Finally the cooled reaction mixture can be separated from excess unreacted metal and the product may be used directly for synthetic applications. Removal of solvent leaves a solvated species from which it is very difficult to eliminate all traces of coordinated ether.

(*b*) *Purity and activation of magnesium.* The magnesium used for these preparations should be of high purity. Grignard himself employed only 99.2–99.4% magnesium but commercial material of >99.8% purity is now readily available and is suitable for most normal preparative reactions. Higher purity, doubly and triply sublimed metal can also be obtained. Some contaminants are not deleterious to reactions and may even be beneficial in activating the metal but others,

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* The formula Mg(R)X will be used throughout this text to represent Grignard reagents in solution when constitutional or structural features of these derivatives are not being discussed.

especially transition metals in some forms, catalyze side reactions giving lower yields of organometallic derivative.[8-11] The presence of such impurities may be more significant in their influence on the course of subsequent chemical reactions of the organomagnesium product, *e.g.* with carbonyl,[12] α,β-unsaturated carbonyl,[13] nitrile[12] or activated alkene[14] compounds. High purity magnesium has been obtained by repeated sublimation or, probably more effectively, by zone refining (less than 10^{-2} p.p.m. impurity has been reported[12]). For accurate kinetic measurements such ultra pure magnesium should be used. An excess of not more than *ca.* 5–10% magnesium is usually used in preparation but it is advisable to remove unreacted metal and associated precipitates before attempting further reactions since these solids can cause by-product formation.[15]

Magnesium in contact with air forms a thin oxide film so that for reaction with organic halide this must be penetrated and this may contribute to the induction period. Some activation of the metal as turnings may be necessary. Finely divided metal affords a greater surface area but being more easily contaminated it must be freshly prepared and offers no advantages with more reactive organic halides.[5] It has been used effectively with less reactive halides[16] and simply stirring the metal under nitrogen for over a day will produce an active, finely divided form of the metal.[17]

A common activation process is chemical reaction of a halogen compound with the magnesium giving an ether soluble magnesium halide and so exposing active metal surface. Physical examination after such an etching process has shown that smooth, polished surfaces are obtained[18] and that the amount of carbon impurities in the surface is reduced.[19] Pretreatment of metal with iodine or addition of a single crystal of iodine to the unstirred metal suspension at the start of the reaction are widely used methods. Alternatively, prior reaction of the metal with small amounts of Br_2, dilute HCl, MeI, EtBr, CH_2BrCH_2Br, $AlBr_3$, preformed Grignard reagent, $Na[AlH_{4-n}(OR)_n]$ or $Si(OEt)_4$, *inter alia*, usually followed by washing with ethereal solvent, has been recommended. Activation by amalgamation, alloying with copper or by addition of transition metal halides has been used but, especially in the presence of the latter additives, side reactions are also likely to be catalyzed.[20,21] Photoactivation of Grignard preparations has also been reported.[22]

Cocondensation of magnesium vapour with a solvent such as THF or hexane at 77 K followed by warming to ambient temperatures gives a slurry of finely divided magnesium which reacts readily with normally inert aryl halides.[23] Using this form of metal it is also possible to carry out reactions with the more reactive halides at low temperatures in THF. A very active form of magnesium has been produced by reduction of magnesium halide with alkali metal in refluxing THF. The most activated magnesium is formed from $MgCl_2$ with excess of potassium metal in the presence of KI (in a 1 : 1 molar ratio with RX).[24] Using this mixture *in situ* many Grignard reactions proceed to high conversion at low temperatures, and reactions also occur with unreactive halides such as *p*-fluorotoluene and 1-chlorobicyclo[2.2.1]heptane. Other methods that have been reported as suitable for producing reactive magnesium metal include reduction of magnesium halide by potassium–graphite (KC_8)[25] or sodium–naphthalene.[26]

(*c*) *Nature of halogen.* The reactivity of a given organic halide RX with magnesium invariably decreases in the order $I > Br > Cl > F$; in fact earlier literature reports the inactivity of fluorides.[5,6] By using magnesium in the presence of a catalytic amount of iodine, or other halide, fluoroalkanes will form compounds Mg(R)F in THF or DME and in some cases high yields are obtainable (R = Me, 95%; Et, 13%; n-C_6H_{13}, 97%) but aryl fluorides fail to react.[27] Using activated magnesium prepared by Rieke's method,[24] aromatic derivatives can be synthesized by direct reaction, *e.g.* Mg(*p*-tol)F (69%), and high yields of alkylfluoromagnesium compounds are also reported.

Although organic iodides are most reactive they generally produce more side products so that for a particular organyl group it is usually advisable to use the chloro or bromo compound in ethereal solvent (except some aromatic iodides and MeI). The 'entrainment method' for preparation of Grignard compound from an inert organic halide, which involves mixing this halide with a more reactive halogenated compound in approximately stoichiometric quantities, is often a useful synthetic procedure. Originally proposed by Grignard himself,[28] simple reactive halides, *e.g.* EtBr and MeI, were employed as 'entrainers' but since the final product contained a mixture of two organometallic compounds it is preferable to use CH_2BrCH_2Br which produces only ethylene and magnesium bromide as side products.[29] The usual procedure for such reactions is to add all the inert organic halide to the magnesium at the start and add 1,2-dibromoethane gradually over a suitable reaction period. The auxiliary halide in these procedures must activate the metal surface by constant renewal during the reaction, but its presence in such a high concentration may also function directly to activate the radical reaction between inert halogen compound and magnesium.

(*d*) *Solvents.* Diethyl ether has been the most used solvent for preparations and if an alternative solvent is required for further reactions it is usually sufficient to effect exchange by distillation, although it is likely that at least traces of ether will remain in the system. Other ethers are suitable[5–7] solvents for preparations and for reactions at higher temperatures di-*n*-propyl ether, di-*n*-butyl ether, diisopentyl ether or anisole may be used, but it should be noted that anisole tends to undergo ether cleavage above 100 °C. Diethers may promote the reaction of magnesium with organic halides and DME is suitable but precipitation of sparingly soluble magnesium halide complexes may occur as is the case with 1,4- and 1,3-dioxane. Diglyme has proved useful for reactions of secondary cyclic bromides[30] and acetals and formals have also been reported as suitable solvents in Grignard preparations.[6]

The more basic cyclic ether THF, introduced by Normant,[31] is now being commonly used. It is ideal for preparation of vinylic Grignard reagents, arylchloromagnesium derivatives and reactions involving more inert organic halides. It is not cleaved by magnesium or Grignard under normal preparative conditions (but see side reactions below). The more polar nature of THF promotes coupling reactions of reactive organic halides with Grignard reagents.[32] Thus, a large excess of organic halide should be avoided. Also, allylic halides tend to form biallylic compounds and alkyl iodides undergo extensive side reactions so that the less basic diethyl ether is a recommended solvent for reactions involving these reagents. Other cyclic ether solvents that have been used include 2-methyltetrahydrofuran, tetrahydropyran (THP) and 4-methyl-1,3-dioxane.[5–7]

Reactions in triethylamine give high yields for primary alkyl chlorides or bromides (80–90%) but lower for branched halides or iodides.[33] The tendency of alkyl halide to form quaternary ammonium salts can be largely avoided but the solubilities of Mg(R)X compounds are only 0.1–0.9M compared to 2–4M in diethyl ether. Other amines have been used as solvent, including *N*,*N*-dimethylaniline, *N*,*N*-dimethylbornylamine and *N*-methylmorpholine.[5–7] The solubilities of preformed Grignard reagents in various tertiary amines have been determined and it is interesting that they are sparingly soluble in pyridine.[34]

The highly polar solvent HMPT has proved very useful in some reactions of organomagnesium compounds[35] but generally this has been added to Mg(R)X preformed in an ethereal solvent. However, direct preparation of simple Grignard reagents in HMPT has been reported to give good yields at 80 °C.[36] Moreover, in a 9:1 mixture of benzene:HMPT reaction occurs at 30 °C and it has also been reported that a DME–HMPT mixture is superior to THF as a solvent for preparation of chlorovinylmagnesium.[37]

Mixtures of hydrocarbons with coordinating solvents such as THF,[38,39] Et_2O,[39,40] DME[39] or NEt_3[41] can be employed normally in Grignard preparations and as little as one molar equivalent of polar solvent need be present.

Direct reaction of magnesium with organic halide in hydrocarbon solvent produces halogen-containing organometallic species which may be considered as unsolvated Grignard reagents.[42] The soluble products do not have the simple empirical formula Mg(R)X but R:X ratios are invariably greater than unity, increase in the order $X = I < Br < Cl$ and may vary with time.[40,42,43] In fact when X = Cl the organometallic product in some cases may be essentially MgR_2.[40,43] Careful attention to detail in the preparation of these products is necessary to minimize side reactions.[42,44] Only primary alkyl and aryl halides give high yields; the solvents employed have been alkanes (C_5–C_{12}) but aromatic hydrocarbons (benzene, toluene, isopropylbenzene, tetrahydronaphthalene) are also suitable; the magnesium should be in substantial excess (>20%) and freshly ground powder (*ca.* 100 μm) has been recommended although turnings will also react. The lower alkylmagnesium derivatives with R = Et, Pr^n are sparingly soluble, even in benzene. Soluble products can be obtained from Bu^nX only when X = Br or I, but higher *n*-alkyl halides generally produce solutions with concentrations >0.02M. Alkoxides of light metals such as Al, Mg and Ca (*e.g.* $Mg[Al(OPr^i)_4]$) promote the Grignard reaction in hydrocarbon solvents.[42] However, these alkoxo compounds do interact with the organomagnesium product and when quantities greater than approximately 10 mol % are present, the resulting properties are markedly altered (see alkoxoorganomagnesium derivatives, Section 4.1.4.1).

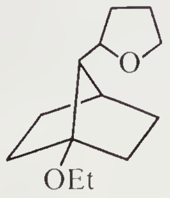
Higher alkyl halides will react with magnesium in the absence of solvent to give amorphous organometallic solids.[45] Also magnesium films react with gaseous alkyl halides at 0 °C to form products which when dissolved in diethyl ether show typical reactivity of Mg(R)X.[46] Cocondensation of magnesium atoms (^1S state) with alkyl halide at 77 K forms a black matrix which on warming up forms colourless orangomagnesium compounds, again unsolvated Grignard reagents.[47] Such organomagnesium compounds have been reported from Pr^nI (76%), Pr^iBr (55%), Bu^tBr (5%), PhCl (58%) and $CH_2{=}CHBr$ (78%) and these react differently to solvated Grignard reagents. It was postulated that at 77 K the black matrix contains a weak complex between magnesium atoms and organic halides.

(*e*) *Side reactions.* The main side reaction often observed during organomagnesium formation is the Wurtz-type coupling of organyl groups (equation 1). This reaction generally becomes more prevalent as the size of a saturated group R increases and when X = I. Allylic and benzylic halides are especially prone to this dimerization. The method of Grignard preparation may have a considerable influence on this coupling and slow addition of halide or, in some cases, a larger excess of magnesium may reduce its occurrence. The dimer R_2 probably results from free radical coupling during Mg(R)X formation (see reaction mechanism below) but it may also arise from a secondary coupling of the first formed organometallic compound (equation 2).[32] This latter reaction is subject to marked catalysis by transition metal compounds, as originally shown by Kharasch,[5] and compounds of Fe(II),[48] Co(II),[49] Ni(II),[50] Pd(II),[50] Cu(I)[48] and Ag(I)[48] are active. The mechanisms of these catalyzed reactions often involve radical intermediates as demonstrated by CIDNP effects in NMR spectra, but organotransition metal intermediates are involved and mechanisms involving oxidative addition and reductive elimination or coupling at the transition metal centre have also been proposed.[48-50] The presence of transition metal impurities in magnesium may promote this side reaction but it has been reported that such metals must be in an oxidized form to be active so that oxidants such as Br_2, I_2 and O_2 in a Grignard preparation may cause increased coupling.[51]

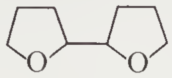
$$2RX + Mg \longrightarrow R_2 + MgX_2 \tag{1}$$

$$Mg(R)X + RX \longrightarrow R_2 + MgX_2 \tag{2}$$

Other products accompanying coupling are usually the radical disproportionation species, alkane (R—H) and alkene R(−H). Their formation is also catalyzed by transition metals including Fe and Cu.[48] An alternative route to the alkane RH is abstraction of an H-atom from the solvent, but in the reaction of 1-halogeno-1-methyl-2,2-diphenylcyclopropane with magnesium carried out in perdeuterated solvents, the alkane was less than 6.7% R—D in $(C_2D_5)_2O$; the total amount of alkane produced was less in d_8-THF but the deuterium incorporation was greater (*ca.* 30%).[52] The fate of solvent radicals produced after H-abstraction has rarely been monitored but in the reaction of 1-ethoxy-7-bromobicyclo[2.2.1]heptane with magnesium in THF, side products (**1**) and (**2**) have been identified, accompanied by alkane and coupled product.[53] In conformity with Bredt's Rule no alkene formation is observed. Alkene R(−H) may also be formed by elimination of hydrogen halide and this is also more prevalent from RX when X = I and when R = tertiary > secondary > primary; hence 2-iodo-2-methylpropane yields 2-methylpropene as the main product.



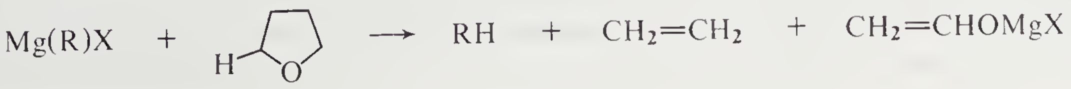
(**1**)



(**2**)

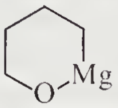
Under normal preparative conditions the ethereal solvents are not readily attacked. Carbonyl-oxygen bond cleavage of THF by Mg(R)X only occurs significantly at elevated temperatures (100–200 °C) and two observed reaction pathways are illustrated by equations (3) and (4).[54,55] It should be noted that activated magnesium formed by Rieke's method[24] does insert into THF to some extent at 65 °C and 1-oxa-2-magnesiocyclohexane (**3**) is produced in 50% yield after 65 h at 100 °C.[56] Non-cyclic ethers also usually require high temperatures for C—O cleavage; thus anisole reacts readily with Mg(R)X at its boiling point (155 °C) and DME is appreciably attacked after 3 h at 95 °C. Allyl aryl ethers themselves react with magnesium to form allylar-

(3)



(4)

yloxomagnesium compounds but it is of interest that during the preparation of Mg(Me)I in allyl phenyl ether a substantial amount of 1-butene is formed. This product shows a second order CIDNP effect in the NMR spectrum indicating that it must be formed by Me· radical addition to the allyl group.[57] Magnesium hydride may also be formed in small amounts in a side reaction which has been shown by deuterium labelling to involve the methylene hydrogen atoms of the diethyl ether solvent.[58] Finely divided metal is more prone to this reaction and a suggested radical mechanism for its formation is given in equation (5).



(3)

$$\mathrm{RBr} \xrightarrow{\mathrm{Mg}} \underset{\text{surface}}{\{\mathrm{R}\cdot\dot{\mathrm{M}}\mathrm{gBr}\}} \xrightarrow{\mathrm{S-H}} \mathrm{RH} + \mathrm{MgHBr} \rightleftharpoons \tfrac{1}{2}\mathrm{MgH_2} + \tfrac{1}{2}\mathrm{MgX_2} \qquad (5)$$

Side reactions involving rearrangement of the organic group during or subsequent to the preparation of the Grignard reagent are discussed in Sections 4.1.1.1(v) and 4.1.1.3(ii).

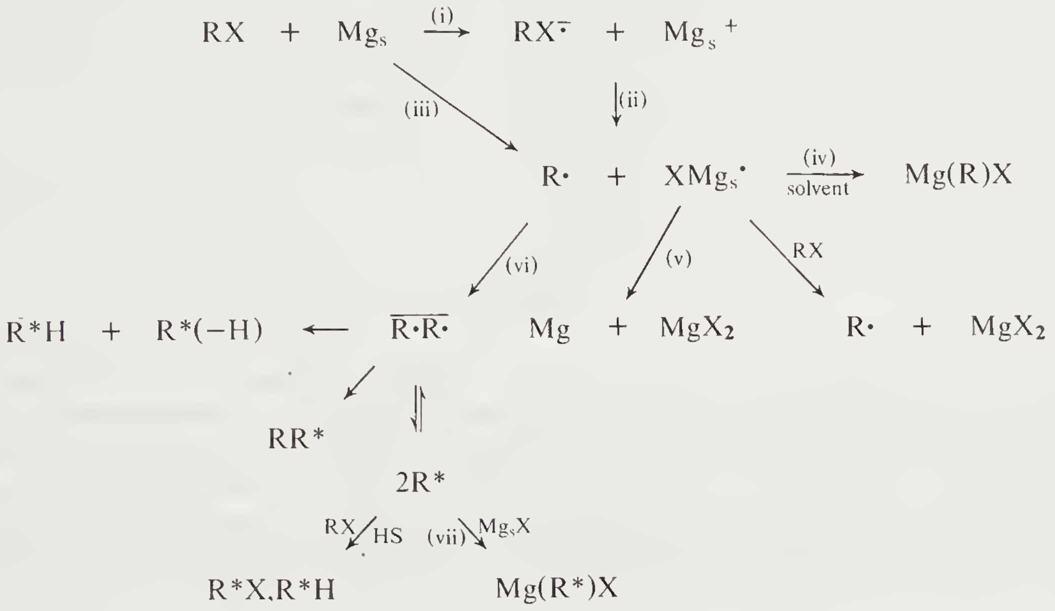
(*f*) *Mechanism of reaction.* The general course of the reaction of magnesium with organic halide and the nature of the side products have for many years been attributed to radical processes.[5] However, it is only relatively recently that analysis of reaction kinetics, examination of the metal surface and spectroscopic studies of intermediates have led to a more detailed, if still incomplete, understanding of the reaction mechanism.

Monitoring the surface of magnesium during the preparative reaction using electron and optical microscopy has shown that initiation is characterized by the formation of isolated corrosion pits, which grow and eventually overlap to form a larger reacting area.[18] Initiation occurs more rapidly at dislocations in comparison to unstrained, intragranular magnesium surfaces. The major part of the reaction, however, takes place at a smooth polished surface and the rate of reaction with organic halide is relatively insensitive to the magnesium lattice plane exposed, to dislocation densities and to grain boundaries.

It is conceivable that species MgR_2 could be formed concurrently or prior to halogeno compounds Mg(R)X. NMR studies of the formation of two products Mg(R)X ($R = C_6F_5$, X = Br and $R = Bu^t$, X = Cl) in THF, both of which are known to disproportionate slowly, proved that the initial organometallic product is the mixed derivative, Mg(R)X. The diorganylmagnesium subsequently forms *via* the Schlenk equilibrium (equation 6).[59]

$$\mathrm{RX} \xrightarrow[\mathrm{THF}]{\mathrm{Mg}} \mathrm{Mg(R)X} \rightleftharpoons \tfrac{1}{2}\mathrm{MgR_2} + \tfrac{1}{2}\mathrm{MgX_2} \qquad (6)$$

Kinetic studies indicate that the metallation reaction shows first order dependence on organic halide concentration and is directly proportional to the surface area of magnesium.[60,61] It has also been claimed that the rate is first order in ethereal solvent concentration.[61] It must be concluded from these results that the rate determining step involves reaction at the metal–solution interface. However, organic iodides and many secondary alkyl bromides react at mass transport and/or diffusion controlled rates in diethyl ether and other ethereal or mixed solvents. For cyclopentyl bromide, the rate of disappearance of bromide shows a dependence $-d[\mathrm{RBr}]/dt \propto [\mathrm{RBr}]A_{\mathrm{Mg}}\omega\eta^{-1}$ (A_{Mg} = surface area of magnesium, ω = stirring rate, η = solution viscosity) and $E_a = 9.6\ \mathrm{kJ\ mol^{-1}}$ in diethyl ether. Transport control is consistent with the absence of a $^{12}C/^{13}C$ kinetic isotope effect in this reaction of MeI with magnesium although, if true, will invalidate the distinction made between outer sphere electron transfer and C—I bond cleavage mechanisms for the rate determining step of this reaction.[62] The reactions of less reactive alkyl bromides (*e.g.* neopentyl, cyclopropyl and cyclobutyl), most alkyl chlorides and aryl bromides in less polar solvents are slower than the transport limited rate and are reagent and medium dependent. Comparison of rate-structure profiles for reactions involving magnesium and alkyl chlorides with those for reductive cleavage reactions of C—X bonds by other homogeneous reagents supports a reaction which is not complicated by adsorption or other heterogeneous phenomena at the metal surface. These studies also suggest that the C—X bond is significantly broken in the transition state. Analysis of reactions involving aryl bromides appears to limit the rate determining step to three possibilities: (a) electron transfer from metal to ArBr (step (i), Scheme 1); (b) aryl radical formation by bromine abstraction (step (iii), Scheme 1) or (c) less probably, concerted insertion of Mg into the C—Br bond.[60] Similar considerations for alkyl halides support the radical mechanisms (a) or (b), rule out carbocation, carbanion or S_N2 processes and suggest an insertion reaction to be unlikely.[60] The formation of an intermediate, free magnesium(I) species does not occur before the rate determining step but cannot be excluded in further or side reactions.



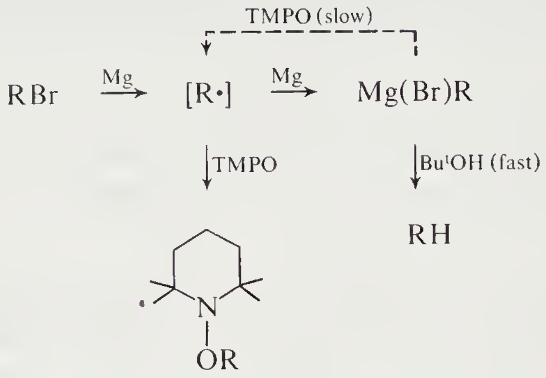
(* - nuclear polarization, s - surface bound species, HS = solvent)

Scheme 1

In the light of the proposed electron transfer process the existence of σ^* radical anions $RX^{\cdot -}$ has been investigated. Reduction of alkyl halides by aromatic radical anions is consistent with a rate determining formation of such intermediates but in some cases cleavage of C—X bonds may occur simultaneously.[63] The electronegatively substituted species $(CF_3)_3CI^{\cdot -}$ has been observed[64] but in the solid state, non-fluorinated species exist as weak charge transfer adducts $\{R\cdot\cdot X^-\}$ and it has been argued that generally $RX^{\cdot -}$ radicals will not be stable but will form planar R· species.[65] Thus a distinction between step (i) followed by (ii) and the alternative step (iii) in Scheme 1 may not be realistic. The concerted insertion mechanism is inconsistent with radical intermediates and can generally be only a partial reaction pathway. A study involving IR and ESR spectroscopy and final product analysis has been reported for the solvent-free reactions of magnesium atoms codeposited with various organic halides at 77 K, followed by controlled heating of the matrix.[66] This supports the formation of R· radicals and also a paramagnetic species which is probably $\{RX^{\cdot -}, Mg^+\}$, the latter especially in the case of chlorobenzene. The formation of Mg—C bonds occurs on warming and is dependent on the phase state of the frozen matrix.[66] It is of interest that IR matrix isolation studies of reaction products between Mg atoms and MeX (X = Cl, Br, I) in argon between 15–45 K have been interpreted as being consistent with the occurrence of insertion of magnesium into the C—X bond at these low temperatures, but no strong IR active Mg—C or Mg—X bonds were observed.[67]

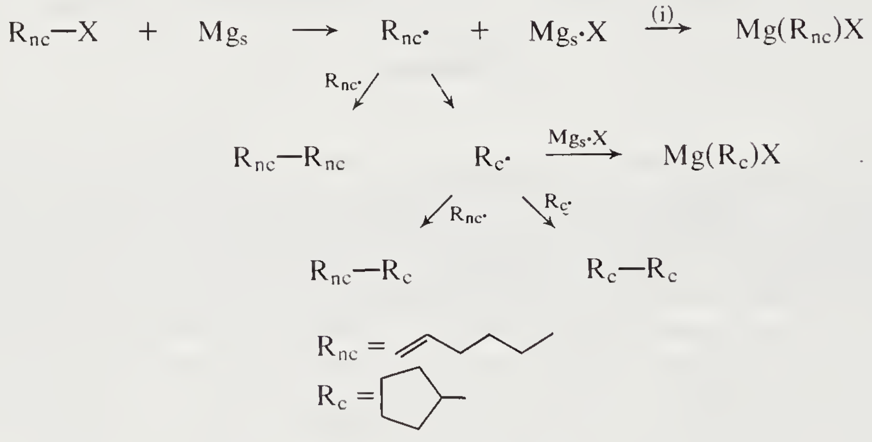
Direct evidence for radical intermediates in the reactions of various alkyl halides in several solvents is provided by the observation of CIDNP phenomena in the NMR spectra of the resulting Mg(R)X and also in the associated by-products.[68,69] The multiplet E/A polarization patterns observed prove that radical pairs of the type $\overline{R\cdot\cdot R}$ are responsible for these effects and not the pair $\overline{R\cdot\cdot MgX}$ so that the complex reactions of Scheme 1 have been proposed. The alternative explanation that the CIDNP effects arise from a metal–halogen exchange reaction following Mg(R)X formation appears to have been ruled out.[69,70] This evidence proves that Mg(R)X is formed in part from $\overline{R\cdot\cdot R}$ precursors but the alternative route, step (iv), producing a non-polarized product is probably the major pathway.

Reaction of bromocyclopentane with magnesium in the presence of a free radical trap, 2,2,6,6-tetramethylpiperidine nitroxyl (TMPO·) results in the cyclopentyl radical R· being trapped as the oxygen bonded species TMPOR. To eliminate the direct formation of this adduct by reaction of Mg(R)X itself with TMPO·, *t*-butanol was added to the system to remove the organometallic component. Assuming that this addition does not influence the reaction mechanism, it may be concluded from the high yield of TMPOR that more than 80% of the reaction proceeds *via* R· radicals (Scheme 2).[71]



Scheme 2

Evidence concerning the relative lifetimes of R· in different solvents has been obtained for the reaction of 6-bromohexene with magnesium. The hexenyl radical (R_{nc}·) formed initially can cyclize to cyclopentylmethyl species (R_c· with rate constant $k = 10^5\ s^{-1}$. Mixed products are shown in the simplified mechanism of Scheme 3 (*N.B.* CIDNP effects are also observed). In more basic solvents, cyclization is less and this may be attributed to efficient solvation of $\dot{\mathrm{Mg}}$X and Mg(R)X species favouring reaction step (i). Retardation of step (i), as by dilution of THF solvent with benzene, promotes the formation of radical pairs and coupling products.[72]



Scheme 3

Several observations support the theory that the radical reactions following the rate determining step take place largely at, or close to, the metal surfaces rather than in bulk solution. During the reaction of 1-bromoadamantane with magnesium, a black layer of thickness up to 7 μm is deposited on the metal surface. X-ray photoelectron spectroscopic studies of C(1*s*), Mg(2*s*) and Br(3*d*) electrons, combined with ion bombardment, have determined the composition of this layer.[19] Except in the outer region of thickness *ca.* 500 Å which contains $MgBr_2$, the principal components of the layer are 1,1′-biadamantane and magnesium metal. Thus, it was suggested that highly reactive Mg(0), formed by disproportionation of the intermediate $\dot{\mathrm{Mg}}$Br (step (v), Scheme 1), is trapped by the coupled by-product and this process must occur at the surface.[19] Also, the small percentage of deuterated hydrocarbon R—D by-product formed from 1-halogeno-1-methyl-2,2-diphenylpropane in perdeuterated diethyl ether solvent and the partial retention of chirality in the resulting Grignard reagent when optically active organic halide is employed (Cl > Br > I) support a reaction at the metal surface.[52] On the other hand, the fact that in at least one case radicals can be trapped efficiently by 2,2,4,4-tetramethylpiperidine nitroxyl in solution suggests that this intermediate species must have a reactivity comparable to that of a free radical in solution.

(*ii*) *Exchange reactions*

(*a*) *Metal–hydrogen exchange.* The metallation of an organic compound by a preformed Grignard reagent (equation 7) occurs for compounds RH which possess a sufficiently acidic hydrogen atom with a pK_a approximately $\leqslant 25$.[5-7] Iotsich[73] first obtained the alkynyl derivatives RC≡CMgX using this method. Acetylene itself will form mono- and di-metallated species HC≡CMgX and XMgC≡CMgX, although the former undergoes some disproportionation in most media and it has been claimed that the best yield is obtained by adding bromoethylmagnesium to a saturated solution of acetylene in THF.[74] Kinetic studies of the metallation of 1-alkynes by Grignard reagents have shown some complex features; the order of reaction varies with solvent,[75] and this must be attributed partly to the different ratios of organometallic entities present in these solutions. Increasing polarity of ethereal solvent has been stated to enhance reactivity[76] and the reaction occurs readily in HMPT,[35] but in another study the rate of metallation of 1-hexyne by bromoethylmagnesium decreased with solvents in the order $Pr^i_2O > Bu^n_2O > Et_2O >$ THF > 2-Me-THF.[77] More recent studies on metallation of acetylene indicate that addition of triethylamine to ethereal solvents increases the rate of reaction but, in the absence of excess amine, $MgBr_2$ retards reaction.[78] In general these results confirm that increasing nucleophilicity of the organic group R′ promotes reactivity but this is complicated by equilibria and association involving organometallic species in solution (see also Section 4.1.1.3(iii)).

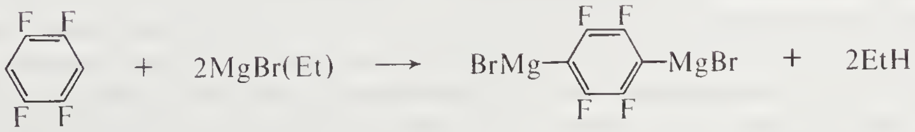
$$RH + Mg(R')X \longrightarrow Mg(R)X + R'H \tag{7}$$

The relatively acidic hydrocarbons cyclopentadiene, indene, fluorene and their derivatives are also metallated but the reactions are slow in diethyl ether and the use of hydrocarbon solvents at higher temperatures has been recommended, *e.g.* C_5H_6 (45–50 °C), C_9H_8 (100 °C) and $C_{13}H_{10}$ (140 °C). Few other simple hydrocarbons are metallated efficiently in ethereal solvents but in HMPT or HMPT–THF mixtures, reaction is promoted.[35] Electrochemical measurements confirm than an increase occurs in the basicity of Mg(R)X compounds when coordinated by up to two moles of HMPT.[79] Thus, in HMPT, the hydrocarbons cyclopentadiene, indene, fluorene and also 9,10-dihydroanthracene and 1,3-diphenylpropene are metallated at temperatures <40 °C by $Mg(Cl)Pr^i$. Triphenylmethane (90 °C) and diphenylmethane (100 ° C) also react.

Electronegative halogenated groups increase the acidity of C—H bonds so that metallation of polyhalogenated organic compounds may occur. However, a competing metal–halogen exchange reaction may also take place. The haloforms CHX_3 (X = Cl, Br) more readily exchange halogen in THF solution but in THF–HMPT (4:1) reactions of equation (8) occur.[80] Metallation is a useful synthetic route to halogeno aromatic magnesium compounds; pentafluorobenzene reacts in THF and 1,2,4,5-tetrafluorobenzene gives a bimetallic derivative (equation 9).[81] Aromatic chloro compounds such as 1,3,5-trichlorobenzene are metallated and it should be noted that in this example direct reaction with magnesium metal initially produces chloro(3,5-dichlorophenyl)magnesium which in turn may react with the original chloride.[82] Similar cross metallation has been observed with trichlorothiophene.[83]

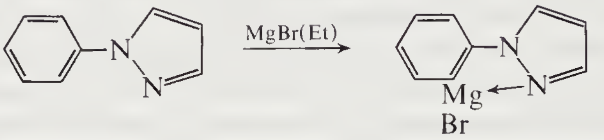
$$CHX_3 + Mg(Pr^i)Cl \xrightarrow{\text{THF/HMPT}} Mg(CX_3)Cl + Pr^iH \tag{8}$$

$$\begin{array}{l} X = Cl, -78\ °C \\ X = Br, -95\ °C \end{array}$$

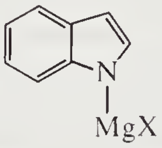


(9)

Aryl ethers such as anisole and phenetole, and also dimethylaniline, can undergo *ortho* hydrogen exchange (3–25%) when heated with Grignard reagents.[5-7] Metallation of the methyl group of α-picoline also occurs. It appears that coordination to the proximal O or N atoms assists such metallations and a related reaction is illustrated by equation (10).[84] Heterocyclic aromatic compounds with active hydrogen atoms react readily with Grignard reagents and the halogenomagnesio derivatives of pyrrole, indole, carbazole and related systems can be prepared. These nitrogen-containing species are useful synthetic intermediates and often undergo further reaction at carbon atoms of the aromatic ring but structurally, in the ground state, they contain N—Mg bonds as in (**4**) so they are not truly organometallic compounds.[85] Grignard compounds of *N*-alkylimidazoles and benzothiazoles have similarly been formed.[86]



(10)

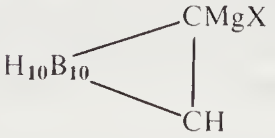


(**4**)

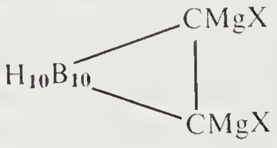
Although Grignard reagents tend to react with compounds containing carbonyl groups by addition processes, there are many cases when α-hydrogen metallation occurs to form enolates and with ketones the solvent HMPT promotes this enolization.[87a] These species are primarily oxygen-bonded derivatives so will not be discussed here.[87b] Ivanov has developed the chemistry of bimetallic species obtained by metallation of substituted acetic acids (equation 11).[88] These Ivanov reagents are also predominantly in the oxygen-bonded enolate form (**5**). Numerous examples of enolates, prepared by hydrogen exchange, have been reported from esters, acids, amides, ketones and cyclic systems including sydnones.[5–7,89] Similar α-metallation reactions occur with sulphonic acids, sulphones and sulphoxides and with phosphonyl and phosphinyl compounds.[5–7,90] The Grignard reagents (**6**) and (**7**) formed by metallation of 1,2-dicarba-*closo*-dodecacarborane and related carboranes should also be noted.[91]

$$\mathrm{RCH_2CO_2H} \xrightarrow{\mathrm{Mg(Pr^i)Cl}} \mathrm{RCH(MgCl)CO_2MgCl} \rightleftharpoons \mathrm{RCH{=}C(OMgCl)_2} \qquad (11)$$

(R = alkyl, aryl, alkynyl, allenyl, cyano) (**5**)



(**6**)



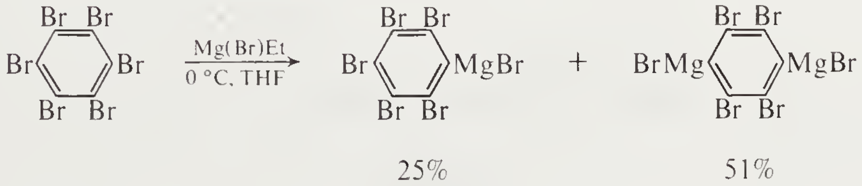
(**7**)

(*b*) *Metal–halogen exchange.* Although exchange of halogen for metal between organolithium reagents and organic halide has been a standard method for preparation of a range of new organolithium compounds, the related reaction for magnesium (equation 12) found relatively little application in early research work. The exchange is complicated by the possible concurrent occurrence of Wurtz-type coupling and the fact that, being an equilibrium process, complete conversion to product may not be achieved.[32,76,92] It has been found to be a useful process for exchange with organic halides bearing electronegative groups, including polyhalogenated and aromatic heterocyclic compounds.

$$\mathrm{RX} + \mathrm{Mg(R')X'} \longrightarrow \mathrm{Mg(R)X'} + \mathrm{R'X} \qquad (12)$$

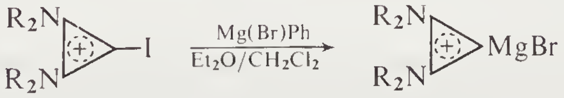
Various halogenomethyl Grignard compounds of general formula $Mg(CH_{3-n}X_n)Cl$ (X = Cl, Br, I; $n = 1$–3) which decompose in the temperature range −75 to −45 °C can be prepared from the appropriate halogenomethane at temperatures 20 °C below the decomposition point using chloroisopropylmagnesium in THF or a 50:50 THF–diethyl ether mixture.[80] The products are insoluble in the medium and this precipitation probably enhances the high equilibrium yields of up to 80%. It is claimed that the more basic secondary Grignard reagent $Mg(Pr^i)Cl$ is more satisfactory than a primary reagent for this exchange. The organometallic species $Mg\{CX_2(MMe_3)\}Cl$ (M = Si, X = Br; M = Sn, X = Br, I) have been made by similar exchange reactions[93] but it is interesting that $Mg(CF_3)Cl$ and $Mg(CHF_2)Cl$ have not been prepared by this method. Higher perfluoroalkylmagnesium compounds $Mg(C_nF_{2n+1})X$ ($n \geqslant 2$) have been formed from the corresponding halides R_fX in various ethereal solvents at low temperatures and the ease of preparation reflects the C—X bond strength, I > Br > Cl, so that chlorides are ineffective but virtually quantitative yields are obtained from iodides.[94,95,96] The preparations by exchange of α,ω-dihalogenomagnesioperfluoroalkanes[95] and of vinyl compounds $R_fCF{=}CF(MgX)$[97] have been described.

Perfluoroaryl Grignard reagents are obtainable from rapid, high yield exchange between $Mg(Et)X$ and C_6F_5X' (X′ = Cl, Br, I) or p-$C_6F_4Br_2$. Hexafluorobenzene itself exchanges with $Mg(Et)Br$ in the presence of $CoCl_2$.[81,98] Similarly C_6Cl_6[98] and C_6Br_6[99] undergo exchange and with excess metallating agent, the *para* dimagnesium compound (accompanied by a little *meta* derivative) can be obtained (equation 13).



(13)

2-, 3- or 4-Halogenomagnesiopyridine may be prepared in high yield by metal–halogen exchange with $Mg(Ph)X$ (X = Br, I) in THF or diethyl ether since the heterocyclic organometallic products are insoluble.[100] A study of the rates of exchange between $Mg(Pr^i)Cl$ and bromopyridines, bromothiophenes, bromofurans or bromoselenophene shows that the reaction follows a second order rate law and that the reaction is faster for bromopyridine than for bromothiophene derivatives.[101] Since highly electronegative substituents facilitate halogen–metal exchange it is not surprising that an iodocyclopropenium ion reacts as in equation (14).[102]



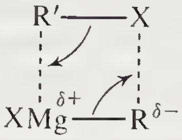
(14)

A special type of organomagnesium reagent comprises the α-halogenoenolates which have found use in synthetic organic reactions but may contain Mg—O rather than Mg—C bonds.[103] These species may be formed by the general exchange process of equation (15).

$$CA(B)Cl_2 \xrightarrow[-78\ ^\circ C/THF]{Mg(Pr^i)Cl} Mg\{CA(B)Cl\}Cl \tag{15}$$

$$(A = Cl, CO_2R;\ B = CO_2R', COR')$$

Exchange between simple alkyl and aryl groups does take place but Wurtz coupling is often significant. In resulting equilibrium mixtures, the aryl magnesium is favoured over the alkyl species but the rate of reaction may be slow. The rate of reaction increases with the solvating properties of the solvent ($Et_2O < EtOCH_2CH_2OEt < MeOCH_2CH_2OEt <$ diglyme < THF < DME) and also with the polarization of halogen (or decreasing C—X bond strength): C—Cl < C—Br < C—I.[92] These observations and the fact that highly electronegative organic groups promote the reaction suggest a heterolytic mechanism involving nucleophilic attack at halogen, electrophilic attack at carbon or alternatively a combined attack *via* a four centre mechanism (**8**). However, Fe(II) catalyzes exchange between $Mg(Br)Pr^i$ and Bu^nBr and the product $Mg(Br)Bu^n$ exhibits CIDNP E/A polarization in the NMR spectrum so that at least some exchange takes place by a radical mechanism involving radical pairs. The mechanism of Scheme 4 has been proposed.[70a] In the non-transition metal catalyzed system involving alkyl groups only iodides RI showed significant exchange, but weak CIDNP signals were observed[70b] and CIDNP effects in exchange between benzylic halides and bromoethylmagnesium in THF/d_6-benzene also gave evidence for a pathway involving radical pairs.[69] Thus, the mechanism of metal–halogen exchange is not clear; it is likely that both heterolytic and radical pathways (involving either caged species or chains) may occur.[32] The predominant pathway is probably dependent on reactants, solvent, catalyst and conditions.



(8)

$$\mathrm{RX} \xrightarrow[\mathrm{Fe(II)}]{\mathrm{Mg(R')X}} \mathrm{R\cdot}$$

$$\mathrm{R\cdot} \quad + \quad \mathrm{R\cdot} \xrightarrow[\text{encounters}]{\text{diffusive}} \overline{\mathrm{R\cdot R\cdot}}$$

$$\overline{\mathrm{R\cdot R\cdot}} \longrightarrow \mathrm{R^*H,\ RR^*,\ R^*(-H)}$$

$$\overline{\mathrm{R\cdot R\cdot}} \xrightarrow{\mathrm{Mg(R')X}} \mathrm{Mg(R^*)X} \quad + \quad \mathrm{R'\cdot}$$

Scheme 4

(*c*) *Miscellaneous exchange reactions.* In spite of earlier misleading isotopic exchange experiments it has been established that an equimolar mixture of the diorganylmagnesium and the anhydrous magnesium halide in an ethereal solvent undergoes exchange to form a product with the same constitution and reactivity as the corresponding Grignard reagent.[104] Hence, it is possible to use this exchange, *via* the Schlenk equilibrium, as a synthetic route (equation 16). However, this does not occur when X = F.

$$\mathrm{MgR_2} \quad + \quad \mathrm{MgX_2} \rightleftharpoons \mathrm{2Mg(R)X} \tag{16}$$

Reaction of an organolithium compound with one equivalent of magnesium halide, $MgBr_2$ or MgI_2, may be a useful route to Grignard reagents that are difficult to prepare directly (equation 17). The reaction occurs with retention of stereochemistry and the chiral Grignard reagent (*S*)-bromo(1-methyl-2,2-diphenylcyclopropyl)magnesium has been obtained by exchange from the corresponding lithium derivative.[105] Similarly iodo(triptycyl)magnesium has been prepared from MgI_2.[106] Other organoalkali metal derivatives may be employed; thus benzylhydrylpotassium and also 1,1′-disodioferrocene have provided the corresponding bromomagnesio derivatives by exchange with $MgBr_2$.[6,7]

$$\mathrm{LiR} \quad + \quad \mathrm{MgX_2} \longrightarrow \mathrm{Mg(R)X} \quad + \quad \mathrm{LiX} \tag{17}$$

Exchange between organic derivatives of less electropositive metals or metalloids and either magnesium metal in the presence of halide or a preformed Grignard reagent can also be employed in certain preparations. Some interesting synthetic applications are illustrated in equations (18),[107] (19)[108] and (20).[109] Exchange with silyl groups has proved useful for preparation of perfluoroorganomagnesium compounds[94] (equations 21 and 22). Another special case involving exchange of a sulphur leaving group is shown in equation (23).[110]

$$\mathrm{CH_2{=}C{=}CH_2} \xrightarrow{\mathrm{i,\ ii,\ iii,\ iv}} \mathrm{RHg(CH_2)_3HgR} \xrightarrow[\mathrm{THF}]{\mathrm{Mg/MgBr_2}} \mathrm{BrMg(CH_2)_3MgBr} \tag{18}$$

i, B_2H_6; ii, $Hg(OAc)_2$; iii, NaCl; iv, LiR

$$\mathrm{SiMe_3(CHBr_2)} \xrightarrow{\mathrm{Zn/Cu}} \mathrm{Me_3SiCH(ZnBr)_2} \xrightarrow{\mathrm{Mg}} \mathrm{Me_3SiCH(MgBr)_2} \qquad (19)$$

$$\mathrm{BR_3} + \mathrm{2BrMg(CH_2)_5MgBr} \longrightarrow \mathrm{3Mg(Br)R} + \mathrm{MgBr[(CH_2)_5\,B\,(CH_2)_5]} \qquad (20)$$

$$\mathrm{Me_{3-\mathit{n}}H_\mathit{n}Si(CF_2)_6SiH_\mathit{n}Me_{3-\mathit{n}}} + \mathrm{2Mg(Br)Et} \xrightarrow[(n\,=\,0,\,1)]{}$$

$$\mathrm{BrMg(CF_2)_6MgBr} + \mathrm{2SiH_\mathit{n}Et(Me)_{3-\mathit{n}}} \qquad (21)$$

$$\mathrm{SiH(C_6F_5)_2Me} + \mathrm{2Mg(Br)Et} \longrightarrow \mathrm{2MgBr(C_6F_5)} + \mathrm{SiHEt_2Me} \qquad (22)$$

$$\mathrm{RC{\equiv}CSOR'} + \mathrm{Mg(R'')X} \longrightarrow \mathrm{RC{\equiv}CMgX} + \mathrm{R'SOR''} \qquad (23)$$

Exchange methods have also proved very useful in preparation of alkyl- and aryl-fluoromagnesium compounds using fluoro compounds of less electropositive elements. In particular, $[\mathrm{BF_3{\cdot}OEt_2}]$, $\mathrm{SiF_4}$ and $\mathrm{SnBu_3F}$ give high yields of magnesium products, but other fluorides also undergo exchanges related to that of equation (24).[111] In this example the triorganylboron by-product can readily be removed from the solid Grignard derivative by washing with hexane.

$$\mathrm{3MgR_2} + \mathrm{Bf_3{\cdot}OEt_2} \xrightarrow[(\mathrm{R\,=\,alkyl,\,aryl})]{\mathrm{THF}} \mathrm{3Mg(R)F} + \mathrm{BR_3} \qquad (24)$$

(*iii*) *Reactions with unsaturated bonds*

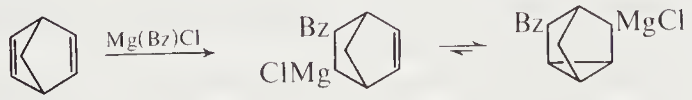
Reactions of preformed Grignard reagents with unsaturated bonds are usually employed as steps in organic syntheses and not as preparative routes to new Grignard reagents. In many cases the products do not contain Mg—C bonds but in others intermediate organometallic compounds are formed and such reactions are discussed briefly in this section.

(*a*) *Alkenes.* In general Grignard reagents are relatively unreactive towards alkenic bonds and in the early literature the only recorded examples of addition reactions were with activated alkenes in highly conjugated systems such as 9,9′-difluorenylidene or 1,2,3,4-tetraphenylfulvene.[6] More recently it has been established that at elevated temperatures and, in the case of volatile alkenes, at moderate pressures, alkyl, benzyl and especially allylic Grignard reagents will add to simple terminal alkenes, dienes and cyclic alkenes.[112]

Primary alkyl- and aryl-halogenomagnesium compounds are unreactive with ethylene in the absence of catalysts or extreme conditions but *s*- and *t*-alkyl derivatives show increasing reactivity. With 1-octene, metal addition to C-1 or C-2 positions can occur but $\mathrm{Mg(Bu^t)Cl}$ and $\mathrm{Mg(Pr^i)Cl}$ predominantly undergo metal to C-2 addition (equation 25).[113]

$$\mathrm{C_6H_{13}CH{=}CH_2} + \mathrm{Mg(R)X} \xrightarrow[(\mathrm{R\,=\,Bu^t,\,Pr^i})]{} \mathrm{C_6H_{13}CH(MgBr)CH_2R} \qquad (25)$$

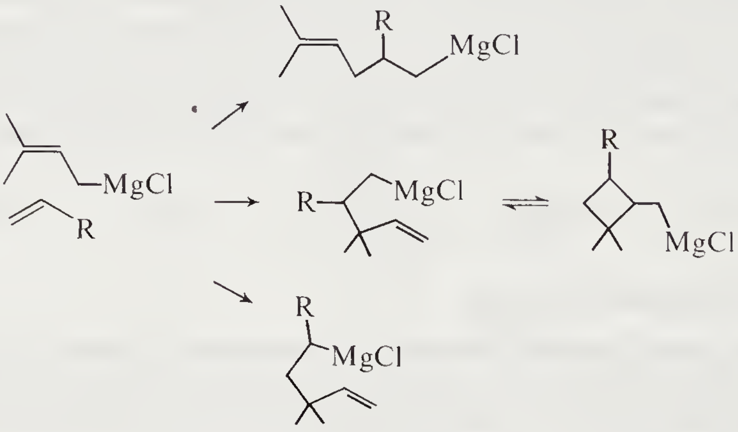
Benzylchloromagnesium, as an etherate, in apolar media at 60–130 °C also forms a 1 : 1 adduct with ethylene, 1-alkenes and bicyclo[2.2.1]hept-2-ene (norbornene). With norbornadiene intramolecular addition to the second double bond gives the nortricyclyl derivative (**9**) as the main product (equation 26).[114]



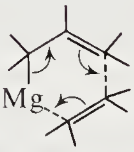
(26)

(**9**)

2-Alkenylhalogenomagnesium species react most readily with non-activated double bonds. Additions to ethylene, 1-alkenes, styrene and norbornene have been investigated.[112,115] A complicating factor is the presence of the unsaturated allyl group which may undergo further intramolecular addition reactions to form cyclobutyl derivatives, *etc.* (see Section 4.1.1.3,ii). In the primary addition process the allylic group may couple with the alkene *via* its C-1 or C-3 positions and with 1-octene the amount of C-3 coupling decreases with increasing temperature and increasing steric hindrance in the allylic group. Furthermore the metal may add to C-1 or C-2 positions of the alkene and a mixture of products can be obtained, *e.g.* Scheme 5. Kinetic investigations of these reactions show first order dependence on organomagnesium compound and on alkene.[116a] Alkene reactivity increases in the order 1-octene < styrene < norbornene and the chloro Grignard reagent is more reactive than the corresponding bromo species. Increased solvation decreases the rate of reaction, Et_2O > THF, and these kinetic analyses, including negative entropies of activation ($\Delta S^{\ddagger} = -75$ to -100 J mol^{-1} K^{-1}), support a non-ionic, non-radical mechanism. A cyclic transition state such as (**10**) has been proposed, probably involving prior complex formation between alkene and magnesium.[116] Addition to styrene is found to be reversible; initially 2-alkenylhalogenomagnesium gives a mixture of products containing metal to C-1 and C-2 bonds, but at 85 °C isomerization to the more thermodynamically stable (1.7 kJ mol^{-1}) benzylic organometallic compound occurs *via* cleavage and readdition of the primary alkylchloromagnesium derivative.[117] In the reaction of perfluorohexylethylene with 2-butenylchloromagnesium, exclusive addition of the metal to the substituted alkene carbon atom occurs but this is followed by MgClF elimination.[118]



(Cut fg023) **Scheme 5**

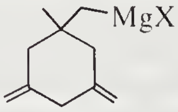


(Cut fg024) (**10**)

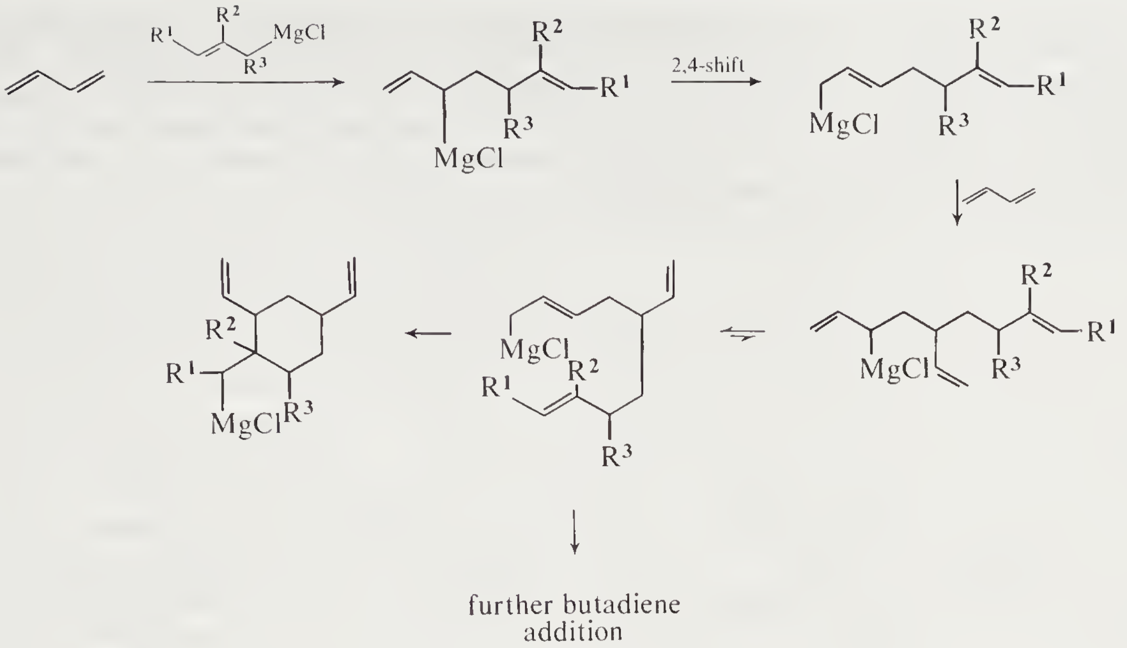
Addition of Grignard reagents to cyclopropenes has also been demonstrated and *cis* addition predominates.[119] Species of the type Mg(R)X (R = Me, Ph, 1-, 2-, 3- or 4-alkenyl) have been shown to react but subsequent addition to form dimeric and higher products may occur. It has also been briefly noted that MgHX will add to alkenes and alkynes and this may prove an alternative preparative route to Grignard reagents.[120]

The proximity of a hydroxyl group activates an alkene bond to addition of Grignard reagent but the organometallic product is believed to be a cyclic oxomagnesium species and not a halogeno organomagnesium compound (see Section 4.1.4.1).[121]

Dienes react with Mg(R)X (R = 2-alkenyl, benzyl, *t*-butyl).[112,114] The initial 1 : 1 addition reactions of 2-alkenylhalogenomagnesium and 1,3-butadiene or isoprene occur with 90% regioselectivity but with excess diene further addition occurs to give 2,4-divinylcyclohexylmethyl derivatives as illustrated for 1,3-butadiene in Scheme 6.[122] The formation of 1 : 3 adducts also occurs. Allenes will react to give 1 : 2 adducts which are also cyclohexane derivatives of the type (**11**).[112]

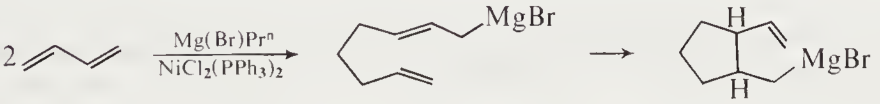


(**11**)

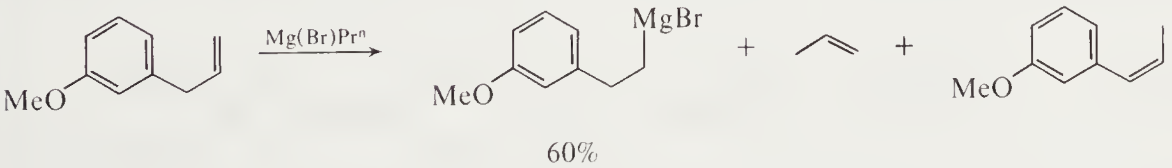


Scheme 6

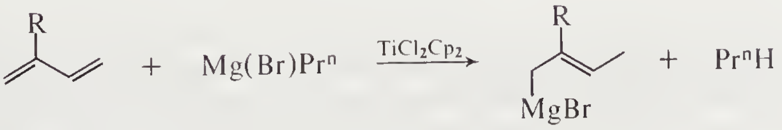
Transition metal-catalyzed reactions of Grignard reagents with alkenes may be useful in organomagnesium synthesis. Nickel(II) chloride catalyzes addition of Mg(Br)Ph to alkenes probably *via* intermediate nickel-π-complexation.[123] An exchange reaction coupled with butadiene dimerization is also catalyzed by an Ni(II) complex (equation 27).[124] Titanium(IV) chloride catalyzes the exchange between terminal alkenes and bromo-*n*-propylmagnesium,[125] as illustrated by the example of equation (28).[124] Using $[TiCl_2Cp_2]$ as catalyst, allylic or α-arylethyl Grignard reagents may be prepared in high yields from respective 1,3-dienes (equation 29) or styrenes.[126] These titanium-catalyzed exchange reactions probably involve intermediates with Ti—H bonds formed by β-hydrogen abstraction from Ti—Pr^n derivatives. Addition reactions of allylic Grignard reagents with dienes are also catalyzed by Ti(IV) compounds.[127]



(27)

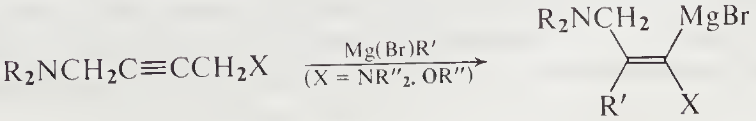


(28)



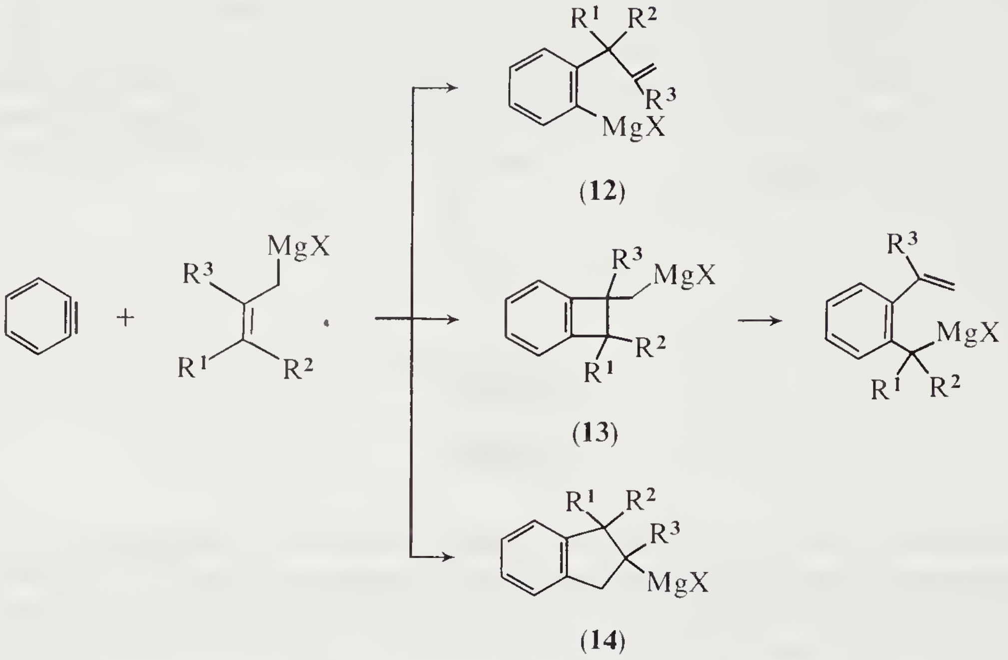
(29)

(*b*) *Alkynes.* Activated 1,4-diamino- or 1-amino-4-alkoxy-substituted 2-butynes undergo a facile addition reaction with Grignard reagents (equation 30). In these reactions, the proximate nitrogen or oxygen containing group gives anchimeric assistance to the addition.[128] Similar reactions occur with propargylic alcohols in which oxomagnesium species are also involved.

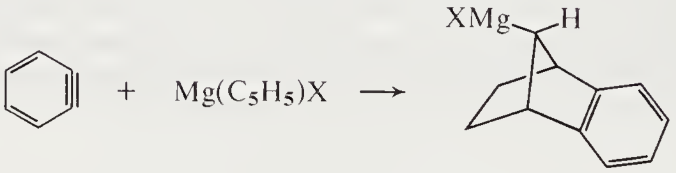


(30)

Cyclohexyne reacts with allylic Grignard reagents solely by addition involving inversion of the allyl group. However, a similar reaction with benzyne produces three products (**12**), (**13**) and (**14**) formed by simple addition, ($\pi^2 + \pi^2$) cycloaddition and ($\pi^4 + \pi^2$) cycloaddition, respectively (Scheme 7).[129] Benzyne reacts with cyclopentadienylmagnesium and related derivatives in a simple Diels–Alder type ($\pi^4 + \pi^2$) addition to the organic ligand, possibly *via* an intermediate σ-bonded cyclopentadienylmagnesium species (equation 31).[130]

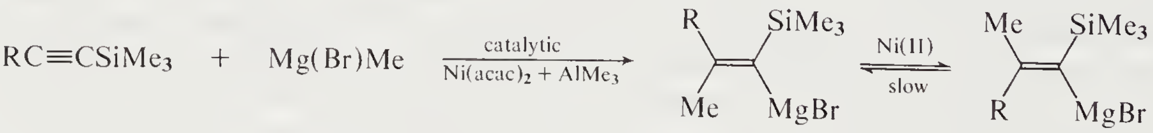


Scheme 7



(31)

There are many recorded examples of Grignard addition to C≡C bonds catalyzed by transition metal complexes, including derivatives of Co, Rh, Ni, Pd and Cu but in most cases the intermediate Grignard has not been identified.[131] An interesting catalyzed addition to a silyl alkyne is illustrated by equation (32).[132]

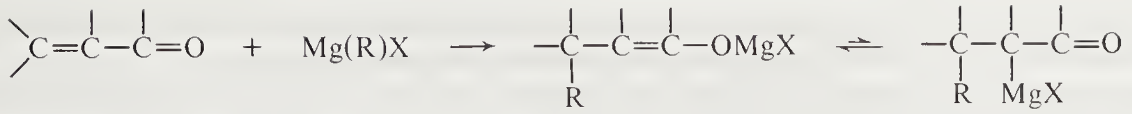


(32)

Additions to conjugated enynes have been the subject of several reports. Saturated, benzylic and allylic Grignard reagents add without catalysts to the double bond of the conjugated system giving a mixture of alkyne and allene derivatives as in equation (33),[133] although the intermediate Grignards have not been isolated. The presence of transition metal salts may direct attack to the alkyne bond.[134]

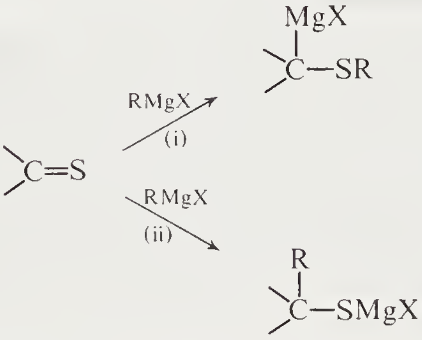
$$\mathrm{XCH_2CH{=}CHC{\equiv}CH} \xrightarrow{\mathrm{Mg(R)X}} \mathrm{XCH_2CH(R)CH(MgX)C{\equiv}CMgX} + \mathrm{XCH_2CH(R)CH{=}C{=}C(MgX)_2} \qquad (33)$$

(*c*) *Other unsaturated bonds.* Reactions of Grignard reagents with most C=X or C≡X systems lead to compounds containing magnesium bonded to the atom X, normally more electronegative than carbon, and a new organometallic product is not formed. In this context, the 1,4-addition to α,β-unsaturated carbonyl compounds should be mentioned where the product is a magnesium enolate which contains an Mg—O bond (equation 34).[5-7,135]

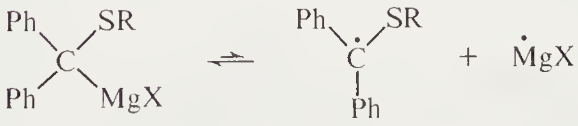


$$\mathrm{>C{=}\overset{|}{C}{-}\overset{|}{C}{=}O} + \mathrm{Mg(R)X} \longrightarrow \mathrm{-\underset{R}{\overset{|}{C}}{-}\overset{|}{C}{=}\overset{|}{C}{-}OMgX} \rightleftharpoons \mathrm{-\underset{R}{\overset{|}{C}}{-}\underset{MgX}{\overset{|}{C}}{-}\overset{|}{C}{=}O} \qquad (34)$$

The thiocarbonyl group reacts with Grignard reagents in several ways including addition, reduction, double condensation and enethiolization.[136] In the addition reaction to thiones, which predominates under some conditions, both thiophilic or carbophilic pathways can occur (steps (i) or (ii) of Scheme 8, respectively). Thiophilic addition of organic groups produces a new Grignard reagent and this reaction has been attributed to bond polarization of the type $^{\delta}\mathrm{C{=}S}^{\delta+}$. The preferred pathway is dependent on the nature of the thione and the Grignard reagent. Thiobenzophenone undergoes mainly thiophilic addition and observations of its reaction with bromo-1-propenylmagnesium rule out a free radical mechanism but favour direct nucleophilic attack at sulphur or possibly a caged radical process.[137] The observation of a free radical in this aromatic system is attributed to the dissociation of equation (35) and the radical may undergo further reactions. The aliphatic thiones, 2,2,4,4-tetramethyl-3-pentanethione and adamantanethione undergo mainly thiophilic addition with saturated aliphatic Grignard reagents but carbophilic addition with unsaturated reagents, although these reactions are accompanied by much reduction.[138] The presence of carbonyl groups α or β to the thione function favours thiophilic attack but the resulting magnesium species contain metal–oxygen links.[139]



Scheme 8



(35)

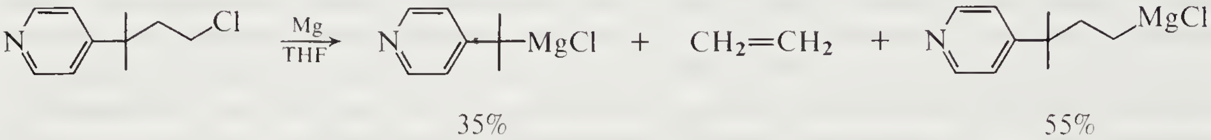
(*iv*) *Simple aryl and saturated alkyl compounds*

There are generally no difficulties in preparing Grignard reagents by direct reaction of metal with simple alkyl and aryl halides.[5–7] As previously mentioned, the use of alkyl chlorides and bromides is better, aryl chlorides react in THF or other strongly basic solvents and reactions in hydrocarbon solvents are also possible. With alkyl halides RX, the reactivity decreases somewhat with chain length and the tendency of secondary and tertiary halides to eliminate hydrogen halide is reduced by using the chloroalkane. Chirality can be introduced into the organic ligand but no examples of non-cyclic Grignard reagents with high enantiomeric purity have been obtained which incorporate the chiral carbon centre bonded to the magnesium atom itself. However, a little optical activity is retained in the magnesium product of exchange between Mg(R)X and a mercury derivative $\mathrm{Hg(R^*)_2}$ with asymmetric α-C centres,[140] and it is also of interest that a product of low optical activity with an Mg—Si bond has also been produced, MgBr(SiMe(1-Np)Ph).[141] Fluoro Grignard reagents Mg(R)F can be prepared directly using activated magnesium[24,27] or by exchange methods.[111] Aryl halides with bulky substituents in the *ortho* positions are relatively inert to reaction with magnesium and activation procedures or the use of the 'entrainment method' may be necessary for these reagents. Heterocyclic aromatic halides may also require activated conditions or exchange methods for preparation of their Grignard reagents.

Care is necessary in the reaction of benzylic halides to avoid substantial Wurtz coupling, and di- and tri-arylmethyl derivatives are best made indirectly *via* exchange of $MgBr_2$ with the corresponding alkali metal derivative[142] or by metallation in HMPT medium.[35]

Few rearrangements are observed during the preparation of simple Grignard reagents. A little 1,2 phenyl migration (1–6%) has been reported in the preparation of the neophyl compound $PhCMe_2CH_2MgX$[143] but significant amounts of 1,2 radical rearrangement (up to 41%) are observed in polyphenylated species such as 2-chloro-1,1,1-triphenylethane (equation 36).[144] Also cyclization and C—C fragmentation have been reported for reactions involving 1-chloro-3-(pyridyl)alkanes, as illustrated by equation (37).[145,146]

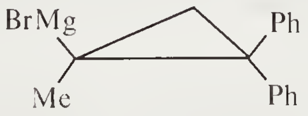
$$Ph_3CCH_2Cl \xrightarrow{Mg} [Ph_3C\dot{C}H_2\dot{M}gCl] \longrightarrow Ph_3CCH_2MgCl + Ph_2C(MgCl)CH_2Ph \quad (36)$$



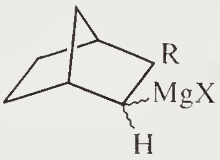
(37)

(*v*) *Cycloalkyl and unsaturated compounds*

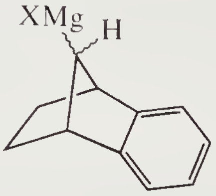
Grignard reagents in which the magnesium is directly bonded to a carbon atom in a simple alicyclic ring are generally readily prepared.[5–7] The rate of inversion of configuration at the metal-bonded carbon atom in such cyclic, secondary derivatives is relatively slow.[30] Thus, an enantiomer of (**15**) has been prepared in high optical purity from the corresponding lithium derivative,[105] *endo* and *exo* forms of norbornyl compounds (**16**) interconvert very slowly at low temperatures[147] and *anti* and *syn* isomers of (**17**) maintain configuration even at elevated temperatures.[148] Moreover, the *anti* isomer of (**17**) is formed with >85% retention of stereochemistry by direct reaction of metal with the *anti*-7-halogenobenzonorbornadiene although reactions with the *syn* isomers are less stereoselective. Often halides of bi- and tri-cyclic compounds are relatively inert to reaction with magnesium so that reactions with highly activated magnesium[24] or exchange of MgX_2 with the lithium derivative are useful preparative routes.



(**15**)

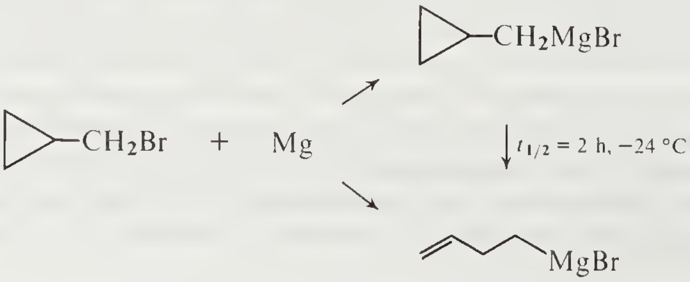


(**16**)



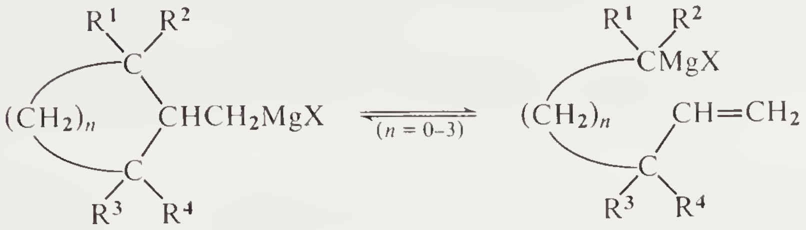
(**17**)

Exocyclic Grignard reagents may show abnormal properties and undergo rearrangements to non-cyclic unsaturated derivatives (see also Section 4.1.1.3,ii).[143] Cyclopropylmethyl halides ring open on reaction with magnesium to form 3-butenylmagnesium derivatives and this process occurs partly *via* radical intermediates formed during the preparation but also by subsequent rearrangement of the cyclopropylmethyl Grignard compound (equation 38).[149] On the other hand



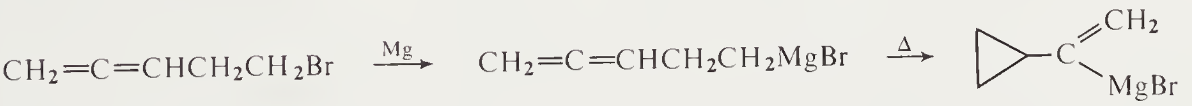
(38)

chloro-2,2,3,3-tetramethylcyclopropylmethylmagnesium is stable.[150] In general, equilibria of equation (39) are set up and the cyclic product is favoured for five- and six- but not for three- and four-membered rings. However, increasing alkylation (R^1–R^4) to provide substituents at β-ring positions in the cyclic form or, correspondingly, secondary or tertiary open chain organometallic derivatives stabilizes the cyclic product, and in this manner, cyclopropylmethyl- and cyclobutylmethyl-magnesium derivatives have been obtained.[150,151] These rearrangements usually proceed at elevated temperatures subsequent to initial Grignard formation but it should be noted that 1-cyclobutylethyl chloride undergoes 10–20% ring cleavage and 6-halogeno-1-hexenes partly cyclize to the cyclopentylmethyl Grignard reagent by radical mechanisms during the actual preparation of organometallic compound.[143]



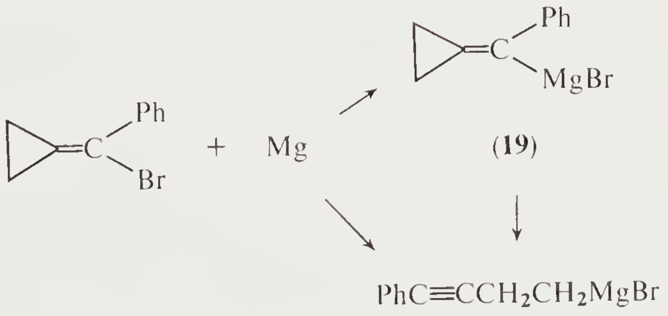
(39)

1-Alkenyl Grignard compounds are prepared in high yields by direct reactions of magnesium and vinylic halides, preferably bromides, in THF.[6,7,31] These reactions are not completely stereospecific and retention of alkene geometry for halides of the type $RR^1R^2CCH{=}CHX$ varies from 60–90% depending on the nature of the substituent group.[152a] Using styryl bromide, retention is higher in THF than in diethyl ether and addition of ethyl bromide is beneficial but iodine reduces the degree of stereoselectivity; products of up to 93% *cis* and 96% *trans* have been obtained.[153] The isomerization occurs during the preparative reaction, probably involving radicals,[152] and the halogenovinylmagnesium compounds themselves are configurationally stable. It is of interest that compound (**18**) can be formed directly and also in low yield by the reaction of equation (40).[154] However, compound (**19**) is unstable with respect to the non-cyclic form (equation 41).[155]



(40)

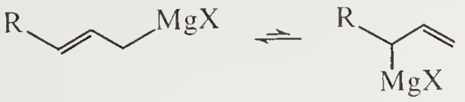
(**18**)



(**19**)

(41)

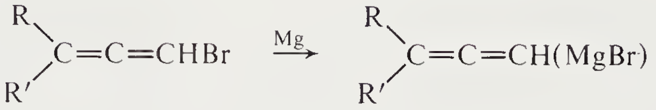
2-Alkenyl-bromo- and -chloro-magnesium compounds are also easily prepared (85–95%) by direct reaction in diethyl ether and the only problem is minimizing the facile associated coupling reaction.[156] These allylic compounds undergo allylic isomerization and the crotyl or similar substituted derivatives are predominantly in the primary form (equation 42), although many reaction products can be considered as being derived from the secondary derivative. 3-Alkenyl and 4-alkenyl Grignards may be prepared but as mentioned above rearrangement equilibria may be set up with cyclic products.



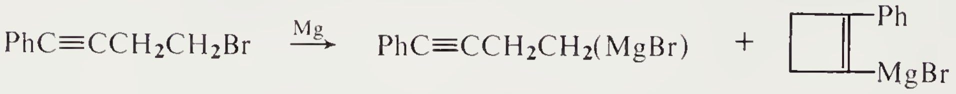
(42)

1-Alkynylhalogenomagnesium compounds RC≡CMgBr and also BrMgC≡CMgBr are readily available by metal–hydrogen exchange reactions as discussed earlier.[73] Propargyl halides react to form an organometallic derivative with the allenic structure (equation 43),[157] although on reaction with substrates isomeric products containing either allenic or alkynic groups may be formed. These products may also be formed directly from bromoallenes (equation 44).[158] A rearrangement involving formation of an alkynyl Grignard reagent is illustrated in equation (41) but in direct preparation of this reagent a cyclobutenyl Grignard is also a minor product (equation 45).[159] It should be noted that cyclizations of 5- and 6-alkynyl Grignard reagents have been observed.[143]

$$HC{\equiv}CCH_2Br \xrightarrow{Mg} H_2C{=}C{=}CHMgBr \tag{43}$$



$$RR'C{=}C{=}CHBr \xrightarrow{Mg} RR'C{=}C{=}CH(MgBr) \tag{44}$$



(45)

1-Halogeno-2,3-dienes react with magnesium in diethyl ether according to equation (46) and the 1,3-diene structure predominates.[160] The Grignard reagents from 5-halogeno-1,2-dienes undergo isomerizations of equation (40) and it is found that 6-bromohexa-1,2-diene cyclizes as shown by equation (47).[161] Conjugated enynes of postulated structure RC≡CCH=CHCH$_2$MgBr have been studied but when the triple bond is terminal the product has the vinylallenic structure as shown in equation (48).[162]

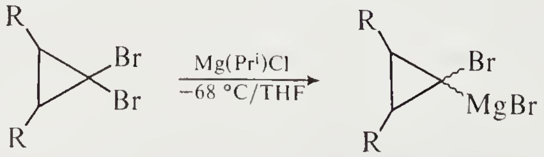
$$RCH{=}C{=}CR'CH_2Br \xrightarrow{Mg} RCH{=}C{=}CR'CH_2MgBr + RCH{=}C(MgBr)CR'{=}CH_2 \tag{46}$$

(47)

$$HC{\equiv}CCR{=}CR'CH_2Br \xrightarrow{Mg} (BrMg)CH{=}C{=}CRCR'{=}CH_2 \tag{48}$$

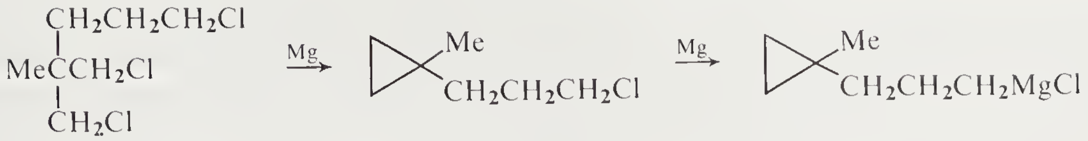
(*vi*) *Halogen substituted compounds*

Grignard reagents with geminal halogen substituents can be prepared by exchange methods at low temperatures. Thus, derivatives Mg(CH$_n$X$_{3-n}$)Cl (X = Cl, Br, I) which decompose *via* carbenoid intermediates at temperatures between −75 and −45 °C have been obtained from the corresponding halogenomethanes and Mg(Cl)Pr^i (see 4.1.1.1,ii).[80,93] These derivatives are somewhat more thermally stable in the presence of HMPT. Although the fluoromethyl Grignards cannot be obtained by similar exchange methods, the unstable compounds Mg(CF$_3$)X (X = Br, I) have been reported as products of low temperature reactions of CF$_3$X and magnesium metal.[163] *gem*-Dibromocyclopropanes also form Grignard reagents, stable at −70 °C (equation 49).[164] Both *anti* and *syn* isomers are obtained but only the *anti* isomer forms a trialkylstannyl derivative stereoselectively on reaction with SnR$_3$Cl.



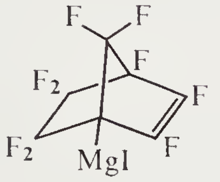
(49)

Grignard compounds with Cl, Br or I substituents in 2- or 3-positions are unstable to alkene or cyclopropane formation, respectively. Reagents of the type X(CH$_2$)$_n$MgX′ ($n \geqslant 4$) can be prepared by careful reaction although side products due to Wurtz coupling or the formation of dihalogenomagnesium species may also be observed.[165] An interesting example which illustrates the tendency to form a cyclopropyl rather than a less strained cyclopentyl ring is shown in equation (50); a radical coupling is considered to account for this ring closure.[166]

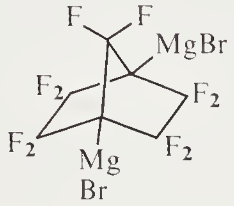


(50)

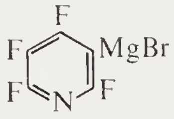
Perfluoroalkyl compounds $Mg(C_nF_{2n+1})X$ ($n \geqslant 2$) can be prepared at low temperatures. Halogen–metal exchange reactions involving $C_nF_{2n+1}X$ (X = Br, I) and Mg(R)X (R = Et, Bu, Ph) at *ca.* −70 to −30 °C are usually the best preparative methods[94,95,96] but direct reaction has been reported for some species, *e.g.* $Mg(C_3F_7)I$.[163a] These perfluoroalkyl Grignards decompose exothermically at *ca.* 0 °C to give alkene products, mainly *trans*-$R_fCF{=}CFX$.[94] However, in some cases, alkenes $R_fCF{=}CF_2$ are formed and these may result by direct elimination from $C_nF_{2n+1}X$ without intermediate organometallic formation.[167] Decomposition catalyzed by Mg(Br)Ph produces a variety of alkenes and alkynes.[168] It is of interest that the bridgehead derivatives (**20**) and (**21**) are undecomposed after several hours at 35 °C.[169]



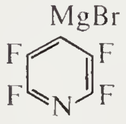
(**20**)



(**21**)



(**22**)



(**23**)

The compounds *trans*-$R_fCF{=}CFX$ (X = Br, I) obtained as described above will form *trans*-perfluoro-1-alkenyl magnesium derivatives stereospecifically either by metal–halogen exchange (using Mg(Br)Ph in Et_2O at 0–5 °C) or by direct reaction (THF/Et_2O, 1 : 1 at 10 °C).[94,97] The simple vinyl compounds $CF_2{=}CFMgX$ have also been well reported,[163a] as have alkynyl derivatives $R_fC{\equiv}CMgX$.[170]

Polyhalogenated aromatic compounds have long been known to form Grignard reagents.[6,7] The compounds C_6F_5X, where X = Cl (in THF, −10 °C)[171] and X = Br (in Et_2O),[172] react directly with magnesium to give high yields of $Mg(C_6F_5)X$. These species can also be obtained by metal–halogen exchange from C_6F_5X (X = F, Cl, Br or I) or metallation of C_6F_5H.[21,81,98] Perfluoro Grignards of heteroaromatic systems such as (**22**) and (**23**) can also be obtained.[173] One thermal decomposition pathway for these compounds is the elimination of magnesium halide and formation of aryne intermediates but these organomagnesium reagents are more stable than the analogous lithium reagents and decompose only at elevated temperatures.[174] Perchloro- and perbromo-aryl derivatives $Mg(C_6X_5)X'$ (X = Cl, Br) can also be formed.[21,99,175,176] The pentachloro derivatives are significantly more stable than the pentafluoro compounds with respect to thermal decomposition to form tetrahalogenobenzyne and are unchanged in boiling benzene after 12 h.[175] The pentabromoaryl Grignards also require elevated temperatures for decomposition. Perchloro- and perbromo-halogenomagnesio derivatives of pyridine and thiophene have also been prepared.[83,176,177,178] Miscellaneous examples of Grignard reagents from partially halogenated arenes have been reported and of particular interest are the simple *ortho* halogeno(halogenomagnesio)benzene compounds which are precursors to simple benzyne.[179]

Other halogenated Grignard reagents of note are the α-halogenoenolates, although probably containing Mg—O bonds,[103] and related arylsulphonyl derivatives $ArSO_2CHCl(MgBr)$ which are thermally stable and undergo usual Grignard reactions.[180]

(*vii*) *Compounds with functionally substituted organic ligands*

Grignard reagents can be prepared from chloromethyl ethers by reaction in THF or methylal at −30 to −20 °C (equation 51).[80,165,181] These reagents decompose forming ethylene and

$$ROCH_2Cl \xrightarrow[-30\ ^\circ C]{Mg} Mg(CH_2OR)Cl \qquad (51)$$

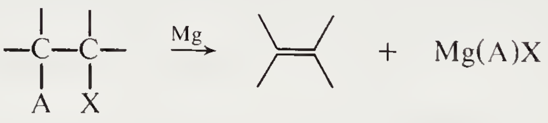
$MgCl(OR)$ at temperatures above −15 °C but the thermal stability is enhanced in HMPT and increases in the order R = Me < Et < Pr^i < Bz ≈ $Cl(CH_2)_2$, the latter being stable at room temperature. There is no good evidence for carbene intermediates in the decomposition reactions but the insertion reactions of equation (52) do occur. It is of interest that the aromatic derivative (**24**) isomerizes by a 1,2 shift as in equation (53).[182] Analogous thioether derivatives $Mg(CH_2SR)Cl$ are also reported.[165,183]

$$Mg(CH_2OR)Cl \quad + \quad Mg(R')X \longrightarrow Mg(CH_2R')X \dashrightarrow Mg\{(CH_2)_nR'\} \qquad (52)$$

$$\underset{(\mathbf{24})}{MgBr\{CPh_2(OPh)\}} \xrightarrow{THF/HMPT} MgBr(OCPh_3) \qquad (53)$$

Other stable Grignard reagents with substituents in the 1-position include $Mg(CH_2MRR'R'')X$ (M = Si, Sn).[93,184] Also, the halogenomagnesio derivatives of carboranes, formally, have α-boron substituents,[91] and enolates such as (**5**) formed from α-methylene groups bonded to C(O)Y (Y = R, OR, OH, *etc.*), S(O)R, $S(O)_2R$, $P(O)R_2$ and related systems fall into this category, although they are primarily O—Mg bonded derivatives.

Functional substituents in the 2-position usually undergo ready elimination on attempted Grignard formation, as shown in equation (54) with for example A = NR_2, PR_2, OR, SR.[165] However, in compounds where such elimination is not favoured, stable Grignard reagents (**25**),[185] (**26**)[53] and (**27**)[186] can be formed. Also, the perfluoro derivative (**28**)[187] has been reported and Grignards with the SiR_3 function in the β-position are preparable.[188] In fact it has been possible to prepare derivatives $Mg(CH_2CH_2NR_2)Cl$ in THF at −100 to −75 °C using highly activated magnesium and these compounds decompose in the temperature range −90 to −20 °C by elimination of ethylene with stability increasing in the order R_2 = PhMe < Ph_2 < Cy_2.[189]



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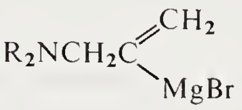
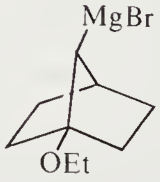
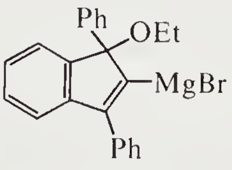


(**25**)



(**26**)



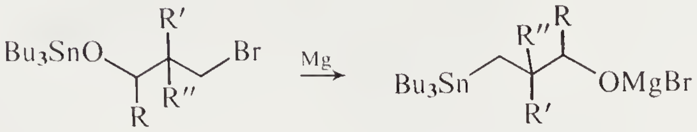
(**27**)

$(CF_3)_2CFOCF_2CF_2MgI$

(**28**)

Organomagnesium derivatives with unreactive substituents in the 3-position of the organic ligand can usually be prepared without difficulty, unlike the corresponding halogen-substituted analogues. Thus, the compounds $Mg\{(CH_2)_3Y\}X$ (Y = NR_2,[190] PR_2,[191] AsR_2,[192] OR,[165] SR,[193] SiR_3,[183] SnR_3[194]) and related systems have been described. It is of interest that when Y = NR_2 the reaction can be carried out readily in an aromatic solvent. Grignards with such substituents at positions higher than 3 are generally readily formed.

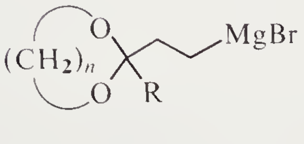
Substituents that are reactive with Grignard reagents usually need protection. The hydroxyl function is often transformed into the 2-tetrahydropyranyl or *t*-butyl ether[165] although it is of interest that the rearrangement of equation (55) may occur for trialkylstannyl ethers.[195] It is, however, possible to form hydroxyl-containing reagents as oxomagnesium derivatives by consecutive reactions (equation 56).[196] The carbonyl group in ketones or aldehydes is normally protected by ketal or acetal formation,[54,165] as in (**29**) for which the 1,3-dioxacyclane with n = 3 is stable in refluxing THF.[197] The carboxylic acid group can be protected as an oxazoline derivative, as in (**30**),[198] and may be subsequently regenerated by hydrolysis.



(55)

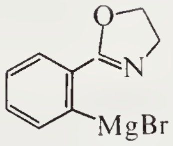
$$Cl(CH_2)_nOH \xrightarrow[\text{ii, Mg/THF}]{\text{i, Mg(R)Cl}} ClMg(CH_2)_nOMgCl \qquad (56)$$

(n = 3, 4, 6)



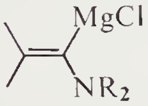
R = H, Me

(**29**)

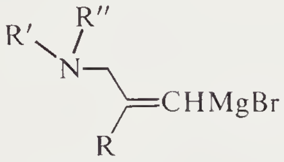


(**30**)

Many examples of unsaturated Grignard reagents with functional group substituents are known, including (**31**),[199] (**32**)[200] and (**33**);[201] see also earlier sections. Functionally substituted aromatic Grignards are also common.[5–7]



(**31**)



(**32**)

$BrMgC{\equiv}C(CH_2)_2CO_2MgBr$

(**33**)

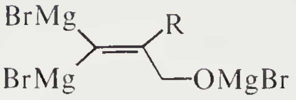
(*viii*) *Dimagnesium compounds*

Reactions between organic substrates and CH_2X_2 with magnesium are often carried out by an *in situ* procedure[202] (Barbier method) and although this may lead to introduction of CH_2 units into the product, there is doubt whether true $CH_2(MgX)_2$ intermediates are involved.[203] Also, it should be noted that CBr_4 will react *in situ* with trimethylchlorosilane as if trimagnesium (39%) and tetramagnesium reagents (20%) are involved but such derivatives are unproven.[204] However, the dimagnesium compounds $CH_2(MgX)_2$ (X = Br, I) can be formed and are stable at 0 °C for weeks,[205] whereas the homologous $MeCH(MgX)_2$ cannot be prepared. The derivative $Me_3SiCH(MgBr)_2$ has also been reported[108] (equation 19).

Aliphatic α,ω-dimagnesium derivatives $XMg(CH_2)_nMgX$ are preparable when $n \geqslant 3$. When n = 3 an exchange route involving equation (18) has been employed[107] but when n = 4–12 normal direct methods may be used.[165,206] Using the chlorides in refluxing THF, the best yields are obtained when n = 4–6 and the poorest for n = 8, 9.[206] It is interesting that 1,2-bis(halogenomagnesio)cyclopropane has been reported.[207] Perfluoro α,ω-species $XMg(CF_2)_nMgX$ (n = 6, 8) have been obtained by exchange reactions at low temperatures, *e.g.* equation (21),[94] but decomposition to α,ω-dialkenes occurs at −10 °C when n = 8. The dimagnesium derivatives $(Mg(Br)(CH_2)_3)_2O$[208] and $(Mg(Br)CH_2SiMe_2\text{+}_2$[209] are also of interest. The vinyl compound (**34**) is formed by addition of Grignard to $BrMgC{\equiv}CCH_2OMgBr$.[210]

Aromatic derivatives, especially compounds with polycyclic rings, containing di- or poly-halogenomagnesio substituents have long been known.[5–7] Two examples which could prove useful in organometallic synthesis are (**35**)[211] and (**36**).[212] At a single benzene nucleus, *para-*, *meta-*

ortho dimagnesium derivatives can be formed, but in preparation of the latter much diphenylene may be produced.[179,213]



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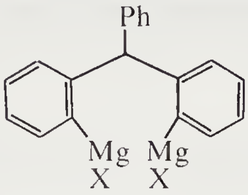

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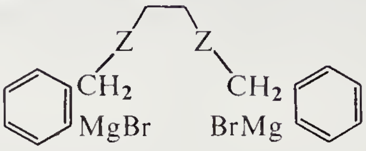


Z = O, (NMe)

(36)

4.1.1.2 Structural and physical properties

(i) Solid state

Halogenoorganomagnesium compounds are mainly employed in solution and rarely isolated as solids. Thus, from a chemical viewpoint the structures and properties in solution are important but studies over many years have shown that these are complex and dependent on concentration and the nature of the solvent as well as of the organic and halogen ligands.[42,104] More definitive studies of solid species have been carried out by X-ray diffraction and structural conclusions derived from such investigations should be relevant to aspects of solution chemistry. In certain cases it has been possible by spectroscopy to identify analogous systems in both phases.

(*a*) *Composition.* On controlled evaporation or by means of other techniques for inducing crystallization from halogenoorganomagnesium solutions, products are obtained which are sometimes colourless, crystalline solids but may be viscous liquids which solidify only at subambient temperatures.[214] Such solid Grignard reagents containing a simple saturated organic group R show significant decomposition of this ligand only at elevated temperatures, usually above 100–150 °C.[215] The solids obtained from ethereal or other coordinating solvents in many cases have R:Mg:X ratios of 1:1:1 but in others the product may separate with excess halide, *e.g.* with stoichiometry Mg_2Cl_3Et from THF, leaving the more soluble dialkylmagnesium (in this case $MgEt_2$) in solution.[42,104] In extreme cases, solvated MgX_2 is precipitated leaving the organometallic compound totally in solution as MgR_2 and this is the basis of the method of preparation of the latter compounds by addition of dioxane to diethyl ether solutions. It should be noted that fluoro species Mg(R)F do not undergo such dissociation and dioxane precipitates the unchanged organometallic derivative.[216] The solid products invariably contain coordinated solvent molecules and although most of these may be removed by heating *in vacuo* it is virtually impossible, even with the most stable products such as Mg(Et)X, to remove all traces of coordinated ether at temperatures below 100 °C or before some decomposition of the organic ligand occurs.[215,217] X-ray diffraction of M(R)X (R = Me, Et; X = Cl, Br) which had been desolvated to constant weight at temperatures in the range 90–120 °C at 10^{-3} Torr, indicated that the solid species is a mixture of MgX_2 and $[MgR_2]_n$.[218] Studies by vibrational spectroscopy have also shown that such a dismutation occurs on desolvation and solid $[MgBr(Me)(OEt_2)_2]$ is stable to this disproportionation only at temperatures below 300 K;[214] it was also suggested by these authors that the ease of solid state disproportionation reflects the ease of ligand bridging: Cl > Br > I and Me > Et.

The preparation of halogenoorganomagnesium compounds in non-coordinating hydrocarbon solvents usually results in the precipitation of MgX_2 and the soluble organometallic when obtained as a solid has a ratio $R:X > 1$.[42] The composition may be close to Mg_2R_3X, especially when freshly prepared, and in fact a soluble crystalline material $[Mg_2ClPh_3]_n$ has been described but no definitive structural information has been obtained for these species.[219] The normally solvated solid species contain varying quantities of solvent; stoichiometric Mg:solvent ratios of 1:1 and 1:2 are common but a range of compositions has been reported and the formation of various solvated species derived from a mixture of associated and disproportionation products will explain such divergences.

(*b*) *Structures.* The molecular structures of several crystalline derivatives have been determined by X-ray analysis (see Table 1). The dietherates $[MgBr(Ph)(OEt_2)_2]$,[220] $[MgBr(Et)(OEt_2)_2]$[221]

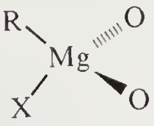
Table 1 Bond Lengths of some Halogenoorganomagnesium Complexes in the Solid State[1]

Complex	Mg—C	*Bond lengths* (Å) Mg—halogen	Mg—O/Mg—N
$MgBr(Et)(OEt_2)_2$	2.15	2.48	2.03, 205
$MgBr(Ph)(OEt_2)_2$	≈2.2	2.44	2.01, 2.06
$MgBr(Me)(THF)_3$	2.53(2.41)[a]	2.41(2.53)[a]	2.04, 2.06, 2.28
$MgBr(Cp)(Et_2NCH_2CH_2NEt_2)$	2.55(2.21)[b]	2.63	2.17, 2.35
$[MgBr(Et)OPr^i_2]_2$	2.094	2.582, 2.576	2.019
$[MgBr(Et)NEt_3]_2$	2.18	2.566, 2.567	2.15
$[Mg_2Cl_3(Et)(THF)_3]_2$	2.19	(i)[c] 2.50,[d] 2.51,[d] 2.79[c] (ii)[f] 2.40,[c] 2.41,[c] 2.47,[d] 2.51[d]	2.04,[d] 2.11,[d] 2.14[c]

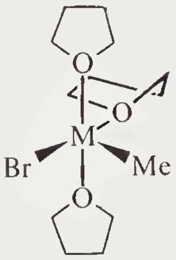
[a] Disordered Me and Br groups. [b] To plane of Cp ring. [c] μ_3-Cl. [d] Octahedral Mg. [c] 5-coordinate Mg. [f] μ-Cl.

1. From refs. 220, 221, 223, 224, 225, 227 and 229; see text pages 178–180.

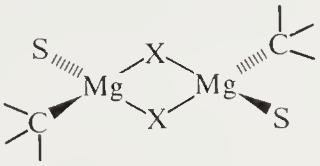
and $[MgBr(Ph)(THF)_2]$[222] are isolated, monomeric units with the magnesium atom at the centre of a distorted but essentially tetrahedral arrangement of four ligands (**37**). The angle C—Mg—Br in the ethyl derivative is 125°. Although Mg(Br)Ph crystallizes as a diadduct with THF the corresponding methyl compound forms a solid complex $[MgBr(Me)(THF)_3]$ which is also monomeric but has approximately trigonal bipyramidal ligand geometry around the magnesium atom (**38**).[223] The methyl and bromide groups are disordered so that a precise Mg—C bond length was not obtainable. Bromoethylmagnesium crystallizes from diisopropyl ether as a dimeric product $[MgBr(Et)(OPr^i_2)]_2$ with bridging Br ligands (**39**) ($S = OPr^i_2$, X = Br).[224] Each magnesium atom is four-coordinate and with O—Mg—C = 120.7° and Br—Mg—Br = 93.2°. The same Grignard crystallizes from ethereal solvents containing triethylamine as a dimer $[MgBr(Et)(NEt_3)]_2$ with similar structure (**39**) ($S = NEt_3$) in which the angle N—Mg—C = 116.2°.[225] It is of interest that in a solution of triethylamine, MgBr(Et) is monomeric[33] whereas in diisopropyl ether, dimeric species exist.[226]



(**37**)

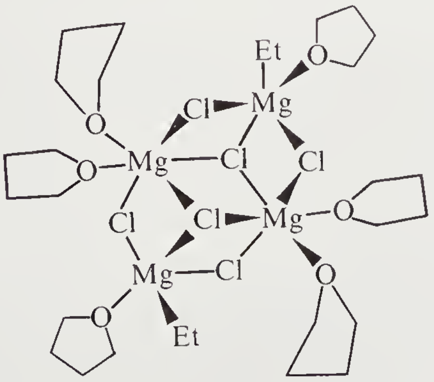


(**38**)

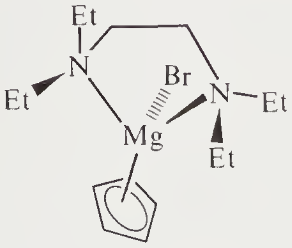


(**39**)

Chloroethylmagnesium crystallizes from THF as the more complex derivative $[Mg_2Cl_3(Et)(THF)_3]_2$ shown by crystallography to have a tetrameric molecular structure (**40**) with two approximately trigonal bipyramidally, five-coordinate magnesium atoms each directly bonded to



(**40**)



(**41**)

terminal ethyl groups and two six-coordinate magnesium atoms bonded only to chloro and THF ligands.[227] The chloro ligands are either doubly (μ) or triply (μ_3) bridging. Cell constants and space groups have also been determined by X-ray analysis for several 2-pyridyl Grignard reagents.[228]

One other halogeno derivative of which the molecular structure has been determined by X-ray analysis is $[MgBr(C_5H_5)(Et_2NCH_2CH_2NEt_2)]$ (**41**), obtained by adding the diamine to an ethereal solution of $MgBr(C_5H_5)$.[229] The cyclopentadienyl group is η^5-bonded to the metal and the metal may be considered as four-coordinate with angle Br—Mg—N = 94.9 ± 3.5°. The long Mg—C distance (2.55 Å) compared to that of related compounds and even $[Mg(C_5H_5)_2]$ (2.304 Å) and the ring C—C distances (1.43 Å (av.)) are consistent with an essentially ionic interaction between $(C_5H_5)^-$ and Mg(II). This ionic model is supported by IR, UV and NMR studies of $Mg(C_5H_5)X$ species in THF solution.[230]

In the alkyl and aryl complexes, the Mg—C bond lengths mainly lie in the range 2.1–2.2 Å and this compares with an expected covalent bond length of 2.17 Å.[220] The terminal Mg—Br lengths (2.44–2.48 Å) are increased to 2.58 Å in the dimeric μ-Br species and the relatively short Mg—O bonds imply strongly coordinated ether groups. The variation of coordination number and association of the magnesium has been attributed to the steric requirements of the solvating ether or amine[227] and the effective volumes of bases appear to follow the order $NEt_3 > OEt_2 >$ THF but the coordinating ability of such ligands must also be important. Diisopropyl ether is a much poorer coordinating ligand than NEt_3 and although both form related dimeric molecules in the solid state, the former may be related more to its inability to displace μ-Br groups than to steric hindrance.[224] It is of interest also that diorganylmagnesium compounds MgR_2 in the solid state are only found as four-coordinate derivatives (see 4.1.2.2,i) whereas Mg(R)X centres have been observed in four- and five-coordinate environments. The simple halides and related non-organometallic complexes are four- to six-coordinate[231] as in $MgBr_2(OEt_2)_2$, $MgBr_2(THF)_2$, $MgBr_2(THF)_4$ and in the six-coordinate centre in $[Mg_2Cl_3Et(THF)_3]_2$. Thus, increasing the number of electronegative halogen ligands promotes higher solvation. No examples of three-coordinate magnesium atoms have been demonstrated for Mg(R)X species although such a geometry has been proposed for some associated $[MgR_2]_n$ and $[Mg(NR_2)R]_2$ derivatives.[232] The variation in coordination number between species MgR_2, Mg(R)X and MgX_2 and with varying coordinating solvents, *e.g.* higher coordination numbers for THF than OEt_2, may be related to differences in the Schlenk equilibrium in solution (see below).

Raman and IR studies on isolated, solvated Grignards $[Mg(Et)X(OEt_2)_2]$, $[Mg(Me)X(OEt_2)_2]$ (X = Br, I), $[Mg(Et)Cl(OEt_2)]_2$, $[MgBr(Et)(OPr^i_2)]_2$ and $[Mg(Br)Ph(S)_2]$(S = OEt_2, THF) have been carried out and extensive vibrational assignments were aided by deuteration of alkyl groups.[214,233] The monomeric diethyl etherates, having a distorted tetrahedral geometry, all contain coordinated *gauche*,*gauche* Et_2O ligands but for $[MgMeBr(OEt_2)_2]$ an alternative form coexists at 90 K with *trans*,*gauche* or *trans*,*trans* conformation for these ligands. Bands attributed mainly to $\nu_{Mg—C}$, $\nu_{Mg—X}$ and symmetric and antisymmetric ν_{OMgO} modes occur at 485, 248 (X = Br), 224 (X = I), 317 and 301 cm^{-1}, respectively, for the ethyl compounds. Similar spectra are observed for these derivatives in diethyl ether solution, thus supporting the presence of four-coordinate complexes in this medium. The compound $[Mg(Et)Cl(OEt_2)]_2$ as a liquid at 300 K or a glass at low temperatures has the dimeric structure (**39**) (X = Cl) of approximate C_{2h} symmetry and frequencies attributable to the bridging chloro system, Mg_2Cl_2, are in the range 288–241 cm^{-1}. However, in a crystalline phase at 90 K, the spectral analysis supports a form containing both bridging and terminal ethyl groups.[214] A variation of the coordinating ether in related complexes shows that $\nu_{Mg—Br}$ and $\nu_{Mg—C}$ frequencies decrease with increasing donor capacity of the ether, and this reflects a corresponding increase in the ionic character of these ligand–metal bonds.[233]

NQR measurements of $^{79}Br/^{81}Br$ nuclei in several derivatives $[Mg(Br)R(OR'_2)_n]$ (R = Et, Ph, Bu^t) at 77 K show resonances (30–42 MHz) which are very much lower than typical covalent C—Br resonances (220 MHz) and suggest high ionic character (*ca.* 0.86) for Mg—Br bonds.[234] The frequency is decreased by 2 MHz on replacing R = Ph by the less electronegative R = Et and also by replacing coordinated Et_2O by THF; both of these trends may be attributed to a slight increase in Mg—Br ionicity.

Raman and IR studies of allylic compounds $Mg(C_3H_5)X$ (X = Cl, Br) which had been desolvated by heating *in vacuo* at 100 °C have been reported at 298 K and 93 K. Bands assignable to metal–allyl vibrations occur in the range 430–310 cm^{-1} and calculated force constants indicate significant ionic character for this bonding but less than for corresponding allyl-lithium and -sodium compounds.[235] In solution, however, the magnesium is bonded in a monohapto manner.[236]

(*ii*) *Solution*

(*a*) *Composition, aggregation and ionization.* In solution the halogenoorganomagnesium derivatives do not have a simple constitution but exist as an equilibrium mixture which may involve various mono-, bi- and poly-nuclear solvated components. The primary equilibrium, known generally as the Schlenk equilibrium,[237] is the dismutation process, expressed simply by equation (16). This was initially proposed on the basis of dioxane precipitation experiments. In this equilibrium the organyl and halogeno ligands are exchanged between two metal centres. The extent of this equilibrium and the rate of the exchange were controversial subjects of earlier research work.[6,7,42] In spite of some misleading experiments it has been established using ^{28}Mg or ^{25}Mg that exchange does occur readily between labelled $MgBr_2$ and both $MgEt_2$ and Mg(Br)Et.[42] Stoichiometric mixtures of MgX_2 and MgR_2 in ethereal or amine solvent give products essentially identical to Grignard reagents although under some situations the rate of attainment of equilibrium could be slow.[33,42,238]

The Schlenk equilibrium has been the subject of various physical investigations. Calorimetric studies of the heats of reaction between MgX_2 and MgR_2 in dilute solutions of THF and Et_2O have provided thermodynamic parameters and equilibrium constants for several systems[238] (see Table 2 for examples). Analysis by NMR spectroscopy is also possible since MgR_2 and Mg(R)X species can be distinguished provided exchange is slow on the NMR time scale. When R = Bu^t or perfluoroaryl this occurs at ambient temperatures in THF but for systems where R is a simple alkyl or aryl group or in a less coordinating solvent such as Et_2O, slow exchange only occurs at low temperatures.[104,239,240] Variable temperature NMR studies have provided thermodynamic parameters and qualitative kinetic data for the exchange process. Schlenk equilibrium constants have also been determined for some systems by IR spectroscopy in THF solutions[241] and other less precise methods of analysis have involved polarography[242] and analysis of kinetic investigations of Grignard reactions.[243]

Table 2 Thermodynamic Parameters for Schlenk Equilibria of some Grignard Reagents[1]

Grignard reagent	*Solvent*	K^a	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})
Mg(Br)Me	Et_2O	*ca.* 320[2]	—	—
	THF	*ca.* 3.5–4[3,b]	—	—
Mg(Br)Et	Et_2O	480–484	−15.6	−1.3
	THF	5.09	25.5	99.1
Mg(Et)Cl	THF	5.52	15.9	67.3
Mg(Et)I	Et_2O	>630	−20.6	−5.0
Mg(Ph)Cl	THF	1.66	11.4	42.2
Mg(Br)Ph	Et_2O	55–62	−8.4	5.0
	THF	3.77	11.8	50.6
		4.0[4]	13.3[4]	56[4]
$Mg(Br)(C_6F_5)$	Et_2O	2.0[4,c]		
	THF	4.0[4,c]		

[a] Equilibrium constant for $MgR_2 + MgX_2 \rightleftharpoons 2Mg(R)X$, at 25 °C unless otherwise stated. [b] At ambient temperature. [c] At 22 °C.

1. From ref. 238 unless otherwise stated.
2. T. Holm, *Acta Chem. Scand.*, 1969, **23**, 579.
3. From refs. 239 and 241.
4. From ref. 240.

The values of K, $\Delta H°$ and $\Delta S°$ (Table 2), although rather approximate, show that in Et_2O the mixed species Mg(R)X is prevalent ($K \approx 10$–10^3) but in THF the values of K (1–10) indicate a more random distribution of components close to the statistical value $K = 4$. It should also be noted that in THF at low temperatures, the equilibrium shifts to the left. Whereas $\Delta H°$ values are negative in Et_2O and corresponding $\Delta S°$ changes are negligible, in THF both $\Delta H°$ and $\Delta S°$ are positive. The six-coordination of the isolated THF adduct $MgX_2(THF)_4$ compared to lower coordination numbers for Et_2O adducts suggests that the principal differences between these two solvent systems is the degree of solvation, especially of MgX_2 and Mg(R)X. In fact enthalpy changes on going from Et_2O to THF for $MgEt_2$, Mg(Br)Et and $MgBr_2$ are respectively −19.2, −29.3 and −79.8 kJ mol^{-1}. An equilibrium of the type shown by equation (57) may occur in THF

$$MgR_2(THF)_2 \quad + \quad MgX_2(THF)_4 \quad \rightleftharpoons \quad \underset{(n = 2\text{–}3)}{2Mg(R)X(THF)_n} \quad + \quad \underset{(m = 0\text{–}2)}{m\,THF} \qquad (57)$$

and it has been reported that differing solvation with concentration can effect the Schlenk equilibrium of $Mg(Bu^t)Cl$.[244] In Et_2O lower solvation is to be expected and equilibria may involve only four-coordination in the primary sphere as found in solid state structures (equation 58), but the presence and influence of associated species must also be important and precipitation of less soluble MgX_2, especially at low temperatures, may occur. The presence of excess halide ions displaces the Schlenk equilibrium and the electrochemically determined basicity of the Grignard reagent is lowered as a consequence of the reduction in concentration of MgR_2.[245] A theoretical relationship between the Schlenk equilibrium constant and solvation effects has been reported.[246]

$$MgR_2(OEt_2)_2 \quad + \quad MgX_2(OEt_2)_2 \rightleftharpoons 2Mg(R)X(OEt_2)_2 \tag{58}$$

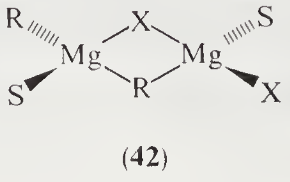
In less coordinating ethereal solvents such as diisopropyl ether and 1-ethoxy-2-methylbutane, Mg(Br)Et is present essentially in this mixed form but association occurs.[226,247,248] In triethylamine the Schlenk equilibrium lies principally to the right when X = Cl or Br but less so when X = I.[33] In the highly coordinating solvent HMPT the mixed species Mg(R)X is the main form but there may be extensive ionization of the C—X bond.[249] The soluble organomagnesium products formed in non-coordinating hydrocarbon solvents cannot involve simple halides MgX_2 which are virtually insoluble in such media so that any derivatives containing halogen must be complexes, probably associated, with the halogen ligand coordinated to organomagnesium centres.

It should be noted that in both THF and Et_2O the fluoro Grignard reagents $[Mg(R)F]_2$ exist solely as the mixed dimeric form and there is no evidence for the Schlenk equilibrium for these derivatives.[216]

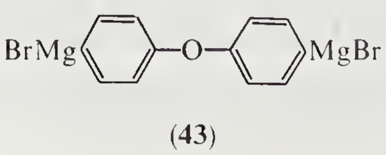
Schlenk equilibrium constants for allylic Grignard reagents have been measured in Et_2O by NMR at low temperatures (*e.g.* for $Mg(CH_2CH{=}CHBu^t)Cl$ values range from $K = 0.44$ (−86 °C) to $K = 14$ (−47 °C)) and extrapolation to standard temperatures gives values (*ca.* 50) consistent with normal monohapto species $Mg(\eta^1\text{-}R)X$.[236b] However, compounds Mg(Cp)X have much larger values for K in Et_2O and these have been attributed to the delocalized ionic nature of the Cp—Mg bonding.[230] Also, the equilibrium of equation (59) involving a cyclic species in THF has a high K value of $299 \pm 30\ \mathrm{l\ mol^{-1}}$ at 28.25 °C.[250]

$$(CH_2)_5Mg \quad + \quad MgBr_2 \rightleftharpoons BrMg(CH_2)_5MgBr \tag{59}$$

Rates for ligand exchanges involved in the Schlenk equilibrium have been monitored qualitatively by NMR and in general for Mg(R)X these decrease in the order X = Cl > Br > I and with increasing branching at α-C atoms of the R group, *i.e.* R = primary > tertiary.[239,240] Substitution by bulky *ortho* groups when R is an aryl ligand also decreases the exchange rate as does polyhalogenation. The rate falls in more coordinating solvents Et_2O > THF > triglyme > HMPT and the addition of small quantities of TMEDA or HMPT to less polar solvents retards the exchange rate.[249,251] These findings support a transition state (**42**) formed by displacement of coordinated solvent S, and favoured by more effective bridging ligands X and R. It should also be noted that oxo species formed by the presence of oxygen will catalyze the exchange since alkoxo ligands are good bridging groups.



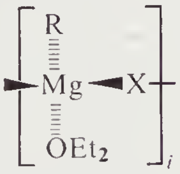
(**42**)



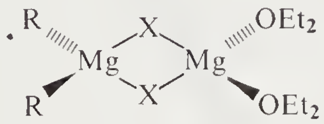
(**43**)

The extent of the aggregation of the complex species $[Mg(R)X]_i$ and the simple binary derivatives $[MgX_2]_i$ and $[MgR_2]_i$ in solution (i = degree of association) have been investigated by studies of colligative properties appropriate to the solvent including ebullioscopy, cryoscopy and rates of quasi-isothermal distillation of solvent.[42,104] Ashby and co-workers have carried out extensive studies and some results are summarized in Figure 1;[104] these are in broad agreement with results of other workers. In THF, species Mg(R)X (X = Cl, Br, I) are monomeric over a wide concentration range and must exist only as solvated adducts of equation (57). Similar monomeric species are present in NEt_3 and in more coordinating solvents such as HMPT.[252] However, $[Mg(R)F]_2$ compounds are dimeric in THF and spectroscopic and related studies support a structure of type (**39**) (X = F) in solution with the strongly bridging F-ligands not displaced by THF, although the degree of solvation (four-coordination or greater) is not known.[216] The dimagnesium reagent of equation (59) is monomeric in THF[250] but (**43**) is a rod-like polymer in the same solvent even at low dilutions although the actual composition of this reagent in solution also involves $MgBr_2$ present in a 1:1 mole ratio.[253]

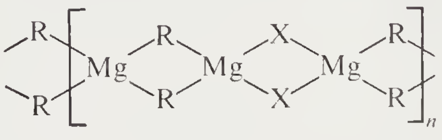
Reagents MgR(X) (X = Cl, F) in Et_2O solvent are both predominantly dimeric over a wide concentration range and thus probably have structure (**39**) (X = F, Cl) with Et_2O incapable of displacing even bridging chloro ligands. Derivatives Mg(R)X (X = Br, I) in Et_2O show a more complex association pattern; at low dilution $i = 1$ and species of equation (58) probably exist but association increases to values of i significantly greater than two with higher concentration. The curvature of the lines of Figure 1(c) have been attributed to deviations from ideality and though it is possible that when $i = 2$ structures of type (**39**) may occur, Ashby argues in favour of linear association of the type (**44**) with $i \geqslant 2$. Associated species of the type (**45**) may also be present but the Schlenk equilibrium in Et_2O lies mainly to the side of the mixed compound Mg(R)X. As shown in Figure 1(d), MgX_2 and MgR_2 also associate in Et_2O. A conflicting report based on IR and Raman studies states that $[MgBr(Et)(OEt_2)_2]$ has a monomeric structure even at high concentrations in Et_2O.[233]



(**44**)

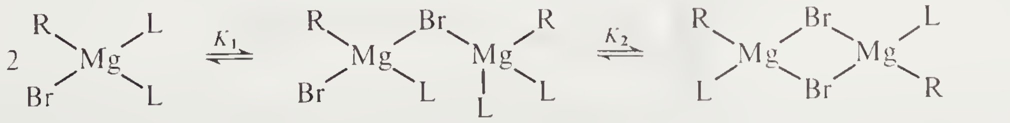


(**45**)



(**46**)

In a less coordinating ether such as Pr^i_2O associated structures are more prevalent and MgBr(Et) exists as a dimer even at 0.04M concentration and it is also of interest that a binuclear complex $[Mg_2BrEt_3]$ is formed from a mixture of Mg(Br)Et and $MgEt_2$ in this solvent.[226] With (+)-(*S*)-1-ethoxyl-2-methylbutane (L) the equilibria of equation (60) have been demonstrated by optical rotatory studies; when R = Et, $K_1 = 103\ \mathrm{mol\ l^{-1}}$ and $K_2 = 1.41\ \mathrm{mol\ l^{-1}}$ at 25 °C.[248] Similar equilibria (60) are observed by adding ligands L (L = NEt_3, OEt_2, THF) to Mg(R)X (R = Me, Et, Bu^i) in 1:1 to 2:1 ratios in benzene solvent.[254] The halogen deficient unsolvated Grignard reagents made entirely in non-coordinating hydrocarbon solvents have been postulated to possess associated structures of type (**46**).[42]



(60)

Another feature of halogenoorganylmagnesium compounds is the solvent dependent degree of ionization of Mg—X and/or Mg—R bonds. Ethereal solutions of Grignard reagents do conduct electricity but the extent of ionization is small (molar conductivities Λ_M of *ca.* $10^{-5}\ \Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}$) in either Et_2O or THF.[42] Electrolysis shows that magnesium migrates towards both cathode (where it plates out) and anode but there is a net transfer of Grignard species towards the anode and the amount transported considerably exceeds the equivalent coulombs passed. In these ethereal media there is little indication of carbanionic species and ionizations represented by equations

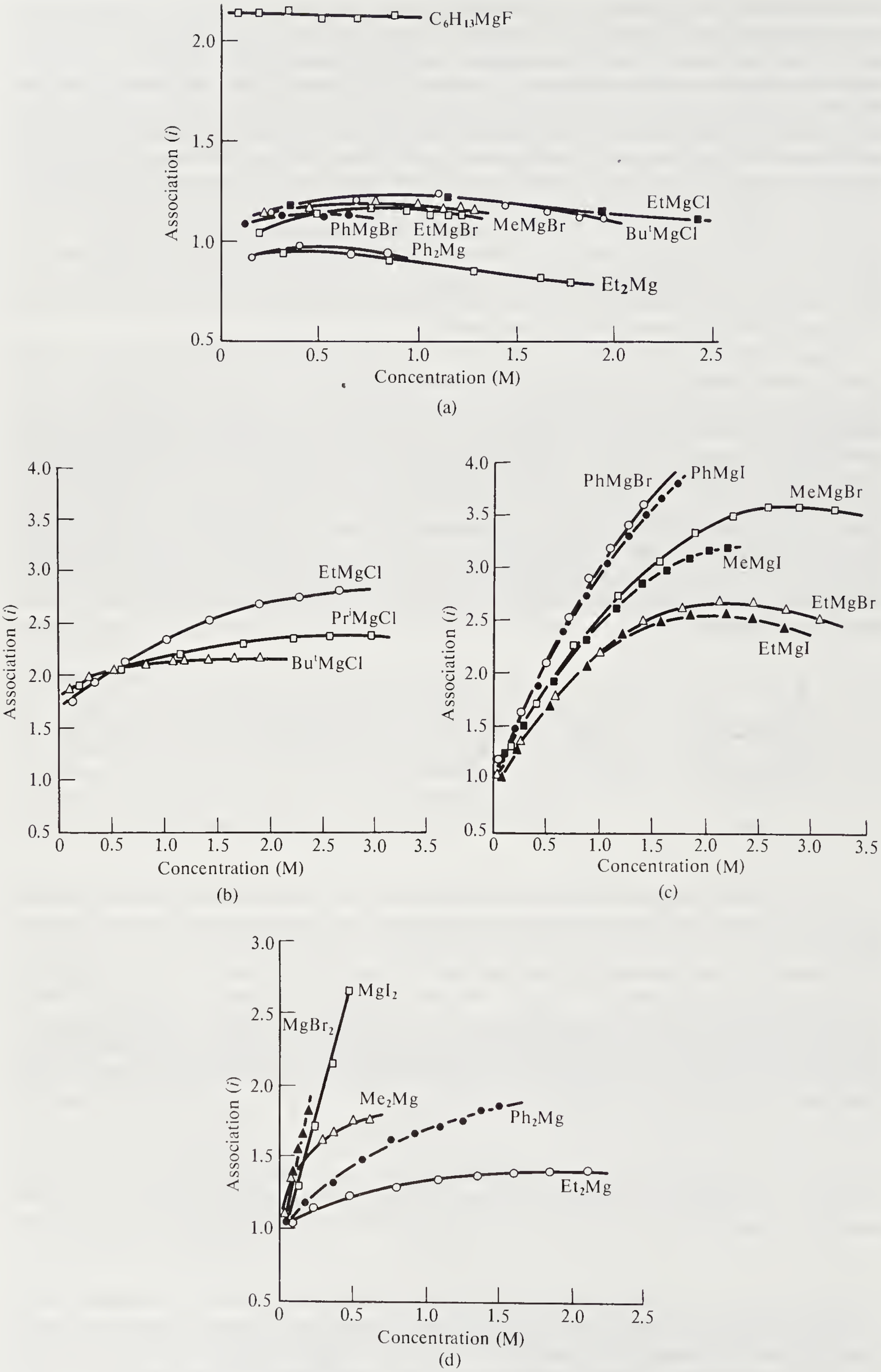


Figure 1 Degree of association (*i*) as a function of concentration: (a) for MgR_2 and Mg(R)X in THF; (b) for Mg(R)Cl in Et_2O; (c) for Mg(Br)R and Mg(R)I in Et_2O; (d) for MgR_2 and MgX_2 in Et_2O ((a)–(c) from E. C. Ashby, *Pure Appl. Chem.*, 1980, **52**, 545; (d) from E. C. Ashby, *Bull. Soc. Chim. Fr.*, 1972, 2133 (reproduced by permission))

(61) and also (62) have been proposed, all organometallic ions being solvated and possibly associated. However, with delocalized organic ligands as in Mg(Cp)X ion pairs, Cp^-Mg^+X, are probably present.[230]

$$\mathrm{Mg(R)X} \rightleftharpoons \mathrm{M\overset{+}{g}R} + \mathrm{X^-} \tag{61}$$

$$\mathrm{2Mg(R)X} \rightleftharpoons \mathrm{M\overset{+}{g}R} + \mathrm{Mg(R)X_2^-} \tag{62}$$

In HMPT ionization is extensive;[252] $MgBr_2$ itself is completely dissociated and Mg(Br)Et shows high conductivity ($\Lambda_M > 20$) and the cryoscopically determined degree of association $i \approx 0.7$ confirms approximately 30% ionization according to equation (61). The dimagnesium reagents $BrMg(CH_2)_nMgBr$ ($n = 4, 5, 6$) are dissociated as 1 : 1 electrolytes.[255] On the other hand chloro compounds Mg(Cl)R are weakly ionized.[252] The absorption maxima in the UV spectra of Grignard reagents in ethereal solutions is shifted to lower energy on addition of HMPT. When more than two molar equivalents of HMPT are present the benzylic-type derivatives Mg(R)X (R = Bz, Me_2PhC, Ph_2CH, Ph_3C) show visible maxima $\lambda_{max} \approx 450$ nm, assignable to the presence of carbanions in this coordinating solvent.[142]

(*b*) *Electrochemical studies.* Polarographic studies of Grignard reagents in DME show two reduction waves, one (at −2.47 V, relative to 10^{-3} M $AgClO_4/Ag$) corresponding to reduction of MgX_2 and the second (−2.7 to −2.8 V) corresponding to Mg(R)X.[242] The product of reduction in ethereal solvents is metallic magnesium. Oxidation of Grignard reagents occurs readily and has been studied at various metal electrodes. With inert electrodes such as Pt or Au the ease of oxidation of Mg(R)X in THF diminishes in the order $R = Bu^t > Et > Pr^i > \text{vinyl} > Bu^n > Me > Ph$.[256] This oxidation reaction has also been studied in relation to the formation of radical anions of aromatic hydrocarbons and by this method the following values have been assigned to this potential for several species, Mg(R)X: $Mg(Cl)Pr^i$, Mg(Cl)Et ≈ −2.6 V; $Mg(CH{=}CH_2)Cl < -2.5$ V; $Mg(Br)Et < -2.45$ V; $Mg(Bu^n)Cl \approx -2.45$ V; $Mg(Cl)Me < -2$ V; Mg(Cl)Ph, $Mg(Br)Me > -2$ V.[256] The oxidation reaction (equation 63) involves R· radical formation and typical radical products are obtained or, in the presence of unsaturated reactants, radical processes are initiated.[7] If the electrodes are reactive metals, radical attack may produce new organometallics; compounds PbR_4 have been synthesized by this method[257] and unstable organosilver compounds have been reported.[258]

$$\begin{aligned}\mathrm{Mg(R)X} &\longrightarrow \mathrm{M\overset{+}{g}X} + e + [\mathrm{R\cdot}]\\ &\longrightarrow \mathrm{R_2} + \mathrm{RH} + \mathrm{R(-H)} + \text{other radical products}\end{aligned} \tag{63}$$

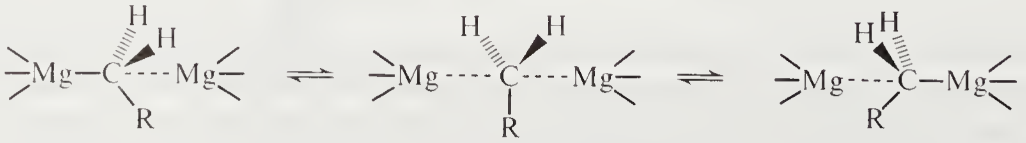
By determining zero current potentials of a hydrogen electrode in a solution of Grignard reagent undergoing reaction with active hydrogen compounds such as BuOH or $PhNH_2$, a scale of basicity for some species Mg(R)X has been proposed. In THF the basicity falls in the sequence X = Cl > Br and $R = Me > Et > Bu^n > Ph$ (values for Mg(Cl)R ($R = Pr^i, Bu^t$) probably being higher but not obtainable by this technique).[245,259] By addition of HMPT the basicity is increased and this is associated with a decrease in oxidizing properties.[79]

(*c*) *Spectroscopic properties.* Many spectroscopic studies of Grignard reagents have been carried out and a number of examples relating to structure and reactivity are discussed elsewhere in this chapter. In ^1H NMR spectra the α-H atoms of a magnesium bound alkyl group R characteristically resonate at slightly higher fields than TMS in the range $\delta = -2$ to 0 p.p.m. Under conditions of fast exchange this is a weighted mean for species involved in the Schlenk equilibrium.[104] At low temperatures, when separate α-H resonances occur for Mg(R)X and MgR_2, the former are found at lower field, being more deshielded by the electronegative halogen ligands (*e.g.* Mg(Br)Me, $\delta = -1.55$ p.p.m.; $MgMe_2$, $\delta \approx -1.70$ p.p.m. in Et_2O at -100 °C).[239] Solvation affects the resonance and increasing donation by solvent shifts the α-H resonance to higher fields;[249,260] a sequence of increasing solvent basicity has been devised on this basis from the CH_2 resonance of Mg(Br)Et: anisole $< Pr^i_2O < Et_3N < Bu^n_2O < Et_2O <$ THF $<$ DME with δ varying from -0.115 to -0.785 p.p.m.[260] ^{13}C NMR spectra have been recorded for many Mg(R)X species and α-C resonances for alkyl derivatives occur mainly in the range +25 to -15 p.p.m. and for Mg(Br)Ph at 164.4 p.p.m.[261,262] Fluoroaryl Grignards have been subjected to analysis by ^{19}F NMR spectroscopy.[240]

IR and Raman studies of Grignard reagents in solution have identified Mg(R)X as the main species of the Schlenk equilibrium in Et_2O and, at least at low concentrations when X = Br or I, these are monomeric and probably disolvated.[214,233,241] It has been reported from Raman studies that at higher concentrations halogen-bridged and alkyl-bridged associated species exist[263] (but contrast ref. 233). When X = Cl or F the vibrational spectra have been attributed to dimeric halogen-bridged species in solution (**39**).[214,249] In THF, both Mg(R)X and MgR_2 have been distinguished by IR spectroscopy.[241] Typical ν_{Mg-C} bands occur in the range 480–535 cm^{-1} when R = alkyl and in the range 365–400 cm^{-1} when R = aryl but the latter may be coupled with other aryl vibrational modes.[233,264] Also, as in the solid state, bands assignable to ν_{Mg-X} (*e.g.* 240 cm^{-1} for Mg(Br)Et in Et_2O) and coordinated ethers have been reported.[214,233]

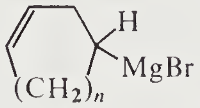
The electronic spectra of most saturated alkyl Grignards and of Mg(Cp)X do not exhibit a $\lambda_{max} >$ 210–220 nm (N.B. $\lambda_{max} = 228$ ($\log \epsilon = 3.31$) has been reported for Mg(Br)Me in THF[230]) but all show an absorption tail that extends to wavelengths above 254 nm.[265] Aryl Grignards have a strong absorption at *ca.* 260 nm (*e.g.* 248 nm for Mg(Br)Ph in Et_2O[142]) assignable to a $\pi \rightarrow \pi^*$ transition, a long tail extending towards 350 nm, assigned to a $\sigma_{C-Mg} \rightarrow \pi^*$ transition, and also a shoulder moving to higher wavelength with increasing solvent polarity.[266] Benzylic Grignards show maxima varying from 266–318 nm in Et_2O for the sequence R = Bz $<$ $PhMe_2C$ $<$ Ph_2CH $<$ Ph_3C.[142] Addition of HMPT in up to two molar equivalents to these reagents shifts λ_{max} to higher wavelength but with greater amounts of HMPT absorbances occur in the visible at *ca.* 450 nm and this is attributed to the presence of free benzylic-type carbanions. Allylic Grignards also show well defined UV absorbances with λ_{max} *ca.* 250 nm (*e.g.* Mg(allyl)Br, 246 nm ($\epsilon = 4300$) in Et_2O).[267]

(*d*) *Dynamic structural interconversions.* The configurational stability of α-C atoms in alkyl Grignard reagents is of interest. As noted in Sections 4.1.1.1,iv and v, no optical isomers with chirality at this centre have been separated for simple alkyl derivatives although this has been possible for a cyclic secondary Grignard. Ready inversion of the primary α-CH_2 occurs in $Mg(CH_2R)X$ (RCH_2 = 2-methylbutyl or 3,3-dimethylbutyl) and this has been monitored by variable temperature ^1H NMR spectroscopy.[268,269,270] The rate is faster when X = Cl than X = Br and is slower in more strongly electron-donating solvents. In Et_2O, under conditions when species $Mg(CH_2R)X$ (X = Br, I, CH_2R) are monomeric the inversion rate shows second order dependence on organomagnesium concentration but for the predominantly dimeric reagent with X = Cl first order kinetics are observed.[269] All the evidence supports a non-ionic mechanism involving a bridged intermediate as shown in equation (64). This mechanism is related to that proposed for exchange of alkyl groups in the Schlenk equilibrium but it has not been established with certainty whether inversion occurs with each exchange or whether exchange with retention of configuration also takes place as found for diorganylmagnesium derivatives (see Section 4.1.2.3).



(64)

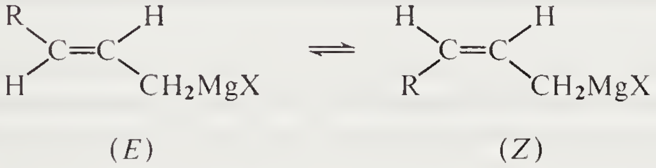
Cyclic secondary Grignards normally undergo slow inversion at the α-C atom on the NMR time scale even at high temperatures up to 175 °C[30] and this has been attributed to the poor bridging ability of these secondary groups.[30,147,148,268] Exceptions to this are cyclic homoallylic compounds (**47**) for which rapid inversion has been observed at ambient temperatures and it is argued that the double bonds enhance the electrophilicity of the magnesium centre to promote the S_E2 mechanism.[271]



$n = 1, 2$

(47)

NMR studies show that allylic Grignard reagents undergo a rapid 1,3-shift of magnesium atoms, equation (42).[236,272] On the basis of some spectroscopic studies a largely ionic structure has been assigned to these allyl reagents[235,262] but analysis of both ^{1}H NMR and also ^{13}C NMR, using a deuterium isotopic perturbation technique, supports a monohapto covalent (but undoubtedly polar) instantaneous structure for these magnesium derivatives in Et_2O and THF, in contrast to structures of alkali metal derivatives.[236] Also, the $\nu_{C=C}$ vibrations (1565–1588 cm^{-1}) are intermediate in magnitude between related vibrations in ionic and simple covalent allylmetal species.[272] In unsymmetrical compounds of equations (42) and (65), the primary form predominates in solution and there is a rapid equilibrium between the *Z*- (*cis*) and *E*- (*trans*) forms even at −80 °C.[236] The ratio $(Z)/(E)$ can be determined from ^{1}H NMR coupling constant measurements and by analysis of the products obtained by protonation of the organometallic compound. In the absence of steric effects the (*Z*)- form is slightly preferred but as shown by the following results for $Mg(CH_2CH{=}CHR)Cl$ steric hindrance favours the (*E*)- isomers: $(Z)/(E) = 60/40$, 45/55, 30/70 and 3/97 for R = Me, Et, Pr^i and Bu^t respectively.[236] It should be noted that in the gas phase the (*E*)-form of the butenyl anion is more stable by 0.8 kJ mol^{-1}.[273]



(65)

(*e*) *Theoretical and thermochemical studies.* A number of theoretical studies of halogenoorganylmagnesium compounds have been carried out using extended Hückel, CNDO/2, SCF and *ab initio* MO calculations.[274,275] In the gas phase, a linear geometry is predicted for $[Mg(Me)X]$ (X = F, Cl) with an Mg—C bond dissociation energy of ≈163 kJ mol^{-1}. Charge distribution and bond lengths in these derivatives have also been calculated. Approximate calculations involving solvation by ethereal solvents and the effects of dimerization *via* halogen bridges have been reported.[275] Experimentally the enthalpies of formation ΔH_f° of a number of Mg(R)X compounds have been measured calorimetrically and from these results it can be concluded that on variation of the organic group R the Mg—C bond dissociation energy increases in the sequence: $R = Bu^t < \text{allyl} < Bz < Bu^s < Pr^i < Et < Bu^i < Bu^n < Me < Ph$.[276] Absolute values for *D*(Mg—R) have not been accurately obtained but an early study reported an approximate value of 280 kJ mol^{-1} for MgMe(I).[277]

4.1.1.3 Reactions

The main usage of Grignard reagents is in organic synthesis, especially in reactions at functional carbon centres, and these reactions are discussed in detail in Chapter 44. A number of reactions have been mentioned in Sections 4.1.1.1,ii and iii as indirect methods for preparation of new Grignard reagents. Thus, this section will be limited to a discussion of the simpler reactions of these compounds and an outline of their use in organometallic and related syntheses, although this latter topic will also be covered in chapters devoted to the specific metal or metalloid element.

(*i*) *Decomposition and related reactions*

Grignard reagents containing saturated alkyl ligands decompose thermally at temperatures over 100 °C and the main products are alkene and magnesium hydride.[215,217,278] The reaction proceeds by β-elimination and the intermediate MgHX disproportionates in the solid state under these conditions into a mixture of binary products (equation 66). The presence of coordinating HMPT stabilizes a Grignard reagent to thermal decomposition by blocking a coordination vacancy necessary for β-elimination.[249] Other side products are formed depending on temperature and reaction conditions. Thus, Mg(Et)X also produces ethane, probably by a radical cleavage followed by dismutation or H-abstraction.[215] It is relevant that thermal decomposition of $\mathrm{Mg(Bu^t)_2}$ in solution occurs primarily by radical fission.[279] 1-Butene is another major side product in the decomposition of Mg(Et)X, formed *via* insertion of ethylene into an Mg—Et bond at high temperature, and C_3–C_6 hydrocarbons are also formed in smaller quantities. The solid pyrolysate on hydrolysis yields primarily H_2 from MgH_2 but also small amounts of acetylene and propyne from carbides MgC_2 and Mg_2C_3.[215]

$$2\mathrm{Mg(CH_2CH_2R)X} \xrightarrow{\Delta} 2\mathrm{CH_2{=}CHR} + \mathrm{MgH_2} + \mathrm{MgX_2} \qquad (66)$$

Thermal decomposition of *ortho* halogenoaryl Grignard reagents usually involves elimination of magnesium(II) halide and formation of an aryne intermediate, but generally the magnesium compounds are more stable than organolithium analogues.[174] An intramolecular *ortho* elimination mechanism probably occurs although it is noted that for $\mathrm{MgBr(C_6F_5)}$ intermolecular nucleophilic displacement of fluorine also takes place on thermolysis.[280] α-Halogenoalkyl Grignard compounds decompose at relatively low temperatures and carbene intermediates appear to be implicated[80,93,174] although perfluoroalkyl compounds $\mathrm{Mg(C_nF_{2n+1})X}$ form alkenes, mainly *trans*-$\mathrm{R_fCF{=}CFX}$, and the experimental evidence does not favour carbene or simple anionic organic intermediates.[96,281] Thermal stabilities of other functionalized Grignard reagents are discussed in Section 4.1.1.1,vii.

Photolysis at 254 nm of Grignard reagents with 3-phenyl-1-propyl or 1-phenyl-2-propyl ligands causes fragmentation into terminal alkene, MgH_2 and MgX_2, with a quantum yield of *ca.* 0.1.[265] This reaction also probably involves β-elimination and in support of this, benzyl(halogeno)-magnesium compounds without β-H atoms show high stability to such photolysis.

Autoxidation by molecular oxygen initially produces alkylperoxo derivatives, which may be isolated as hydroperoxides by carefully controlled experiments at low temperatures,[282] but finally forms alkoxo species.[5–7] The radical chain mechanism of Scheme 9 is believed to account for this reaction and explains typical radical side reactions such as the cyclization of 6-hexenyl Grignard reagents.[283] Chemiluminescence is observed in the reaction of oxygen with $\mathrm{MgBr(}p\mathrm{\text{-}C_6H_4X)}$ (X = H, Cl) in ethers and the main emitting species are brominated biphenyls[284a] but *p*-terphenyls are involved in other systems.[284b] Sulphur and selenium will also yield products Mg(YR)X (Y = S, Se).[5–7]

$$\mathrm{Mg(R)X} \xrightarrow{O_2} \mathrm{R\cdot}\ \text{(initiation)}$$

$$\left.\begin{array}{l} \mathrm{R\cdot} + \mathrm{O_2} \longrightarrow \mathrm{ROO\cdot} \\ \mathrm{ROO\cdot} + \mathrm{Mg(R)X} \longrightarrow \mathrm{Mg(OOR)X} + \mathrm{R\cdot} \end{array}\right\}\ \text{(chain process)}$$

$$\mathrm{Mg(OOR)X} + \mathrm{Mg(R)X} \longrightarrow 2\mathrm{Mg(OR)X}$$

Scheme 9

Reactions of Grignards with compounds containing proton active groups are commonplace and most derivatives with OH, SH, NH, PH and AsH bonds, as well as more acid hydrocarbons (Section 4.1.1.1,ii), liberate RH from Mg(R)X. This reaction is the basis for determination of active hydrogen in organic compounds by the Chugaev–Zerewitinoff method or, conversely, usually by addition of H_2O or MeOH, for quantitative analysis of a Grignard solution.[5–7,285] Titration of the Mg—C bond by butan-2-ol using an indicator such as 1,10-phenanthroline has been recommended for analysis.[286]

Reaction of dihydrogen with Grignard reagents occurs at temperatures of 75–150 °C and pressures of *ca.* 350 atm according to equation (67).[7,287] Reactions with molecular halogens (Cl_2, Br_2 and I_2) occur readily by a formally similar reaction (equation 68), but when $X'_2 = Cl_2$ or Br_2 and $X \neq X'$ mixed organic halides are produced.[7,288] Concurrent dimerization to R—R may occur and this may cause inaccuracy if an iodometric method is used to analyze Grignard solutions. The reactivity to halogenation follows the order R = vinyl ≈ aryl > alkyl > alkynyl.

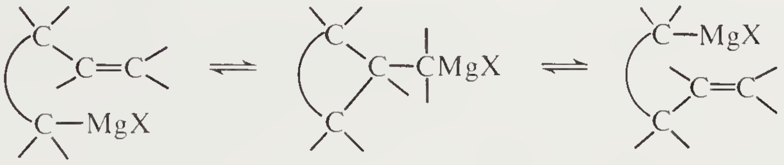
$$2\text{Mg(R)X} + H_2 \xrightarrow[350\ \text{atm}]{\Delta} 2\text{RH} + \text{MgH}_2 + \text{MgX}_2 \qquad (67)$$

$$2\text{Mg(R)X} \xrightarrow{X'_2} \text{RX} + \text{RX}' + \text{MgX}'_2 + \text{MgXX}' \qquad (68)$$

Decomposition of Grignard reagents by reactions with the solvent has been mentioned previously (Section 4.1.1.1,i(e)). The cleavage of C—O bonds of ethers and related compounds by Grignard reagents has been reviewed[54] and studies of this reaction with 1,3-dioxolanes show that preliminary coordination to the magnesium occurs and the mechanistic course is dependent on the degree of association of the Grignard.[289]

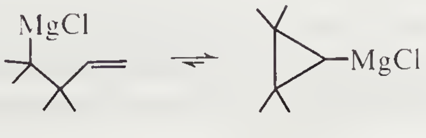
(*ii*) *Rearrangement reactions*

Two relatively recent reviews give a comprehensive coverage of rearrangements of organomagnesium compounds.[143] The principal class of rearrangements observed for Grignard reagents includes ring formation by intramolecular addition to a carbon–carbon multiple bond, its reverse reaction of β-cleavage involving rupture of a strained ring or a sequence of reactions with a combination of these steps as illustrated generally in equation (69). Such a reaction may occur during preparation of reagent (see 4.1.1.1,v), when a radical mechanism may operate, but in many examples the process takes place after formation of the organometallic compound by a non-radical mechanism and may require a relatively high temperature. Rings of three to six carbon atoms have been implicated in such processes and the unsaturated entity may alternatively be an alkyne or allene group.[143]

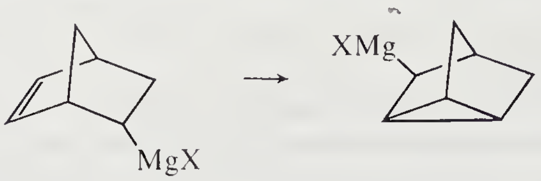


(69)

The facile ring cleavage rearrangement of the cyclopropylmethyl Grignard has previously been mentioned[149] (equation 38), and this typical cyclopropylmethyl–3-butenyl interchange has been studied for a wide variety of substituted cases.[143] In general the acyclic organometallic is more stable than the strained ring species and ring cleavage occurs. However, in the equilibrium of equation (70) the cyclic form is present in >99.9% since the open chain species are destabilized as tertiary derivatives and the ring stabilized by the Thorpe–Ingold '*gem*-dimethyl' effect.[150] Another exception (equation 71) has the three-membered ring incorporated into the nortricyclyl system[290] and the vinyl Grignard of equation (40)[154] stabilizes the cyclopropyl ring. For other 3-enyl Grignard reagents the cyclopropylmethyl species may be an intermediate (or possibly transition state) in rearrangement reactions of general equation (69). The more stable acyclic Grignard (primary > secondary > tertiary) will predominate in the equilibrium; a specific example is given in equation (72), the enthalpy difference between secondary and primary functions being estimated to be 15.5 kJ mol^{-1}.[291] Rearrangements of isotopically labelled species (equation 73) have been demonstrated and a cyclic intermediate with finite lifetime is supported by the fact that *cis–trans* isomerization at the double bond occurs at a similar rate to label rearrangement.[292]



(70)



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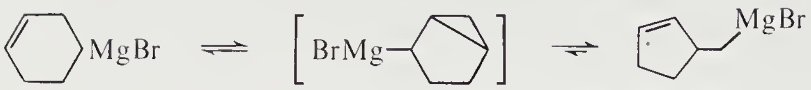

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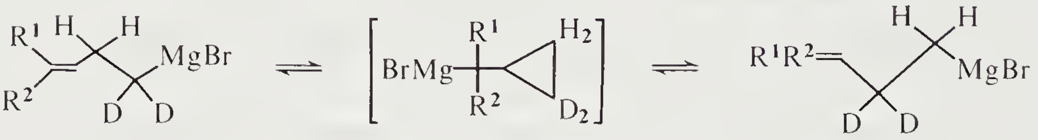
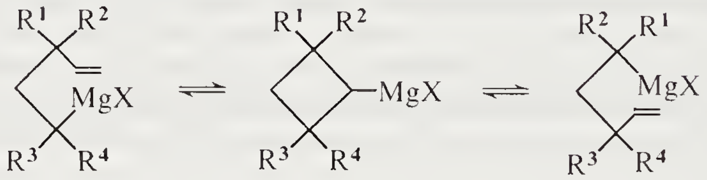
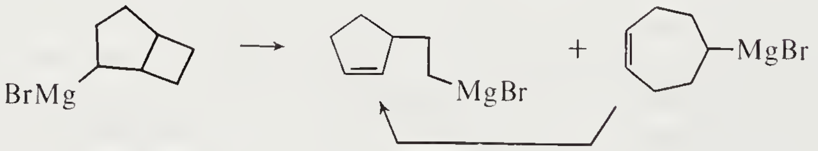


(73)

In systems involving four-membered rings the equilibrium again usually lies on the side of the acyclic organometallic but a combination of ring alkylation and the formation of secondary or tertiary open-chain species may stabilize the cyclic system. In equation (74) when $R^1 = R^2 = R^3 = R^4 = Me$, essentially complete cyclization occurs at 70 °C,[151] when $R^1 = R^2 = R^3 = R^4 = H$, the equilibrium constant $K = 1.8\text{–}5.6 \times 10^{-4}$ (100 °C), and when $R^1 = R^3 = Me$, $R^2 = R^4 = H$, $K = 6.9$ (100 °C) in THF.[293] Secondary 4-enyl Grignards (*e.g.* equation 74, R^3 = alkyl, $R^1 = R^2 = R^4 = H$) may be converted into the more stable primary derivatives *via* a cyclic intermediate. Rearrangements involving cyclobutyl ring cleavage have been observed in bicyclic systems as shown by equation (75)[294] and in addition reactions of allylic Grignards to norbornene (*e.g.* Scheme 10)[115] or benzyne (Scheme 7).[129]



(74)



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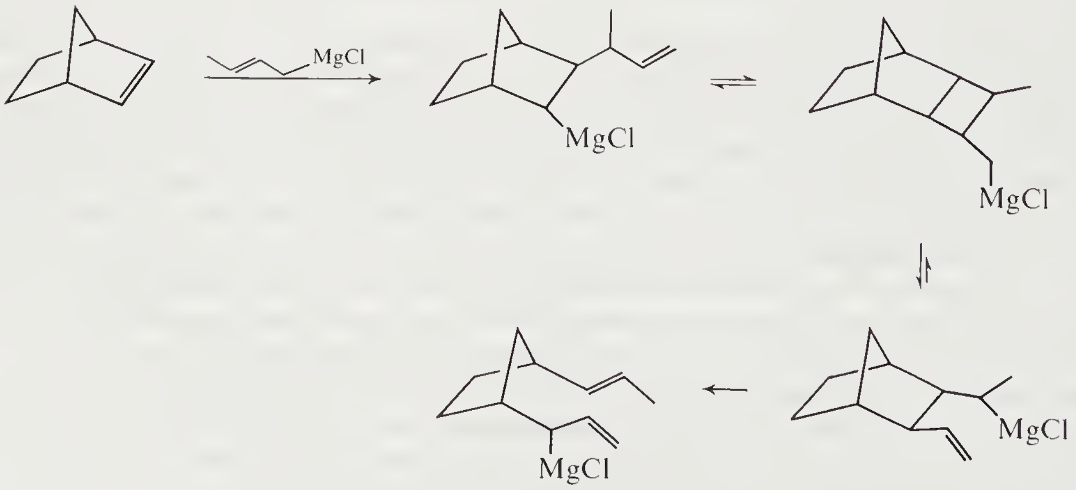
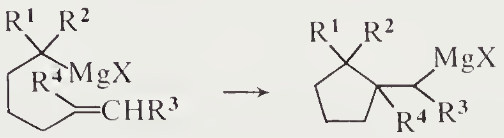


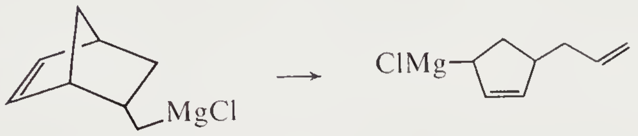
Scheme 10

The reduced ring strain of five-membered rings causes the cyclic product to be more stable than the open chain form in most cases although ring closure of the latter may be slow and high temperatures may be necessary, especially for primary to secondary Grignard conversions.[143,295]

Studies on 5-hexenyl derivatives (equation 76) have been reported and when a substituent is present, the cyclic *trans* product is favoured. A further example of cyclization with an allylic system has been quoted earlier (equation 27)[124] and reactions with alkynyl Grignards are also known.[143] Rare examples involving cleavage of five-membered ring systems are found in relatively strained bicyclic systems when allylic Grignards are the final products (Scheme 10[115] and equation 77).[143]

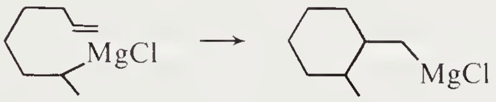


(76)



(77)

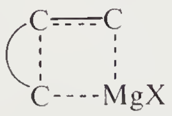
The stability of six-membered rings precludes simple cleavage rearrangements and the rate of ring closure to six-membered systems is low so that few examples are known. The reaction shown in equation (78) is 2800 times slower than the analogous cyclopentyl reaction but as in the latter reaction the *trans* product predominates[296] Further examples are shown in Scheme 6[122] and by the alkynyl derivative of equation (79).[143]



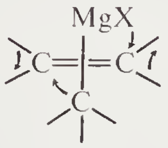
(78)

(79)

Generally these rearrangements occur less readily in THF than Et_2O and in relatively dilute solutions are simple first order reactions. Rates are relatively insensitive to the purity of the magnesium and correlations with substituent groups and ring sizes have been reported. The mechanism for addition/elimination is not established unequivocally but (see ref. 143) simple radical or heterolytic fission of the Mg—C bond is inconsistent with the experimental data and a concerted, intramolecular process involving a four-centre transition state (**48**) has been proposed, possibly preceded by an intermediate π-complex formation between alkene and Mg. To account for stereochemical effects it has also been suggested that the Mg—C function approaches the unsaturated bond perpendicularly, followed by a rotatory motion prior to addition (**49**), cleavage occurring by a reverse process.[143] However, it should be noted that other workers support a bimolecular carbanionic mechanism involving solvated species of the types RMg^+ and $RMgX_2^-$ to account for the dependence of rates on Grignard concentration in more concentrated solutions.[292]



(**48**)



(**49**)

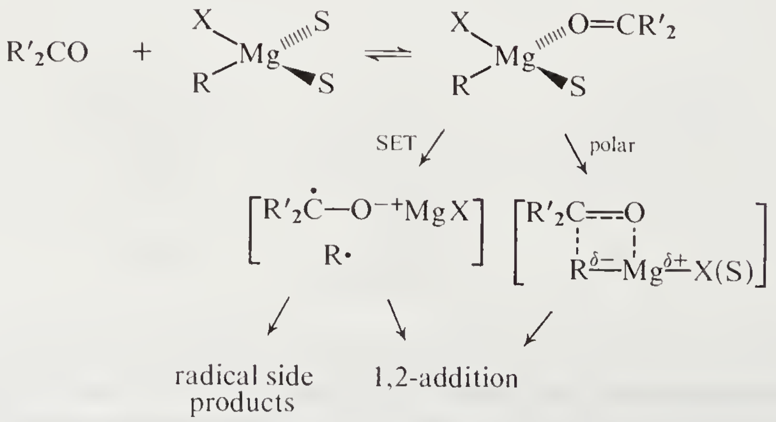
The stereochemical isomerizations and structural non-rigidity of allylic Grignard reagents in solution have been discussed in Section 4.1.1.2,ii(d). Under thermal conditions cyclization of allylhalogenomagnesium compounds does not occur at temperatures up to 200 °C but cyclopropyl derivatives are formed under UV photolysis (high pressure Hg arc lamp in quartz apparatus) as shown by equation (80), the products being analyzed by carboxylation.[267] The *trans*-cyclopropyl isomers were the major product when R = Ph or CH=CH$_2$, with respective *trans*:*cis* ratios of 49:1 or 6:1.

(80)

Few other uncatalyzed rearrangements of Grignard reagents have been observed although previously mentioned 1,2 shifts of Mg{C(OPh)Ph$_2$}X (equation 53) and the radical rearrangement of equation (36) may be noted here. Thermodynamically controlled isomerizations of secondary to primary Grignard reagents are catalyzed by Ti(IV) compounds, including Ti(OR)$_4$ and TiCl$_4$.[297,298] Thus, chloro(4-octyl)magnesium produces chloro(1-octyl)magnesium in up to 62% yield in the presence of Ti(OBu)$_4$. The conditions for isomerization are 3–5% catalyst added continuously during reaction in THF solution at a temperature in the range −10 to 60 °C. The mechanism probably involves the formation of alkene and a titanium hydride from β-elimination of a titanium alkyl with subsequent reinsertion of alkene into the Ti—H bond, and Ti(III) species have been suggested as the active catalyst. The *cis–trans* isomerization of 1-alkenyl Grignard reagents catalyzed by Ni(II) complexes such as NiCl$_2$(PPh$_3$)$_2$ has also been described and nickel π-complexes are suggested as intermediates.[299]

(*iii*) *Reactions with organic compounds*

Since organic syntheses involving Grignard reagents are discussed in detail in Chapter 44 only a few general comments on the reactivity and mechanism of such reactions will be made here. The most studied reactions involve the organic carbonyl function, especially in ketones, and of the many contributors to this field[5–7] the more recent researches of Ashby,[104,243] Holm,[300] Tulmets[301] and associates should be mentioned. The initial step normally involves coordination of the carbonyl oxygen atom to magnesium. Two extreme mechanisms are then possible; a polar, heterolytic reaction or a single electron transfer (SET) homolytic process as illustrated for 1,2-addition in Scheme 11 taking, for simplicity, the monomeric Mg(R)X as the active species. Any MgR$_2$ or oligomeric entities present will also react. In the SET process the radical pair may not necessarily separate to form free radicals. Other side reactions do take place and under some conditions may predominate. These reactions include conjugate addition to aryl or unsaturated systems (R′), reduction to form Mg(OCHR′$_2$)X by Grignard β-H transfer or by ketyl radical H-abstraction, radical coupling to form pinacol derivatives or enolization by abstraction of an α-proton from R′. Similar SET or polar mechanisms may occur for other functional group reactions. Transition metal-catalyzed reactions often involve radical intermediates and such processes may also occur in the presence of adventitious impurities. Homolytic and SET mechanisms have been observed in the absence of known catalysts for reactions of certain compounds containing C=S,[136] N=O,[302] N=N[300] and NO$_2$[303] groups, especially aryl derivatives which are more readily reduced, and also in oxidation reactions with R$_2$O$_2$[304,305] or R$_2$S$_2$,[305] in exchange or coupling reactions with halogenated organic compounds[306] and in simple electron transfer to aromatic hydrocarbons.[307]

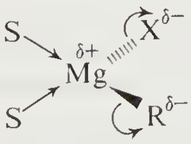


Scheme 11

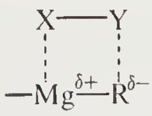
The relative reactivity of Grignard reagents Mg(R)X to SET mechanisms in reactions with $Bu^t_2O_2$[304] or Ar_2CO[104] follows the order R = Bu^t > Pr^i > Et > Me > Ph, which is essentially the same as the electrochemically measured decreasing ease of oxidation and is aided by more polar solvents, HMPT > THF > Et_2O. The same order reflects the decreasing basicity of the group R so that reactions which are simply dependent on Mg(R)X acting as a base, such as hydrocarbon metallation, should show a similar trend. This is essentially found for reaction with phenylacetylene[308] — reactivity sequence R = allyl ≫ Pr^i > Et > Pr^n > Me with alkyl > vinyl > aryl > 1-alkynyl and also X = Cl > Br > I. However, in reaction with halogens, chlorotrimethylsilane, 2-methylpropanol, carbon dioxide and formaldehyde, the reactivity order is different; R = vinyl > aryl > alkyl > 1-alkynyl.[308] Ketones which are difficult to reduce (*e.g.* Me_2CO) react primarily by the heterolytic pathway and show a reversed reactivity sequence to that of the SET process (R = Me ≈ Et > Pr^i > Bu^t), the R group forming the most stable carbanion being the most reactive.[104] Earlier studies of benzonitrile or esters, although exhibiting some differences show an essentially corresponding order for alkyl group reactivity.[6,7] The reactivity sequence for PhCN was found to be allyl > Ph > Et > Pr^n > Pr^i > Bu^n > Bu^s > Bu^i ≫ Bu^t ≫ C≡CPh.

In all the above comparisons there must be consideration of the constitution of the Grignard in solution as determined by the physical conditions, reagent concentrations and presence of potentially coordinating groups. In particular, solvent changes markedly affect the reactivity.[42,309] Solvent influences on the position of the Schlenk equilibrium and degree of aggregation have been discussed in Section 4.1.1.2,ii. For monomeric species $Mg(R)Y(S)_n$ (Y = halogen or R; S = coordinating solvent), present in dilute Et_2O solutions and more polar solvents, the coordinated solvent induces more polarity in Mg—R and Mg—X bonds, as depicted in (**50**). The better coordinating solvents increase the basicity of group R and hence increase the reactivity for processes in which the carbanionic character is the rate determining factor. This increased reactivity in some coordinating solvents is found for Wurtz coupling,[76] metallation,[35,76] halogen–metal exchange[310] and polymerization of styrene.[311]

The possible concomitant increase of positive charge on magnesium by solvation (**50**) may lead to increasing electrophilicity of this centre and many mechanisms have been interpreted as involving a combination of the nucleophilic nature of R groups and electrophilic character of Mg.[42,309] A cyclic intermediate has been suggested for many reactions at a polarized $X^{\delta-}$—$Y^{\delta+}$ bond (**51**). However, strong complex bonding between solvent molecules and magnesium will effectively block coordination sites and prevent electrophilic attack by Mg at reacting functional groups. Thus, additions to ketones[104,243] or nitriles[312] and oxirane ring openings,[313] in which complexation with metal precedes reaction, are generally slower in more coordinating solvents. In highly coordinating HMPT the alternative proton abstraction–enolization of ketone is promoted.[87a]



(**50**)

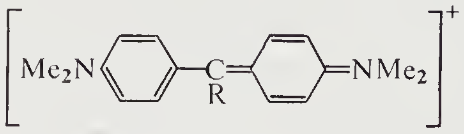


(**51**)

Gutman[309] has classified solvents according to their electron donicity and acceptor properties and pointed out that for Grignard reactions ethereal solvents are ideal media due to their pronounced donor properties, absence of electrophilic character and their reluctance to undergo induced bond polarization on coordination to magnesium.

Other effects of solvents on carbonyl addition reactions are also manifest in asymmetric syntheses using optically inactive Grignard reagents in chiral solvents[42,314] and also in variations in geometric isomers of products from cyclic ketones in differing solvents.[42,315]

Reactions of Grignard reagents with organic functional groups are useful in analysis. Gilman's qualitative test I,[316] using the reaction with bis(*p*-dimethylaminophenyl)ketone (Michler's ketone) to give a green–blue/green colour due to cation (**52**), formed by 1,2 addition and acid work-up, is suitable for detection of Mg(R)X and has been modified to distinguish between various R groups including R = aryl.[317] Gilman's test III, using $BiPh_3X_2$ (X = Cl, Br), which gives a transitory purple colour, is also suitable for detection of aryl derivatives.[318] 1,10-Phenanthroline and 2,2′-biquinoline give violet–green colours with small amounts of Mg(R)X and have been used as indicators in quantitative titration with *s*-butanol.[286] Quantitative analysis of Grignards by total base analysis after acid hydrolysis, although useful for freshly made solutions,[319] often gives high results due to presence of alkoxide, *etc.*, but a second titration after initially reacting all Grignard with tetrachloromethane has been employed to determine the inactive base.[320] Methods based on spectrophotometric determination of unreacted ketone (*e.g.* Ph_2CO, Me_2CO) after addition of excess of the carbonyl compound have been described.[319] Also, the distinct colour change between deeply coloured bis(arylimido)sulphur compounds and colourless product of equation (81) has been proposed as the basis of an analytical procedure.[321]



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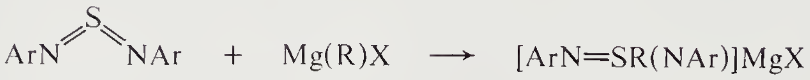


$$ArN{=}S{=}NAr \quad + \quad Mg(R)X \quad \longrightarrow \quad [ArN{=}SR(NAr)]MgX \qquad (81)$$

(*iv*) *Synthesis of organometallic compounds*

The principal use of Grignard reagents or diorganylmagnesium compounds in organometallic chemistry is in synthesis of new metal–carbon bonds. The formation of M—C σ-bonds occurs by the general sequence of reactions (equation 82), with X being halogen or similar uninegative ligand, such as an alkoxy group. The reaction is thermodynamically favoured for elements M which are more electronegative than Mg, with the stability of the by-product MgX_2 being the dominating factor in this exchange. Thus, in principle, alkylations of all main group elements, other than alkali or alkaline earth metals, and of transition metals can be carried out. Moreover it should be noted that Group I metals and organomagnesium compounds form 'ate' complexes (Section 4.1.6.1).

$$MX_n(L)_m \xrightarrow{Mg(R)X'} MR(X)_{n-1}(L)_m \xrightarrow{Mg(R)X'} MR_2(X)_{n-2}(L)_m$$
$$\longrightarrow \text{ further alkylation} \qquad (82)$$

Metal alkylation by Grignard reagents was realized within a few years of their discovery and alkyl derivatives of Si, Sn, Pb, As, Sb, Bi and Hg were reported in 1903–4.[322] The relative ease of formation of Grignards Mg(R)X with a wide variation of group R has led to their continued use for such reactions and organolithium reagents are the only other compounds used to a comparable extent. Organolithiums are generally more reactive and this may be an advantage but they show greater tendency to form anionic 'ate' complexes. Grignards may sometimes be usefully employed to obtain products with lower degrees of alkylation. The presence of the additional halide or of a coordinating solvent may be other disadvantages in the use of Grignards when compared to organolithium reagents, but it should be noted that hydrocarbon solutions or suspensions of the Grignard reagents can be prepared, albeit less easily, and also the use of diorganylmagnesium reagents may be preferable to Mg(R)X (see Section 4.1.2.3).

A short general review[323] and articles outlining the use of cyclopentadienyl[324] and allyl[325] Grignards in organometallic synthesis have been published. The use of dimagnesium derivatives, such as $BrMg(CH_2)_nMgBr$[206] or 1,2-$C_6H_4(CH_2MgCl)_2$[326] to form metallocyclic organometallic compounds should also be noted. The *in situ* method for formation of Si—C bonds using SiR_3Cl or SiR_2Cl_2 and Mg metal with an organic compound in HMPT is of interest,[327a] as are similar *in situ* methods for Sn—C bond formation, although organomagnesium intermediates have not been definitively established for these reactions. In general metal alkylations are facilitated by more polar solvents, DME > THF > Et_2O, as found for reactions with halides of Te, Si and Sb[310] and HMPT promotes reactions of $SnPh_3Cl$.[327b]

Of main group elements, Group II metals Be, Zn, Cd and Hg readily form organometallic compounds from the halides (equation 83), as for example in preparations of $Zn(Bu^t)_2$[328] and

$Cd(CH_2)_n$.[329] An advantage in using Mg(R)X over LiR for zinc derivatives is the higher tendency of the latter reagents to form zincates. Organic derivatives of Group III metals are also prepared from Grignards; thus reactions of BX_3 (X = halide, alkoxide) with Mg(R)X will give BR_3 compounds and controlled sequential displacement of alkoxo ligands is possible but further alkylation to $[BR_4]^-$ (especially R = Ar) can occur. Organic compounds of aluminium are less commonly prepared from Grignards and it should be noted that Mg—Al 'ate' complexes are isolable. Reaction of TlX_3 with Grignards in Et_2O normally only proceeds to TlR_2X but in THF complete alkylation is promoted.[310]

$$MCl_2 + 2Mg(R)X \longrightarrow MR_2 + 2Mg(Cl)X \tag{83}$$

Grignard synthesis of Group IV organometallic compounds is a standard procedure and alkylation of $SiClMe_2Ph$ or $SnBu_3Cl$, followed by GLC, has been recommended for quantitative analysis of some Grignard reagents.[285] For silicon, sequential alkylation of derivatives such as $SiCl_2R_2$ can be controlled to give $SiClR_2R'$ or $SiR_2R'_2$. Alkylation of Si—OR bonds also occurs and displacements at chiral centres such as $Si(OR)R^1R^2R^3$ often proceed with retention of stereochemistry, probably by equatorial attack, although allyl and benzyl Grignard reagents have been reported to cause inversion in some cases; in $SiF(OR)R^1R^2$ the fluoro ligand is displaced in more polar solvents by inversion of configuration.[330] Alkylations of halogen or alkoxo containing compounds of Ge(IV), Sn(IV) and Pb(IV) by Grignards are standard and control of reaction conditions may lead to partial or complete alkylation, or in some cases to dimeric or oligomeric products. The transformations of lead(II) chloride (equation 84) *via* an unstable PbR_2 intermediate are useful in preparations, in specific cases, of tetraalkyllead, hexaalkyldilead or the bimetallic intermediate[323,331a] (compounds MR_2, stabilized with sterically bulky R groups, have as yet only been prepared from lithium reagents[331b]).

$$PbCl_2 \xrightarrow{Mg(R)X} [PbR_2] \longrightarrow PbR_3(MgX) \longrightarrow Pb_2R_6 \xrightarrow{\Delta} PbR_4 \tag{84}$$

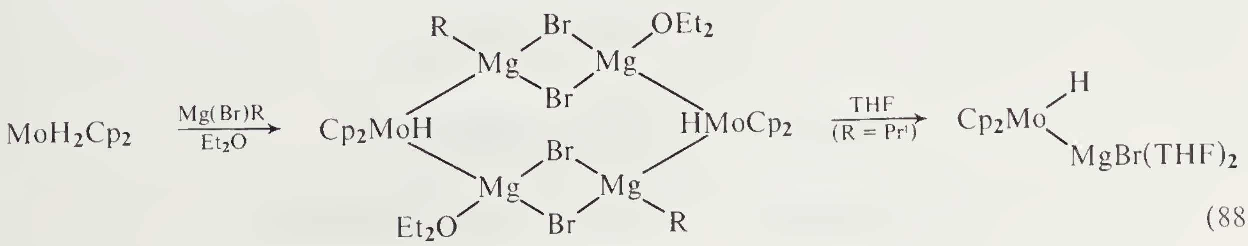
Preparation of tertiary phosphines by Grignard reaction with halogeno phosphorus(III) compounds PX_nR_{3-n} is a well established method and similar processes for As(III), Sb(III) and Bi(III) compounds are useful.[192a,332] The P—OR bond may also be displaced and $P(OPh)_3$ is a good precursor for PR_3.[333] Phosphorus(V) compounds PR_5 cannot be prepared and reaction of PCl_5 with Grignards gives primarily PCl_2R_3 which undergoes further reduction reaction to PR_3 and RCl or is hydrolyzed to $P(O)R_3$.[334] Alkylations of $PR_n(X_{3-n})(Y)$ (Y = O, S, Se) also occur and in PO(OR)(Ph)(SMe), depending on the nature of R, methylation using Mg(Me)I occurs either at the P—S bond with retention or at the P—O bond with inversion of configuration at phosphorus.[335] Preparations of aryl derivatives of As(V), Sb(V) and Bi(V) by Mg(Ar)X are also known although LiAr reagents are generally more useful for such reactions. Gilman's colour test III for Mg(Ar)X using $BiPh_3X_2$ should be noted here.[318]

Metal–hydrogen exchange of M—H bonds with Mg(R)X to form MMgX bimetallic species also occurs when M = B, Ge, Sn, P, As and Sb, as illustrated by equations (85),[323] (86)[323] and (87).[332a] Less common for transition metal hydrides, the transformations of equation (88) are also of interest here.[336] Properties of such compounds are discussed in the relevant chapters of this work. The Ni(II)-catalyzed reaction of $SiHR_3$, however, with non-reducing Grignard reagents (R′ = Me, Ph, Bz, allyl, vinyl) is an alkylation (equation 89), mechanistically probably related to hydrosilylation.[337]

$$B_{10}H_{14} \xrightarrow{Mg(R)X} B_{10}H_{13}(MgX) \xrightarrow{Mg(R)X} B_{10}H_{12}(MgX)_2 \tag{85}$$

$$SnHR_3 \xrightarrow{Mg(R)X} SnR_3(MgX) \tag{86}$$

$$PH_2Ph \xrightarrow{Mg(R)X} PPh(MgX)_2 \tag{87}$$



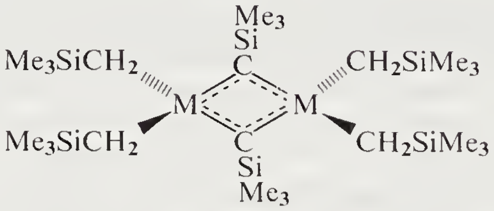
(88)

$$\mathrm{SiHR_3} \xrightarrow[\mathrm{(NiX_2(PPh_3)_2\ catalyst)}]{\mathrm{Mg(R')X}} \mathrm{SiR_3R'} \tag{89}$$

Alkylation by Grignard reagents of transition metals with halogeno or, less commonly, alkoxo or other oxygen-bonded ligands is widely used for synthesis of σ-bonded organometallic compounds although the more reactive, hydrocarbon soluble organolithium reagents have often been preferred. Examples of preparations using magnesium derivatives by general equation (82) have been reported for all *d*-block and some *f*-block elements. The relative instability of transition metal alkyls has found application in the widespread use of compounds of these elements, especially Fe, Co, Ni, Pd, Cu, Ti and Mn, as catalysts for organic reactions of Grignard reagents (see Chapter 44).[48,49,50,124]

The early reported compounds $[\mathrm{AuBrEt_2}]_2$ and $[\mathrm{PtMe_3I}]_4$ were formed using Mg(R)X[338] but development of such syntheses for other metals was slow due to the instability of products and tendency for coupling or other reductive radical reactions to take place. The first binary ('homoleptic') alkyl $\mathrm{TiMe_4}$ was formed from $\mathrm{TiCl_4}$ and the Grignard or LiMe at −78 °C[339] but for later, related methylations the lithium reagent has more generally been employed. Grignard reagents Mg(R)X in which R is stabilized to β-hydrogen elimination,[340] including R = benzyl, neopentyl, trimethylsilylmethyl, neophyl and 1-adamantylmethyl,[341] have proved useful in forming simple, relatively stable alkyl compounds, *e.g.* equation (90) (M = Ti, Zr, V). Other binary alkyls formed from such Grignard and metal halides include $[\mathrm{CrR_4}]$,[340] $[\mathrm{M_2(CH_2SiMe_3)_6}]$ (M = Mo, W)[340] and electron deficient bridged species $[\mathrm{Mn_2(CH_2CMe_2Ph)_4}]$ and $[\mathrm{Mn(CH_2SiMe_3)_2}]_n$.[342] However, even β-stabilized Grignards may undergo α-abstraction and reactions of $\mathrm{MCl_5}$(M = Nb, Ta) or $[\mathrm{ReCl_4(THF)_2}]$ with Grignards give products (**53**) (M = Nb, Ta, Re).[343]

$$\mathrm{MCl_4} \;+\; \mathrm{4Mg(R)X} \longrightarrow \mathrm{MR_4} \;+\; \mathrm{4MgClX} \tag{90}$$



(**53**)

Aryl compounds formed from Mg(Ar)X include $\mathrm{TiPh_4}$, more readily prepared from $\mathrm{TiCl_4L_2}$ (L = py, piperidine, quinoline), and $\mathrm{CrPh_3(THF)_3}$. The instability of the latter and its reduction to Cr(0) species [Cr(PhH)(arene)] caused early difficulties in characterization.[340] The reagent Mg(Mes)X has also proved useful.

The formation of coordination stabilized transition metal complexes containing other ligands as well as ligands with σ-carbon bonds by the general process of equation (82) with L = Cp, CO, $\mathrm{PR_3}$, diene, cot, NO, bipy, *etc.* is a well established procedure.[340] Equations (91)–(95)[344a–e] suffice to illustrate the scope of this reaction but again more reactive organolithium reagents are often preferred, especially for higher degrees of alkylation. Sequential chloro ligand displacement in $[\mathrm{TiCl_2Cp_2}]$ occurs with Grignard reagents and the monoalkyl complexes may be isolated.[340] The degree of alkylation of Pt(II)–diene complexes $[\mathrm{PtI_2(diene)}]$ is dependent on the nature of the diene ligand.[340]

$$\mathrm{NiCl(PPh_3)Cp} \xrightarrow{\mathrm{Mg(Me)I}} \mathrm{Ni(Me)(PPh_3)Cp} \tag{91}$$

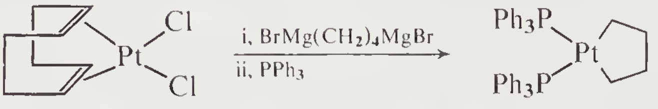
$$\mathrm{ZrCl_2(cot)} \xrightarrow{\mathrm{Mg(R)X}} \mathrm{ZrR_2(cot)} \tag{92}$$

$$\mathrm{CrI(NO)_2Cp} \xrightarrow{\mathrm{Mg(Me)I}} \mathrm{CrMe(NO)_2Cp} \tag{93}$$

$$\mathrm{CrCl_2(Me_2dtc)(bipy)} \xrightarrow{\mathrm{Mg(Br)Ar}} \mathrm{Cr(Ar)_2(Me_2dtc)(bipy)} \tag{94}$$

$$\mathrm{Th(Cl)Cp_3} \xrightarrow{\mathrm{Mg(R)X}} \mathrm{Th(R)Cp_3} \tag{95}$$

A wide variety of groups R have been bonded to transition metals using the Grignard synthesis. Of σ-bonded η^1-ligands mention should be made of the use of bimagnesium reagents to form metallocycles, *e.g.* equations (96)[345] and (97),[326] of the introduction of unsaturated ligands, *e.g.* in $[Fe(CO)_2R(Cp)]$ (R = vinyl, alkynyl)[346] and $[Ru(2\text{-alkenyl})(PR_3)_2Cp]$[347] prepared from the corresponding halogeno complexes, and of the formation of σ-bonded ligands with functional groups that may also chelate to the metal, *e.g.* using the product of equation (10) or reagent (**36**). Fluorocarbon Grignard reagents have been less used than the lithium analogues but it is interesting that the reaction shown in equation (98) gives the *trans* product whereas LiC_6F_5 gives the *cis* derivative.[348]



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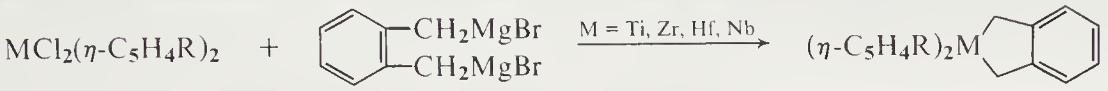
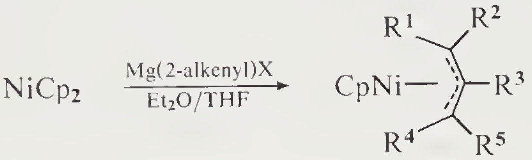


(97)

$$trans\text{-}\mathrm{PtCl_2(SEt_2)_2} \xrightarrow{\mathrm{MgBr(C_6F_5)}} trans\text{-}\mathrm{Pt(C_6F_5)_2(SEt_2)_2} \tag{98}$$

The introduction of π-bonded organic ligands using Grignard reagents is also useful. η^5-Cyclopentadienyl compounds may be produced using Mg(Cp)X but generally sodium, thallium or lithium reagents or dicyclopentadienylmagnesium are often more convenient.[324] Reactions of 2-alkenyl Grignards with appropriate metal halides have produced compounds $[M(\eta^3\text{-alkenyl})_n]$ (M = Ni, Cr, Mn, $n = 2$; M = Ti, V, Cr, Fe, Co, $n = 3$; M = Mo, W, $n = 4$).[349] Substitution of an η^5-cyclopentadienyl group may occur (equation 99).[350]

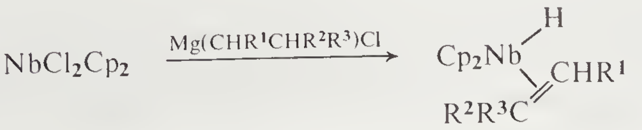


(99)

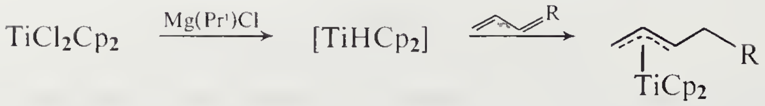
Formation of alkylated transition metal anions is less common from organomagnesium than from organolithium reagents but excess Grignard may form such 'ate' species. In the reaction of $CrCl_3(THF)_3$ with Mg(R)X (R = CH_2CMe_3, CH_2SiMe_3) intermediate anionic species $[CrR_4]^-$ are formed which oxidize to $[CrR_4]$.[340] The reaction of manganese may also be noted (equation 100).[351] Although simple alkylcopper(I) compounds may be prepared using Grignards, of synthetic importance are the complex magnesium cuprates formed from interaction of copper(I) or reduction of Cu(II) compounds with Grignards.[352] These cuprates of magnesium are less well characterized than lithium analogues but derivatives of general formulae $[MgCuR_2X]$ or $[MgCuRX_2]$ may exist and dynamic equilibria are set up in solution. The widespread uses of catalytic quantities of Cu(I) compounds in Grignard reactions with organic compounds probably involve such species as active intermediates.

$$\mathrm{MnCl_2} \xrightarrow{\mathrm{Mg(R)Cl}} \mathrm{MnR_3(MgCl)} \tag{100}$$

Reduction of organotransition metal complexes by Grignard reagents commonly occurs, either by an electron transfer mechanism or by alkylation followed by reductive elimination. Such reductions are often the cause of poor yields in simple metal alkylation reactions. However, some synthetically useful reductions have been mentioned earlier in this section and others include formation of M(III) organometallic compounds from Ti(IV), V(IV) or Nb(IV); an example of equation (101) also involves a β-hydrogen abstraction reaction in the formation of alkene and hydrido ligands.[353] The reduction of $[TiCl_2Cp_2]$ in the presence of alkenes and dienes yields organometallic complexes by a related mechanism (equation 102).[354] Reactions of $[IrCl(cod)]_2$



(101)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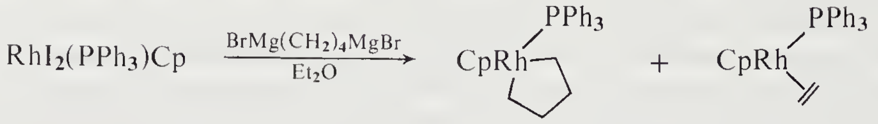

(103)

with $\mathrm{Mg(Br)Pr^i}$ in the presence of dienes also gives products *via* Ir—H intermediates.[355] In the reaction of equation (103) the unexpected product has an ethylene ligand derived from the solvent, $\mathrm{Et_2O}$, which is cleaved by Grignard under the mild conditions of the reaction — the metallocyclopentane coproduct is not the precursor.[356]

Attack of Grignard reagent at coordinated groups can also be observed as in reactions with carbonyl,[357] alkene,[358] cyclopentadienyl,[359] phosphine[360] and related ligands. The reaction of equation (104) is of interest.[361] The formation of transition metal–magnesium bonded species is discussed in Chapter 42.

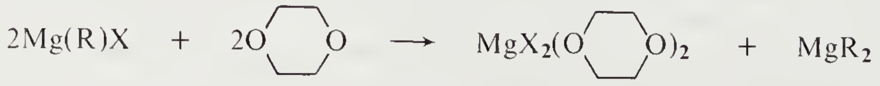
$$\mathrm{Cr(GeCl_2)(CO)_5(THF)} \xrightarrow{\mathrm{Mg(Br)(Mes)}} \mathrm{Cr\{Ge(Mes)_2\}(CO)_5} \qquad (104)$$

4.1.2 Diorganylmagnesium Derivatives

4.1.2.1 Preparation

Since the preparations of Grignard reagents have been well developed several methods for the synthesis of related diorganylmagnesium derivatives involve interconversion from the corresponding halogen-containing compound. The existence of the Schlenk equilibrium in solution indicates the presence of some $\mathrm{MgR_2}$ in Grignard reagents themselves and simple fractional crystallization has led to the separation of the diorganylmagnesium. Thus, crystallization of $\mathrm{[Mg_2Cl_3(Et)(THF)_3]_2}$ by addition of benzene to THF solutions of Grignard reagent Mg(Cl)Et leaves $\mathrm{MgEt_2}$ in solution.[362]

A convenient and simple laboratory synthesis is achieved by addition of 1,4-dioxane to an ethereal Grignard solution.[237] An insoluble dioxanato complex of magnesium halide is precipitated (equation 105). In effect the Schlenk equilibrium has been displaced in favour of the disproportionation products. In practice, dioxane in slight excess (5–10%) of a 1:1 molar ratio is added dropwise to a well stirred Grignard solution in $\mathrm{Et_2O}$ and the reaction left stirring for 12–24 h.[184b,363,364,365] The precipitate is separated by filtration or, more easily owing to its fineness, by centrifugation and the clear solution of $\mathrm{MgR_2}$ may be used directly for chemical reactions. In principle, derivatives with a variety of functionally substituted groups R may be formed by this method. The solution is labile to contain some residual halogen and also some dioxane. Evaporation of solvent leaves a colourless, normally solid product. Removal of any coordinated dioxane requires heating *in vacuo* at 100–170 °C; this is possible for example when R = Me, Et, Pr, $\mathrm{Pr^i}$, $\mathrm{Bu^n}$, Ph, $\mathrm{Me_3CCH_2}$, $\mathrm{Me_3SiCH_2}$ and $\mathrm{PhMe_2CCH_2}$, but when R = $\mathrm{Bu^i}$, $\mathrm{Bu^t}$, hexyl and some higher homologues decomposition of the organometallic compound occurs at or below such temperatures so that pure dioxane-free products are unobtainable.[363,366] For instance if $\mathrm{Mg(Bu^t)_2}$ is required free of dioxane a slight deficiency must be added in the precipitation stage and the soluble product contains at least 2–4% halogen.[365] Excess dioxane forms isolable complexes $\mathrm{[MgR_2(dioxane)]}$.


(105)

An interesting application of the dioxane reaction is the formation of cyclic organomagnesium compounds (equation 106).[255,367] This cyclization reaction has been carried out in THF by addition of excess dioxane but it has been reported in the formation of $\mathrm{MgEt_2}$ from Mg(Br)Et that incomplete halide precipitation (as low as 80%) can occur in THF when approximately stoichiometric amounts of dioxane are added.[368] However, it should be noted that $Mg(Mes)_2(THF)_2$ has been formed directly by the dioxane method in a THF medium.[369] Also it is of interest that dioxane will precipitate MgX_2 from hydrocarbon solutions of Grignard reagents.[40]

$$BrMg(CH_2)_nMgBr \xrightarrow[n\,=\,4,\,5,\,6]{\text{dioxane}} (CH_2)_n\,Mg + MgBr_2(dioxan)_2 \qquad (106)$$

(54)

The use of diglyme as a precipitant for $MgCl_2$ has been reported in the formation of divinylmagnesium in THF solutions.[7] Precipitation of MgX_2 as a pyridine complex also occurs from Grignard solutions and by addition of pyridine it has proved possible to obtain solutions of complexes $MgR_2(py)_2$ ($R = Et, Bu^n, Bu^t$).[370] Moreover, $Mg(Ph)_2(py)_2$, although coprecipitated with MgX_2 by pyridine, may also be obtained by its selective extraction with dioxane but the pyridine procedure fails for Grignard reagents $Mg(R)X$ ($R = Me, Bz$). A related preparation is the reaction of 1-chlorobutane with magnesium in hexane containing TMEDA (equation 107). The halide complex is insoluble but $Mg(Bu^n)_2(TMEDA)$ (21%) is a soluble, volatile liquid (b.p. 175–180 °C, 0.8 Torr) which may be purified by distillation.[371]

$$2Bu^nCl + 2Mg \xrightarrow[\text{hexane}]{\text{TMEDA}} MgCl_2(TMEDA) + MgBu^n_2(TMEDA) \qquad (107)$$

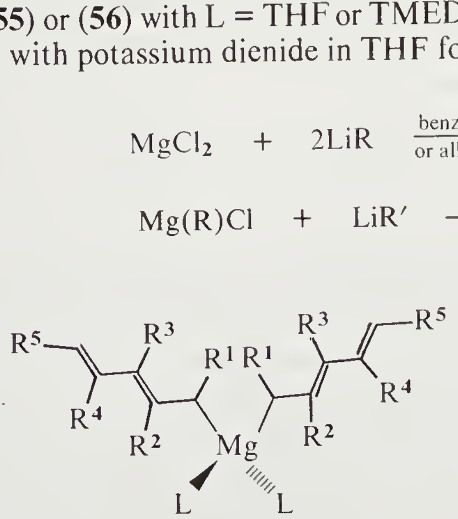
The second most widely utilized route to MgR_2 derivatives is transmetallation between excess magnesium and organomercury compounds (equation 108).[372] Using this procedure both halide and strongly coordinating solvents are avoided and the pure product, extracted from the reaction mixture by an appropriate solvent, is most suited for critical physical studies.[364,373] The reaction is usually carried out in the absence of solvent and, after an induction period, occurs exothermically and readily for alkyl derivatives, *e.g.* when $R = Me$ heating to *ca.* 60 °C is required; higher temperatures are necessary when $R = Ar$ (*ca.* 150 °C).[373] Diarylmagnesium derivatives are also formed in ether solutions by stirring at ambient temperatures but these reactions take many days.[372] Cyclic species such as (**54**) have also been prepared from the corresponding mercury derivatives in THF.[250]

$$HgR_2 + Mg \longrightarrow MgR_2 + Hg \qquad (108)$$

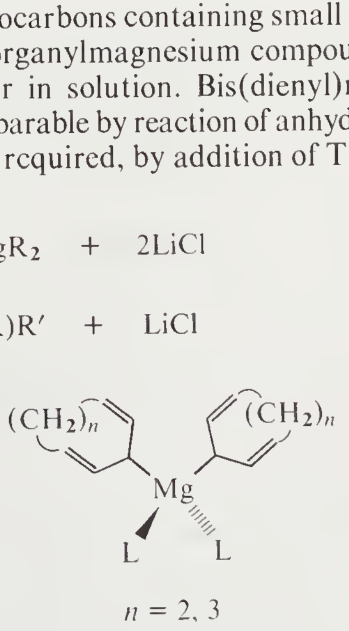
Preparation of MgR_2 in hydrocarbon solvents from anhydrous 'activated' $MgCl_2$ (*e.g.* prepared by reaction of $Mg(R)Cl$ and $BzCl$) has been reported (equation 109).[374,375] This procedure has been described fully for $R = Bu^s$ and $Me_3CCH_2CH{=}CHCH_2$, both of which form hydrocarbon soluble organometallic compounds. Other examples are quoted in patents.[376] Organolithium reagents will also react with Grignards in ether or in hydrocarbons containing small amounts of ether (equation 110). In this manner formally mixed diorganylmagnesium compounds can be produced,[374] although alkyl group exchange may occur in solution. Bis(dienyl)magnesium compounds (**55**) or (**56**) with L = THF or TMEDA are preparable by reaction of anhydrous MgX_2 ($X = Cl, Br$) with potassium dienide in THF followed, if required, by addition of TMEDA.[377]

$$MgCl_2 + 2LiR \xrightarrow[\text{or alkane}]{\text{benzene}} MgR_2 + 2LiCl \qquad (109)$$

$$Mg(R)Cl + LiR' \longrightarrow Mg(R)R' + LiCl \qquad (110)$$



(55)



(56)

Metal exchange equilibria are set up between organomercury and organomagnesium compounds (equation 111).[378] The organic group which forms the most stable carbanion is preferentially attached to Mg and normally this exchange is not of preparative value. However, in some cases quantitative production of MgR'_2 is achieved, *e.g.* when R = Me, $R' = C{\equiv}CPh$; $R = Pr^i$, R′ = Ph;[378] R = Et, $R' = C_6F_5$.[240b] Exchange equilibria between MgR_2 and BR'_3 also occur and selective distillation of volatile coproduct BR_3 may be used to synthesize MgR'_2.

$$MgR_2 + HgR'_2 \rightleftharpoons MgR'_2 + HgR_2 \qquad (111)$$

The direct reaction of halogeno organic compounds with magnesium in polar solvents affords Grignard reagents but in hydrocarbons the products are deficient in halogen (Section 4.1.1.1,i(d)) and chloroalkanes give species which are essentially MgR_2. Thus, in benzene, 1-chloropentane forms $Mg(C_5H_{11})_2$ in solution with ratio of concentrations [R] : [Cl] = 116, although soluble products from the corresponding bromides and iodide contained increasing amounts of halogen.[43] Reaction of 2-chlorobutane with magnesium in hexane containing 10% dimethyl ether yields soluble $Mg(Bu^s)_2$, which may be essentially freed of ether by its codistillation with benzene or cyclohexane and this also precipitates any remaining soluble chloride.[374] A detailed study of preparation of Grignard reagents from C_2–C_8 *n*-alkylhalides in various hydrocarbon solvents suggests that in general chlorides give products of the type MgR_2 with [R] : [Cl] ratios of *ca.* 30 but that such reactions only occur readily for higher alkyl chlorides ($\geqslant C_5$).[40] The low solubilities of C_1–C_4 species MgR_2 in hydrocarbons and their precipitation with $MgCl_2$ renders such preparations inappropriate for lower alkyl derivatives. It should be noted that addition of trialkylaluminium compounds to these hydrocarbon suspensions solubilizes MgR_2 compounds by forming mixed metal derivatives (Section 4.1.6.3).[379] The preparation of MgR_2 in hydrocarbons in the presence of Al, Cu and other metal compounds has also been reported in the patent literature.[380]

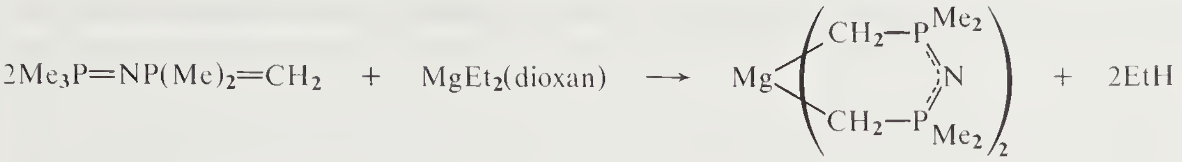
Direct reaction between cyclopentadiene, or alkyl substituted cyclopentadienes, and magnesium metal occurs at 450–600 °C (equation 112). A detailed preparation of $MgCp_2$ has been described involving passage of cyclopentadiene vapour over heated magnesium turnings in an inert atmosphere.[381] In the presence of catalytic amounts of $TiCl_3Cp$, cyclopentadiene and magnesium react at 0 °C and the product $MgCp_2$ (60%) is isolable from the reaction mixture.[382] It should also be noted that pyrolysis of Mg(Br)Cp also leads to formation of $MgCp_2$ which is obtained after sublimation *in vacuo*.[383] The analogous indenyl compound $Mg(C_9H_7)_2$ is obtained by thermal decomposition (190 °C) of $Mg(Br)(C_9H_7)$ *in vacuo* and is also purified by sublimation.[384]

$$2C_5H_6 + Mg \longrightarrow MgCp_2 + H_2 \qquad (112)$$

Reactions of dialkyl sulphates with Grignard reagents form solutions of dialkylmagnesium compounds in Et_2O, as illustrated by equation (113).[385] The reaction of magnesium with dialkyl sulphates may also yield MgR_2, especially in Et_2O, but in more polar solvents such as THF, the mixed species $Mg(R)\{OSO_2(OR)\}$ (R = Me) has been reported as the major product.[386]

$$2SO_2(OBu^n)_2 + 2Mg(Br)(Bu^n) \longrightarrow Mg\{OSO_2(OBu^n)\}_2 + MgBu^n{}_2 + 2Bu^nBr \qquad (113)$$

Metallation of hydrocarbons has not been extensively used to prepare diorganylmagnesium derivatives. 1-Hexyne reacts with dialkylmagnesium compounds in two steps, the first occurring more rapidly but giving finally $Mg(C{\equiv}CBu)_2$. The activity order of compounds MgR_2 for such metallation follows the sequence $R = Pr^i > Et > Pr^n$, as found for corresponding Grignards.[387] Metallation reactions of diaryl species $Mg(C_6H_4X)_2$ (X = H, *m*- or *p*-Me, Cl) with various 1-alkynes have been studied in Bu_2O, Et_2O and THF solvents and the mechanism interpreted in terms of a four-centre transition state.[388] The formation of ylide compounds by metallation is illustrated by equation (114) and similar metallation of $Me_3P{=}CH_2$ forms a polymeric product.[389] A related mixed product $[Mg(R)CH_2P(Me)_2CH_2\text{]}_n$ is formed by reaction between Mg(R)X and $Li[P(Me_3)_2(CH_2)_2]$.



(114)

Metallation of fluorene (FlH) with an equimolar quantity of $MgEt_2$ occurs very slowly in Et_2O solvent but is promoted by the addition of 1 : 1 mole ratio of HMPT.[390] The active species in the presence of HMPT is believed to be $[MgEt_2(HMPT)_2]$ and using a 2 : 1 ratio $[HMPT]:[MgEt_2]$ the reaction is first order in concentration of both fluorene and $[MgEt_2]$. With equimolar quantities of reagents the mixed product Mg(Et)(Fl) is formed and this shows little tendency to disproportionate (equation 115). The reaction of equimolar amounts of $MgMe_2$ and cyclopentadiene does occur in Et_2O over 5 d at 20–25 °C and the mixed derivative Mg(Cp)(Me) is similarly formed.[391] Related mixed cyclopentadienyl compounds Mg(Cp)(R) (R = Me, Ph) have been obtained by exchange reactions in Et_2O between $MgCp_2$ and MgR_2.[392] Metallation of C_6F_5H by $MgEt_2$ has also been reported.[98]

$$2Mg(Et)(Fl) \rightleftharpoons MgEt_2 + Mg(Fl)_2 \qquad (115)$$

Metal–halogen exchange reactions involving diorganylmagnesium compounds are very few but the formation of bis(pentafluorophenyl)magnesium by exchange from C_6F_5Br[98] and of bis(2-(5-diethoxymethyl)furanyl)magnesium from the corresponding bromide[393] may be noted.

Magnesium hydride will react with alkenes to form Mg—C bonds. Reaction between MgH_2 and ethylene in Et_2O at 100 °C forms $MgEt_2$ in yields of up to 28% but products of further insertion and polymer are also obtained.[394] Similar reactions have been reported for 1-octene and isobutene and the process is catalyzed by alkyl compounds of boron, aluminium or zinc. Hydrometallation by MgH_2 of terminal alkenes and both terminal and internal alkynes is catalyzed by $[TiCl_2Cp_2]$ in THF at 60 °C, although no specific diorganylmagnesium compounds have been isolated from such reactions.[395] Ethylene will also insert into Mg—C bonds of $MgEt_2$, and in Et_2O (100 °C, 740 p.s.i.) $Mg(Bu)_2$ has been formed in yields of 25–35%.[394] Diisopropyl ether is a better solvent[396] but in hydrocarbons higher oligomers and polymer are obtained.

It should be noted here that addition compounds between unsaturated organic compounds and magnesium (Section 4.1.5) may also be considered as diorganylmagnesium derivatives.

4.1.2.2 Structural and physical properties

(i) Solid state

Simple diorganylmagnesium compounds are usually colourless solids which react readily with oxygen and water. Most derivatives decompose without melting at elevated temperatures but distinct melting points have been reported for others, *e.g.* MgR_2 (R = Bu^tCH_2, 111–113 °C; R = $PhMe_2CCH_2$, 143–147 °C; R = Me_3SiCH_2, 200–205 °C; R = Cp, 176 °C).[366,381] Most binary species are non-volatile although vacuum sublimation of some MgR_2 compounds (*e.g.* R = Bu^tCH_2,[366] Cp,[381] In[384] (In = indenyl)) has been reported. Another exception is $Mg(Bu^s)_2$ which is a light yellow mobile liquid at ambient temperature.[374] The compounds usually crystallize from polar media with coordinated solvent or ligands as species of stoichiometry $MgR_2(L)$ or $MgR_2(L)_2$ (L = unidentate, neutral ligand such as Et_2O, THF, HMPT, $\frac{1}{2}$DME, $\frac{1}{2}$TMEDA). However, in contrast to Grignard reagents, solvated ether can generally be readily removed by heating under vacuum and dimethylmagnesium crystallizes unsolvated from Et_2O at ambient temperatures.[268] The complexes $MgR_2(TMEDA)$ are particularly stable, usually show distinct melting points and may be sublimed *in vacuo*.[365,397]

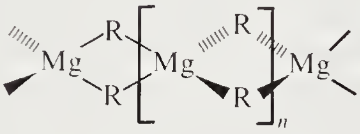
The X-ray determined crystal structures of solids MgR_2 (R = Me, Et) show these to be linear polymeric molecules with symmetrically bridging alkyl groups (**57**).[398] The bonding may be formalized in terms of electron-deficient three-centre two-electron covalent (but polar) links and each metal atom acquires an approximately tetrahedral coordination of four ligands (see Table 3 for relevant structural data). The structural parameters leave the question of the presence or absence of interactions between Mg atoms unanswered. Raman and IR spectra of solids $[MgR_2]_n$ (R = Me, Et) at 90 K and 300 K have also been interpreted in terms of the symmetrical polymeric chain structure (**57**) although at 90 K $[MgEt_2]_n$ shows a distinctly lower symmetry which was attributed to a change in chain conformation.[399] Analyses of the vibrational data gave a force constant for Mg—C bonds of 1.05×10^{-8} N Å and in $[MgMe_2]_n$ there appeared to be evidence for an interaction between neighbouring Mg atoms.[399] Crystal structures have not been reported for other uncomplexed derivatives but it is probable that hydrocarbon soluble species with bulky R groups may possess oligomeric, trimeric or dimeric structures (see solution properties, Section 4.1.2.2,ii).

Table 3 Structural Parameters for some Diorganylmagnesium Derivatives in the Solid State[1]

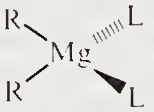
Compound	*Bond length* (Å) Mg—C	*Other bonds*	*Bond angle* (°) C—Mg—C
$[MgMe_2]_n$	2.24	2.72 (Mg—Mg)	105
$[MgEt_2]_n$	2.26	2.67 (Mg—Mg)	108
$MgMe_2(TMEDA)$	2.166	2.257, 2.227 (Mg—N)	130.0
$MgMe_2(quinuclidine)_2$[a]	2.163, 2.224	2.231, 2.247 (Mg—N)	129.0
$MgPh_2(TMEDA)$	2.167	2.199, 2.205 (Mg—N)	119.4
$Mg(C_7H_{11})_2(TMEDA)$[b]	2.179	2.202 (Mg—N)	113.1
$[Mg(CH_2)_5(THF)_2]_2$	2.13, 2.15	2.089, 2.110 (Mg—O)	141.5
$MgCp_2$	2.304	—	—
$Mg(indenyl)_2$	(i) 2.43 (mean η^5-C—Mg) (ii) 2.32, 2.26 (η^1)[c] (ii) 2.33, 2.43, 2.40, 2.44 (η^2)[d]	—	—

[a] Quinuclidine = 1-azabicyclo[2.2.2]octane. [b] C_7H_{11} = 2,4-dimethyl-2,4-pentadienyl. [c] Structure (**62**), see text. [d] Structure (**63**), see text.

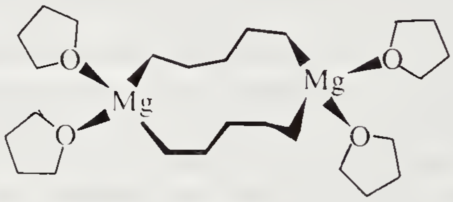
1. From refs. 277, 384, 398, 400–404.



(**57**)



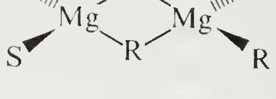
(**58**)



(**59**)

X-ray determinations of the crystal structures of adducts $[MgR_2(L_2)]$ (R = Me, L = quinuclidine[400] or L_2 = TMEDA;[401] R = Ph, L_2 = TMEDA;[402] R = 2,4-dimethyl-2,4-pentadienyl, L_2 = TMEDA[377]) have established monomeric structures (**58**) with distorted tetrahedral geometry around the magnesium (see Table 3 for some dimensions). It is of interest that the pentadienyl complexes (**55**) and (**56**) adopt the η^1-bonded structures, as is also the case for allyl compounds in solution but in contrast to pentahapto bonding in $Mg(Cp)_2$.[403] The IR and Raman spectra of solid diallylmagnesium have been reported and assigned to a centrosymmetric dimer $[Mg(C_3H_5)_2]_2$ with marked ionic character.[235] The molecular structure of the dinuclear cyclic derivative $[Mg(CH_2)_5(THF)_2]_2$ in the crystal also involves four-coordinate magnesium (**59**) but has a large angle C—Mg—C.[404] $[MgPh_2(OEt_2)_2]$ is also reported as monomeric in the crystalline state.[220]

No X-ray structural determinations of 1 : 1 adducts of the type $MgR_2(L)$ have been reported although such complexes can be isolated from ethereal solutions (L = Et_2O) and in solution are usually dimeric. IR and Raman studies of $[MgEt_2(OEt_2)]_2$ crystallized from Et_2O at −50 °C have established a centrosymmetric structure of the type (**60**) for this complex.[405,406] A phase diagram for the system Et_2O–$MgEt_2$ has been constructed and only at low temperatures in dilute solutions does monomeric $[MgEt_2(OEt_2)_2]$ crystallize — a triple point occurs at *ca.* −70 °C with mole fraction of about 24% $MgEt_2$.[406] The properties of $[Mg(Bu^t)_2(1,4\text{-dioxane})]_n$ suggest a polymeric structure, probably with bridging dioxane ligands.[365]



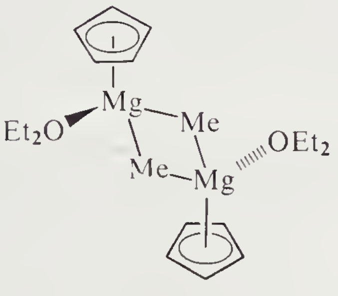
(**60**)

The report of crystalline species $[\mathrm{Mg(C{\equiv}CPh)_2(THF)_4}]$, for which X-ray evidence suggests that both *cis* and *trans* octahedral isomers can be formed, constitutes a rare example of a six-coordinate diorganylmagnesium derivative.[407] This may be related to the higher electronegativity of the η^1-phenylethynyl groups.

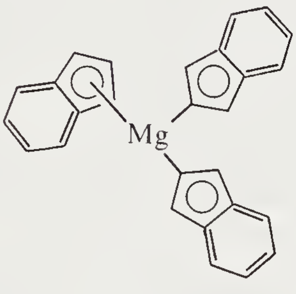
The extremely thermally stable derivative $\mathrm{Mg(Cp)_2}$ has been shown to possess a typical monomeric sandwich structure with staggered, parallel $\mathrm{C_5H_5}$ rings in the solid state.[403] The Mg—C distance (Table 3), allowing for differences in metal ion radii, is relatively long in comparison to $\mathrm{M(Cp)_2}$ (M = Fe, Co), albeit shorter than in $\mathrm{Ca(Cp)_2}$, and from such comparisons significant ionic character to the bonding, $\mathrm{C\bar{p}}\ \mathrm{Mg^{2+}}\ \mathrm{C\bar{p}}$, has been inferred. More recent IR and Raman studies on $\mathrm{Mg(Cp)_2}$ as solid or melt in which $\nu_{\mathrm{Mg—Cp}}$ is assigned at 218 $\mathrm{cm^{-1}}$ also support an ionic model,[408] as do He(I) UV PES studies in the gas phase.[409] However, the question of the covalent contribution to the bonding is still open.[410] From thermodynamic data a mean bond energy for the Mg—Cp interaction has been estimated as 228 ± 50 kJ $\mathrm{mol^{-1}}$.[411]

The mixed derivative Mg(Cp)(Me) is isolable as a solid, dimeric adduct $[\mathrm{Mg(Cp)(Me)(OEt_2)}]_2$ and vibrational studies indicate the presence of methyl bridges ($\nu_{\mathrm{Mg—C}}$ in the region 308–575 $\mathrm{cm^{-1}}$) and structure (**61**) is probable.[391] On desolvation, however, changes in the coordination of the cyclopentadienyl rings occur to form a less symmetrical structure.

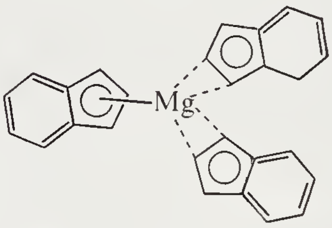
Solid $\mathrm{Mg(In)_2}$ (In = indenyl) possesses a complex molecular structure. In the crystalline lattice the magnesium atoms are found in two environments (**62**) and (**63**) with both terminal and bridging In groups.[384] Both magnesium atoms are bonded symmetrically to one η^5-In ligand but in (**62**) there are also two η^1-In bonds and in (**63**) two η^2-In interactions (Table 3). The closest η^1-C interaction approaches a normal Mg—C bond length. The complexity of the structure is probably determined by the most effective packing of unsymmetrical planar indenyl groups in the lattice. This could arise if the bonding is either essentially ionic or is only weak but largely covalent.



(**61**)



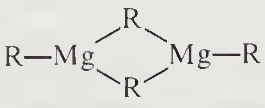
(**62**)



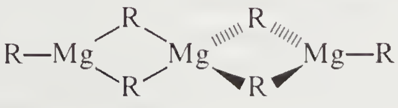
(**63**)

(*ii*) *Solution*

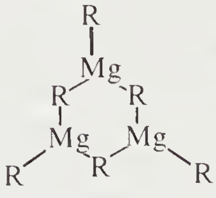
For simple diorganylmagnesium compounds the complications of processes related to the Schlenk equilibrium do not exist in solution but equilibria involving differing associated and solvated species do occur. The solubilities of pure $\mathrm{MgR_2}$ compounds in hydrocarbon solvents are slight when R is a lower alkyl or aryl group. Thus, $[\mathrm{MgMe_2}]_n$ and $[\mathrm{MgPh_2}]_n$ show negligible solubilities in benzene or alkanes and compounds $\mathrm{MgR_2}$ (R = Et, $\mathrm{Pr^n}$, $\mathrm{Pr^i}$, $\mathrm{Bu^n}$) form only *ca.* 10^{-2} M or 10^{-3} M solutions in benzene or heptane, respectively.[7,363] However, derivatives $\mathrm{MR_2}$ (R = $\mathrm{Bu^s}$,[374] $\mathrm{Bu^tCH_2}$,[366] $\mathrm{C_5H^n_{11}}$,[43] $\mathrm{Bu^tCH_2CH{=}CHCH_2}$,[375] Cp[381]) are significantly soluble in benzene and other hydrocarbons and derivatives with R = In[384] or 1-adamantyl[341] show slight solubility in aromatic solvents. In such media solvation should be negligible so that molecular weight measurements may be related to simple binary structures; in hydrocarbon solvents derivatives $[\mathrm{MgR_2}]_n$ are dimeric when R = $\mathrm{C_5H^n_{11}}$ or $\mathrm{Bu^s}$ and trimeric when R = $\mathrm{Bu^tCH_2}$ so that structures (**64**) and either (**65**) or (**66**) are possible.[366,374] These structures involve three-coordinate magnesium atoms.



(**64**)



(**65**)



(**66**)

Most MgR_2 derivatives are soluble in ethereal solvents (*e.g.* $MgMe_2$ forms 0.8M solutions in Et_2O) but solvation occurs so that alkyl bridges of polymeric or oligomeric structures may be broken by coordinated solvent molecules. Molecular weight variations of typical derivatives, determined by ebullioscopy, in THF or Et_2O are shown in Figures 1(a) and 1(d).[104] In THF, monomeric forms predominate over a wide concentration range. In Et_2O, monomeric species are prevalent in dilute solutions but some association generally occurs in more concentrated solutions. Raman spectral studies of $MgEt_2$ in Et_2O provide evidence for an equilibrium between a dimeric form $[MgEt_2(OEt_2)]_2$ and a monomer $[MgEt_2(OEt_2)_2]$ (equation 116) with $\Delta G° = +7.3$ kJ mol^{-1}.[406] Additional evidence for an equilibrium of the type shown in equation (116) comes from ^1H NMR studies in various solvents (S = Et_2O, THF or $\frac{1}{2}$DME) with equilibrium constants of 6.31, 13.5 or 4.5 l mol^{-1}, respectively.[412] When S = $\frac{1}{2}$TMEDA the transformation to the monomer is complete. In the less basic solvent Pr^i_2O, diethylmagnesium has a degree of association $i = 2.28$ and an equilibrium (dimer) $\rightleftharpoons$ (tetramer) is set up with equilibrium constant $K = 24.9$ l mol^{-1} at 27.7 °C.[226] The structure of the tetramer presumably involves ethyl bridges and less solvation.

$$[Mg(Et)_2S]_2 \quad + \quad 2S \quad \rightleftharpoons \quad 2[Mg(Et)_2S_2] \qquad (116)$$

Coordination adducts $[MgR_2(L)_2]$ (L_2 = 2THF, 2HMPT, TMEDA, DME)[365,366,369,412] dissolve in benzene as monomeric species. With a deficiency of HMPT, soluble benzene dimeric products of type (**60**) are also observed[412] and it has been reported that partial dissociation of THF from $[Mg(Bu^t)_2(THF)_2]$ occurs in benzene.[365] The dimeric species $[Mg(Cp)Me(OEt_2)]_2$ (**61**) dissolves in benzene without cleavage of the methyl bridge bonds, as shown by both IR and ^1H NMR spectra, but some dissociation of coordinated Et_2O occurs; in more polar solvents such as THF a monomeric solvated structure predominates.[391]

The monomeric metallocyclic derivative $Mg(CH_2)_5$ in THF solution is in equilibrium with the dimeric form[250] for which the crystal structure has been determined (**59**).[404] The equilibrium constant, $K = 531 \pm 81$ l mol^{-1} (28.27 °C) has been reported for this (monomer) $\rightleftharpoons$ (dimer) interconversion.[250] In dioxane the cyclic species $Mg(CH_2)_n$ (n = 4, 5, 6) are also partly associated with degrees of association i = 1.3–1.4, although such solutions are somewhat unstable to gel formation.[367] In HMPT, $Mg(CH_2)_n$ derivatives are essentially monomeric.[367]

The electrical conductivities of MgR_2 derivatives in Et_2O or THF are low[7] and even in HMPT, in which halogen containing species are appreciably dissociated into ions, the ionization of MgR_2 into free solvated ions and R^- (or associated ions) is negligible when R = Et or Bu^n.[252] Studies by ^1H NMR of the effect of addition of HMPT to the mixed derivative Mg(Et)(Fl) (Fl = fluorenyl) suggest that the Mg—Fl bond is covalent in Et_2O or THF but when three moles of HMPT coordinate to the magnesium a solvent separated ion pair is formed, $[MgEt(HMPT)_3]^+//Fl^-$.[390]

Dicyclopentadienylmagnesium in ethereal solvents appears from various spectral studies to be essentially a contact ion triple but on addition of HMPT the formation of solvent separated ions occurs in a two step process (equation 117), the fully separated species arising when the ratio $[HMPT]:[MgCp_2]$ is >3.[390]

$$Cp^-Mg^{2+}Cp^- \quad \overset{\text{HMPT}}{\rightleftharpoons} \quad Cp^-//Mg^{2+}Cp^- \quad \rightleftharpoons \quad Cp^-//Mg^{2+}//Cp^- \qquad (117)$$

^1H NMR studies on various diorganylmagnesium compounds have been reported. For $MgMe_2$ in Et_2O it is possible to distinguish between bridging (δ −1.0 to −1.5 p.p.m.) and terminal (δ −1.69 to −1.74 p.p.m.) methyl groups and similar distinctions can be made for dimeric species in toluene.[239] Shifts of ^1H NMR resonances of α-H atoms in $MgEt_2$ in differing solvents have been related to the solvent basicity.[260] Variable temperature ^1H NMR studies of inversion of configuration at α-C atoms in MgR_2 (R = 3,3-dimethylbutyl, 2-methylbutyl) have been reported and under conditions when monomeric species are present it has been established that the process occurs *via* a bimolecular mechanism involving an alkyl-bridged intermediate as discussed for Grignard reagents (Section 4.1.1.2,ii(d)).[268,269]

Diallylmagnesium compounds are η^1-bonded in solution but undergo rapid 1,3-shifts as also observed for corresponding Grignard reagents.[236b] Bis(3-neopentylallyl)magnesium shows dynamic allylic behaviour in the ^{1}H NMR spectrum at room temperature and above, but slow exchange is observed at low temperatures in ethereal solvents and both (Z) and (E) isomers are present in approximately equal proportion.[375] Bis(dienyl)magnesium species are also fluxional in solution and undergo 1,3-rearrangements.[377] ^{13}C NMR spectra have been reported for some compounds MgR_2,[261] and for $Mg(Bz)_2$ chemical shifts indicate less ionic character for this compound than for analogous derivatives of Ca, Sr or Ba.[413] In the UV spectrum, $Mg(Bz)_2$ shows an absorption band at 277 nm ($\epsilon \approx 1.86 \times 10^4$) in THF.[142]

IR spectra of several MgR_2 species in solution exhibit bands assignable to Mg—C vibrations and bridging or terminal groups can be distinguished but superposition of bands, vibrations of coordinated solvent and combination bands make precise assignments unclear.[264,406] In ethereal solutions distinctive bands occur for alkyl species in the region 450–600 cm^{-1} and for $MgPh_2$ at 381 cm^{-1} [241,391]

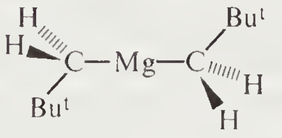
Polarographic studies on solutions of MgR_2 in DME solvent show oxidation waves corresponding to two electron transfer but reduction by a one electron process in this medium is only observed when the organic group R forms a significantly stable carbanion (*e.g.* R = Cp, Bz, allyl).[242] A mechanism may be given as in equation (118).

$$MgR_2 \quad + \quad e \longrightarrow R^- \quad + \quad [\dot{M}gR] \longrightarrow Mg(0) \quad + \quad [R\cdot] \longrightarrow \text{radical products} \qquad (118)$$

(*iii*) *Gas phase*

Few simple MgR_2 compounds are volatile but $MgCp_2$ (b.p. 220 °C) readily sublimes *in vacuo*[381] and electron diffraction studies support the metallocene sandwich structure with Mg—C bond distance 2.339 Å, similar to that found in the solid state. However, the data are more consistent with an eclipsed geometry for the two C_5H_5 rings in contrast to the staggered form in the crystal.[410] Positive and negative ion mass spectra for $MgCp_2$ have been reported and the ions $MgCp_2^+$, $MgCp^+$, Mg^+ or $MgCp^-$, Cp^- detected.[414] He(I) PES spectra of $MgCp_2$ have been reported.[409] The mixed compound Mg(Cp)(Me) also sublimes and the molecular ion has been identified by mass spectroscopy but marked thermal decomposition occurs and volatile $MgCp_2$ and involatile $MgMe_2$ are formed.[391,392]

Bis(neopentyl)magnesium is volatile and an electron diffraction examination of this molecule in the gas phase at 160 °C shows a linear monomeric structure (**67**) with Mg—C bond length 2.126 Å and angle M—C—C 118.3°.[415]



(**67**)

It has been reported that $MgMe_2$ itself will sublime but this may only be in the presence of traces of coordinating solvent. The ready sublimation of derivatives MgR_2(TMEDA) should be noted here.[397] *Ab initio* MO calculations have been reported for linear monomeric $MgMe_2$.[274]

4.1.2.3 Reactions

The most thermally stable binary dialkylmagnesium compound is $[MgMe_2]_n$ for which decomposition only occurs in the region 220–260 °C with liberation of one molar equivalent of methane leaving a residue of stoichiometry '$MgCH_2$', formally a methylenemagnesium compound but probably polymeric in nature.[391,416] At temperatures over 300 °C further decomposition to hydrogen and a carbide 'MgC' has also been reported.[391] Dialkyl compounds MgR_2 (R = Et, Bu^n) decompose at 170–210 °C to form MgH_2 and alkene, probably by β-H abstraction.[363] Secondary and tertiary alkyl compounds decompose at lower temperatures but it is to be noted that compounds stabilized to β-elimination are relatively more stable and may even sublime unchanged.[366] A study of $MgEt_2$ by thermogravimetric analysis indicated no decomposition below 210 °C and endotherms at 290 °C (MgH_2 and C_2H_4 formation) and 370 °C (Mg and H_2 formation).[417] Bis(*t*-butyl)magnesium decomposes at 80 °C and 1-butene has been reported as the main volatile product[374] but NMR studies in hydrocarbon solvents have shown CIDNP effects and products (isobutene, isobutane and dimer) typical of a radical process.[279] Decomposition of $MgPh_2$ at 280 °C forms, primarily, biphenyl and free metal,[278] but $Mg(Mes)_2$ decomposes at 178–190 °C to liberate mesitylene and leave a residue 'MgC_9H_{10}'.[369] It should be noted that $Mg(Cp)_2$ is exceptionally stable to thermolysis but that $Mg(In)_2$ decomposes at *ca.* 170 °C and can only be sublimed with accompanying decomposition.[384]

Complexes [MgR_2(TMEDA)] are relatively stable but most other adducts with ethereal and other O- or N-ligands can be dissociated thermally *in vacuo.* It is of interest that [$MgMe_2$(DME)] decomposes above 120 °C but this may occur in the gas phase since heating *in vacuo* at 160 °C gives a condensate of free $MgMe_2$.[365] Also, in the presence of Et_2O thermal decomposition of $MgEt_2$ forms sublimable Mg(Et)(OEt).[418]

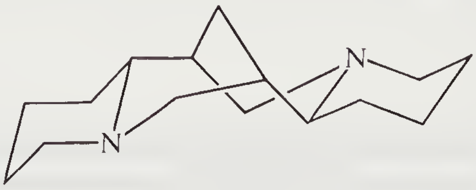
Decompositions by other reagents such as O_2, CO_2, H_2, active hydrogen containing compounds and halogens follow similar courses to Grignard reagents (Section 4.1.1.3,i) although the reactivity of MgR_2 species is generally greater.

Rearrangements observed for diorganylmagnesium compounds are analogous to those of the corresponding Grignard reagents but when studied in detail have been shown to occur at faster rates.[143] Thus, in MR_2 (R = 5-hexenyl) the conversion of alkenyl group to cyclopentylmethyl occurs 45 times more rapidly than in Mg(Br)R[295] and in fact bis(cyclopentylmethyl)magnesium is the product of reaction between magnesium and bis(5-hexenyl)mercury.[419]

Several exchange reactions of MgR_2 compounds have been studied. Organic ligand exchange between $MgPh_2$ and $Mg(CH_2Bu^t)_2$ may be monitored by NMR line shape analysis and follows typical second order kinetics.[420] The rate decreases with increasingly coordinating solvents, *i.e.* Et_2O > THF > TMEDA, and a mechanism involving an organyl bridging dimer is likely. The mixed species $Mg(CH_2Bu^t)(Ph)$ is only slightly thermodynamically favoured ($\Delta G° = -7.2$ kJ mol^{-1}) unlike products Mg(Cp)R (R = Me, Ph) which predominate on mixing $Mg(Cp)_2$ and MgR_2 in solution. The rate of alkyl group exchange between MgR_2 and Mg(Cp)R is fast, although it is slower in more polar solvents (TMEDA or DME), and is accelerated by addition of $MgBr_2$.[392] The fact that exchange takes place 10^4 times more rapidly than inversion at α-C atom when R = $Bu^tCH_2CH_2$ indicates that the exchange process takes place with retention of configuration at this carbon centre.[392] The formation of species [$MgEt_2$·Mg(Br)Et][226] and [$MgMe_2$·MgMe($OCPh_2Me$)][421] in solution may also be noted. Also, halide and pseudohalide adducts have been obtained and vibrational spectra reported for complex anions $[MgMe_2X]_2^{2-}$ (X = Cl, N_3, NCS), $([MgMe_2]_2X)_2^{2-}$ (X = F, CN, N_3, NCO) and $[MgMe_2CN]_4^{4-}$, obtained as tetramethylammonium salts.[422]

Intermetallic exchange between MgR_2 and HgR'_2 (equation 111) shows reversible, second order kinetics and thermodynamic control favours the magnesium bonded to the alkyl group with lowest pK_a; when R′ = Ph, equilibrium constants vary from $K > 6$ ($R = Pr^i$) to $K \ll -3$ (R = PhC≡C).[378] Fast exchange also occurs between $MgMe_2$ and $CdMe_2$, $ZnMe_2$ or $InMe_3$ (see also Section 4.1.6).

Although exchange of neutral ligands L in solutions of [MgR_2L_2] is usually fast and useful in preparation of more thermodynamically stable adducts, it may be noted that exchange of ethereal ligands with (−)-sparteine (**68**) is slow and this is related to conformational changes in this polycyclic dinitrogen donor.[423]

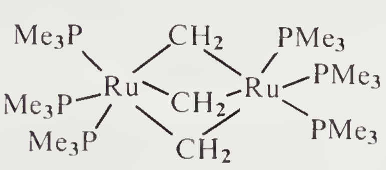


(**68**)

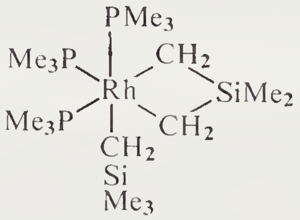
Reactions of MgR_2 and Mg(R)X species with organic molecules are similar but reactivity of the former is normally greater. Thus, metallation of 1-hexyne by $MgEt_2$ is three times as rapid as by $Mg(Br)Et^6$ and addition of $MgMe_2$ to the C=O function of diaryl ketones shows an approximately tenfold increase in rate when compared to Mg(Br)Me.[104] Under some conditions differences in reaction pathways between MgR_2 and Mg(R)X species may be observed; examples of such differences include: the occurrence of simple addition to ketones by MgR_2 in HMPT when Grignards mainly cause enolization or reduction,[424] 1,2-addition to α,β-unsaturated ketones in more basic solvents when Grignards give substantial amounts of 1,4-addition products[425] and less rearrangement products in reaction with oxiranes than observed with the analogous Grignard reagent.[426] The steric inability of cyclic derivatives $Mg(CH_2)_n$ (n = 4, 5) to cause reduction of ketones by β-H transfer has also been described.[255]

Species MgR_2 have two potentially active organyl groups per magnesium atom and generally these react by a sequential, two-step process. Thus, it is possible to produce intermediate mixed organomagnesium compounds of the type Mg(R)(Y) where Y is a uninegative group such as OR, SR or NR_2 and it should be noted that mixing MgR_2 with MgX_2 (X = Cl, Br, I or H) forms the Grignard reagent or Mg(H)R.

Formation of organometallic compounds by alkylation of metal halide or related derivative using MgR_2 may be carried out as with Grignard reagents. Particular applications to synthesis of main group organometallic compounds have not been stressed in the literature but reactions of MgR_2 species with more electronegative metallic compounds occur. Also 'ate' complexes are formed with alkali metals and aluminium (Section 4.1.6). Alkyl or aryl compounds of transition metals may often be obtained in cleaner, higher yield reactions by using MgR_2 rather than Grignard reagents for alkylation.[184b] Reactions with MgR_2 may, if necessary, be carried out easily in hydrocarbon solvents. The tendency for MgR_2 compounds to cause reduction of transition metal compounds is less than for analogous Mg(R)X species and thus undesired side reactions may be avoided, especially in preparations of organotransition metal compounds in higher oxidation states. Examples of compounds for which the recommended preparation is reaction of transition metal precursor with MgR_2 rather than Grignard reagent include: $[TiR_4]$ (R = Bz, Cy, CH_2SiR_3),[427] $[V(Bz)_4]$,[428] $[Ta(Bz)_5]$,[429] $[Ta(CH_2SiMe_3)_2Me_3]$,[430] $[WMeCl_3O]$,[431] $[Cr_2(CH_2SiMe_3)_4(PMe_3)_2]$,[432] $[Mo_2Me_4(PMe_3)_4]$,[432] $[Re_2(2\text{-}MeOC_6H_4)_6]$[433] and $[Mn(CH_2CMe_2Ph)_2]_2$.[342] However, even in preparations with MgR_2 further H-abstraction reactions may occur as illustrated by the formation of (**69**) from $MgMe_2$[434] and (**70**) from $Mg(CH_2SiMe_3)_2$.[432]



(**69**)



(**70**)

Dicyclopentadienylmagnesium has been used to form a range of η^5-cyclopentadienyl metal compounds and although not often preferred as a reagent it is readily obtained as a solid and so easily mixed with the transition or main group metal precursor in a suitable solvent.[324,435] The use of $MgCp_2$ in the preparation of $[ScCl(Cp)_2]$[436] and $[MCl_4Cp]$[437] (M = Nb, Ta) may be noted. In related reactions diindenylmagnesium has been used to form lanthanoid and actinoid η^5-indenyl compounds.[384]

4.1.3 Hydridoorganomagnesium Derivatives

4.1.3.1 Simple hydrido compounds

Hydridoorganomagnesium compounds of type Mg(H)R have been postulated as unstable intermediates in several reactions of organomagnesium reagents.[268] Thus, a species Mg(H)Et was reported, with little supporting evidence, as an intermediate in the formation of Mg(H)(OEt) by reaction of $MgEt_2$ with silane in Et_2O.[438] Derivatives Mg(H)R are also probably involved in the formation of dialkylmagnesium compounds by hydrometallation of alkenes using MgH_2[394,395] or, conversely, in the decomposition of dialkylmagnesium compounds by pyrolysis[278,363,374,417] or hydrogenolysis.[394] However, hydridoorgano intermediates have not been positively identified in such processes.

Reaction of $MgEt_2$ with sodium triethylhydroborate in Et_2O at −78 °C was reported to follow equation (119) to form Mg(H)Et, stable in this medium at low temperatures but apparently unstable to disproportionation (equation 120) at temperatures >−20 °C.[365a] White solids isolated from this reaction were formulated as MgH_2, although analyses showed the presence of residual ethyl groups, attributed to occlusion of $MgEt_2$ in the solid lattice.

$$MgEt_2 \quad + \quad Na[BHEt_3] \xrightarrow{Et_2O} Mg(H)Et \quad + \quad Na[BEt_4] \qquad (119)$$

$$2Mg(H)Et \xrightarrow{Et_2O} MgH_2 \quad + \quad MgEt_2 \qquad (120)$$

The reactions of MgR_2 (R = Et, Ph) with LAH in Et_2O normally produce insoluble MgH_2 accompanied by $Li[AlH_{4-n}R_n]$ (n = 1–4, depending on ratio of reactants).[439,440] Only when R = Ph and the ratio of concentrations $[MgPh_2]:[LiAlH_4]$ is 4:1 has evidence been presented for the formation of the hydrido derivative $Mg_2(H)_3Ph$ mixed with $Li[AlPh_4]$.[440] However, if related reactions are carried out in THF, species Mg(H)R or $Mg_2(H)_3R$ are formed (equations 121 and 122).[440,441] These hydrido products are soluble in THF and not conveniently separated from $Li[AlH_{4-n}R_n]$ by-products.

$$4MgR_2 \quad + \quad LiAlH_4 \xrightarrow[R\,=\,Me,\,Ph]{THF} 4Mg(H)R \quad + \quad Li[AlR_4] \qquad (121)$$

$$2MgPh_2 \quad + \quad LiAlH_4 \xrightarrow[r.t.]{THF} Mg_2(H)_3Ph \quad + \quad Li[AlHPh_3] \qquad (122)$$

A simple preparative route to pure compounds Mg(H)R (R = Me, Et, Pr^i, Cp or Ph) is the reaction of active MgH_2 with MgR_2 in THF solvent (equation 123).[441] If MgR_2 (R = Me, Ph) is added to an active MgH_2 slurry in THF in a 1:3 molar ratio, a solution of $Mg_2(H)_3R$ is produced (equation 124).[441]

$$MgH_2 \quad + \quad MgR_2 \xrightarrow{THF} 2Mg(H)R \qquad (123)$$

$$3MgH_2 \quad + \quad MgR_2 \xrightarrow{THF} 2Mg_2(H)_3R \qquad (124)$$

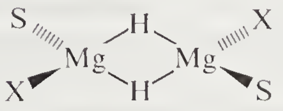
Both hydridoorganylmagnesium derivatives Mg(H)R and $Mg_2(H)_3R$ can be isolated as white crystalline solvated solids, although disproportionation into MgH_2 and MgR_2 may occur on desolvation and X-ray powder data appear to be unclear on this point. Solutions of Mg(H)R in THF are stable at ambient temperatures. Although resonances of magnesium bound organic groups are present in ^1H NMR spectra, no resonances attributable to Mg—H hydrogen atoms can be observed but broad bands in the region 1250–1300 cm^{-1} in IR spectra are assignable on the basis of deuteration studies to $\nu_{Mg—H}$ vibrations, probably in a bridging environment. Vibrational frequencies have also been assigned to $\nu_{Mg—C}$ modes in the range 370–662 cm^{-1} for R = Ph, Pr^i, Et, Me and Cp. Molecular weight measurements in THF indicate dimeric structures for Mg(H)R (R = Me, Et) or a monomeric structure for Mg(H)Ph at infinite dilution but for all derivatives association increases markedly with concentration (degree of association $i > 4$ at 0.2M). It has been noted that Mg(H)Ph undergoes disproportionation of equation (125) when stirred in a solution of Et_2O at room temperature.[440,441]

$$3Mg(H)Ph \longrightarrow MgPh_2 \quad + \quad Mg_2(H)_3Ph \qquad (125)$$

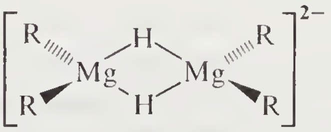
$Mg_2(H)_3Ph$ is obtainable as a solid which completely redissolves in THF but is insoluble in Et_2O and thus cannot be a physical mixture of $MgPh_2$ and MgH_2. However, it slowly cleaves THF and on refluxing in this solvent, a product of composition $Mg_2Ph(OBu^n)_3$ is formed. Solid $Mg_2(H)_3Me$ disproportionates on solvent removal to Mg(H)Me and MgH_2. IR spectra of these species $Mg_2(H)_3R$ in solution also exhibit strong $\nu_{Mg—H}$ bands in the range 1270–1300 cm^{-1}, suggesting the presence of bridging hydrido ligands.[440,441]

The solids obtained after desolvation of these hydrides decompose around 300 °C to liberate RH from Mg(H)R, or RH from H_2 from $Mg_2(H)_3R$. In their reactions with ketones both alkylation and reduction of the carbonyl group is observed.[441] Reactions of Mg(H)R with alane or borane in THF produce complex bimetallic hydrides MgH(MH_3R) (M = Al, B; R = Et, Pr^i, Ph) or Mg(MH_3R)$_2$ (M = Al, B; R = Me).[442]

It is of interest to note that the simple mixed hydrides Mg(H)X (X = Cl, Br) may be formed from equimolar quantities of active MgH_2 and MgX_2 in THF.[443] The species Mg(H)X are soluble and stable in THF solution but disproportionate on desolvation. They are dimeric in solution with $\nu_{Mg—H}$ in the IR spectra at 1280 ± 20 cm^{-1} so that a bridged structure (**71**) has been suggested and this may be related to the dimeric form of $[Mg(H)R]_2$. It has been briefly mentioned that Mg(H)Me can be prepared by reaction of Mg(H)X (X = Cl, Br) with LiMe.[441]



(**71**)



(**72**)

4.1.3.2 *Bimetallic hydrido complexes*

Reactions of MgR_2 (R = Me, Et) with alkali metal hydrides in ethereal solvents do not afford isolable hydridoorganomagnesium species although under some conditions extensive solvent cleavage has been reported.[365a] When $MgPh_2$ and KH are mixed in Et_2O, however, a stable, isolable complex [$KMg_2(H)Ph_4$] is formed.[444] In benzene solution related reactions with MgR_2 (R = Bu^s, Bu^n) and MH (M = Na, K) form stable, soluble complexes [$NaMg_2(H)Bu^s_4$] or [$KMg(H)R_2$]. [$KMg(H)Bu^s_2$] forms stable solutions in THF at low temperature and in this medium it is possible to effect metathetical exchange of cation using LiBr, NaI or NR_4Br to give [$MMg(H)Bu^s_2$] (M = Li, Na, NR_4). By a similar exchange reaction involving LiBr in Et_2O the derivative [$LiMg_2(H)Bu^s_4$] has been produced.[444]

Alternative preparations of lithium-containing hydrido complexes involve reactions of alkyllithium reagents.[445] Thus, [$LiMg(H)R_2$] is produced by the reaction of equation (126). Reactions of active MgH_2 with varying molar ratios of alkyllithium compounds have also produced species of formulae [$LiMg(H)_2R$], [$LiMg_2(H)_3Bu^n_2$] and [$Li_2Mg(H)_2(Me)_2$].

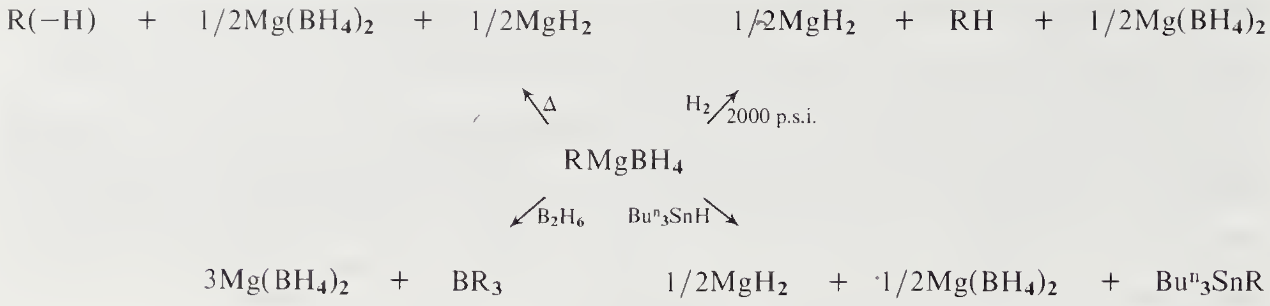
$$\mathrm{LiR} + \mathrm{Mg(H)R} \xrightarrow{\mathrm{THF}} \mathrm{LiMg(H)R_2} \qquad (126)$$

The solid alkali metal hydrido species [$MMg(H)R_2$] and [$MMg_2(H)R_4$] have distinct X-ray powder patterns and ^1H NMR spectra of soluble species exhibit hydridic resonances at $\delta \approx 3.4$ p.p.m. IR spectra show broad absorptions in the region 600–1200 cm^{-1}, tentatively assigned to bridging hydrogen atoms, and also bands at approximately 520 cm^{-1} (assigned to $\nu_{Mg—R}$). Molecular weights of [$MMg(H)R_2$] in benzene (M = K, R = Bu^s, Bu^n) or THF (M = Li, R = Me, Et) show essentially dimeric association over a wide concentration range so that structures of type (**72**) were suggested.[444,445] The interaction between M^+ and anion may be as an ion pair or could involve an electron deficient covalent link.

Few reactions of these complex hydrides have been reported. Hydrogenolysis at 25 °C or pyrolysis at 80 °C of [$KMg(H)Bu^s_2$] forms either butane or 1-butene, respectively, and solid $KMgH_3$.[446] Reaction of [$KMg(H)Bu^s_2$] with excess KH in benzene forms an organometallic intermediate which metallates the solvent (equation 127).[444]

$$\mathrm{KH} + \mathrm{KMg(H)Bu^s_2} \longrightarrow \mathrm{K_2Mg(H)_2Bu^s_2} \xrightarrow{\mathrm{C_6H_6}} \mathrm{K_2MgH_2(Bu^s)Ph} \qquad (127)$$

Diborane and Grignard reagents form species $Mg(BH_4)X$ (X = Cl, Br, I) as the major products, isolable as bis(THF) adducts.[447] Grignard reagents and sodium tetrahydroborate in THF or Et_2O form $Mg(BH_4)R$ (R = Et, Bu^s), identified only in solution, and typical reactions are illustrated in Scheme 12.[447a,448]



Scheme 12

Hydridoaluminium compounds and organomagnesium derivatives also produce bimetallic complexes. Thus, alane and $MgEt_2$ react in THF to form derivatives of formulae $AlMgH_{5-n}Et_n$ (n = 1–5, depending on ratio of reactants).[449] The structures of these species are not clear and when $n < 5$ it is not certain whether the H or Et ligand is terminally bound to the magnesium atom — an equilibrium of the type of equation (128) was proposed on the basis of IR studies. When $n = 4$ the equilibrium probably lies predominantly to the left. Reactions between $MAlH_4$ (M = Li, Na) and Mg(Br)R have been studied and a complex hydrido organic product of formula $[AlMg_2(H)_4Br(R)_2]$ (R = Bu^n) isolated.[450]

$$HMgAlH_{4-n}Et_n \underset{(n\,=\,1-4)}{\rightleftharpoons} EtMgAlH_{(5-n)}Et_{(n-1)} \qquad (128)$$

4.1.4 Oxo-, Thio- and Amido-organomagnesium Derivatives

4.1.4.1 Alkoxo and aryloxo derivatives

(i) Preparation

The first characterized alkoxoalkylmagnesium compound was MgEt(OEt), formed by cleavage of solvated ether during pyrolysis of $MgEt_2$,[418] but alkoxo derivatives can be more readily synthesized by partial alcoholysis of MgR_2 compounds, using an equimolar ratio of reactants (equation 129).[268,392,421,451] Reaction of chloro Grignard reagents in hydrocarbons with alcohol or the related direct reaction of equation (130) are other useful preparative reactions;[42,452] in these procedures methylcyclohexane is a suitable solvent for higher alcohols but for less soluble lower alkoxo products, toluene is recommended. A variation on this basic method is reaction of magnesium with alkyl halide and sodium alkoxide.[452] Preparation of $MgMe(OCEt_2Me)$ by exchange between $MgMe_2$ and $Mg(OCEt_2Me)_2$ has also been described.[392]

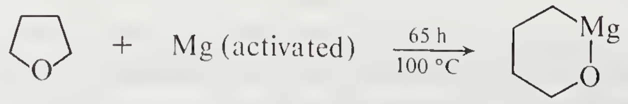
$$MgR'_2 + ROH \longrightarrow MgR'(OR) + R'H \qquad (129)$$

$$2R'Cl + ROH + 2Mg \xrightarrow{\text{hydrocarbon}} MgR'(OR) + R'H + MgCl_2 \qquad (130)$$

Cleavage of allyl phenyl ethers[453] or allyl naphthyl ethers[454] by magnesium can give excellent yields of allyl(aryloxo)magnesium compounds (equation 131), and in refluxing THF negligible amounts of Wurtz-type coupling products are formed. Non-aromatic allyl ethers also react but give poorer yields of alkoxo products.

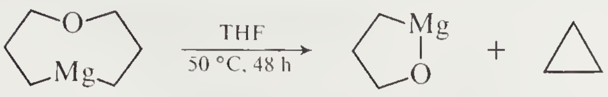
$$ArOCH_2CR{=}CH_2 + Mg \xrightarrow[\text{reflux}]{\text{THF}} ArOMgCH_2CR{=}CH_2 \qquad (131)$$

Under mild conditions saturated ethers are not readily cleaved by magnesium but using activated metal (from $MgBr_2$/K) the reaction of equation (132) occurs; the cyclic product (**3**) can also be synthesized by dioxane addition to $XMg(CH_2)_4OMgBr$.[56] A formally related cyclic species (**73**) is formed by internal C—O bond cleavage (equation 133).[208]



(132)

(**3**)



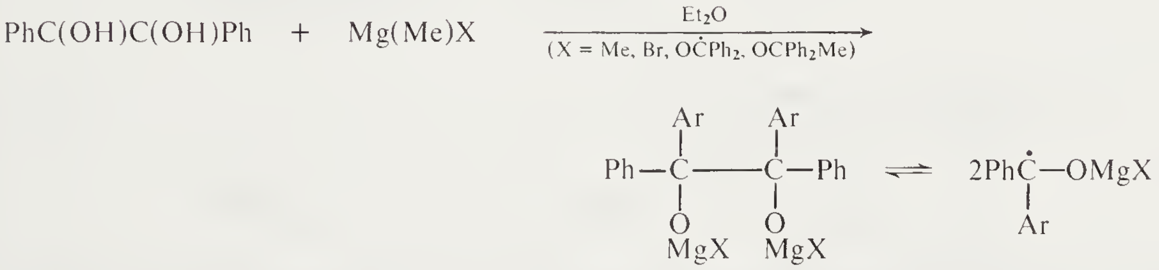
(73)

(133)

Oxiranes normally react with MgR_2 by simple ring opening to form alkoxoalkylmagnesium compounds in the first step[5–7,426] and further reaction of this product with excess oxirane is extremely slow.[313,455] With unsymmetrical oxiranes, in the absence of dominant electronic effects, the mode of ring cleavage appears to be influenced by steric effects. Thus, from $PhCH_2CHCH_2O$ and MgR_2 the exclusive product is $PhCH_2CH(OMgR)CH_2R$. These reactions do not proceed in HMPT and occur faster in Et_2O than THF and so probably involve initial complex formation between epoxide and magnesium.[313]

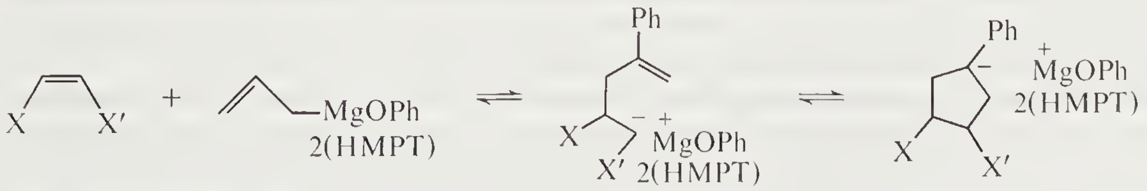
Alkoxo species are formed as intermediates in the addition of organomagnesium derivatives to organic carbonyl groups, and using equimolar quantities of MgR_2 and ketone this reaction may be used preparatively (equation 134).[392,421,451,456] Such alkoxoalkylmagnesium compounds are also present as one of several intermediates in reactions of ketones with Grignard reagents.[104] When ketones react by an electron transfer (SET) mechanism a magnesium ketyl is produced and this may lead to pinacol formation (see Scheme 10). Using a reverse reaction (equation 135), such ketyl species have been produced in equilibrium with dialkoxo derivatives.[457] The ketyl species displays characteristic ESR and electronic spectra (λ_{max} = 537–543 nm, X = Me) but is probably itself dimeric.

$$R_2CO \quad + \quad MgR'_2 \longrightarrow R_2R'COMgR' \qquad (134)$$



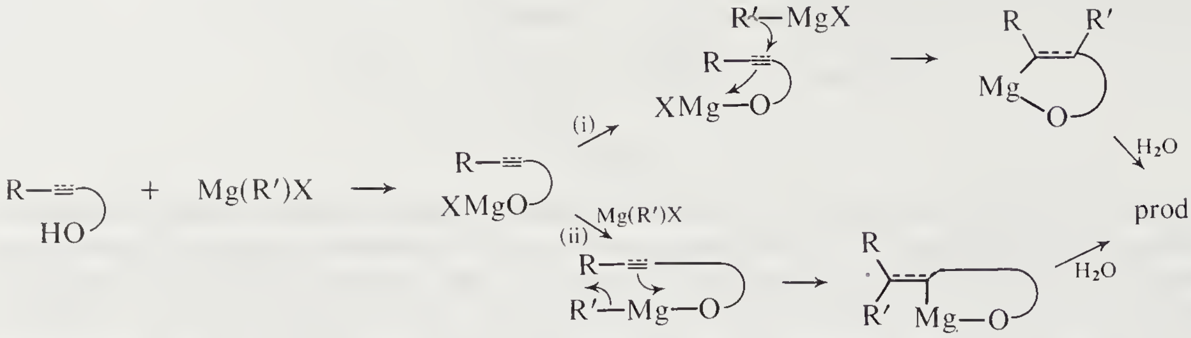
$$PhC(OH)C(OH)Ph \quad + \quad Mg(Me)X \xrightarrow[(X\,=\,Me,\,Br,\,O\dot{C}Ph_2,\,OCPh_2Me)]{Et_2O} Ph-\underset{\underset{MgX}{O}}{\overset{Ar}{C}}-\underset{\underset{MgX}{O}}{\overset{Ar}{C}}-Ph \rightleftharpoons 2Ph\underset{Ar}{\dot{C}}-OMgX \qquad (135)$$

Addition of preformed alkoxoallylmagnesium to alkenes activated by electron withdrawing substituents occurs in the presence of HMPT or a macrocyclic complexing agent such as cryptand[2.1.1].[458] With *trans*-stilbene, styrene, methylstyrenes or phenanthrene, $Mg(CH_2CPh{=}CH_2)(OPh)$ reacts by a formal [3 + 2] cycloaddition of the allyl group to the unique C=C bond. With other unsaturated reactants such as acenaphthylene, only a single C—C bond is formed, and with anthracene initial addition to the 9-position is followed by 9,10-cyclization. A stepwise carbanion mechanism is consistent with all these products (equation 136).[458]



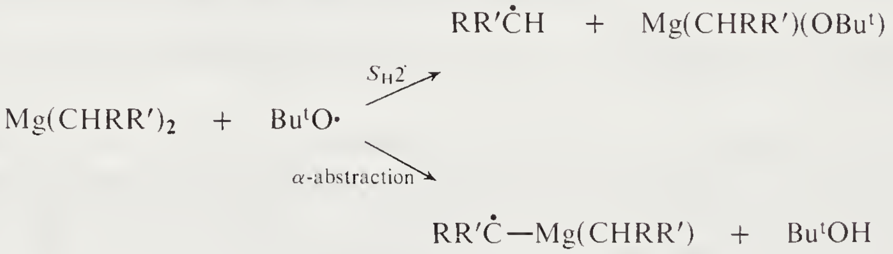
(136)

First observed for the alcohol $Ph_2C(OH)CH_2CH{=}CH_2$,[459] it has since been established that other allyl alcohols,[121,460,461] alkynols,[128,462] allenols[463] and alkenes with proximate hydroxyl groups[460,464] will undergo addition reactions with allyl-, benzyl- and *t*-butyl-magnesium compounds. The organometallic products of such reactions, prior to hydrolysis, are cyclic oxomagnesium derivatives. The mode of addition to the unsaturated bond has been reported by different workers to be predominantly either *cis* (*syn*)[121,460,464] or *trans*.[461,462] A report claims addition to alkynes is usually *trans*[462] but for alkenes, at least in some cases, *cis* (*syn*)[464] addition does occur. Two possible mechanistic pathways must be considered, the intermolecular route (i) *trans* or the intramolecular route (ii) *cis* (Scheme 13). In either case, the oxygen bonded magnesium intermediate provides anchimeric assistance to the addition reaction.



Scheme 13

Autoxidation of organomagnesium compounds occurs *via* alkylperoxo and, subsequently, alkoxo species (see Scheme 9). Although not normally used as a synthetic route to organometallic compounds the initial product of reaction of dioxygen with $MgEt_2$ was reported as trimeric $[MgEt(OEt)]_3$,[465] but this could have also contained peroxo groups. Studies on reactions of $MgPh_2$ with organic and organosilicon peroxides have also implicated alkoxophenylmagnesium intermediates.[466] Photolytically generated butoxy radicals can either cause S_H2 substitution or α-H elimination from dialkylmagnesium compounds; the former process produces unisolated butoxo compounds, (equation 137).[467] Other peroxomagnesium compounds that have been reported include derivatives of formula RMgOOMgR.[468]



$$\mathrm{Mg(CHRR')_2} + \mathrm{Bu^tO\cdot} \begin{cases} \xrightarrow{S_H2'} \mathrm{RR'\dot{C}H} + \mathrm{Mg(CHRR')(OBu^t)} \\ \xrightarrow{\alpha\text{-abstraction}} \mathrm{RR'\dot{C}{-}Mg(CHRR')} + \mathrm{Bu^tOH} \end{cases} \qquad (137)$$

Reactions of dialkyl sulphates $SO_2(OR)_2$ (R = Me, Bu^n) with magnesium in Et_2O or THF give MgR_2 and $Mg(OSO_3R)_2$ but also probably some mixed oxygen bonded product, $Mg(OSO_3R)R$.[385,386]

(*ii*) *Structural and physical properties*

Alkoxoalkylmagnesium compounds are generally crystalline solids, although liquids such as $MgBu^n(OPr^i)$ exist,[452] and with higher alkyl groups they show solubility in saturated hydrocarbons such as methylcyclohexane. Most are soluble in aromatic solvents. Crystallization from Et_2O may produce etherates but, unlike corresponding Grignard reagents, desolvation occurs readily. They are rather involatile but sublimation of some methyl and ethyl derivatives occurs *in vacuo* at *ca.* 200 °C, usually accompanied by decomposition.[421,451,469]

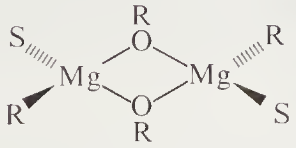
Molecular weight and spectral studies of these alkoxo compounds in various solvents have shown them to possess a variety of associated structures, favoured by the bridging ability of oxygen ligands (see Table 4). The steric bulk of the alkoxo ligand and the coordinating ability of the solvent determine the thermodynamically preferred form.[421,451] In THF, solvated dimers predominate but in Et_2O higher oligomers, including tetramers, are found, provided alkoxo groups are not too bulky. In benzene, tetramers are formed with relatively bulky alkoxo ligands OR (R = Pr^i, Bu^t), but with less sterically demanding groups, oligomers containing between seven and nine monomer units are present. Probable structures for dimer and cubane tetramer are (**74**) and (**75**). The other oligomeric species are probably either linear species with both μ-alkoxo and μ-alkyl bridge bonds or more complex species also involving μ_3-alkoxo ligands as found, for imino groups, in $[AlMe(NMe)]_7$.[470] The μ-alkoxo dimeric structure is supported by X-ray structural analysis of $[MgBr(OBu^t)(OEt_2)]_2$.[471]

The rate of interchange between dimer or 'linear oligomer' and the cubane tetramer is slow for *t*-butoxo derivatives and can be monitored by ^1H NMR spectroscopy.[421] Rapid interconversion

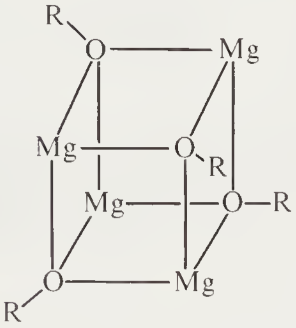
Table 4 Degree of Association of Some Alkoxoorganomagnesium Compounds in Solution

Compound	Et$_2$O	*Solvent* THF	C$_6$H$_6$
MgMe(OPr^n)[1]	3.5–4.3	1.9–2.3	7–9
MgMe(OPr^i)[1]	2.8–3.7	1.8–2.1	4.1–4.3
MgMe(OBu^t)[1]: **A**	2.0–3.8	1.9–2.0	insoluble
MgMe(OBu^t)[1]: **B**			4.0–4.4
MgMe(OCEt$_2$Me)[2]	2.8		
MgMe(OCMePh$_2$)[1]	2.0		
MgEt(OEt)[3]	4.05[a,b]		
MgEt(OPr^n)[3]	~6.5		7.0–7.2
MgEt(OPr^i)[3]			4.1–4.2
MgEt(OBu^t)[3]	3.9–4.0[a]		3.9
MgEt(OCEt$_3$)[3]	2.0		
MgEt(OCEt$_2$Me)[3]	2.1		
MgPr^i(OMe)[3]			7.0–8.3
MgPr^i(OEt)[3]			7.5–8.1
MgPr^i(OPr^i)[3]			4.1–4.2
MgBu^n(OPr^i)[4]			≈3
$\overline{\text{MgO(CH}_2)_3}$[5]		≈3	
[MgMe(OBu^t)MgMe$_2$][1]	1.0		

[a] Low concentration. [b] Note: *i* = 3, ref. 465 .
1. From ref. 421 .
2. From ref. 392 .
3. From ref. 451 .
4. From ref. 452 .
5. From ref. 208 .

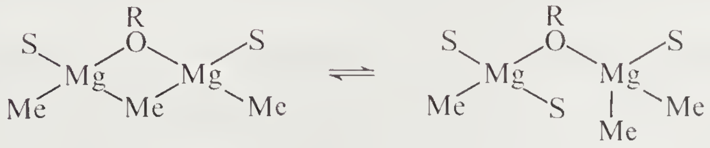


(74)



(75)

between the various forms in equilibrium concentrations occurs for less bulky alkoxo species. The cubane form is inert and does not exchange or interact with MgMe$_2$ but in solvents where the dimer ('linear oligomer') structures are present, mixed derivatives are formed and, in Et$_2$O, NMR spectra indicate an equilibrium between species of the type shown in equation (138)[421] when R = OCPh$_2$Me. In the solid state the desolvated species MgMe(OCPh$_2$Me) exhibits IR bands characteristic of bridging methyl groups and this suggests a linear oligomeric structure.[421]



(138)

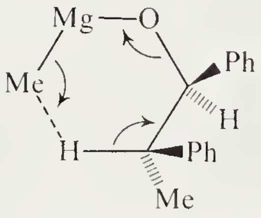
The tendency of Mg(OR)R′ species to undergo disproportionation analogous to the Schlenk equilibrium to form MgR′$_2$ and Mg(OR)$_2$ appears to be slight and is unlikely to occur in most hydrocarbon solvents since $Mg(OR)_2$ compounds are insoluble in such media. It has been suggested that $MgBr_2$ might catalyze such disproportionation; in fact the interchange of equation (139) takes place in which the Grignard reagent is formed and $[MgBr(OBu^t)(OEt_2)]_2$ can be crystallized from solution.[451] However, sterically hindered $MgMe(OCBu^t_2Me)$ does not react with $MgBr_2$.[472] Also, $Mg(OBu^t)X$ catalyzes the rate of alkyl exchange between $Mg(Bu^t)_2$ and $Mg(Bu^t)X$.[239]

$$MgMe(OBu^t) + MgBr_2 \xrightarrow{Et_2O} MgBr(OBu^t) + Mg(Br)Me \qquad (139)$$

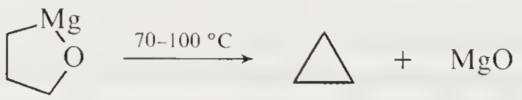
(*iii*) *Reactions*

Pyrolysis of $Mg(OR)R'$ compounds in the range 195–340 °C forms alkane, alkene and magnesium oxide (equation 140).[469,473] This constitutes a convenient method for dehydration of alcohols *via* reaction with MgR_2. DTA and TGA studies show that pyrolysis occurs in one endothermic step with no apparent intermediate. When OR = OPr^i, increasing decomposition temperature follows the order $R' = Me < Bz < Ph$ but no simple pattern was observed for change in alkoxo group. The process follows first order kinetics, the alkene is formed by *syn* elimination and the kinetic parameters suggest a cyclic six-centred transition state, as illustrated for the *threo*-1,2-diphenyl-1-propoxo derivative (**76**) which yields *cis*-alkene. However, simple β-H abstraction is not the rate determining step which must involve both C_α—O and C_β—H bond rupture to varying extent depending on the groups present in the molecule.[469] It is interesting that the cyclic species (**73**) decomposes above 70 °C[208] (equation 141) but (**3**) is stable to 100–120 °C.[56]

$$MgR'(OR) \xrightarrow{\Delta} MgO + R'H + R(-H) \qquad (140)$$



(**76**)

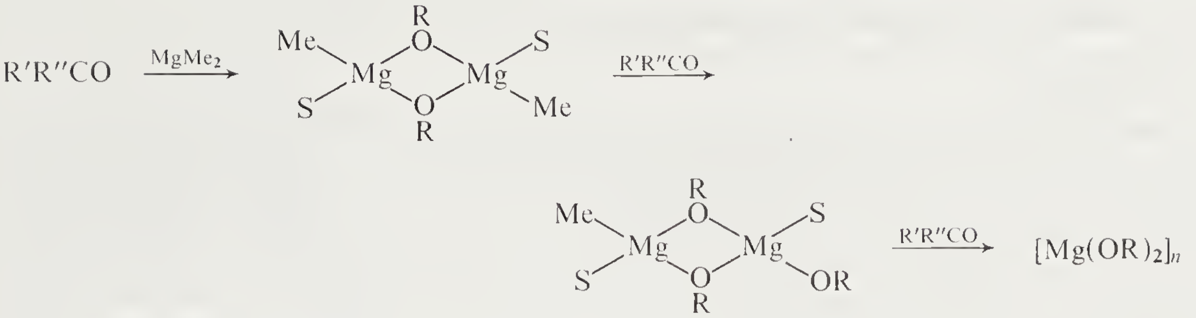


(141)

(**73**)

Hydrogenolysis of $Mg(OBu^t)R$ ($R = Et, Pr^i$) at 300 p.s.i. affords the disproportionation products MgH_2 and $Mg(OBu^t)_2$ but not $MgH(OBu^t)$ unlike the related reaction with $Mg(NR_2)R'$.[474] However, $MgH(OR)$ species may be readily formed from MgH_2 and ROH.[475]

Alkyl addition by $Mg(OR)R'$ species to C=O bonds occurs but less readily than by MgR'_2 species and more by-products of enolization and reduction have been reported.[476] A study of addition of $MgMe_2$ to 2-methylbenzophenone identified three products arising from sequential addition to the carbonyl group (equation 142).[456] Stereoselective equatorial methylation of substituted cyclic ketones has been demonstrated by using bulky aryloxo derivatives $MgMe(OAr)$[477] and optically active tertiary alcohols may be obtained from reactions of unsymmetrical ketones with ethylmagnesium derivatives of chiral amino alcohols such as *N*-methylephedrine.[478]



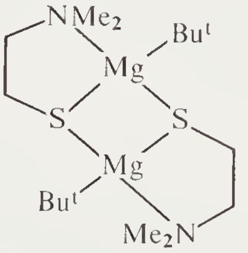
(142)

4.1.4.2 *Alkylthio and arylthio derivatives*

Although reactions of MgR_2 compounds with elemental sulphur or selenium are a route to organic sulphur and selenium compounds, intermediates of the type $MgR'(YR)$ ($Y = S, Se$) have not been isolated from such reactions. The alkylthio derivatives have been prepared by reaction of MgR_2 with alkanethiol in equimolar proportions in THF or Et_2O at or below ambient temperatures.[479] Solvated species $[MgR'(SR)(THF)]_2$ ($R = Bu^t$, $R' = Me, Et$) and $[Mg(Bu^t)(SPr^i)OEt_2]_2$ have been isolated and shown to be dimeric by cryscopy in benzene; structures of type (**74**) but with μ-SR groups are likely. Attempts to isolate other diethyl etherates were thwarted by the tendency to disproportionation (equation 143). This tendency is particularly favoured by μ-methyl bridge formation which is prevented by the more coordinating solvent THF. From toluene the tetrameric derivative $[Mg(Et)(SBu^t)]_4$ is obtained which is presumed to have a cubane structure,[479] *cf.* (**75**).

$$2MgR'(SR) \longrightarrow MgR'_2 + Mg(SR)_2 \qquad (143)$$

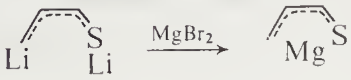
2-Dimethylaminoethanethiol with an internal, potentially coordinating amino group forms products $[MgMe(SC_2H_4NMe_2)]_4$, probably having a cubane structure with or without coordinating amino groups, and $[MgBu^t(SC_2H_4NMe_2)]_2$ of likely structure (**77**).



(77)

Reaction of allyl phenyl sulphides and related species with magnesium metal in THF is a preparative route to $MgR(SPh)$ (R = 2-alkenyl, benzyl, 2-cyclopentyl, 1-propenyl).[480] It is to be noted that only phenyl sulphides possessing a hydrocarbon group R with an sp^2-carbon atom in the β-position show reactivity in this direct reaction and a mechanism involving electron transfer to the sulphur atom was postulated.

An interesting thio compound useful in organic synthesis is formed as illustrated by equation (144).[481]



(144)

4.1.4.3 Dialkylamido and diarylamido derivatives

(*i*) *Preparation*

Compounds of the type $MgR(NR^1R^2)$ can be most simply synthesized by the reaction of secondary amines with MgR_2, usually in Et_2O at low temperature (equation 145).[482,483] The reaction proceeds with a variety of groups R, R^1 and R^2 but with dimethylamine only the disproportionation of equation (146) was observed.[482] With higher dialkylamines, ethyl derivatives $MgEt(NR^1R^2)$ are obtained from which all solvated Et_2O is not readily removed but displacement by THF gives viscous liquids of formula $[\{MgEt(NR_2)\}_2THF]$ (R = Et, Pr^i).[482] Polymeric ether-free species $[MgR(NPh_2)]_x$ (R = Et, Pr^i) are formed but monomeric etherates may also be isolated $[MgR(NPh_2)S_2]$ (S = Et_2O, THF). From $Mg(Pr^i)_2$ and $NH(Pr^i)_2$ an unsolvated product $[MgPr^i(NPr^i_2)]_2$ is formed as is a similar compound from 2,2,6,6-tetramethylpiperidine, $[MgMe(NC_5H_6Me_4)]_2$.[482] The products from *N*,*N*,*N′*-trimethylethylenediamine, $[MgR(NMeCH_2CH_2NMe_2)]_2$ (R = Me, Pr^i, Bu^t) should also be noted.[365] Many other products $MgR(NR^1R^2)$ (R = Me, Bz, Ph) have been reported either as etherates or unsolvated species but without full characterization.[483]

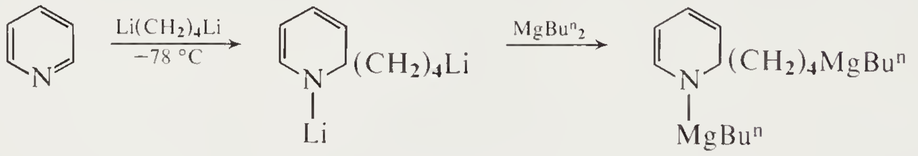
$$MgR_2 \quad + \quad R^1R^2NH \quad \longrightarrow \quad MgR(NR^1R^2) \quad + \quad RH \qquad (145)$$

$$Me_2NH \quad + \quad MgEt_2 \quad \longrightarrow \quad [MgEt(NMe_2)] \quad \longrightarrow \quad \tfrac{1}{2}Mg(NMe_2)_2 \quad + \quad \tfrac{1}{2}MgEt_2 \qquad (146)$$

It is of interest to note here that no related organo-phosphido- or -arsenido-magnesium species have been identified but the reaction of $MgEt_2$ with $AsHPh_2$, which forms $Mg(AsPh_2)_2$, probably involves an intermediate $Mg(AsPh_2)Et$.[484]

Addition of $MgEt_2$ to benzylideneaniline produces $[MgEt\{NPh(CHEtPh)\}]_2$.[482] Similar addition of MgR_2 to benzonitrile forms $MgR(N{=}CRPh)$ (R = Me, Et)[482,485] but with *t*-butyl cyanide no addition was reported with $Mg(Pr^i)_2$ and the coordination compound $Mg(Pr^i)_2(NCBu^t)$ was isolated.[482]

The transformations of equation (147) are also relevant to this section.[145] The synthetically useful Grignard reagents formed from pyrrole, indole and related nitrogen heterocycles contain N—MgX linkages although reactions often occur at carbon atoms of the aromatic rings.[85] It is possible that N—MgR species may be present in solutions of such derivatives but no characterized indolyl- or pyrrolyl-alkylmagnesium compounds have been reported.



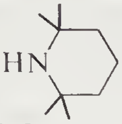
(147)

(*ii*) *Structural and physical properties*

The dialkylaminomagnesium derivatives are mainly involatile solids which decompose thermally above 150 °C.[482,483] Exceptions are solvates such as $[\{MgEt(NR_2)\}_2THF]$ (R = Et, Pr^i)[482] which are viscous liquids and, also, sublimation occurs for $[MgMe(NMeCH_2CH_2NMe_2)]_2$[365] and, partially, $[MgMe(NPh_2)]$.[483] If not polymeric the compounds are soluble in aromatic hydrocarbons and $[MgPr^i(NPr^i_2)]_2$ is readily soluble in hexane. Association data have been obtained in solution (see Table 5) and unsolvated dimeric species are found although the more insoluble derivatives are probably polymeric. Desolvation does not always occur readily and stoichiometric solvates are monomeric, $[MgR(NR'_2)S_2]$,[482] or dimeric, as found for $[MgMe(N{=}CPhMe)(OEt_2)]_2$.[485]

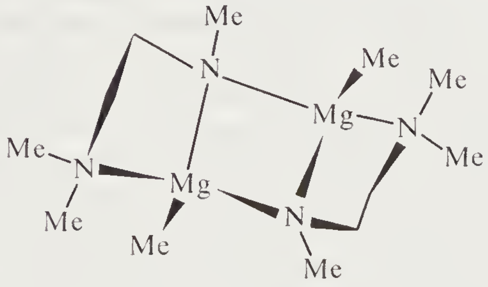
The X-ray determined structure of $[MgMe(NMeCH_2CH_2NMe_2)]_2$ in the solid state shows that the two monomethylamido groups are bridging and the ligands act as chelates giving a four-coordinate, approximately tetrahedral environment around each magnesium atom (**78**).[486] The X-ray determined structure of $[\{MgBr(N{=}CPh_2)(THF)\}_2THF]$ (**79**), a product of Grignard addition to benzonitrile, also contains bridging N-ligands.[487] More unusually a bridging bidentate THF group is present so that formally the magnesium atoms achieve five-coordination but this

Table 5 Amido- and Imido-organomagnesium Compounds[1]

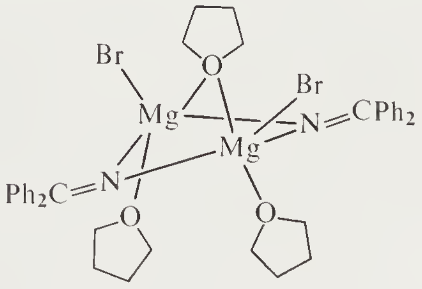
Reactants[a]	*Product*	*Degree of association*[b]
$MgEt_2 + HNEt_2$[c]	$\{MgEt(NEt_2)\}_2THF$	1[d]
$MgEt_2 + HNPr^i_2$[c]	$\{MgEt(NPr^i_2)\}_2THF$	1[d]
$MgEt_2 + HNPh_2$[e]	$MgEt(NPh_2)(THF)_2$	1
$MgEt_2$ + 	$MgEt(NC_5H_6Me_4)$	2
$MgR_2 + HNMeCH_2CH_2NMe_2$	$MgR(NMeCH_2CH_2NMe_2)$ (R = Et, Pr^i, Bu^t)	2[f]
$MgPr^i + HNPr^i_2$	$MgPr^i(NPr^i_2)$	2
$MgPr^i_2 + HNPh_2$	$MgPr^i(NPh_2)(Et_2O)_2$	g
$MgEt_2 + PhCH{=}NPh$	$MgEt\{N(CHEtPh)Ph\}$	2
$MgMe_2 + PhCN$	$MgMe(N{=}CMePh)$	2[h]
$MgEt_2 + PhCN$	$MgEt(N{=}CEtPh)$	13–21

[a] In Et_2O solution. [b] In benzene unless otherwise stated. [c] Residual solvated Et_2O displaced by THF. [d] Slightly associated. [e] THF added to unsolvated, probably polymeric product. [f] When R = Bu^t, slightly dissociated. [g] Dissociation of Et_2O and precipitation of $MgPr^i(NPh_2)$ occurs. [h] In Et_2O, 0.15M ($i < 2$ at low concentrations).
1. From refs. 365, 482 and 485.

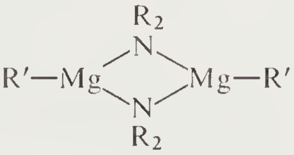
bridging THF group is easily removed. It is of interest that species $[\{MgEt(NR_2)\}_2THF]$ are isolated and these could also contain a similar bridging THF unit giving the magnesium a favoured four-coordinate structure. However, the unsolvated dimeric derivatives can only reasonably be assumed to possess three-coordinate magnesium in a structure such as (**80**).[482]



(**78**)



(**79**)



(**80**)

Low temperature ^1H NMR spectra of dimeric $[MgMe(N{=}CMePh)Et_2O]_2$ suggest that both *trans* and *cis* isomers exist in solution in the ratio 4 : 1 at −100 °C.[485] In this system there is no evidence for disproportionation into $MgMe_2$ and $Mg(N{=}CMePh)_2$[485] and the contrast with complete disproportionation of equation (146) may reflect the insolubility of $Mg(NMe_2)_2$ in Et_2O.[482] On the other hand the redistribution reaction of equation (148) occurs readily and extensively.

$$MgMe(N{=}CMePh) + MgBr_2 \longrightarrow MgBr(N{=}CPhMe) + Mg(Br)Me \qquad (148)$$

(iii) Reactions

Pyrolysis of $MgR(NR^1R^2)$ (R = Me, Bz, Ph; R^1, R^2 = various) in the temperature range 150–250 °C occurs by overall equation (149).[473,483] The residual solid $Mg(NR^2)$ can be hydrolyzed to form primary amine. As with analogous alkoxo species, after loss of coordinated solvent, the main decomposition occurs in a single step without formation of an intermediate. A unimolecular mechanism involving a six-centre transition state and *syn* elimination has been proposed for the process (*cf.* (**76**)) but unlike the corresponding decomposition of alkoxo derivatives a kinetic deuterium isotope effect shows that β-H abstraction is the rate determining step.[483] One exception to this one-step mechanism is the decomposition of MgMe(NEtPh) which eliminates methane at an early stage (215 °C) and subsequently ethylene (270 °C). It may also be noted that pyrolysis of the chelated complex $[(MgR(NMeCH_2CH_2NMe_2)]_2$ forms alkane RH as the only volatile hydrocarbon.[365]

$$MgR(NR^1R^2) \xrightarrow{\Delta} RH + R^1(-H) + [Mg(NR^2)]_x \qquad (149)$$

Hydrogenolysis of $MgR'(NR_2)$ at 3000 p.s.i. in benzene or reaction with LAH in Et_2O forms the hydrido species $MgH(NR_2)$[474] which can also be readily prepared by reaction of active MgH_2 with $Mg(NR_2)_2$.[488] When bulky groups R are present these hydrides have found application in stereoselective reduction of cyclic ketones.[488] Similarly, stereoselectivity in addition to cyclic ketones is found for $MgMe(NR_2)$ containing bulky R groups and interestingly triphenylphosphine enhances the yield of axial alcohol, suggesting that PPh_3 interacts with these magnesium reagents.[477]

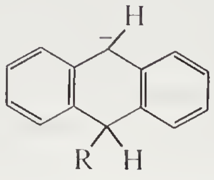
4.1.5 Electron Transfer–Addition Compounds with Unsaturated Organic Molecules

4.1.5.1 Aromatic derivatives

Organometallic compounds formed by electron transfer from magnesium to aromatic systems have been relatively little studied in comparison to the readily formed derivatives of alkali metals. It was first reported that magnesium in liquid ammonia forms a dark green, paramagnetic product with naphthalene, $Mg[C_{10}H_8]_2$, which can be isolated as a solid solvated by ammonia.[489,490] Desolvation causes decomposition into naphthalene and magnesium but this residue will redissolve in HMPT and, slightly, in DME to reform the organometallic product. The electronic spectrum (λ_{max} = 327, 371, 464 nm, in HMPT)[491] is similar to that of the naphthalene radical anion with an alkali metal counter ion. In liquid ammonia, protonolytic decomposition after *ca.* 60 h yields mainly a 1:1 mixture of naphthalene and dihydronaphthalene and only small quantities of tetralin, indicating little reaction of the organometallic compound with solvent but after 142–196 h more extensive ammonolysis does occur and some hydrogenated binaphthyl derivatives may be isolated.[489] A separate study of the stability of naphthalene–magnesium in 1,2-diaminoethane and liquid ammonia showed that decomposition occurred relatively easily in the former medium but although ammonolysis does occur, solutions in liquid ammonia possess a marked stability at −60 °C.[491] Magnesium will give similar addition compounds in liquid ammonia with biphenyl, phenanthrene and anthracene, forming initially solutions of radical anions with high electrical conductivity but ammonolysis slowly takes place.[492]

The aprotic solvent HMPT is a good solvent for reactions of arenes with magnesium films, and radical anions have been reported from naphthalene, biphenyl, anthracene, pyrene and *p*-terphenyl.[491,493,494] The conversion of *p*-terphenyl to the radical anion using excess Mg is 45–55% at ambient temperature. The relative activity of Group II metals follows the order Ba > Mg ≫ Ca.[494] Magnesium species formed in HMPT show expected ESR spectra[493] and IR studies indicate the presence of solvent separated ion pairs.[495] Solutions of napththalene–magnesium in HMPT are quite stable (8% decomposition in 100 h *in vacuo*).[491] The blue anthracene radical ion, in the presence of excess magnesium, changes after 5–10 d into a yellow product (λ_{max} = 450 nm) to which is ascribed a structure of type (**81**) where R is probably a radical product formed by metal and solvent.[494] Solutions of the naphthalene derivative $Mg[C_{10}H_8]_2$ in HMPT have been used preparatively to form radical anions by electron exchange with more readily reduced aromatic compounds.[490]

Hydrocarbons with low electron affinities are reported not to react with magnesium in ethereal solvents such as THF or DME. Tetracene and magnesium in THF form an organometallic species but the product is neither radical anion or simple dianion and a probable structure is of type **(82)** with R being H or $(CH_2)_4O^-$ derived from the solvent.[496] Magnesium organometallic products have been reported for other C_{12}–C_{40} aromatic compounds in THF.[497]



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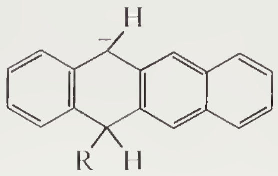


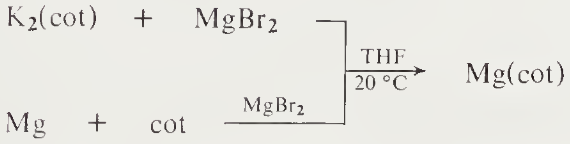
(82)

The few recorded reactions of these ionic magnesium species include metallation of indene, fluorene and benzyl cyanide,[498] the dimerization of α-bromoesters to succinic esters by naphthalene–magnesium[499] and initiation of polymerization of styrene by an anionic mechanism in HMPT.[490,494]

Magnesium metal and pyridine form a paramagnetic coupled product bis(4,4′-bipyridyl)-magnesium isolable as an adduct with pyridine, Mg(4,4′-bipy)$_2$·4.8py.[500]

4.1.5.2 Cyclooctatetraene

The magnesium derivative Mg[cot] can be prepared by reactions of equation (150).[501] The product is insoluble in THF and isolable as a solvate Mg[cot]·2.5THF (m.p. > 250 °C). Hydrolysis forms 1,3,5- and 1,3,6-cyclooctatriene. The compound has found application in organotransition metal synthesis as illustrated by equation (151). An alternative *in situ* reaction is electrogeneration using a magnesium anode (equation 152).[501]



$$\left.\begin{array}{l} K_2(\text{cot}) + MgBr_2 \\ Mg + \text{cot} \xrightarrow{MgBr_2} \end{array}\right] \xrightarrow[20\,°C]{THF} Mg(\text{cot}) \qquad (150)$$

$$HfCl_4 + 2\text{cot} + 2Mg \longrightarrow Hf(\text{cot})_2 + 2MgCl_2 \qquad (151)$$

$$Mg(\text{anode}) + 2\text{cot} + ZrCl_4 \xrightarrow[THF]{\text{electrolysis}} Zr(\text{cot})_2 + 2MgCl_2 \qquad (152)$$

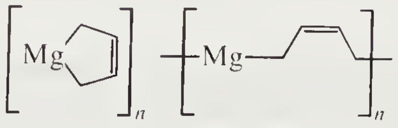
4.1.5.3 Diene and related derivatives

Dienes such as butadiene,[502] isoprene[503] and myrcene[504] react directly with magnesium in the presence of suitable catalysts.

In general diamagnetic compounds of stoichiometry $[Mg(\text{diene})_n]$ (n = 1, 2, 3) have been isolated and deuterolyses of these species gave unsaturated hydrocarbons incorporating two deuterium atoms, thus establishing the presence of two formal Mg—C bonds to a dinegative organic ligand.[502,503] In THF, preparation requires the presence of either iodine or an organic halide such as MeI, EtI, PhI or Bu^{t}Br in 0.1–1.0 mol%. Activated magnesium also reacts in the presence of $B(OR)_3$.[505] Alternative catalysts are compounds of Fe(III), Ti(IV), Ni(II), Cu(II), or Zn(II), usually employed in the presence of a reducing agent.[503] However, when some transition metal complexes such as $[NiBr_2(PPh_3)_2]$ are used partial hydrogen transfer may occur, probably *via* a transition metal–hydrido complex, to form simple allylmagnesium compounds which yield monodeuteriated hydrocarbons on reaction with D_2O.[503] It is also of interest to note that propyne and allene are self-hydrogenated on magnesium films and in such reactions MgH_2 formed *in situ* hydrometallates the unsaturated hydrocarbon.[506]

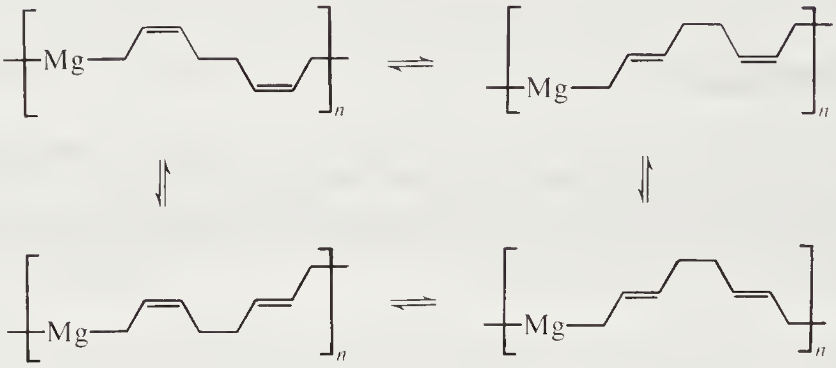
An investigation of butadiene–magnesium adducts shows that 1:1, 1:2 and 1:3 products

$[MgC_4H_6]$, $[MgC_8H_{12}]$ and $[MgC_{12}H_{18}]$ can be isolated as THF solvates.[502] These species are formed sequentially by addition of increasing amounts of butadiene. The 3:1 complex is relatively inert to further addition but at 120 °C a 4:1 species is claimed to be formed. The 1:1 adduct is insoluble but the other species are soluble in THF and the 2:1 adduct shows a high degree of association ($i \approx 11$) so that polymeric structures have been assigned to these species. IR and NMR spectra suggest that magnesium is bonded to a primary carbon atom and *cis*:*trans* ratios for unsaturated groups are 15.5:1 for $[MgC_4H_6]_n$ and 1.3–1.4:1 for $[MgC_8H_{12}]_n$ although rapid *cis–trans* isomerization takes place for the latter complex in solution at −80 °C. Postulated structures are (**83**) and (**84**) for 1:1 and 2:1 adducts, respectively. The 3:1 complex produces cyclic hydrocarbons on hydrolysis so that structures involving ring closed groups such as (**85**) or (**86**) have been proposed.[502]

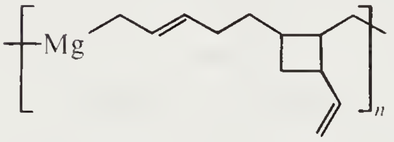


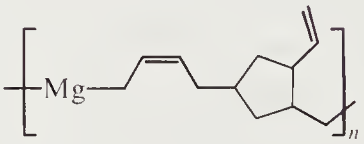
(a) (b)

(83)



(84)

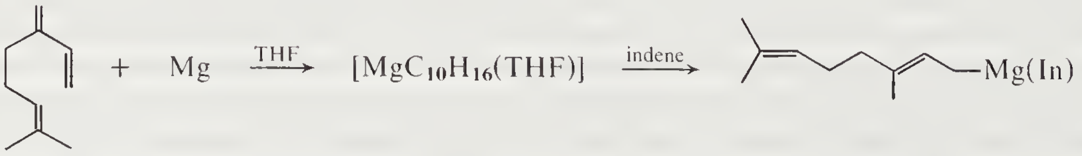




(85) (86)

Although primary C—Mg bonding is indicated, 1,3-allylic rearrangements can take place and, as for simple allylmagnesium compounds, some reactions take place at the 3-carbon atom.[502]

Isoprene forms 1:1 and 2:1 adducts and similar structures to those of butadiene derivatives probably obtain with the added complexity of the occurrence of head-to-head or tail-to-head combinations of the diene in the 2:1 derivative.[503] Myrcene–magnesium, essentially as a 1:1 adduct, has been described[504] and applied in the synthesis of organic products by reactions with ketones, oxiranes, carbon dioxide, esters, acetyl chloride and acetic anhydride.[507] The reaction of myrcene–magnesium with indene gives a mixed organomagnesium compound (equation 153).



(153)

The 2:1 adducts of butadiene and isoprene will react by addition with ethylene in THF at 80–100 °C.[112] Also the 1:1 adduct $[MgC_4H_6]_n$ has found application in the synthesis of transition metal butadiene complexes, including $[Mo(\eta^4\text{-}C_4H_6)_3]$.

Magnesium adds to the activated monoenes, styrene and 1,1-diphenylethene, in liquid ammonia or HMPT.[508]

4.1.6 Organobimetallic Derivatives

In this section 'ate' complexes of general formula $Mg_xM_yR_z$ where M is a typical metal from Groups I–III will be discussed. Bimetallic complexes containing hydrido ligands are mentioned in Section 4.1.3.2 and species containing bonds between magnesium and transition metals or silicon are discussed in Chapter 42 or 9.1, respectively.

4.1.6.1 Alkali metal compounds

Wittig reported the first example of a magnesium 'ate' complex, $LiMgPh_3$, a solid (dec. 209–212 °C) formed by combination of equimolar quantities of phenyllithium and diphenylmagnesium in Et_2O.[509] Adducts are formed with 1,4-dioxane ($LiMgPh_3(diox)_2$)[509] and TMEDA ($LiMgPh_3(TMEDA)$).[510] A related mesityl derivative $LiMg(Mes)_3(THF)_4$ has also been isolated.[369] Studies of mixtures of LiPh and $MgPh_2$ in Et_2O solution show that when the ratio Li : Mg is less than two only $LiMgPh_3$ forms, when the ratio is greater than two the 2 : 1 species Li_2MgPh_4 is produced but there is no evidence for 3 : 1 complexes.[511]

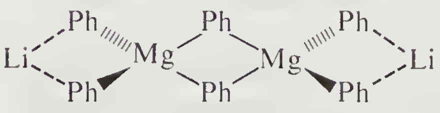
A 1 : 1 mixed alkyl 'ate' complex $LiMgBu^nMe_2{\cdot}Et_2O$ may be prepared as a viscous liquid by reaction of $LiBu^n$ with $MgMe_2$ in ether.[365a] However, studies of LiMe and $MgMe_2$ in ethereal solutions by ^1H and ^7Li NMR spectroscopy showed no evidence for a stable complex $LiMgMe_3$[512] (*N.B.* such a species has been mentioned in a synthetic paper[513]), but species of formulae Li_2MgMe_4 and Li_3MgMe_5 do form. In Et_2O both species exist depending on the reagent concentrations but in THF the 2 : 1 complex predominates.[512] Mixed complexes $Li_2MgMe_{4-n}Ph_n$ ($n = 1$–3) are also formed in a virtually statistically random distribution from LiMe–$MgPh_2$ or LiPh–$MgMe_2$ mixtures in ether.[514]

Direct reaction of alkali metals with MgR_2 compounds in hydrocarbon solvent produces 1 : 1 complexes $MMgR_3$ (M = Li, Na, K, Rb, Cs; R = Bu^n, Bu^s and/or Bu^t) (equation 154).[515] When R = Bu^s or Bu^t, the products are soluble in hydrocarbons, but when R = Bu^n the presence of a small quantity of solubilizing polar solvent is necessary. A simple one pot synthesis of such a complex is the reaction of Bu^nCl with magnesium in cyclohexane with a small amount of TMEDA, followed by addition of potassium (equation 155). In the reaction with lithium metal the 3 : 1 complex $Li_3MgBu^s_5$ can also be produced and sodium will also form a second species $NaMg_2Bu^n_5$.[515]

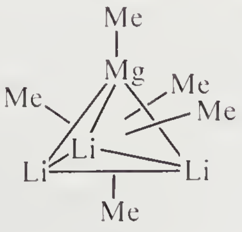
$$3M + 2MgR_2 \xrightarrow{\text{cyclohexane}} 2MMgR_3 + Mg \qquad (154)$$

$$Bu^nCl + Mg + 4K \xrightarrow[\text{(+TMEDA)}]{\text{cyclohexane}} 2KMgBu^n_3 + 3KCl \qquad (155)$$

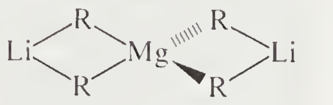
The X-ray determined structure of $LiMgPh_3(TMEDA)$ in the solid state shows the species to be dimeric and to contain phenyl-bridged magnesium atoms for which three-centre bonding may be assumed (**87**).[510] Mean bond distances are: terminal C—Mg = 2.18 Å, bridging C—Mg = 2.31 Å, Mg—Mg = 2.88 Å. The species $[Mg_2Ph_6]^{2-}$ is isoelectronic and isostructural with $[AlPh_3]_2$ and the interaction with $[Li(TMEDA)]^+$ entities is at least partially ionic but solubility in hydrocarbon solvents suggests some covalent character for these bonds. Other solvated species



(**87**)



(**88**)



(**89**)

$LiMgR_3(ether)_n$ probably have related dimeric structures and unsolvated derivatives probably possess phenyl- or alkyl-bridged structures. The 3:1 complex Li_3MgMe_5 in Et_2O exhibits NMR resonances corresponding to three non-equivalent types of methyl group at −57 °C so that structure (**88**), related to that of $[LiMe]_4$, has been proposed which dissociates in THF solution.[512] The electron deficient structure (**89**) has been suggested for the 2:1 complexes.[512]

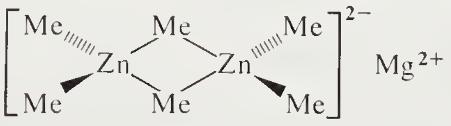
Exchange processes occurring in solution have been monitored by variable temperature ^1H and ^7Li NMR spectroscopy.[511,512,514] The equilibrium (156) is set up with $\Delta H = +11.7 \pm 3.3$ kJ mol^{-1}. When the Li:Mg ratio is greater than two, Li and Me group exchanges between Li_nMgMe_{2+n} complexes and $[LiMe]_4$ occur at comparable rates in both Et_2O and THF. When Li:Mg is less than two, exchange involving $MgMe_2$ and 'ate' complex is also quite rapid.[512] For the aryl species Li_2MgPh_4 in Et_2O the exchange of Ph groups between complex and LiPh is slower than Li exchange and it was suggested that the former process involves dissociation into $MgPh_2$ and $[LiPh]_2$ in a rate determining step whereas the latter process occurs simply *via* formation of solvent separated ion pairs $Li^+//LiMPh_4^-$.[511]

$$\tfrac{1}{4}[LiMe]_4 \;+\; Li_2MgMe_4 \;\rightleftharpoons\; Li_3MgMe_5 \qquad (156)$$

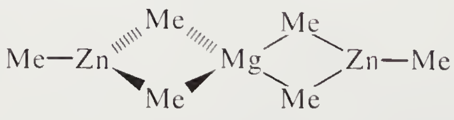
The few reactions reported for these lithium 'ate' complexes include metallation of fluorene by $LiMgPh_3$[509] and addition to ketones.[513] It is of interest that additions to cyclic ketones by Li_nMgMe_{2+n} show essentially the same overall stereochemistry as expected for mixtures of the separate reagents LiMe and $MgMe_2$.[513] Hydrogenolysis of Li_nMgMe_{2+n} produces MgH_2 and LiH but reactions of $LiMgPh_3$ with $LiAlH_4$, depending on the conditions and stoichiometry of reactants, produce MgH_2, $LiMgH_3$ or $LiMgH_2Ph$ accompanied by aluminium containing products.[445]

4.1.6.2 Zinc compounds

Species of overall compositions $MgZnMe_4$ and $Mg(ZnMe_3)_2$ have been reported.[516] They are formed by mixing $ZnMe_2$ and $MgMe_2$ in appropriate proportions or by reaction of $ZnMe_2$ with MgH_2. However, ^1H NMR studies of solutions of these species over a range of temperatures down to −107 °C show that rapid exchange is taking place[512] and an equilibrium between free dimethylmetal compounds and complex is set up.[516] IR spectra of solutions show bands attributable both to a complex and the dissociated species.[516] Possible structures for 2:1 complexes are (**90**) or (**91**).



(**90**)



(**91**)

Reaction of $MgZnMe_4$ with MgH_2 or LAH gives the complex hydride $MgZnH_4$.[517]

4.1.6.3 Aluminium compounds

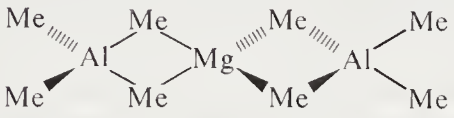
Reaction of de-etherated Grignard with trialkylaluminium in hexane occurs by equation (157) forming $Mg(AlR_4)_2$ (R = Me, Et).[518] Products obtained in this manner are viscous oils but reaction of completely ether- and halide-free $MgMe_2$ and $(AlMe_3)_2$ in a 1:1 molar ratio gives a crystalline product $Mg(AlMe_4)_2$ (m.p. 39 °C) sublimable *in vacuo* at room temperature.[519] Thermal decomposition of $Mg(AlR_4)_2$ (R = Me, Et) occurs to form $MgR(AlR_4)$ (equation 158)[518] and this product can also be obtained from a 2:1 mixture of $MgMe_2$ and $(AlMe_3)_2$ (R = Me).[519] The reaction of diethoxomagnesium with triethylaluminium produces MgEt(OEt) and not an 'ate' complex as in related reactions involving ethoxides of Ca, Sr or Ba (Section 4.2.4.3).[520] Reaction of dienes with magnesium and triethylaluminium will also produce 'ate' complexes, *e.g.* equation (159), isolated as adducts with THF.[521] The addition of AlR_3 or $MAlR_4$ (M = Li, Na, K) to MgR'_2, prepared in hydrocarbon solvents, using various ratios of Mg:Al from 1:2 to 20:1 forms hydrocarbon soluble species of overall composition $(MgR'_2)_n(AlR_3)_m$ which have proved useful components of catalytic systems for polymerization of alkenes, especially ethylene.[379,522]

$$2Mg(R)Cl \quad + \quad [AlR_3]_2 \xrightarrow[100\,°C]{\text{hexane}} Mg(AlR_4)_2 \quad + \quad MgCl_2 \tag{157}$$

$$Mg(AlR_4)_2 \xrightarrow{\Delta} MgR(AlR_4) \quad + \quad AlR_3 \tag{158}$$

(159)

X-ray analysis of solid $Mg(AlMe_4)_2$ shows an electron deficient structure with approximately tetrahedral coordination around each metal and four μ-methyl groups (**92**).[519] The Mg—C bridge bond length, 2.21 Å, compares with 2.25 Å in $[MgMe_2]_n$ and the Mg—Al distance of 2.703 Å may indicate some metal–metal interaction. A similar structure may exist in non-polar hydrocarbon solvents. Cryoscopic measurements on species $(MgBu^n_2)_n(AlEt_3)_m$ (n/m = 0–10.1) in cyclohexane have shown increasing molecular weights with increasing Mg/Al ratio.[379] When n/m = 1.1, a dimeric form $[MgBu^n_2{\cdot}AlEt_3]_2$ is present and the species is a clear mobile liquid, probably with μ-alkyl bridges.



(**92**)

^1H NMR studies have shown alkyl group exchange to occur between Al—R and Mg—R bonds.[519] Intermolecular exchanges between $Mg(AlMe_4)_2$ and $MgMe(AlMe_4)$ (possibly a dimer) (equation 160) and between $Mg(AlMe_4)_2$ and $(AlMe_3)_2$ are fast at ambient temperatures but slow on the NMR time scale at lower temperatures. However, intramolecular alkyl group exchange is still rapid at −100 °C.[519] Polarographic studies of complexes $M(AlEt_4)_2$ (M = Mg, Ca, Sr, Ba) show that the reduction potential is lowest for the magnesium derivative.[523]

$$2Mg(AlMe_4)_2 \rightleftharpoons [MgMe(AlMe_4)]_2 \quad + \quad [AlMe_3]_2 \tag{160}$$

The formation of the species $[NMe_4][Me_2Al(N_3)_2MgMe_2]$, studied by IR spectroscopy, may also be mentioned here.[524]

4.2 CALCIUM, STRONTIUM AND BARIUM

Surveys of this field have appeared in two textbooks[6,525] and in a relatively recent review.[526] The organometallic compounds of these elements have, as yet, found little application in general organic synthetic procedures since, in most cases, no advantage is to be gained over comparable reactions of the more readily handled organo-magnesium or -lithium reagents. The organometallic chemistry of calcium has been investigated most deeply but strontium and, especially, barium derivatives have been studied more widely as initiators of polymerization reactions. The reactivity of organometallic compounds shows a general increase in the order Ca < Sr < Ba and this is reflected by a corresponding decrease in stability for the derivatives of the heavier elements.

4.2.1 Halogenoorganometal Derivatives

The metals give compounds which are usually formulated as M(R)X (M = Ca, Sr, Ba; X = Cl, Br, I; R = organic group) although the actual constitution in solution is more complex, as in the case of Grignard reagents, and is generally not clear. The first organocalcium derivative was prepared in 1905[4] but Gilman and co-workers carried out the first series of studies on the reactivities of Ca(R)I derivatives (mainly R = Ph) from 1926.[527]

4.2.1.1 Preparation

(i) Direct reaction

The usual method for preparation of derivatives M(R)X is the direct interaction of metal with organic halide RX in a suitable solvent using a procedure similar to that employed for related Grignard reagents. The reactions are not as facile as for magnesium and careful attention to conditions is necessary to obtain reasonable yields.

In the preparation of calcium compounds it is found that the nature of the metal is important. Commercial calcium contains significant amounts of impurities including Mg (often approx. 0.4%), Al (*ca.* 0.01%) and Na (from 0.002%). Transition elements such as Fe and Mn may be present in trace amounts. Several workers have confirmed that the presence of Na leads to lower yields of Ca(R)X,[528,529,530] although in a recent study special purification of calcium from sodium only led to a 10–15% improvement.[529] The presence of Mg is beneficial and studies in which some of the highest yields of Ca(R)X were obtained used calcium containing 0.0019% Na and 0.49% Mg.[530] The metal is usually employed in a finely divided state, produced by mechanical milling or rasping, but alternative processes involve the desolvation of $Ca(NH_3)_6$ or rapid cooling with argon gas of vaporized metal.[531,532] To initiate reactions, calcium is often activated and, as for Grignard preparations, the addition of a little iodine has been employed[533,534] and this has been recommended as the best procedure.[535] Activation by amalgamation of calcium with mercury metal or $HgCl_2$ is also useful.[528,534,536] Other reactions have been initiated by the addition of a little preformed organocalcium or organomagnesium compound.[526] However, for simple organic iodides provided the purest finely divided calcium is used activation is unnecessary; for organic bromides and chlorides the addition of 1 mol% RI has been found effective.[530]

Fewer studies of Sr and Ba reactions have been made. Activation by amalgamation has been most used although addition of either I_2 or Mg has also been reported.[537,538,539,540] Again, reactions of unactivated finely divided metal have been found satisfactory for reactions with R^nI.[541]

Ethereal solvents are usual and both THF and Et_2O have been widely used. Other ethers, such as 1,4-dioxane and diglyme, amines and other polar solvents have been reported to be less satisfactory.[535] Highest yields have been obtained in THF but reactions need to be carried out at low temperatures to minimize the tendency for Wurtz-type coupling and reactions with the solvent.[526,530] Wurtz coupling is also reported to be reduced by using lower concentrations of RI.[529] The higher solubilities of CaI_2 and Ca(R)I in THF probably promote reaction in this solvent.[529] Hydrocarbon solvents containing ethers have been used for preparation of both calcium and strontium compounds.[536,542] It is also possible to prepare Ca(R)X derivatives in good yields solely in hydrocarbon solvents such as toluene, or cyclohexane.[530b] The products are virtually insoluble in the hydrocarbon media. Reaction times are longer but since reaction with solvent is unlikely, higher temperatures may be employed and Wurtz-type coupling does not appear to be a serious side reaction.

Simple alkyl derivatives M(R)X (R = alkyl) are most readily formed when X = I and many workers have reported no success with other halides although reaction does occur with calcium. Table 6 outlines the highest reported yields for typical compounds in different solvents. Primary alkyliodocalcium compounds are formed relatively easily. Analogous primary derivatives of strontium and barium may be formed in good yield in THF at −78 °C but at higher temperatures the yields are lower.[537,541] These compounds, $M(R^n)I$ (M = Sr, Ba), are thermally less stable than the calcium derivatives and no other alkylhalogenometal species of the heavier elements have been prepared in solution. Secondary alkyl iodides react with calcium and organometallic compounds have been prepared in reasonable yields.[530] Tertiary alkyliodocalcium compounds are very difficult to prepare and most workers report only trace amounts[526] although a more recent paper claims $Ca(Bu^t)I$ in 15% yield.[529] Disproportionation of the Bu^t group into alkane and alkene appears to be the main reaction.[530]

Table 6 Some Halogenoorganometallic Derivatives of Calcium, Strontium and Barium prepared by Direct Reaction

	Maximum yield % (Reaction temperature °C)		
Compound	THF	Et_2O	Toluene[1]
Ca(Me)I	93(−70)[2]	61(35)[2]	84(40)
Ca(Br)Me	81(−35)[3]		
Sr(Me)I	80(−78)[4]		
Ba(Me)I	25(r.t.)[5]		
Ca(Et)I	68(−70)[2]	49(r.t.)[6]	64(60)
Ca(Br)Et	46(r.t.)[7]		
Ca(Et)Cl	20(50)[3]		
Sr(Et)I	87(−78)[4]		
Ba(Et)I	86(−78)[4]	trace[8]	
Ca(Pr^n)I	73(r.t.)[7]	50(r.t.)[6]	88(95)
Ca(Br)Pr^n	45(−70)[2]		72(65)
Ca(Pr^n)Cl	29(0)[2]		50(45)
Sr(Pr^n)I	68(−78)[4]		
Ba(Pr^n)I	30(r.t.)[5]	20(r.t.)[5]	
Ca(Pr^i)I	67(0)[2]	low yield (⩾35)[9]	78(85)
Ca(Br)Pr^i	78(0)[2]		75(55)
Ca(Pr^i)Cl			75(33)
Ca(Bu^t)I	15(r.t.)[7]	0(35)[3,9]	0(95)
Ca(Br)Bu^t	14(−10)[2]		
Ca(Ph)I	97(−30)[2]	80(35)[10]	3(160)[a]
Ca(Br)Ph	55(0)[2]		5(160)
Ca(Ph)Cl	14(0)[2]		3(130)
Sr(Ph)I	97(r.t.)[11]		
Ba(Ph)I	30(r.t.)[5]		

[a] In tetralin at 180 °C, yield = 15%.
1. Ref. 530(b).
2. Ref. 530(a).
3. Ref. 528.
4. Ref. 541.
5. Ref. 537.
6. Ref. 534.
7. Ref. 529.
8. Ref. 540.
9. Ref. 547.
10. Ref. 533.
11. Refs. 538 and 542.

Perfluoroalkyl iodides R_fI ($R_f = C_2F_5$, C_6F_{13}) react with calcium amalgam in THF at −40 to −20 °C presumably forming Ca(R_f)I intermediates but these reactions have only been used for *in situ* (Barbier type) fluoroalkylations of ketones and aldehydes.[543]

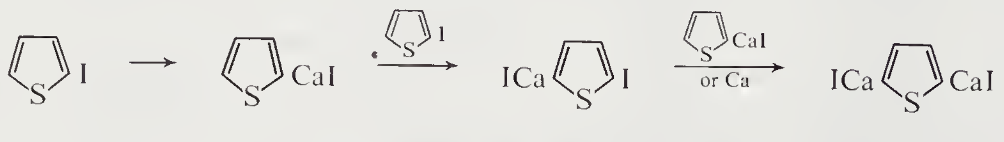
The preparation of Ca(R)X (X = Br, Cl) usually requires activated calcium; few examples have been reported and, as shown in Table 6, overall yields tend to be lower. The ease of direct reaction with calcium follows the order RI > RBr > RCl but it appears that the thermal stability of the resultant organometallic products follows the opposite trend, *i.e.* Ca(R)X, X = Cl > Br > I, and Ca(Bu^n)Cl is stable in boiling THF.[528]

Cocondensation of a range of alkyl halides with Ca, Sr or Ba vapour at −196 °C and subsequent warming *in vacuo* gives products which contain solvent-free alkylhalogenometal species in 10–25% yield, mixed with other products including metal hydride and halide.[541] In this manner primary, secondary and tertiary alkyl and also iodo, chloro and bromo species of all three metals have been obtained but hydrolysis produces a range of hydrocarbons. Related cocondensations of dimethyl ether with Ca, Sr and Ba vapour give organometallic intermediates, probably including M(Me)OMe, which on hydrolysis form C_1–C_8 organic products;[544] deuterolysis yields products incorporating between one and three deuterium atoms.

Diiodomethane reacts with calcium in THF at −30 °C to give the bimetallic species of equation (161) in 17% yield, although dibromomethane and dichloromethane do not form similar organometallic compounds.[545]

$$CH_2I_2 \quad + \quad 2Ca \quad \xrightarrow{THF} \quad CH_2(CaI)_2 \tag{161}$$

Aryliodometal compounds M(Ar)I (Ar = Ph, *o*-, *m*- and *p*-tolyl, 1-naphthyl) are prepared by direct reaction when M = Ca (in THF, Et_2O or hydrocarbon)[528,529,530,533] or Sr (in THF or solvents containing 1 mol THF).[538,542] Only one barium species Ba(Ph)I has been reported.[537] Chloro and bromo derivatives Ca(Ph)X (X = Cl, Br) have also been formed[528,530] (see Table 6 for typical examples and yields). The aryl coupling side reaction is not important in these reactions although attack of ethereal solvent may occur so that low temperature preparations are best in THF. Poorer yields are obtained in hydrocarbon solvents.[530] It is interesting that 2-iodothiophene reacts normally with mercury activated strontium in THF to form iodo-2-thienylstrontium[538] but with calcium the reaction is complicated by a subsequent metallation (equation 162) forming products (**93**) and (**94**) as indicated by subsequent carboxylation to the respective acids.[528] Cocondensation of calcium metal vapour with hexa- or mono-fluorobenzene at −196 °C leads to reaction and on warming in the presence of water C_6F_5H or C_6H_6, respectively, is formed.[546] It is probable that species $Ca(C_6F_5)F$ or $Ca(C_6H_5)F$ are present initially but these are unstable, and on warming the former in the absence of water CaF_2 is eliminated and a polymeric product obtained, possibly formed *via* a tetrafluorobenzyne intermediate. It should be noted that perfluoro-2-butene is defluorinated to hexafluoro-2-butyne under similar conditions.[546]



(162)

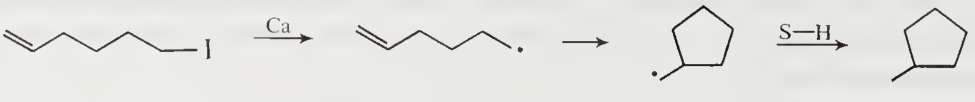
(**93**) (**94**)

Benzyl halides give poor yields of organometallic compounds and Wurtz-type coupling is the major reaction. The following compounds have been formed by careful reaction: Ca(Bz)I (13% in THF at −70 °C), Ca(Bz)X (X = I, 6%; X = Br, 6%; X = Cl, 2% in benzene at 90 °C).[530] Allyl iodide reacts with calcium in Et_2O to produce $Ca(C_3H_5)I$ in a smooth reaction[547] and the strontium complex $Sr(Br)(C_3H_5)(THF)_2$ has also been isolated.[539] No 1-alkenylhalogenometal compounds have been described.

Triphenylmethyl chloride reacts readily with calcium as finely divided metal or amalgam giving a deep red crystalline solid adduct from THF, $Ca(CPh_3)Cl(THF)_2$ in yields >90%.[548] The reaction also occurs in Et_2O, DME, dioxane and other polyethers. Compounds $M(CPh_3)X$ (M = Ca, X = Br; M = Sr, X = Cl, Br; M = Ba, X = Cl) have also been prepared as THF adducts in similar reactions[539] and a range of species M(CArAr′Ar″)X (M = Ca, Sr; X = Cl, Br, I) have been mentioned in a patent.[549]

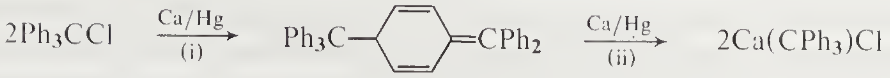
The mechanism of the direct reaction between Ca, Sr or Ba and organic halide has not been well investigated but may be analogous to the reaction of Mg (Scheme 1). In the reaction between 1-iodohexane and calcium, Wurtz-type coupling affords $C_{12}H_{26}$ as the major product (60–70%) and the organometallic $Ca(C_6H_{13})I$ is formed in only 25–30%.[536] Both species are produced concurrently and coupling is not the result of a reaction of the type shown in equation (163). Such a conclusion is supported by the slowness of reaction (163) when R = Me and R′ = Bz.[550] Radicals R· are thus implicated in the formation of both R—R and smaller amounts of the dismutation products RH and R(−H) during the direct preparation of Ca(R)I ($R = C_6H_{13}$). Supporting evidence for radical intermediates in calcium reactions includes the formation of methylcyclopentane from 6-iodo-1-hexene by cyclization of the hexenyl radical (equation 164) and the trapping by 2-methyl-2-nitrosopropane of Me· radicals during the preparation of Ca(Me)I[536] (although it is possible that the *t*-butylmethyl nitroxide could alternatively result from a subsequent reaction of Ca(Me)I itself). CIDNP effects have been observed in reactions between EtBr and Ca so that radical reactions must be occurring but it is of interest that the organometallic compound itself was not identified by its ^1H NMR spectrum.[551]

$$\mathrm{Ca(R)I} \quad + \quad \mathrm{R'I} \quad \longrightarrow \quad \mathrm{RR'} \quad + \quad \mathrm{CaI_2} \tag{163}$$



(164)

The formation of $Ca(CPh_3)Cl$ has been proposed to occur *via* ‘hexaphenylethane’ (equation 165) since step (ii) has been demonstrated to take place.[548] However, the coupled product of CPh_3 is actually the *para* adduct and this is in equilibrium with free trityl radicals so that a radical mechanism involving an intermediate such as $\{Ph_3C\cdot\ \cdot Ca_sX\}$, probably also obtains here.



(165)

The apparently ready thermal decomposition and tendency for solvent attack by compounds M(R)X (R = alkyl), increasing in the order M = Ca < Sr < Ba, complicates any mechanistic studies, especially for the heavier metals.[541]

(*ii*) *Indirect reactions*

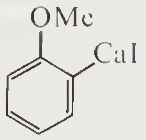
Indirect methods for formation of halogenoorganometal compounds have included metallation, halogen–metal exchange and addition to certain unsaturated organic compounds using more readily available preformed organometallic reagents.

Metallation of more acidic hydrocarbons has been demonstrated for Ca(R)X (R = Me, Ph, Ph_3C) and Sr(Ph)I. The general reactivity for metallation by Group I and II organometallic compounds follows the order KR > NaR > LiR > Ca(R)I > Mg(R)X[552] and for calcium R = Me > Ph.[528,553,554] The phenyl derivatives are activated for metallation when complexed as Ca(Ph)I(L) (L = TMEDA, DABCO (1,4-diazobicyclo[2.2.2]octane))[555] or Sr(Ph)I·0.5TMEDA.[556]

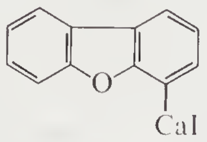
Fluorene is metallated by Ca(Me)I,[553] Ca(Ph)I·L[555] and also by $Ca(CPh_3)Cl$,[557] the latter yielding chloro-9-fluorenylcalcium in high yield from THF as the sparingly soluble adduct $Ca(Fl)Cl(THF)_2$ (Fl = fluorenyl). Likewise Sr(Fl)I·0.5THF is isolated from Sr(Ph)I·0.5TMEDA and fluorene.[556] Indene and thiophene are metallated by both Ca(Me)I[528,553,554] and Ca(Ph)I·L,[555] as indicated by carboxylation to indene-3-carboxylic acid or thiophene-2-carboxylic acid, respectively. The intermediate organometallic products were not identified. It should be noted that $Ca(CPh_3)Cl$ gives the soluble diindenylcalcium as the product of metallation of indene and this may be related to the relative solubilities of $Ca(In)_2$ and $CaCl_2$ compared to Ca(In)Cl (In = indenyl) in the Schlenk equilibrium.[557] Also, the triphenylmethyl reagent forms $CaCp_2$ from cyclopentadiene whereas Ca(Me)I and cyclopentadiene in THF at 60 °C form the sparingly soluble $Ca(Cp)I(THF)_2$ in 40% yield.[529]

Reactions of 1-alkynes with Ca(Ph)I in Et_2O give the corresponding alkynyliodocalcium compound in good yields (46–91%), Ca(C≡CR)I (R = Ph, Pr^n, Bu^n, CH_2OEt, $Me_2CHCH_2C(Me)O$—THP).[558] $Ca(CPh_3)Cl$ similarly reacts with phenylacetylene in THF to give an adduct of $Ca(C_2Ph)Cl$.[557] These crystalline solids are sparingly soluble in usual organic solvents and melt at temperatures in excess of 250 °C.

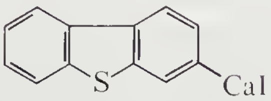
In Et_2O solvent, low yield metallation reactions have been observed for anisole, dibenzofuran, dibenzothiophene and *N*-ethylcarbazole producing, respectively, compounds (**95**), (**96**), (**97**) and (**98**).[552] The formation of 2-(iodocalcium)dibenzothiophene is unusual. Using the activated complexes of Ca(Ph)I with TMEDA or DABCO metallation occurs for triphenylmethane and pentafluorobenzene.[555] It is also probable that, as for magnesium compounds, HMPT would promote metallation reactions.



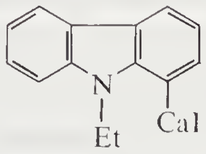
(**95**)



(**96**)



(**97**)



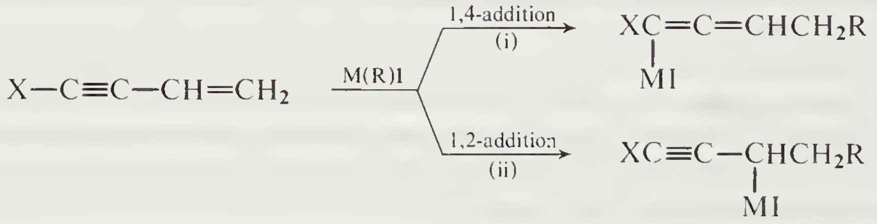
(**98**)

Metal–halogen exchange reactions are less well documented. The reaction of equation (166) occurs in high yield.[528] On the other hand exchanges between iodomethylcalcium and halogenobenzenes are slow and yields of products from the reaction of equation (167), determined by carboxylation using CO_2, are X = Cl, 21%; X = Br, 42%; X = I, 38%.[553] $Ca(Pr^n)I$ is more reactive in this reaction and benzoic acid (80%) is produced after 60 h at 20 °C from bromobenzene but since excess Ca metal was present in these latter studies some Ca(Ph)X may also have resulted from direct reaction of PhX and metal.[553]

(166)

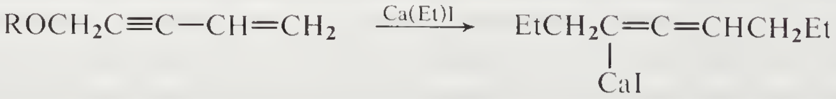
$$\mathrm{PhX} \xrightarrow[\text{THF, 49 h, 23 °C}]{\mathrm{Ca(Me)I}} \mathrm{Ca(Ph)I} \qquad (167)$$

Addition of Ca(R)X to simple alkenes does not occur readily. No reaction is observed between cyclohexene and Ca(Me)I after 60 h at 20 °C and with 1,1-diphenylethylene in THF a deep red colouration is produced, attributable to $Ca(CEtPh_2)I$, but formed in very low yield.[550] Alkyl- and aryl-iodometal compounds, however, react with conjugated enynes in ethereal solvents. Cherkasov and co-workers have reported many examples of such reactions and the basic pathways are 1,4 or 1,2 addition as shown by equation (168).[526,559] The compounds studied have included M = Ca, R = Et, Pr^n, Bu^n, Ph, Bu^i, *n*-pentyl and *i*-pentyl, and M = Ba, R = Et, Ph, Pr^n and Bu^n. When X = alkyl, $Me_2C(OH)$, RS, $CH_2{=}CH$, $MeCH{=}CH$, $CH_2{=}CMe$ or Me_2NCH_2, the only isolable product after hydrolysis is the allene formed *via* route (i),[559] although when X = CH_2OR the alkoxy group is also replaced (equation 169).[560] When X = $SiMe_3$ or $GeEt_3$ both allene and alkyne are produced by pathways (i) and (ii) in virtually 1 : 1 ratio.[561] This difference in reactivity has been attributed to the more electropositive character of Si and Ge and to the possibility of *d*-orbital interaction with the alkyne group. The general pattern of reactivity of M(R)X (X = Ca, Ba) with enynes resembles the reactions of alkyllithium compounds but not Grignard reagents.



(168)

$$\mathrm{X{-}C{\equiv}C{-}CH{=}CH_2} \xrightarrow{\mathrm{M(R)I}} \begin{cases} \xrightarrow[\text{(i)}]{\text{1,4-addition}} \underset{\mathrm{MI}}{\mathrm{XC}}\mathrm{{=}C{=}CHCH_2R} \\ \xrightarrow[\text{(ii)}]{\text{1,2-addition}} \mathrm{XC{\equiv}C{-}}\underset{\mathrm{MI}}{\mathrm{C}}\mathrm{HCH_2R} \end{cases} \qquad (168)$$



(169)

$$\mathrm{ROCH_2C{\equiv}C{-}CH{=}CH_2} \xrightarrow{\mathrm{Ca(Et)I}} \mathrm{EtCH_2}\underset{\mathrm{CaI}}{\mathrm{C}}\mathrm{{=}C{=}CHCH_2Et} \qquad (169)$$

4.2.1.2 Constitution, properties and reactions

Very little is known concerning the structures of halogenoorganometal compounds of calcium, strontium and barium. In solution even the stoichiometries of the products are not clear.

Derivatives have been isolated in the solid state having the simple 1 : 1 : 1 stoichiometry M(R)X.[529,533,541,548] These are normally obtained as solvated adducts from ethereal solutions. Alkyl complexes with THF, $M(R)X(THF)_n$ (M = Ca, $n = 2$; M = Sr, $n = 2$ or 3; M = Ba, $n = 1$) have been described.[529,541] The complex $Ca(Et)I(Et_2O)$ was first reported by Beckmann,[4] although later disputed.[527,547] More recently $Ca(Bu^n)I(Et_2O)$ has been isolated and this can be desolvated at 110–120 °C *in vacuo* to give free $Ca(Bu^n)I$ which is apparently stable at this temperature.[533] It should be noted that the alkyl derivatives of strontium and barium are thermally unstable and desolvation without decomposition was not achieved.[541] Complexes between Ca(R)I (R = alkyl) and 1,4-dioxane or triethylamine have also been isolated.[529]

Aryl derivatives have also been obtained as complexes, *i.e.* $Ca(Ar)I(L)_n$ (L = 1,4-dioxane, $n \leqslant 1$; L = TMEDA, $n = 1$; L = DABCO, $n = 1$; L = NEt_3, $n = 1$)[529,533,555] and $Sr(Ar)I(L)_n$ (L = THF, $n = 1, 2$; L = TMEDA, $n = 0.5$),[538,556] and heating the dioxane adducts of calcium (110–120 °C, $2\text{–}3 \times 10^{-3}$ Torr) forms free Ca(Ar)I. Other isolated complexes include triphenylmethyl derivatives $Ca(CPh_3)Cl(L)_n$ (L = THF, Et_2O, 1,4-dioxane, DME, $n = 2$; L = THF, $CH_2(OMe)_2$, $n = 1$),[548] $M(CPh_3)X(THF)_n$ (M = Ca, Sr, Ba; X = Cl, Br; $n = 2$–5)[539] and fluorenyl compounds $M(Fl)X(THF)_n$ (M = Ca, X = Cl, $n = 2$; M = Sr, X = I, $n = 0.5$).[556,557] Desolvated solid $Ca(CPh_3)Cl$ can also be obtained and since it will not reform an adduct with THF a polymeric structure was proposed for this species.[548]

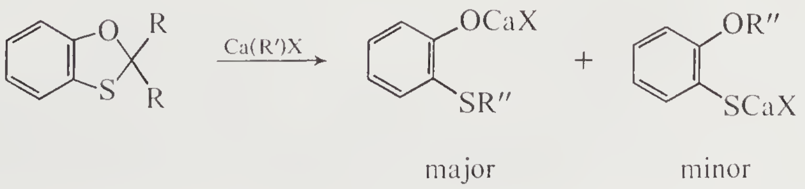
The degrees of aggregation of simple alkyl and aryl derivatives in solution have not been determined. In the preparation of Ca(R)I species in THF, especially at low temperatures, both soluble and insoluble products are formed. In many studies of such systems the combined suspension has been employed but if the solution and precipitate are separated it is found that the soluble fraction reacts with ketones by addition and the insoluble fraction only by reduction.[562] It has also been suggested by other studies of reactions that two different organocalcium species may be formed.[528] Analyses of the soluble fraction indicate a base to iodide ratio R : I > 1 and this has been attributed to a mixture of Ca(R)I and CaR_2 derivatives in solution.[528,529] The precipitate consists of solvated species CaI_2 and Ca(R)I in a mole ratio > 1.[529] This evidence supports the existence of a Schlenk-type equilibrium (equation 170) which may be shifted to the left with the low solubility of species such as $CaI_2(THF)$. Contrary to this interpretation, however, the soluble product was found by other workers to have an R : I ratio <1, a formula nCa(R)I·$m$$CaI_2$ being assigned.[563]

$$CaR_2 + CaI_2 \rightleftharpoons 2Ca(R)I \qquad (170)$$

Electrical conductivities of alkyl and aryl derivatives Ca(R)I in THF are somewhat higher than for analogous Mg(R)I species (Λ_M in the range 10^{-5}–10^{-4} Ω^{-1} cm^2 mol^{-1}) indicating greater ionic character in Ca—I and Ca—R bonds. The molar conductivity also falls with increasing concentration and this is attributable to the formation of insoluble complex species.[529] 1 : 1 Complexes are formed between dibenzo-18-crown-6 and Ca(R)I (R = Me, Et, Ph) in solution and absorption bands at 294 and 363 nm in the UV spectrum are assigned to the methyl complex.[564]

The compound $Ca(CPh_3)Cl(THF)_2$ is monomeric in benzene but dissociation of THF occurs at low concentrations.[548] The deep red colour of this compound compared to the colourless magnesium analogue in THF suggests ionic character for the $Ph_3\bar{C}(\overset{+}{C}aCl)$ bond but the conductivity is low so that ion pairs or higher associated ions must exist in solution.

Ethers are attacked by M(R)X species. Decomposition of Ca(R)I species in THF follows first order kinetics and the following stability order is observed R = Bu^n > n-hexyl > n-pentyl > Et > Pr^n > Me.[563] For the methyl derivative, decomposition half lives at 20 °C in THF have been quoted as varying from 10 h[550] to 13 d.[528] In Et_2O the rate of decay is approximately 50% lower.[530] The main product from Et_2O and Ca(R)I is reported to be $Ca(OEt)_2$ but from THF no simple ring opened products have been observed.[528] Ca(Me)I and THF at 20 °C liberate gaseous products CH_4 (9 mol%), C_2H_6 (1 mol%) and C_2H_4 (90 mol%), much involatile tarry material and a little 2-propanol. In THF, decompositions of $Ca(C_6H^n_{13})I$[536] and M(Me)I (M = Sr, Ba)[541] form corresponding 2-alkyltetrahydrofuran compounds in 3–6% yield, probably by a radical mechanism. The cleavage of C—O bonds by Ca(R)X has been shown to be the main reaction of 1,3-benzodioxole and 1,3-benzooxathiole derivatives, although a small amount of C—S bond cleavage does occur for the latter compounds (equation 171).[565]



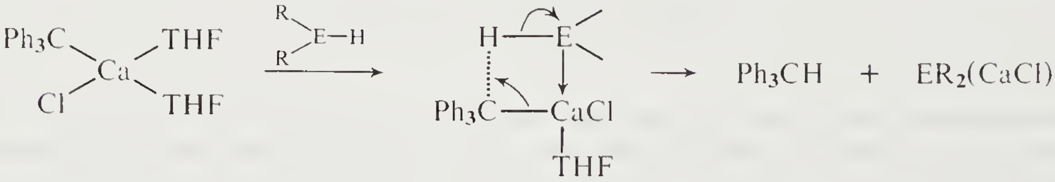
(171)

Decomposition by reaction with O_2 has not been generally investigated but in the case of $Ca(CPh_3)Cl$ in THF the peroxide $(Ph_3C)_2O_2$ is formed.[548]

Reactions with unsaturated organic groups are discussed in Chapter 44. It is relevant here to note that carboxylation with CO_2 forms the corresponding acid $ArCO_2H$, after hydrolysis, in nearly quantitative yields from aryl derivatives M(Ar)X (M = Ca, Sr).[528,538] However, only low yields of RCO_2H are formed from alkyl derivatives when ketones are the main product at ambient temperatures.[528] In reactions with ketones, aldehydes or other carbonyl compounds addition, reduction and enolization reactions can occur but yields of products tend to be low except from aromatic carbonyl compounds.[528,541,550,562]

Addition reactions to unsaturated C=C bonds have been discussed in Section 4.2.1.1(ii) but such processes are also involved in the initiation and propagation steps of vinyl polymerization. Butadiene, isoprene and styrene are polymerized by $Ca(Bu^n)I$ by a typical anionic mechanism — the initiation step is slow compared to the propagation process and the microstructure of the resulting polymer is solvent dependent.[566] Also, derivatives $M(CPh_3)X$ (M = Ca, Sr, Ba) and Ca(Fl)Cl are polymerization initiators for vinyl monomers.[539,567]

Metallation and metal–halogen exchange reactions are outlined in Section 4.2.1.1(ii). The reactions of M(R)I (M = Ca, Ba) with alcohol have been found useful in the preparation of diarylmethoxoiodometal compounds.[534,537] Polymeric species $Ca(ER_n)Cl$ (E = N, P, As, $n = 2$; E = O, S, Se, $n = 1$) are formed from reaction of $Ca(CPh_3)Cl(THF)_2$ with the active hydrogen in $EH(R)_n$ and a mechanism involving a four-centre S_Ei transition state was suggested for these reactions (equation 172).[568] Interactions of diborane with Ca(Ar)X, prepared *in situ*, form arylboron intermediates which after oxidation with H_2O_2 give low yields (1–48%) of the corresponding phenols.[569] The formation of 2-phenylpyridine, accompanied by smaller quantities of 2,5- or 2,6-diphenylpyridine, by reaction of Ca(Ph)I with pyridine is also of interest.[528]



(172)

Analyses of organoalkaline earth metal compounds in solution have been carried out in several ways and some quoted preparative yields may be liable to error. Simple analysis by acid titration usually gives high values since basic impurities, including alkoxides, are often present. A double titration method has been recommended in which the residual base is also titrated after completely decomposing Ca(R)X with chloroform.[570] Analysis of the amount of carboxylic acid obtained by carboxylation is essentially quantitative for many aryl compounds but for alkyl derivatives is not satisfactory. The determination of hydrocarbon RH liberated on hydrolysis of freshly prepared reagents is a reliable method and gas chromatography is a useful technique for this analysis[571] but RH may also form by decomposition on standing in solution and, if involatile, it will remain in the system to invalidate subsequent hydrolytic analyses. Methods for determination of C and H in organoalkaline earth metal compounds have been described.[319]

4.2.2 Diorganylmetal Derivatives

4.2.2.1 Dialkyl and diaryl derivatives

Simple dialkyl and diaryl compounds of calcium, strontium and barium have been prepared by transmetallation with HgR_2 in THF or Et_2O (equation 173). The following have been reported in fair to good yields: MR_2 (M = Ca, R = Me, Et, Ar; M = Sr, R = Me, Et, Ph; M = Ba, R = Me, Ph).[572,573] Alkyl derivatives are formed between −35 and 0 °C and are relatively unstable in solution at ambient temperatures. In particular, $CaMe_2$ reacts readily with pyridine so that it is highly unlikely that compounds MMe_2 (M = Ca, Sr, Ba) can be prepared by reaction of MeI with metal in refluxing pyridine as claimed earlier[574] — the products are probably hydrido species.[526] Also, products of reaction between ZnR_2 and alkaline earth metals are complex 'ate' derivatives (see Section 4.2.3.2) and not simple MR_2 compounds as often described in the literature. It may also be noted that reactions between alkenes and metal hydrides MH_2 (M = Ca, Sr, Ba) may involve organometallic intermediates.[394,526]

$$HgR_2 + M \longrightarrow MR_2 + Hg \qquad (173)$$

Mixtures of $Ba(OR)_2$ and organomagnesium compounds, in particular MgR'_2, lead to formation of organobarium compounds by exchange and although the products have not been characterized the presence of derivatives BaR'_2 and $BaR'(OR)$ has been proposed.[575]

Compounds MR_2 (R = alkyl) show α-H ^1H NMR resonances in the range δ −0.4 to −1.8 p.p.m.[572] They metallate relatively acidic hydrocarbons such as indene and act as catalysts for anionic polymerization of styrene, lower alkyl acrylates and dienes. No structural information has been obtained for these alkyl compounds but solid $CaMe_2$ does not readily dissolve in THF, DME or TMEDA so that it may have a polymeric structure, as found for $MgMe_2$.[572]

Aryl compounds MAr_2 are more stable than alkyl derivatives and may be prepared at temperatures 0–40 °C in THF or other ethers, being fairly soluble in such solvents but sparingly soluble in hydrocarbons in the absence of coordinating ethers.[573] Reaction of $CaPh_2$ with THF, however, does occur slowly at 23 °C. Calcium compounds have been isolated as complexes $CaAr_2{\cdot}nL$ (n = 1, L = DABCO; n = 0.5, L = THF, 1,4-dioxane) but weakly coordinated THF can be removed under vacuum. The structures of these solid products are unknown. The compounds MAr_2 react by addition with benzophenone and CO_2 and are also effective in metallation of acidic hydrocarbons including indene, fluorene, triphenylmethane and diphenylmethane.[573] The use of $CaAr_2$ as initiator for polymerization of epoxides[576] and vinyl monomers[567] has also been reported.

4.2.2.2 Dialkenyl, dialkynyl and di-α-arylalkyl derivatives

The divinyl compounds $M(CH{=}CH_2)_2$ and diallyl compounds $M(C_3H_5)_2$ have been prepared by metal exchange between alkaline earth metal and tetravinyl- or tetraallyl-tin or -lead using a trace of $HgBr_2$ as initiator (equation 174).[577] The orange–yellow vinyl compounds decrease in stability Ca > Sr > Ba. The basically colourless diallyl compounds can also be prepared from diallylmercury (equation 173),[572] and $Ca(C_3H_5)_2$ shows ^1H NMR resonances of an AX_4 pattern consistent with an essentially ionic or fluxional allyl group.

$$M'R_4 \quad + \quad 2M \quad \xrightarrow[M' = Sn,\ Pb]{THF\ (0\text{–}40\ ^\circ C)} \quad 2MR_2 \quad + \quad M' \qquad (174)$$

Dialkynyl compounds $M(C{\equiv}CR)_2$ (M = Ca, Sr, Ba, R = Ph; M = Ca, Ba, R = H) have been described and may be prepared by direct reaction in liquid ammonia (equation 175).[578,579] Reaction of $Hg(C{\equiv}CPh)_2$ with alkaline earth metal (equation 173) also gives quantitative yields of the bis(phenylethynyl)metal compounds[572] but metallation of $PhC{\equiv}CH$ with simple MR_2 compounds, although feasible, has not yet been reported except with the 'ate' complexes $MZnEt_4$.[580] Solvates $M(C{\equiv}CR)_2(NH_3)_n$ (R = H, $n \leqslant 4$; R = Ph, n = 1–2) are obtained from liquid ammonia. When R = H the solvated ammonia may be removed at low temperatures but the compounds are relatively unstable and decompose to form simple carbides even at room temperature (equation 176).[579] On the other hand, when R = Ph desolvation can be carried out *in vacuo* at elevated temperatures and the products $M(C{\equiv}CPh)_2$ are thermally very stable with decomposition temperatures 320 °C (Ca), > 360 °C (Sr), 195 °C (Ba).[578]

$$2RC{\equiv}CH \quad + \quad M \quad \xrightarrow{\text{liquid } NH_3} \quad M(C{\equiv}CR)_2 \quad + \quad H_2 \qquad (175)$$

$$M(C{\equiv}CH)_2(NH_3)_n \quad \longrightarrow \quad MC_2 \quad + \quad HC{\equiv}CH \quad + \quad nNH_3 \qquad (176)$$

Desolvated $Ca(C{\equiv}CPh)_2$ dissolves in THF and ebullioscopic molecular weight studies show that slow depolymerization occurs in solution to give a final species which is predominantly dimeric. Therefore, it is probable that the compound is polymeric in the solid state and the X-ray powder analysis suggests similar solid state structures for strontium and barium analogues, although IR evidence supports increasing ionic character of the M—C bond down the group.[578] Adducts of $M(C{\equiv}CPh)_2$ with THF and TMEDA are isolable. A few reactions of $Ca(C{\equiv}CPh)_2$ have been investigated including addition to C=O bonds and the formation of $CaCp_2$ (>80%) by metallation of cyclopentadiene or of $Hg(C{\equiv}CPh)_2$ (80%) from $HgCl_2$.[578]

Dibenzylmetal and related compounds $M(CH_2Ar)_2$ can be prepared in high yields by the transmetallation reactions of equations (173) and (174).[413,572,577,581,582] A convenient quantitative synthesis of $Ba(Bz)_2$ is to react a barium film, formed by vaporization *in vacuo*, with a THF solution of $Hg(Bz)_2$.[581] The compounds $M(Bz)_2$ (M = Ca, Sr, Ba) are yellow–red species having λ_{max} in the region 322–343 nm. Solutions in ethereal solvents decompose at ambient temperatures; thus, $Ba(Bz)_2$ shows significant decomposition in THF after 30–40 h[582] and in DME is 20% decomposed within 1 h at 31.5 °C.[413] The ^1H and ^{13}C NMR spectra of $M(Bz)_2$ have been analyzed and chemical shifts, especially of *para* aromatic C- and H-atoms in THF, indicate an increase in ionic character in the order Mg < Ca < Sr < Ba.[413] Molar conductivity of $Ba(Bz)_2$ in THF over a concentration range of $0.1–10 \times 10^{-3}$ M is approximately constant ($\approx 0.2\ \Omega^{-1}\ cm^2\ mol^{-1}$) and this may be accounted for by a combination of dissociation as a 1:1 electrolyte (equation 177) and association to form 'triplet' anionic species (equation 178).[582]

$$Ba(Bz)_2 \rightleftharpoons BaBz^+ + Bz^- \qquad (177)$$

$$Ba(Bz)_2 + Bz^- \rightleftharpoons Ba(Bz)_3^- \qquad (178)$$

The cumyl derivatives $M(CMe_2Ph)_2$ (M = Sr, Ba) are formed by the reaction of equation (179).[583] The insoluble $M(OMe)_2$ is also produced and there is no evidence for mixed species of the type $M(CMe_2Ph)(OMe)$. Benzylic compounds react by addition with activated C═C bonds and several reports have appeared of their application in polymerizations of styrene and butadiene.[582,583] Reaction of α-methylstyrene in *ca.* 3.5 fold excess with $Ba(Bz)_2$ forms an oligomeric species $Ba(CMePhCH_2(CMePhCH_2)_nBz)_2$ which has also found use as a polymerization initiator.[581] Studies of the active ends in monofunctional living polystyrene initiated by such benzylic barium compounds have been carried out and conductivity measurements of BaS_2 (S = monoanionic polystyryl chain) support the existence of ions BaS^+, BaS_3^- and S^- in THF. S^- is the only effective propagating species and addition of $Ba(BPh_4)_2$ inhibits its formation, so retarding polymerization.[581]

$$2\,PhCMe_2(OMe) \xrightarrow{M} M(CMe_2Ph)_2 + M(OMe)_2 \qquad (179)$$

Organometallic compounds with diaryl- or triaryl-methyl ligands $M(CRAr_2)_2$ (R = H, alkyl, aryl) are relatively stable. They are preparable by direct reaction of metal with organic compounds,[549,585,586] *e.g.* equations (180) and (181), by metallation of Ph_3CH or Ph_2CH_2 with $CaPh_2$[573] and by addition of MR_2 (M = Sr, Ba) to 1,1-diphenylethylene (DPE) giving $M(CPh_2CH_2R)_2$.[588] All of these compounds are active polymerization initiators but the compounds $M(CPh_3)_2$ have been most studied. The calcium derivative has been isolated as a red solid adduct from THF solution, $Ca(CPh_3)_2{\cdot}7THF$, for which IR spectral evidence indicates that most THF is coordinated to calcium but a minor portion remains free in the crystal lattice.[585] $Ba(CPh_3)_2$ in dilute ethereal solutions acts as a 1:1 electrolyte with values of K_{diss} (25 °C; determined by conductance measurements) of $3.6 \times 10^{-7}\ mol\ l^{-1}$ (THF) and $3 \times 10^{-5}\ mol\ l^{-1}$ (DME).[587] The undissociated species probably exists as an ion triple, $Ph_3\bar{C}\ Ba^{2+}\ \bar{C}Ph_3$, and the shift in visible λ_{max} from 455 nm in THF to 475 nm in DME indicates greater solvation in the latter medium. Polymerizations of vinyl monomers with $Ba(CPh_3)_2$ show abnormal features associated with the bulky nature of the CPh_3 groups.[589] Initiation rates are slow for both butadiene and styrene and most growing chains are associated with a barium counter ion combined with an unreacted trityl group, $Ba(CPh_3)$(polymer). With the more bulky monomer, styrene, steric hindrance by the remaining CPh_3 group in the propagation steps leads to low molecular weight polymer — chain transfer is a competing process — and in anionic copolymerization of butadiene with styrene by $Ba(CPh_3)_2$ a polymer richer than normal in butadiene is obtained.[589] Few other reactions of these compounds have been investigated but protonation of $Ca(CPh_3)_2$ by H_2O gives 60% Ph_3CH and carboxylation with CO_2 only 5% Ph_3CCO_2H.[585]

$$2Ar_3CCl + 2M \longrightarrow M(CAr_3)_2 + MCl_2 \qquad (180)$$

$$2Ph_2CH_2 + Ba \xrightarrow[80\ °C]{HMPT} Ba(CHPh_2)_2 + H_2 \qquad (181)$$

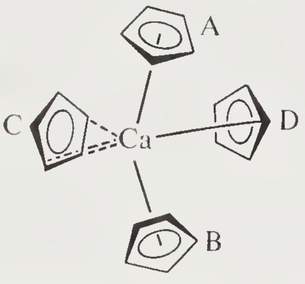
4.2.2.3 Dicyclopentadienyl, diindenyl and difluorenyl derivatives

Dicyclopentadienylcalcium and ring substituted derivatives were the first well characterized organoalkaline earth metal compounds, produced initially by reaction of CaC_2 with cyclopentadiene in liquid NH_3 or other amine solvents (equation 182).[590] Calcium and strontium compounds can also be prepared by direct reaction of metal with cyclopentadiene in THF, liquid NH_3 or DMF (equation 183).[591,592] The barium compound is not so easily obtained by normal solution techniques; it has been formed in very low yields from BaH_2 and cyclopentadiene at 350–400 °C.[591] However, cocondensation of Ca, Sr or Ba vapour with cyclopentadiene at −196 °C and subsequent warming produces all derivatives MCp_2 in high yields.[541] Other methods of formation include reaction of Ca or Sr with $HgCp_2$ (equation 173)[572] or metallation of cyclopentadiene by organocalcium compounds including $Ca(CPh_3)Cl$ and $Ca(C{\equiv}CPh)_2$.[557,578]

$$2C_5H_6 \quad + \quad CaC_2 \quad \longrightarrow \quad CaCp_2 \quad + \quad HC{\equiv}CH \tag{182}$$

$$2C_5H_6 \quad + \quad M \quad \longrightarrow \quad MCp_2 \quad + \quad H_2 \tag{183}$$

MCp_2 compounds are thermally stable colourless solids and sublime at temperatures >250 °C *in vacuo*. The IR spectra have been interpreted in terms of essentially ionic species $C_5H_5^-$ and M^{2+}[408] but there is probably an increase in ionicity down the group as, for example, manifest by shifts in ρ_{C-H} out of plane vibrations in the region 800–700 cm^{-1}. The molecular structure of crystalline $CaCp_2$ determined by X-ray analysis shows that each Ca atom is associated with four C_5H_5 rings, bridging in varying degrees.[593] Three rings are disposed about the Ca atom in a roughly trigonal manner, two being pentahapto (A and B) and one trihapto (C), and the fourth is monohapto with the Ca—C bond (3.100 Å) perpendicular to the plane of the centroids of rings A, B and C (**99**). The bonding is presumably mainly ionic as supported by the long mean Ca—C distances of η^5-C_5H_5 rings (2.80 Å) and steric effects may influence the adoption of this unique structure. However, covalent contributions to the bonding involving Ca 4*s*, 4*p* and 3*d* orbitals have been discussed. Mass spectroscopy of $CaCp_2$ shows high abundances of ions $CaCp_2^+$ and $CaCp^+$, suggesting the presence of a simple sandwich species in the gas phase with a significant Ca—Cp interaction; smaller peaks due to $Ca_2Cp_2^+$ and $Ca_2Cp_3^+$ may arise from ion–molecule interactions between $CaCp_2$ and $CaCp^+$.[593] $CaCp_2$ forms adducts with a number of N- and O-donors and tends to form four coordinate systems $CaCp_2(L)_2$ (L = NH_3, THF, py, $\frac{1}{2}$TMEDA, $\frac{1}{2}$bipy).[591,592,594]

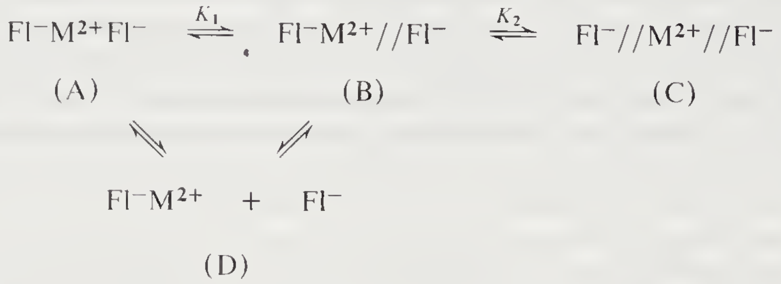


(**99**)

In solution MCp_2 compounds appear to be essentially ionic and ^1H NMR spectra show the expected singlet resonances at temperatures down to −100 °C. Few chemical reactions have been studied but $HgCp_2$, $FeCp_2$ or $TiCl_2Cp_2$ are formed in high yields from $CaCp_2$ and $HgCl_2$, $FeCl_2$ or $TiCl_4$, respectively.[594] Coupling of the C_5H_5 groups of $CaCp_2$ with alkyl halides has been studied[592] and a BF_3-catalyzed electrophilic alkylation to form $Ca(C_5H_4R)_2$ has also been described.[529]

Diindenyl compounds $M(In)_2$ (In = C_9H_7, M = Ca, Sr, Ba) are formed by exchange of metal with $Hg(In)_2$[572] and also by cocondensation of metal vapour with indene at low temperatures.[541] Direct reaction between indene and Ca in liquid NH_3[592] or HMPT, or Ba in HMPT[586] also produces the corresponding $M(In)_2$ compound and syntheses by metallations of indene with $Ca(CPh_3)Cl$ and related organocalcium compounds have also been described.[557,572,573] The structures of $M(In)_2$ are unknown but could be unusual in the solid state (*cf.* $Mg(In)_2$[384]). The ^1H NMR spectra are as expected for a planar In^- anion but coordinating solvents cause shifts in the resonances. In the solid state, complexes $Ca(In)_2L_n$ (n = 1, L = THF, DME; n = 2 L = NH_3, THF) have been characterized[557,573,592] but these solvent molecules can be removed by heating *in vacuo* and free $Ca(In)_2$ itself sublimes. The few reactions that have been reported for $Ca(In)_2$ include initiation of polymerization,[567] alkylation and reactions with some organic carbonyl compounds.[592]

Direct reaction of fluorene with all alkaline earth metals in liquid NH_3[595] or slowly with barium in THF[596] yields $M(Fl)_2$ (Fl = fluorenyl). Other preparative methods for $M(Fl)_2$ are metallation of fluorene with $CaPh_2$[573] or $M[Ph_2CCH_2CH_2CPh_2]$ (M = Sr, Ba).[596,597] The structures of the orange crystalline products have not been determined but in the solid state it is possible that, as in $LiFl(NC_7H_{13})_2$,[598] a simple symmetrical bonding does not occur. In solution, electronic spectroscopic and conductimetric studies have been interpreted in terms of equilibria involving contact ion-triples (A), two types of solvent separated ion-triples (B) and (C) and dissociated species (D) (Scheme 14).[595,596,597] In THF all compounds $M(Fl)_2$ exist as contact ion-triples (A) at ambient temperatures and when M = Ba, contact ion-triples still predominate at −70 °C. When M = Sr, solvent separated ions (B) and (C) are formed at low temperatures (*e.g.* $K_1 = 88$ mol l^{-1}, −50 °C) and a two-step process of solvation occurs, $K_1 > K_2$. $Ca(Fl)_2$ also exists as form (A) in DME at room temperature but solvent separated species occur at low temperatures.[595] Ionization to free Fl^- ions (D) is shown by conductivity studies and fluorescence and excitation spectra with dissociation constants in THF at 20 °C of 5.3×10^{-9} mol l^{-1} for $Ba(Fl)_2$ and 1.73×10^{-7} mol l^{-1} for $Sr(Fl)_2$.[596] HMPT promotes ionization.[595]



Scheme 14

Crown ethers, other polydentate ethers and cryptands form stoichiometric 1 : 1 or 1 : 2 complexes with $M(Fl)_2$ (M = Sr, Ba) in solution.[596,597] Studies of the barium adducts show that 1 : 1 complexes are mixed ion-triples, Fl^-Ba^{2+}(ligand),Fl^- and 1 : 2 complexes and cryptates are fully separated ion triples Fl^-,(ligand)Ba^{2+}(ligand),Fl^-. The rate of exchange between free and complexed crown ether, as $[Ba(Fl)_2(crown)]$ (crown = dimethyldibenzo-18-crown-6), has been shown to be relatively slow by ^1H NMR spectroscopy.

It has been suggested that $Ba(Fl)_2$ is a sandwich-type species in solution but absorption and emission spectra have been analyzed in terms of bands due to exciton exchange and attributed to a structure with two non-parallel, mutually tilted planar fluorenyl units in an $Fl^-Ba^{2+}Fl^-$ ion-triple enabling external coordination of Ba^{2+} by solvent at the exposed side, the angle of tilt being greater in THF than THP.[596]

It may be noted that xanthenyl compounds similar to fluorenyl species have also been reported, $M(C_{13}H_9O)_2$ (M = Sr, Ba).[586]

4.2.3 Electron Transfer–Addition Compounds with Unsaturated Organic Molecules

4.2.3.1 Aromatic compounds

Unlike the well known species formed by alkali metals little work has been reported on addition compounds between alkaline earth metals and arenes. Reactions do occur with polynuclear aromatic compounds but rates tend to be slow and very dependent on the physical state of the metal. In liquid NH_3 the granulated metal may be used[599] but freshly evaporated metal films are recommended[493,494,496,600] and activation by addition of small quantities of halogen-containing promoters[601] has also been employed. The solvent order for decreasing ease of preparation is NH_3 > HMPT > DME > THF. The order of metal reactivity is Ba > Mg ≫ Ca and the irregular position of Mg may be explained by the opposing trends in ionization potentials of the metals and the solvation energies of the resulting metal cations.[494,496]

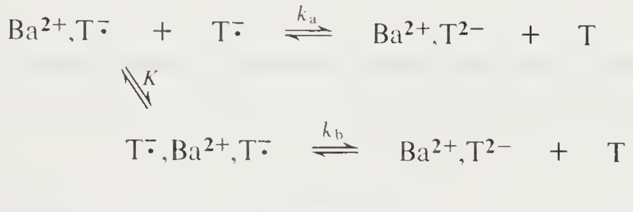
The main reaction follows the well established pathway forming radical anion and dianion (equation 184) with the extent of reaction and the tendency of radical anion to disproportionate

$$2\text{arene} \xrightarrow{M} M^{2+}[\text{arene}]^{-}_{2} \xrightarrow{M} 2M^{2+}[\text{arene}]^{2-} \qquad (184)$$

being dependent on M, arene and solvent. However, other side reactions may take place, including hydrogen transfer from solvent.[496]

In liquid NH_3 and HMPT solvents, diphenyl and *p*-terphenyl react with all alkaline earth metals giving radical anions.[493,494] In HMPT the degree of conversion of *p*-terphenyl is high when M = Ba (87–90%) but low when M = Ca (0.5–2.5%). Other hydrocarbons with greater electron affinities than *p*-terphenyl react in HMPT, including naphthalene and anthracene.

Reactions are less facile in ethereal solvents and the products may have low solubilities.[496] In DME, anthracene, perylene and higher aromatic compounds react with Ba metal[496] and it has also been found that naphthalene forms a radical anion (*ca.* 3%) for which ESR signals have been observed.[602] In THF, naphthalene does not react but in the presence of cryptand[2.2.2] the fully separated ion-triple $[Ba(cryptand)]^{2+},[C_{10}H_8]_2^-$ is formed for which a sandwich-type structure was suggested.[603] Anthracene and higher polynuclear aromatic compounds, including tetracene and perylene, form anions with Ca, Sr and Ba in THF.[496] Tetracene (T) mainly forms the dianion Ba^{2+},T^{2-} for which charge delocalization over the extended aromatic system prevents formation of tight ion-pairs (λ_{max} = 630 nm).[600] The radical anion present as $Ba^{2+},T^- + T^-$ has λ_{max} = 715 nm and the dissociation constant for $Ba^{2+},(T)_2^-$ is 5.7×10^{-6} M (25 °C). Kinetic studies using flash photolysis have shown that the disproportionation of T^- proceeds by two routes (a) or (b) (Scheme 15) with rate constants $k_a \approx 6 \times 10^8\ l\ mol^{-1}\ s^{-1}$ and $k_b \leqslant 10^4\ s^{-1}$.[600]



$$Ba^{2+},T^{\overline{\cdot}} + T^{\overline{\cdot}} \overset{k_a}{\rightleftharpoons} Ba^{2+},T^{2-} + T$$

$$T^{\overline{\cdot}},Ba^{2+},T^{\overline{\cdot}} \overset{k_b}{\rightleftharpoons} Ba^{2+},T^{2-} + T$$

Scheme 15

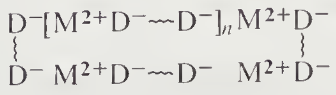
Calcium naphthalenide in liquid NH_3 promotes the coupling of 2-bromoesters but the dicarboxylic acid derivatives formed contain unsaturated C=C bonds and are not succinic esters as formed by magnesium naphthalenide.[499] $Ca(NH_3)_6$ and related anionic adducts can be used as selective reducing agents for aromatic hydrocarbons including benzene derivatives, and organometallic compounds are probably implicated in these reactions.[526,604] Also adducts of all aromatic hydrocarbons with alkaline earth metals have been claimed as polymerization initiators.

Heteroaromatic nitrogen containing compounds (N) including pyridine, substituted pyridines, quinoline, acridine and 1,10-phenanthroline react with calcium in liquid NH_3. The products were not fully characterized but species of the type $Ca(N)_2(NH_3)_x$ and $Ca(N)(NH_3)_x$ (x = 0–2) as well as non-stoichiometric products have been isolated.[599,605] ESR spectra of rigid glasses of $M(N)_2$ species are characteristic of triplet state compounds.[606]

4.2.3.2 Alkenes

Reaction of Ca, Sr or Ba metals in liquid NH_3 or HMPT, or of Sr or Ba in THF or DME, with 1,1-diphenylethylene occurs by electron transfer but the initially formed radical anion dimerizes completely to a diamagnetic 1 : 1 bicarbanionic organometallic (equation 185).[587,607,608,609] An alternative preparation of Ca[D—D](D—D = $Ph_2CCH_2CH_2CPh_2$) is electrolytic reduction of CaI_2 in the presence of $Ph_2C{=}CH_2$ in HMPT.[610] The solution properties of derivatives M[D—D] have been interpreted in terms of aggregated units with a cyclic structure (**100**) and this is supported by changes both in conductivity with concentration and in viscosity changes during reactions.[587,608] An alternative association of chelated entities (**101**) has been proposed by other

$$Ph_2C{=}CH_2 \xrightarrow{M} M^{2+}[\dot{C}H_2\bar{C}Ph_2]_2 \longrightarrow M^{2+}[Ph_2\bar{C}CH_2CH_2\bar{C}Ph_2] \qquad (185)$$



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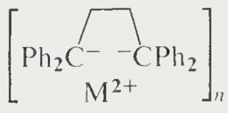
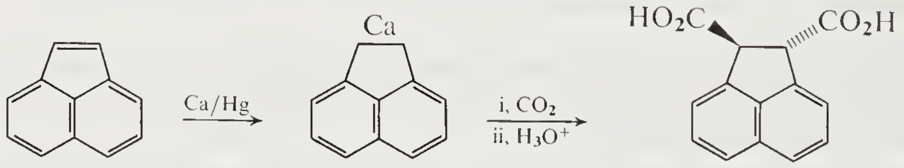


(101)

workers.[609] In THF solution the visible absorption maxima for M[D—D] compounds occur in the region 420–455 nm increasing in the order M = Ca < Sr < Ba and when M = Ba no marked change in λ_{max} is observed over the temperature range −105 to +25 °C so that a contact ion-pair nature is likely for this species.[608,609] When M = Ca or Sr another absorption band (495–500 nm) is observed at temperatures below −70 °C and this is attributed to the presence of some solvent separated ion pairs.[608,609] Two steps are possible in the solvation process (equation 186), and results for Sr[D—D] show $K_1 > K_2$ and addition of HMPT produces solvent separated ions. These bicarbanionic derivatives M[D—D] are effective polymerization initiators of vinyl, diene and epoxide monomers and polymerization by species with M = Sr or Ba have been the subject of several studies.[587,611] In hydrocarbon media butadiene gives up to 70% *cis*-1,4-polymer and the effects of solvent polarity on this stereochemistry have been investigated.

(186)

Alkaline earth metals react with a number of aromatic substituted alkenes including *trans*-stilbene, tetraphenylethylene, 1,4-diphenylbutadiene and acenaphthylene.[496,600,612,613] The product from acenaphthylene and calcium amalgam at −35 °C is dianionic and rapid carboxylation produces acenaphthene-*trans*-1,2-dicarboxylic acid (equation 187), although prolonged reaction leads to some coupled product.[613] Barium in the form of a mirror reacts with tetraphenylethylene in THF or DME by electron transfer but the disproportionation constant for the radical anion (equation 188), studied by flash photolysis, is high (>10^6) and the dianionic species is the product of reaction.[600] Absorption spectra of $Ba[Ph_2C_2Ph_2]$ show two maxima at 345 and 485 nm in THF, or 350 and 485 nm in DME, and on this basis it was proposed that an unsymmetrical structure obtains in solution with Ba^{2+} closely ion-paired with only one $\bar{C}Ph_2$ chromophore with slow exchange between the two sites (equation 189).[600]

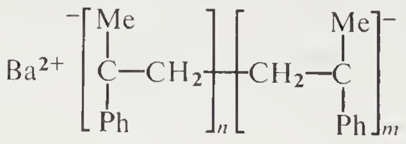


(187)

$$Ba^{2+}[Ph_2C_2Ph_2]^{\overset{.}{-}} + Ph_2C_2Ph_2^{\overset{.}{-}} \rightleftharpoons Ba^{2+}[Ph_2C_2Ph_2]^{2-} + Ph_2C_2Ph_2 \quad (188)$$

$$\underset{\underset{Ba^{2+}}{\vdots}}{Ph_2\bar{C}}-\bar{C}Ph_2 \rightleftharpoons Ph_2\bar{C}-\underset{\underset{Ba^{2+}}{\vdots}}{\bar{C}Ph_2} \quad (189)$$

Reaction of α-methylstyrene with Ba metal occurs readily in THF and the radical anion dimerizes to form (**102**) ($n = m = 1$) but further alkene addition may occur so that α,ω-bicarbanionic oligomers are also obtained ($n \geqslant 1, m \geqslant 1$). However, the conditions of preparation can influence the nature of the product and hydrogen transfer may occur to form monocarbanionic species such as (**103**) and corresponding trimers and tetramers.[614] These oligomeric organometallic compounds are polymerization initiators.



$$Ba^{2+}\,{}^{-}\left[\begin{matrix}Me\\ |\\ C-CH_2\\ |\\ Ph\end{matrix}\right]_n\left[\begin{matrix}Me\\ |\\ CH_2-C\\ |\\ Ph\end{matrix}\right]_m^{-}$$

(**102**)

$[Me_2PhCCH_2CPhMe]^{-}\frac{1}{2}Ba^{2+}$

(**103**)

Styrene reacts with strontium or barium forming α,ω-bicarbanionic living polystyrene associated with the metal cations. Short chain oligomeric species (degree of polymerization, $\overline{DP} < 10$) have been studied by spectroscopy, conductance measurements, kinetics of polymerization and other physical techniques.[615] Absorption maxima, λ_{max}, vary with $\overline{DP} = 2$–10 and ring structures having both anionic ends bound to the same cation have been proposed. These cyclic species appear to undergo the association and dissociation reactions of equations (190) and (191).[615] Deactivation by protonation of α,ω-bicarbanionic oligostyryl metal derivatives occurs on standing in THF but it is interesting that this occurs in a non-random, quasi-simultaneous process in which both ends react so that little mono-functional living polystyrene is formed.[616]

(190)

(191)

Polymerizations of methyl methacrylate, butadiene, isoprene and styrene by direct interaction with alkaline earth metals, and involving addition organometallic intermediates, have been described.[494,496]

Cyclooctatetraene in HMPT forms species $M^{2+}(cot)^{2-}$ (M = Ca, Sr, Ba) and these compounds may be isolated as blue–purple solvated solids. The IR spectra are characteristic of a planar cot^{2-} group.[612,617]

4.2.4 Organobimetallic Derivatives

4.2.4.1 Lithium derivatives

Reactions of alkyl- or aryl-iodocalcium compounds with organolithium derivatives in Et_2O give isolable complex products which are more reactive than the precursors.[526,618] The nature of these products $LiR'\cdot Ca(R)I$ (R, R′ = alkyl, aryl) is not clear. Wittig has reported 'ate' complexes of the type $M'[LiPh_2]$ (M′ = Na, K, Cs)[619] and it is possible that Li is the 'central' atom in the calcium species but they have been formulated as $Li[CaI(R)(R')]$. In solution, equilibria between various species probably exist. Reactions of LiR with $M(OR')_2$ (M = Ca, Sr, Ba) or BaR_2 also produce mixed species of unknown structure which are active as polymerization initiators.[620]

4.2.4.2 Group IIB metal derivatives

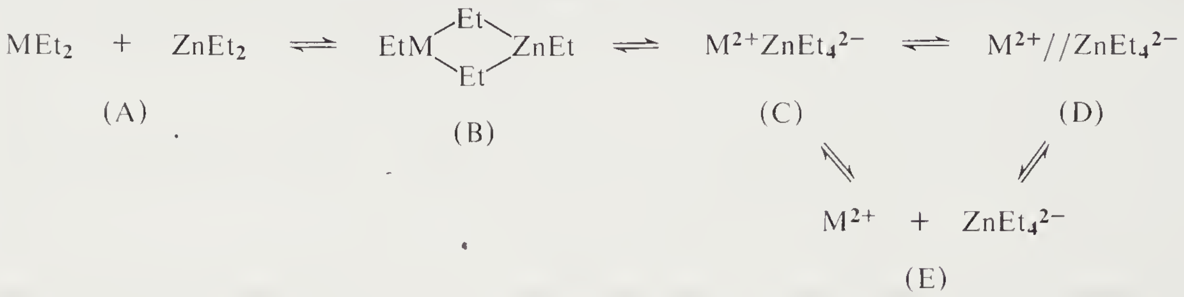
Complexes are readily formed between ZnR_2 and alkali metals, products such as $NaZnEt_3$ being formed. Similarly, reaction of rasped alkaline earth metals, Ca, Sr or Ba, with ZnR_2 (R = Me, Et, Prⁿ) in benzene at 68–105 °C or, when R = Buⁿ, in Et_2O solvent forms complexes $MZnR_4$ (equation 192).[580,621,622,623] The metallation of some hydrocarbons by $MZnR_4$[580,621] or addition to unsaturated C=C bonds as in equation (193) also produces 'ate' complexes[624] but the organometallic products have not been well characterized.

$$2ZnR_2 + M \longrightarrow MZnR_4 + Zn \tag{192}$$

$$MZnR_4 + Ph_2C{=}CH_2 \longrightarrow MZn(RCH_2CPh_2)_nR_{4-n} \tag{193}$$

Complexes $MZnR_4$ are soluble in benzene and ethers, and slightly soluble in saturated hydrocarbons, but decompose slowly in ethereal media. The stability to decomposition is Ca ⩾ Sr ⩾ Ba and, probably for steric reasons, $CaZnR_4$ is more stable when R = Buⁿ than R = Et.[622]

Complexes $MZnEt_4$ and monomeric in benzene (cryoscopy) and, in the absence of association, the solvent dependent equilibria of Scheme 16 are possible.[623] ^1H NMR spectra at ambient temperatures in various solvents show the presence of only one Et resonance (α-CH_2, $\delta = 0.3$ to -0.1 p.p.m.) so that rapid exchange between differing species must be occurring (estimated lifetime, $\tau_e < 0.009$ s). Changes in chemical shifts with solvents indicate that solvation takes place and the appearance of an extra band, absent in benzene, in the UV spectrum of $MZnEt_4$ in THF at 370 nm has been assigned to solvent separated ion-pairs (D) in this ethereal medium. It has been estimated that the concentration of free ions (E) in Et_2O, THF or benzene is low. In cyclopentane solvent, variable temperature ^1H NMR spectra of $CaZnEt_4$ indicate the presence of both free dialkylmetal compounds (A) and a complex species, probably the contact ion-pair (C), in concentration ratio (A) : (C) of 1 : 1.25. Thus, in polar solvents, Et_2O and THF, (C) and (D) are important whereas in non-polar solvents (A) and (C) are present with the electron deficient species (B) as a possible intermediate involved in the exchange reaction.[623]



Scheme 16

Many reactions of $MZnR_4$ species have been attributed to MR_2 compounds and, as noted above, there is evidence that simple dialkylmetal species are present in complex solution equilibria, especially in non-polar media. However, the presence of Zn does influence the reactivity of the system and the reactions must be considered as those of 'ate' complexes and different from binary compounds described in Section 4.2.2.

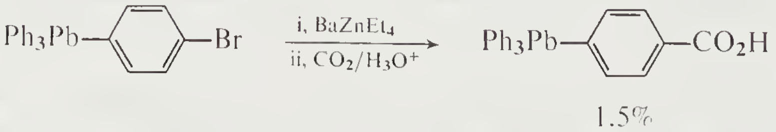
A red solid complex of composition $MZnEt_4{\cdot}4py$ can be obtained from pyridine and this has been suggested to be a mixture of complexes $ZnEt_2(py)_2$ and $MEt_2(py)_2$.[623]

Reactions with unsaturated C═C bonds do occur and as mentioned above 1,1-diphenylethylene undergoes ready reaction according to equation (193).[624] 1,3-Enynes and 1,3,5-dienynes react with $MZnR_4$ to give fair yields of allene (25–50%) after hydrolysis (equation 194) (X = alkyl, RS, R_2N, $CH_2{=}CH$, M = Ba; X = alkyl, M = Sr; X = alkyl, Ph, $RCH{=}CR'$, M = Ca).[625] The application of $MZnR_4$ complexes in anionic polymerization of various monomers has also been described.[626,627,628]

$$X{-}C{\equiv}C{-}CH{=}CH_2 \xrightarrow[\text{ii, } H_2O]{\text{i, } MZnEt_4/Et_2O} XCH{=}C{=}CHCH_2Et \qquad (194)$$

The 'ate' complexes $MZnEt_4$ will metallate the aromatic rings of anisole at the 2-position and dibenzofuran or dibenzothiophene at the 4-positions, but the yields of products are low.[621] The reactivity for metallation is less than for corresponding Ca(R)X compounds and falls in the order M = Ba > Sr > Ca. Phenylacetylene, also, is metallated readily by $MZnEt_4$ to give phenylethynyl derivatives which add to the C≡N bond of benzonitrile.[580]

Metal–halogen exchange between $BaZnEt_4$ and 1-bromonaphthalene gives a very low yield of product, as judged by subsequent carboxylation.[621] Another low yield metal–halogen exchange is illustrated by equation (195) and alkylation of Group IV metal derivatives has also been reported, *e.g.* equation (196).[621]



(195)

$$Ph_3SnCl \xrightarrow{BaZnEt_4} Ph_3SnEt \qquad (196)$$

Reactions of organic compounds containing carbonyl and unsaturated nitrogen bonds with $MZnR_4$ may occur by addition and/or reduction pathways and in some reactions the nature of the products shows that the 'ate' complex rather than MR_2 species is the reactive entity.[629]

It is claimed that $CdPh_2$ reacts in refluxing benzene with Ba metal to form $BaPh_2$, which on carboxylation affords 4.2% benzoic acid,[621] but Wittig has described the 'ate' complex $LiCdPh_3$[509] and it is possible that the corresponding barium derivative may also be a complex in equilibrium with free diphenylmetal compounds (equation 197). Reaction of alkaline earth metals with HgR_2 compounds on the other hand does form simple MR_2 species (Section 4.2.2) and, moreover, no 'ate' complex $LiHgPh_3$ has been identified. However, the derivatives $BaHg(C{\equiv}CR)_4$ (R = H, Ph) have been reported.[630]

$$BaCdPh_4 \rightleftharpoons BaPh_2 + CdPh_2 \qquad (197)$$

4.2.4.3 Group IIIA metal derivatives

Tetraethylborate complexes $M(BEt_4)_2$ (M = Ca, Sr, Ba) can be synthesized by the reactions of equations (198) and (199).[520] The calcium product $Ca(BEt_4)_2$ can be distilled *in vacuo* (75–80 °C, 10^{-3} Torr) but the strontium and barium complexes are less volatile. Thermal decomposition occurs at higher temperatures, as shown by equations (200) and (201).[520]

$$M + HgEt_2 + 2BEt_3 \longrightarrow M(BEt_4)_2 + Hg \qquad (198)$$

$$M/Hg + Mg(BEt_4)_2 \longrightarrow M(BEt_4)_2 + Mg/Hg \qquad (199)$$

$$Ca(BEt_4)_2 \xrightarrow[10\ Torr]{130\ °C} CaH_2 + 2C_2H_4 + 2BEt_3 \qquad (200)$$

$$Ba(BEt_4)_2 \xrightarrow{160\ °C} Ba(BHEt_3)_2 + 2C_2H_4 \qquad (201)$$

A number of aluminium 'ate' complexes of formula $M(AlR_4)_2$ have been characterized. Direct reaction of excess triethylaluminium with alkaline earth metal in the absence of solvent at 85–120 °C using a well agitated vessel gives yields of 78–85% (equation 202).[631] Reactivity falls in the order Ba > Sr > Ca so that higher temperatures are necessary for the lighter metals. A reaction mechanism involving the initial formation of radical anions $[AlEt_3]^{\overline{\cdot}}$ by electron transfer has been proposed.[631] When the reaction is carried out in hydrocarbon solvents lower yields are obtained and ethers are generally unsuitable, forming by-products $AlEt_2(OR)$. An exception is the use of a 1 : 1 mixture of diglyme : $AlEt_3$ when isolable complexes $M(AlEt_4)_2(diglyme)_2$ are obtained in 80–96% yield.[631]

$$3M + 4[AlEt_3]_2 \longrightarrow 3M(AlEt_4)_2 + 2Al \qquad (202)$$

An alternative preparative route is reaction of alkaline earth alkoxide with $[AlEt_3]_2$ (equation 203), in which the by-product $[AlEt_2(OR)]_2$ (R = Et, Pr^n, Bu^n) may be removed by distillation.[520] The intermediate $M[AlEt_3(OR)]_2$ may also be isolated if desired. Other syntheses are outlined in equations (204) and (205).[520] The latter reaction has produced a range of $M[AlR'_3R]_2$ derivatives, and in the presence of solvents adducts of the type $M[AlR'_3R]_2nL$ (L = Et_2O, THF, diglyme, Me_3N, TMEDA, n = 2, 3, 4 or 6) have been obtained.[631] Although CaH_2 does not react with $[AlEt_3]_2$, the reaction of BaH_2 (equation 206) forms a hydrido 'ate' complex.[520]

$$M(OR)_2 \xrightarrow{[AlEt_3]_2} M[AlEt_3(OR)]_2 \xrightarrow{[AlEt_3]_2} M(AlEt_4)_2 + [AlEt_2(OR)]_2 \qquad (203)$$

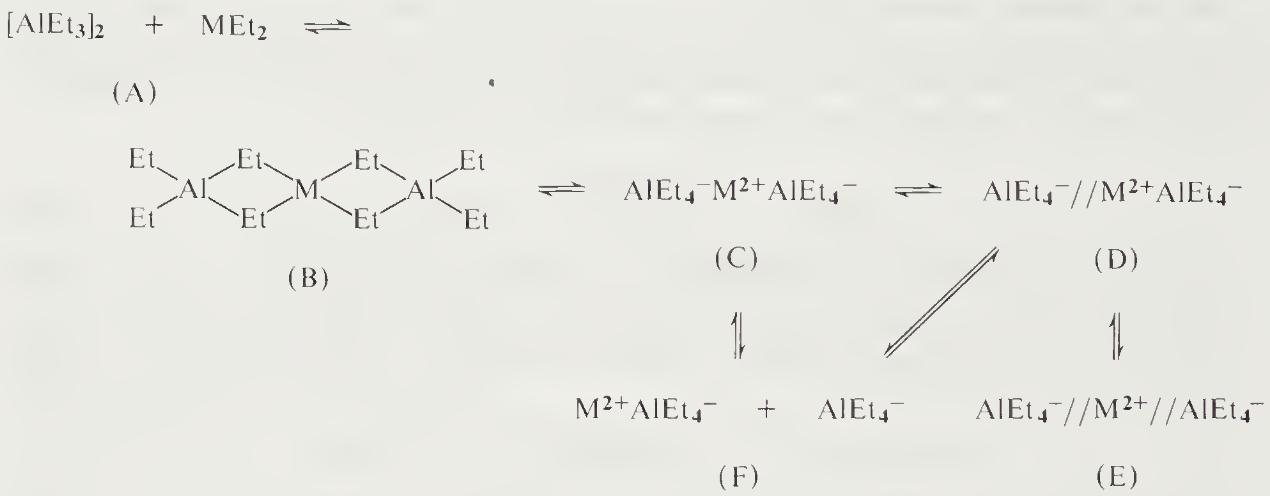
$$MCl_2 + 2NaAlEt_4 \xrightarrow{benzene} M(AlEt_4)_2 + 2NaCl \qquad (204)$$

$$M + HgR_2 + 2AlR'_3 \longrightarrow M(AlR'_3R)_2 + Hg \qquad (205)$$

$$BaH_2 + [AlEt_3]_2 \xrightarrow{120\ °C} Ba[AlHEt_3]_2 \qquad (206)$$

Complexes $M[AlEt_4]_2$ ($M = Ca$ or Sr) can be vacuum distilled whereas when $M = Ba$ decomposition sets in at the b.p. (150–160 °C, 10^{-3} Torr).[520] The thermal decomposition of $Ca[AlEt_4]_2$ follows equation (207) unlike $Mg[AlEt_4]_2$ which forms free $MgEt_2$ and $[AlEt_3]_2$. It is also of interest that with NEt_3 the calcium complex gives $Ca[AlEt_4]\cdot 4NEt_3$[631] whereas $Mg[AlEt_4]_2$ forms adducts of free $AlEt_3$ and $MgEt_2$.[520] In solution electrical conductivities are low and, as for corresponding zinc complexes $MZnR_4$, a constitution involving rapid exchange between species of Scheme 17 is possible. The evidence suggests that in less polar solvents these 'ate' complexes exist mainly as contact ion-triples (C) or as electron deficient species (B).

$$Ca(AlEt_4)_2 \xrightarrow[10\ Torr]{130-160\ °C} CaH_2 + 2C_2H_4 + 2AlEt_3 \tag{207}$$



Scheme 17

Exchange of alkyl groups occurs between $M[AlEt_4]_2$ and $[AlMe_3]_2$. Total displacement of ethyl groups is not observed but complexes of approximate stoichiometry $M[Al(Et)Me_3]_2$ can be formed.[520]

1-Alkynes are metallated to form $M[AlEt_{4-n}(C{\equiv}CR)_n]_2$ in hydrocarbon or a high boiling ethereal solvent.[632] The degree of metallation leads to $n \leqslant 3$. Thus, when $R = Ph$ species with $n = 3$ are isolable and ease of reaction follows the order $M = Ca < Sr < Ba$. When $R = Bu^n$ or n-pentyl, species with $n = 2$ have been isolated for $M = Ca$.[632] Indene is also metallated in hydrocarbon solvents but the final product is a mixed derivative as illustrated by equation (208).[633]

$$Ca(AlEt_4)_2 \xrightarrow{indene} Ca(AlEt_4)\{AlEt_3(In)\} \longrightarrow CaIn(AlEt_4) \tag{208}$$

The complexes $M[AlEt_4]_2$ are cleaved by 2 mol halogen or by aluminium(III) halides to form MX_2 and free $[AlEt_3]_2$.[634]

Reactions of $M[AlR_4]_2$ with organic carbonyl compounds have been reported, and with ketones addition may predominate over reduction.[629] When $M = Ca$ and $R = Ph$ an intermediate complex with benzophenone has been isolated and characterized ($Ca[AlPh_4]_2\cdot Ph_2CO$), but after heating to 90–160 °C addition to the C=O bond occurs although only four of the eight available phenyl groups are involved in this reaction.[635] Six of the alkyl groups of $Ca[AlMe_4]_2$ add to benzophenone. With aldehydes only four of the eight ethyl groups of $M[AlEt_4]_2$ react, mainly by addition, and with benzoyl chloride or acetic anhydride lower yields of the corresponding ketone, accompanied by its reduction and alkylation products, are formed.[635]

$Ba[AlR_4]_2$ complexes are initiators for anionic polymerization of butadiene but are less active than $BaZnR_4$. On the other hand, the polybutadiene formed is more stereospecific, containing up to 99% 1,4-linkages using benzene solvent.[624]

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5.1

Non-cyclic Three and Four Coordinated Boron Compounds

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The first report of the preparation of 'organoboron' compounds appears to be the report[1] in 1846 to the French Academy of Science concerning the preparation of methyl, ethyl and pentyl esters of boric acid from the appropriate alcohol and boron trichloride. Of the many main group elements, boron and its organic compounds probably represent one of the most sturdy bridges between the areas of inorganic and organic chemistry, *i.e.* organometallic chemistry. Recent advances in the field of organoboron chemistry, *e.g.* the hydroboration reaction[2] and its tremendous potential in synthetic chemistry,[3-5] have led to renewed efforts to understand the structure, bonding, synthesis and reactions of organoboranes.[6,7]

Organoboranes in this chapter will be defined as those non-cyclic compounds containing at least one boron–carbon bond. However, one of the very interesting aspects of this class of compounds is that they incorporate a wide range of functionalities, and organoboranes containing, among others, B—N, B—P, B—O, B—S, B—Se and B—Hal bonds will be discussed with respect to physical properties, preparation and reactions.

5.1.1 STRUCTURE, BONDING AND PROPERTIES

5.1.1.1 Physical Constants

A number of relationships exist between organoboron compounds and organic species. For example, tricoordinate organoboranes, $\mathrm{BR_3}$, are isoelectronic with the corresponding carbocations, $\mathrm{^+CR_3}$. Other isoelectronic pairs include $\mathrm{H_3BCO}$ and $\mathrm{CO_2}$, $\mathrm{RB(OH)_2}$ and RC(O)OH, and $\mathrm{(RBNH)_3}$ and symmetrically trisubstituted benzenes ($\mathrm{C_6R_3H_3}$). In many cases, similar structural and chemical properties result. As has been previously pointed out,[8] the similar Pauling electronegativities (boron, 2.0; carbon, 2.5) and the fact that tricoordinate organoboranes are monomeric leads to similar physical constants, particularly boiling points, between boron compounds and the corresponding hydrocarbon. Table 1 lists some physical constants for selected organoboron compounds. Additional physical data may be presented in later sections which deal with specific classes of compounds. A large collection of physical constants of organoboranes which has been compiled from government documents has been published.[9]

Table 1 Physical Constants of Selected Organoboranes[1]

Organoborane	*M.p.* (°C)	*B.p.* (°C)[2]	*Density* (g cm^{-3}) (°C)	*Vapor pressure* (Torr)
$\mathrm{MeBBr_2}$	−110.6	60	—	log $P = 7.692 - 1602/T$ (230–330 K)
$\mathrm{MeBCl_2}$	−127.1	11.1	—	log $P = 7.368 - 1275/T$ (180–282 K)
$\mathrm{MeBF_2}$	−130.4	−63	—	log $P = 5.9680 + 1.75 \log T - 0.00684 T$ log $P = 7.39973 - 843.724\ (T - 23.93)$(140–210 K)
$\mathrm{MeB(OH)_2}$	95(d)	110(d)	—	log $P = 11.6619 - 3347.5/T$
$\mathrm{MeB(OMe)_2}$	—	53.5	—	—
$\mathrm{Me_2BBr}$	−128.9	31.6	—	log $P = 7.363 - 1365/T$ (235–295 K)
$\mathrm{Me_2BCl}$	—	4.9	—	log $P = 7.414 - 1260/T$ (225–273 K)
$\mathrm{Me_2BF}$	−147.3	−42	—	log $P = 7.7370 - 1121.4/T$ log $P = 7.7369 - 1222.2/T$ (175–227 K)
$\mathrm{Me_2BI}$	−107.5	68.8	—	log $P = 7.090 - 1440/T$ (273–300 K)
$\mathrm{Me_2BOH}$	—	0 (36 Torr)	—	36 (0 °C)
$\mathrm{Me_2BOMe}$	—	21	—	log $P = 7.942 - 1492/T$ (195–283 K)
$\mathrm{BMe_3}$	−160	−20.5	0.625 (−100)	log $P = 7.906 - 1250/T$ log $P = 757.649416/T + 11.835236 \log T - 0.01481919T - 18.81106$ (160–250 K)
$\mathrm{Me_2BEt^3}$	<−160	25.5	—	log $P = 7.170 - 1281/T$
$\mathrm{MeBEt_2{}^3}$	−135.5	61	—	log $P = 7.818 - 1647/T$
$\mathrm{BEt_3}$	−92.9	95.4	0.6774	log $P = 7.4856 - 1704.1/T$ (273–350 K)
$\mathrm{EtBCl_2}$	—	50	—	100 (25 °C) 115 (0 °C)
$\mathrm{Et_2BBr}$	−81.0	101	—	log $P = 8.026 - 1920/T$ (273–350 K)

Table 1 (*continued*)

Organoborane	*M.p.* (°C)	*B.p.* (°C)^2	*Density* (g cm^{-3}) (°C)	*Vapor pressure* (Torr)
Et_2BCl	−84.6	78.5	0.85091 (26.5)	$\log P = 7.817 - 1736/T$ (273–340 K)
Et_2BOH	−50	80(d)	0.7921	75 (35–37 °C)
Pr^nBF_2	—	36	—	—
$Pr^nB(OH)_2$	106	—	—	—
BPr^n_3	−65.6	156	0.7204 (24.7) 0.7634 (20)	$\log P = (2085/T) + 7.662$
Pr^iB_3	−52.5	147.4	—	$\log P = 7.862 - 2091/T$
Bu^iBH_2	—	47 (2.5 Torr)	0.7383 (35)	2.5 (47 °C)
Bu^nBH_2	—	—	0.7853 (33)	6 (83–93 °C)
Bu^sBH_2	—	68 (2.5 Torr)	0.7561 (36)	2.5 (68 °C)
$BuBBr_2$	—	150	—	20 (49 °C)
$BuBCl_2$	—	107.9	—	20–25 (25 °C)
$BuBF_2$	—	35	0.851 (25)	—
Bu_2BCl	—	173	—	1 (25 °C)
BBu^i_3	—	188	0.7380 (25) 0.7687 (20)	2.6 (51–52 °C)
BBu^n_3	—	208	0.7583 (33)	14 (98 °C)
BBu^s_3	—	—	0.7687 (20)	2.6 (51–52 °C)
BBu^t_3	—	181.5	—	3.5 (50 °C)
$B(i\text{-}C_5H_{11})_3$	—	119	0.7452 (33)	4.6 (97–99 °C)
			0.76 (23.4)	1.5 (83 °C)
$B(n\text{-}C_5H_{11})_3$	−26.5	—	0.7721 (20)	1.5 (98–99 °C)
	−26.5	—	0.7676 (25)	4.1 (109 °C)
$B(n\text{-}C_6H_{13})_3$	99.1	133 (1.5 Torr)	0.7761 (33.5) 0.7994 (20)	—
$B(CH{=}CH_2)_3$[4]	—	85.7	—	$\log P = 8.2833 - 1810/T - 0.001T$
$MeB(CH{=}CH_2)_2$[4]	—	51.7	—	$\log P = 8.4126 - 1660/T - 0.0013T$
$Me_2B(CH{=}CH_2)$[4]	—	17.1	—	$\log P = 11.9166 - 1890/T - 0.0087T$
$(CH_2{=}CH)_2BBr$[5]	−98	—	—	26 (0 °C)
$(CH_2{=}CH)_2BCl$[4,6]	−109.6	76.4	—	$\log P = 11.4619 - 2230/T - 0.0063T$
$(CH_2{=}CH)_2BF$[6]	−164 to −157	23.8	—	$\log P = 7.416 - 1347/T$
$(CH_2{=}CH)BBr_2$	−95	—	—	26 (0 °C)
$(CH_2{=}CH)BCl_2$[4,6]	−111.1	46.0	—	$\log P = 7.6053 - 1508/T$
$(CH_2{=}CH)BF_2$[4,6]	−133.4	−39.1	—	$\log P = 10.4642 - 1430/T - 0.0063T$
$B(CF{=}CF_2)_3$[7]	−107	104.9	—	$\log P = 8.559 - 2147/T$
$(CF_2{=}CF)_2BCl$[7]	−57.5	100.5	—	$\log P = 7.861 - 1861/T$
$(CF_2{=}CF)BCl_2$[7]	−108	48.0	—	$\log P = 8.008 - 1645/T$
$(CF_2{=}CF)BF_2$	−96	−14.0	—	$\log P = 8.247 - 1389/T$
$B(CH_2CH{=}CH_2)_3$[8]	—	46 (10 Torr)	0.7689 (20)	—
$B(CH_2CH{=}CHCH_3)_3$[8]	—	72 (2 Torr)	0.7857 (20)	—
$B(CH_2CMe{=}CH_2)_3$[8]	—	40 (2 Torr)	—	—
$B(CH_2CH{=}CMe_2)_3$[8]	—	70 (1 Torr)	0.8065 (20)	—
$EtB(CH_2CH{=}CMe_2)_2$[8]	—	40 (1 Torr)	0.7824 (20)	—
$Et_2B(CH_2\text{-}CH{=}CMe_2)$[8]	—	40 (7 Torr)	0.7451 (2)	—
$PhBCl_2$	0	175	—	—
$PhBF_2$	—	70	—	—
Ph_2BCl	—	271	—	—
BPh_3	142	195	—	15 (230 °C)
	136	245	—	2 (175–180 °C)
$B(CH_2Ph)_3$	47	229 (15 Torr)	—	13 (230 °C)
$B(C_6H_4Me)_3$	175	—	—	12 (233 °C)

1. Unless otherwise designated, all values are from R. L. Hughes, I. C. Smith and E. W. Lawless, 'Production of the Boranes and Related Research', ed. R. T. Holzmann, Academic Press, New York, 1967.
2. Unless otherwise designated, boiling point values are quoted at 760 Torr.

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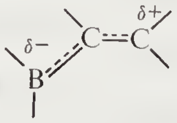
5.1.1.2 Electronic Structure and Bonding

The most important type of bonding between boron and carbon in organoboranes is, of course, B—C σ-bonding involving primarily a 'single' bond. The three atoms attached to boron in tricoordinate organoboron compounds invariably form a trigonal plane around an sp^2 hybridized boron atom with angles close to 120°. Tetracoordinate organoboron compounds are almost always tetrahedral or nearly so and the boron atomic orbitals are considered to be sp^3 hybridized. As expected, boron–carbon bond distances vary depending upon the hybridization of the boron atom and the hybridization of the carbon atom attached to the boron. Thus bond distances decrease in the order alkyl–B > aryl–B > alkenyl–B and tetravalent B > trivalent B. Additionally, when other atoms such as nitrogen, oxygen and halogen which contain one or more unshared pairs of electrons are also bonded to boron in an organoborane, the boron–carbon bond length generally increases.

There have been some data which support the idea of hyperconjugation between the empty p-orbital in a trialkylborane and a neighboring C—H bond, *i.e.* $H\overset{+}{C}H_2{=}\overset{-}{B}R_2$. For example, the B—B distance in tetramethyldiborane, $B_2H_2(CH_3)_4$, is 0.065 Å longer than the corresponding distance in B_2H_6, leading to speculation that a CH_3—B π hyperconjugative interaction reduces the strength of the BHB bridge bond.[10] Also, $B(CH_3)_3$ does not dimerize although BH_3 and $Al(CH_3)_3$ form stable dimers.[11] One explanation for this is that the empty p-orbital on boron in $B(CH_3)_3$ is at least partially satisfied by intramolecular hyperconjugation. Additionally, the C—H bond length in CH_3BF_2 (1.095 Å)[12] is longer than that observed in the isoelectronic CH_3NO_2 (1.089 Å) molecule.[13] Although hyperconjugation could be at least partially responsible, the B—C bond length (1.564 Å) shows no evidence of double bond character. Finally, it should be mentioned that NMR chemical shift data for CH_3BF_2 have been interpreted[14] as implying that π-donation to boron occurs primarily from the methyl group. However, boron quadrupole coupling constants for HBF_2 and CH_3BF_2 are identical within experimental error, which would appear to indicate similar bonding in the two molecules and negate the idea of hyperconjugation in CH_3BF_2.[12]

Another very interesting aspect of bonding in organoboranes concerns the possibility of partial double bond character in boron–carbon bonds in systems where a tricoordinate boron atom is bonded to an electron rich organic group, *e.g.* vinylboranes, phenylboranes and other boron substituted aromatic heterocycles. Many physical techniques have been used to study potential mesomeric interactions, which may involve contributions from structure (A) which may play a substantial role in the ground state properties of these molecules. Although the subject is still somewhat controversial and conflicting data can be found, there seems little doubt from NMR studies, particularly ^{13}C NMR data,[15–17] that some mesomeric interaction is involved. Thus the electronic structures of organoboranes containing one or more unsaturated organic moieties bonded to tricoordinate boron must involve at least some partial B—C double bond character. Various physical studies which have addressed this problem are described in later subsections of 5.1.1.



(A)

5.1.1.3 Thermodynamic Properties

Obtaining reliable thermodynamic data for organoboranes has not been an easy task experimentally.[18,19] The use of bomb calorimetry to determine accurate heats of formation is difficult if the compound does not burn completely, resulting in a complex mixture of products. The experimentally determined numbers then can be meaningful only if the products of combustion can be accurately identified and analyzed. This can produce severe problems, especially when solid products are deposited on different parts of the calorimeter in varying compositions. Liquid trimethylborane, for example, burns in a static bomb calorimeter to form mainly boric oxide (which becomes hydrated to boric acid), but other products are formed which include boron carbide, B_4C, and possibly elemental boron and 'soot'.[20,21] Thermodynamic data for selected organoboranes are presented in Table 2.

Table 2 Heats of Formation and Atomization of Selected Organoboranes[1]

Organoborane	*State*	ΔH_f° (kJ mol^{-1}, 25 °C)	ΔH_a° (kJ mol^{-1}, 25 °C)
BMe_3	l	-142.7 ± 23	
	g	-122.6 ± 23	4781.7
$MeBF_2$	g	-832.6 ± 12.6	2911.6
BEt_3	l	-189.5 ± 10.5	
	g	-152.7 ± 10.5	8264.8
$EtBF_2$	g	-874.4 ± 33.5	4104.4
Pr^iBF_2	g	-887.0 ± 33.5	5267.9
BBu^n_3	l	-345.2 ± 10.5	
	g	-283.2 ± 10.9	15301.2
Bu^n_2BCl	l	-412.9 ± 12.6	
	g	-362.7 ± 12.6	10679.7
Bu^n_2BBr	l	-350.6 ± 10.9	
	g	-298.3 ± 11.3	10606.1
Bu^n_2BI	l	-277.4 ± 10.5	
	g	-223.0 ± 10.9	10525.8
Bu^n_2BOH	l	-609.2 ± 12.6	
	g	-546.4 ± 16.7	11209.8
BBu^i_3	l	-337.6 ± 5.0	
	g	-279.9 ± 5.4	15297.9
BBu^s_3	l	-305.4 ± 25.1	
	g	-245.6 ± 25.1	15263.6
$B(n\text{-}C_6H_{13})_3$	l	-485.3 ± 9.6	
	g	-396.6 ± 10.5	22320.5
$B(n\text{-}C_7H_{15})_3$	l	-559.8 ± 7.5	
	g	-457.7 ± 8.4	25834.5
$B(n\text{-}C_8H_{17})_3$	l	-636.4 ± 7.5	
	g	-520.9 ± 8.4	29350.7
$B(s\text{-}C_8H_{17})_3$	l	-624.6 ± 14.6	
	g	-509.2 ± 16.7	29339.0
$CH_2{=}CHBF_2$	g	-715.4 ± 33.5	3509.4

1. H. A. Skinner, *Adv. Organomet. Chem.*, 1964, **2,** 49.

Some of the most accurate measurements have been made on heats of hydroboration of alkenes, which have then provided reliable heats of formation of trialkylboranes.[22–24] However, even in these cases it was necessary to correct for the fact that boron addition does not occur exclusively at the least hindered carbon atom.[22]

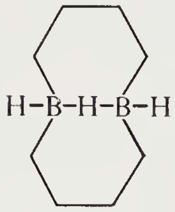
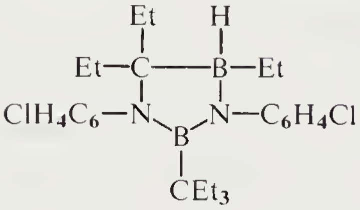
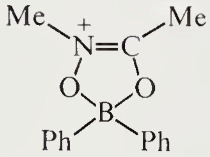
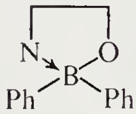
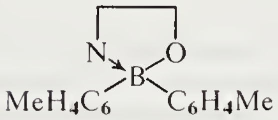
Boron–carbon bond dissociation energies can be obtained from the data in Table 2 for BR_3 molecules by using the equation $\overline{D}_{B-C} = \Delta H^\circ/3$, where $\Delta H^\circ = \Delta H_f^\circ(B_{(g)}) + 3\Delta H_f^\circ(R_{(g)}) - \Delta H_f^\circ(BR_{3(g)})$. Values which are obtained are: BMe_3, 363.2 ± 11.3; BEt_3, 341.8 ± 11.3; BBu^n_3, 343.5 ± 11.3 kJ mol^{-1}. From these values it can be seen that boron–carbon bonds are relatively strong. It should be pointed out that these values are all lower than those which are obtained for the boron–carbon bond dissociation energy in the organoboron difluorides listed in Table 2. These values are: $MeBF_2$, 397.5–418.4; $EtBF_2$, 464.4; $C_2H_3BF_2$, 422.6; Pr^iBF_2, 401.6 kJ mol^{-1}. However, the ΔH_f° values for the difluorides were obtained[25] from mass spectral appearance potential studies and several assumptions were necessary in obtaining the derived values.

The prediction of heats of formation of a number of tri- and tetra-atomic boron molecules including a number of organoboranes has been reported[26] *via* a bond energy decomposition scheme which includes second-order additive terms assigned to each pair of substituents of the central boron atom. Comparison with experimental data shows good agreement.

5.1.1.4 X-Ray Diffraction Studies

Of greatest interest perhaps in X-ray diffraction studies of organoboranes is the boron–carbon bond length. Table 3 lists several organoboranes and the B—C distance which has been determined by X-ray techniques. Available structural data as determined by X-ray and other techniques (*e.g.*

Table 3 Boron–Carbon Bond Lengths Determined by X-Ray Diffraction

Organoborane	*B—C* (Å)	*Ref.*
$Me_3B_3N_3H_3$	1.52–1.53	1
π-$(MeOBC_5H_5)_2Co$	1.526, 1.522	2
p-$BrC_6H_4B(OH)_2$	1.54	3
2,3-$Me_2B_5H_7$	1.55	4
$PhB(OH)_2$	1.565	5
$[C_6H_2Me_3]_3B$	1.573, 1.580	6
Ph_3B	1.577	7
$Cl_2BCH_2CH_2BCl_2$	1.58 ± 0.05	8
$(NMe_2)_3B_3C_3H_6$	1.58	9
$(mesityl)_2BN{=}CPh_2$	1.58	10
1-$EtB_{10}H_{13}$	1.59 ± 0.01	11
π-$(MeBC_5H_5)_2Co$	1.594 (B—Me) 1.505, 1.522 (ring)	12
	1.596–1.610	13
	1.600 ± 0.010 (B—CEt_2) 1.576 ± 0.011 (B—CEt_3)	14
π-$(Et_6B_3N_3)Cr(CO)_3$	1.60 ± 0.03	15
	1.609	16
	1.613, 1.620	17
	1.616, 1.623	17
$Et_2B(pz)_2^-$	1.620	18
$CF_3BF_3^-$	1.625	19
Me_2BNMe_2	1.65 ± 0.02	20
$Rh\{P(OMe)_3\}_2\{\pi$-Ph-$BPh_3\}$	1.66	21
BPh_4^-	1.64–1.69	22

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17. S. J. Rettig and J. Trotter, *Can. J. Chem.*, 1976, **54,** 3130.
18. Average value in diethylbis(1-pyrazolyl)borate taken from the following publications: F. A. Cotton, B. A.

Frenz and A. G. Stanislowski, *Inorg. Chim. Acta*, 1973, **7**, 503; F. A. Cotton, T. LaCour and A. G. Stanislowski, *J. Am. Chem. Soc.*, 1974, **96**, 754; B. W. Davies and N. C. Payne, *J. Organomet Chem.*, 1975, **102**, 245.

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microwave and electron diffraction) suggest that B—C distances in most three-coordinate boron compounds are $\leqslant 1.60$ Å; in four-coordinate compounds the corresponding distance is in the range 1.62–1.65 Å. The bond distances in general can be correlated to the hybridization of the carbon atom. That is, B—C distances increase in the order $sp < sp^2 < sp^3$.

5.1.1.5 Vibrational Spectra

Vibrational spectra of organoboranes have been the subject of many studies. These studies in general have focused either on providing diagnostic group frequencies for a closely related series of compounds (Table 4) or on a detailed investigation of the entire spectrum of a molecule (Table 5). The focus of studies of the latter type has in many cases been an elucidation of the molecular and/or electronic structure of the molecule, with particular emphasis on the nature of the B—C bonding in molecules containing unsaturated organic substituents bonded to a trigonal boron atom (see Section 5.1.1.2). Torsional information (when obtained) has been useful in this context, as have boron–carbon stretching frequencies and force constants. Isotopic labeling has been of some value, as well as the fact that in many cases one is able to observe bands from both ^{10}B and ^{11}B modes since the natural abundance is relatively high for both isotopes (^{10}B, 20%; ^{11}B, 80%). Table 5 lists pertinent vibrational data for many organoboranes which have been studied. In addition much of the early information has been reviewed.[27–30] As expected, assignments for various modes are quite different in some cases and care must be exercised in judging the validity of detailed assignments. It is almost impossible to generalize concerning B—C stretching frequencies. However, in trigonal boron compounds containing two or three B—C bonds the asymmetric stretch generally occurs at ~ 1150 cm^{-1} and the symmetric stretch at ~ 650 cm^{-1}. In trigonal boron compounds containing a single B—C bond the B—C stretching frequency varies widely and can be found from ~ 760–~ 1230. The position of the ν(C=C) mode (1629–1910 cm^{-1}) has been used to postulate a π-interaction between the boron atom and vinyl groups in $(C_2H_3)_{3-n}BX_n$ (n = 1–3; X = F, Cl)[31] and (CH$_2$=CR)BX$_2$ (R = H, OBu; X = OH, Me).[32] Most B—C force constants appear to range from 3.6–4.1 N m^{-1}, although a value of 5.59 N m^{-1} has been reported[33] for $C_2H_3BF_2$ which is a probable reflection of B—C π-bonding.

With regard to the question of B—C π-bonding, several vibrational studies have appeared. Vinylboranes, cyclopropylboranes and phenylboranes have all received attention. Trivinylborane was studied by both IR and Raman spectroscopy in all phases and was found to exist as two conformers in the fluid state, a planar C_{3h} form and a nonplanar form (probably C_3).[34] Tris(perfluorovinyl)borane also exists as two conformers in the fluid states but neither is a planar C_{3h} form.[35] However, the monovinyl compounds $(C_2H_3)BF_2$,[33,36] $C_2F_3BF_2$[37] and $C_2F_3BCl_2$[37] all appear to be planar molecules and the barrier to rotation about the B—C bond in $C_2H_3BF_2$ is 17.43 kJ mol^{-1}. This is essentially identical to the value of 17.6 kJ mol^{-1} determined for $(C_2H_3)B(CH_3)_2$.[38]

A value of 188 kJ mol^{-1} reported for the barrier to internal rotation about the B—C bond in PhBCl$_2$ is incorrect.[39] The correct value[40] is 13.6 kJ mol^{-1}, which is very similar to the value of 13.3 kJ mol^{-1} reported[41] for PhBF$_2$. Both correct values were determined by microwave spectroscopy.

IR[39,42–46] and Raman[42,47] techniques have been used for complete investigations of the phenylhaloboranes Ph$_n$BX$_{3-n}$ (n = 1, 2; X = F, Cl, Br, I), all of which are monomeric. The spectra for all halides except the fluorides can be assigned on the basis of C_2 symmetry in which the phenyl ring(s) is (are) out of the skeletal plane of the molecule.[44] Interestingly, the phenylboron fluorides exhibit spectra which are substantially different from the other phenylboron halides. There are larger than expected differences in ν(B—F) and the other ν(B—X) frequencies and the spectra of the fluorides are simpler than the spectra of the other halides. It is possible that delocalization

Table 4 Series of Compounds Examined by Vibrational Spectroscopy

General formula[1]	*Ref.*
BR_3	2–9
R_2BBr	10
R_2BCl	2, 11–13
R_2BF	14
$RBCl_2$	2, 14–18
R_2BNCO	19–21
R_2BNCS	20, 21
$RB(NCO)_2$	20, 21
$RB(NCS)_2$	20, 21
R_2BNH_2	11, 22
R_2BNHR'	5, 11, 22–25
$R_2BNR'_2$	5, 11, 22–25
$RB(NHR')_2$	26, 27
$RB(NR'_2)_2$	26, 27
$(RBNR')_3$	28–30
R_2BOR'	16, 31, 32
R_2BOAc	33, 34
R_2BOH	31, 35, 36
$(R_2B)_2O$	31
$RB(OR')_2$	16, 26, 27, 32, 37
$RB(OAc)_2$	34
$RB(OH)_2$	32, 38–40
$(RBO)_3$	28, 30, 32, 40, 41
$[R(OAc)B]_2O$	34
$R(R'O)BCl$	16, 37
$B_2H_{6-n}R_n$	42, 43

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Table 5 Boron–Carbon Stretching Frequencies and Force Constants for Selected Organoboranes

Organoborane	$\nu(B—C)$ (cm^{-1})[1]	K (N m^{-1})	*Ref.*
BMe_3	1116–1189; 675–680	3.64	2–9
	1298; 620		10
	1259–1309; 675		11
Me_2BBr	1130; 1052		12, 13
Me_2BCl	1120; 1080	3.64	2, 13
Me_2BF	1152; 710		13, 14
Me_2BNCO	1140; 630		15
Me_2BNH_2	1193; 705	3.73	16–18
Me_2BNHMe	1176; 682		17, 18
Me_2BNMe_2	1163, 1169; 645		16–18
Me_2BOMe	1135; —		19
$Me_2BOCOMe$	1220; 730		20
Me_2BOH	1204; 718		21, 22
$Me_2BC_2H_3$	1119; 680 (B—Me)		23
	663 (B—vib)		
$MeBBr_2$	1060	3.60	12, 13
$MeBCl_2$	1078	3.10	2, 13
$MeBF_2$	779		13, 14, 24
$MeB(OMe)_2$	700		19
$MeB(OH)_2$	815		19
$MeB(C_2H_3)_2$	845 (B—Me)		25
	1120; 666 (B—vib)		
Me_2BEt	1118; 656 (B—Me)		26
	992 (B—Et)		
$MeBEt_2$	994 (B—Me)		27
	1108; 631		
BEt_3	1116–1150; 620–675		7, 10, 28
Et_2BBr	1075; 1010		13
Et_2BCl	1080; 1010		13
Et_2BF	1100; 680		13
$EtBBr_2$	1050		13
$EtBCl_2$	1065		13
$EtBF_2$	746		13, 29
$B(C_2H_3)_2$	1153; 651, 663		30, 31
$C_2H_3BBr_2$	994	4.23	32
$C_2H_3BF_2$	765	5.59	33, 34
$B(C_2F_3)_3$	1135; 666		35
$C_2F_3BCl_2$	1023		36
$C_2F_3BF_2$	1040		36
(cyclopropyl)BF_2	731		37
(cyclopropyl)BCl_2	793		38
$PhBBr_2$	1225		13, 39
$PhBCl_2$	1230		13, 39
$PhBF_2$	728		13, 39
$(Me_2B)_2O$	1128; 815		40
$[(C_2H_3)_2B]_2O$	1166, 1138; 755, 735		41
$(MeBO)_3$	1155		19, 24
$(EtBO)_3$	1265		43
$(PhBO)_3$	1087		43
H_3BCO	691–692		44–46
H_3BCN^-	875–890		47, 48
$C_2H_3BF_3^-$	1107, 1132		49
$CF_3BF_3^-$	1343	3.63	50
Alkyldiboranes	1100–1150; 516–844		51–54
$B(CH_2CH{=}CH_2)$	1342; 942		55

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of the π-electron density of the phenyl ring(s) is more pronounced in the case of the fluorides, resulting in structures having C_{2v} symmetry in which the phenyl ring is in the skeletal plane of the molecule.[44,45] Spectra of mixed halide phenylboron compounds have also been reported.[43]

5.1.1.6 Rotational Spectra

Microwave spectroscopy has been of great benefit in studying gas phase structures of volatile organoboranes which possess dipole moments. In many cases the natural abundance isotopic ratio of ^{10}B and ^{11}B, as well as isotopic labeling, has resulted in very accurate determination of bond lengths and bond angles. Microwave investigations have also resulted in accurate dipole moment determinations as well as quadrupole coupling constants. In favorable cases, boron–carbon torsional barrier heights have been determined.

Difluoroorganoboranes have been extensively investigated by microwave spectroscopy.[17,33,36,48–53] A trend which can be correlated with the hybridization of the carbon atom is observed in the boron–carbon bond lengths of a series of RBF_2 compounds whose structures have been determined by microwave spectroscopy: $(C_2H)BF_2$ (1.513),[48,49] $(C_2H_3)BF_2$ (1.533),[33,36] $PhBF_2$ (1.551),[41] $EtBF_2$ (1.572),[50] $(c\text{-}C_3H_5)BF_2$ (1.589)[17] and $MeBF_2$ (1.60 Å).[12,51–53] In this series only cyclopropyldifluoroborane[17] seems to be out of place since the peculiarities of the electronic structure of cyclopropanes have been extensively treated theoretically[54,55] and in all cases the hybridization of the ring carbons is more similar to that in alkenes than in saturated systems. However, the uncertainty involved in the determination of the B—C bond distance in $c\text{-}C_3H_5BF_2$ would allow it to take its expected place in the series.

Because of the change in hybridization of carbon in the series it is difficult to draw concrete conclusions regarding B—C π-bonding from these bond distances. However, barriers to rotation and especially preferred conformations demonstrate that indeed some mesomeric interaction between the electron-rich organic moiety and the trigonal boron atom must be occurring. Thus, vinyldifluoroborane[33,36] and phenyldifluoroborane[41] are planar molecules while cyclopropyldifluoroborane[17] adopts the 'bisected' conformation, all of which allow for maximum mesomeric interaction. Table 6 lists pertinent data which have been determined by microwave spectroscopy for organoboranes.

Table 6 Organoboranes Studied by Microwave Spectroscopy

Organoborane	*B—C* (Å)	*Dipole moment* (D)	*B—C barrier to internal rotation* (kJ mol^{-1})	*Ref.*
C_2HBF_2	1.513	1.87	—	1, 2
$C_2H_3BF_2$	1.532	1.74	17.4	3, 4
H_3BCO	1.534	1.698	—	5–8
$PhBF_2$	1.551	—	13.3	9
$PhBCl_2$	1.556	—	13.6	10
$MeBF_2$	1.564	1.67	0.05	11–14
H_3BCNMe	1.566	6.73	<0.02	15
$EtBF_2$	1.572	1.69	4.9	16
$c\text{-}C_3H_5BF_2$	1.589	2.18	17.7	17
Me_3BNMe_3	1.698	—	—	18–21

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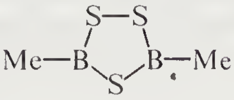
5.1.1.7 Electron Diffraction Spectra

Electron diffraction studies have been just as valuable as microwave spectroscopy in providing gas phase structural data of organoboranes. There has been some duplication of molecules studied by microwave and electron diffraction techniques but the experimental data which have been obtained are very similar. Again B—C bond lengths are found to be 1.60 Å or less for tricoordinate boron compounds with variations depending primarily on the hybridization of the carbon atom bound to boron. However, as more structural data become available it may be that other effects besides hybridization, *e.g.* electron delocalization, steric effects and electronegativity/bond ionicity,[56] will assume increasing importance. Table 7 lists organoboranes which have been studied by electron diffraction.

Table 7 Organoboranes Studied by Electron Diffraction

Organoborane	*B—C* (Å)	*Ref.*
$PhBCl_2$	1.52	1
Me_2BF	1.55	2
$MeB(SMe)_2$	1.567	3
	1.569	4
$Me_3B_3O_3$	1.57	5
Me_2BSMe	1.570	6
Me_2BOBMe_2	1.573	7
$Me_2BSSBMe_2$	1.573	8
BMe_3	1.578	9
cis-$B_2H_4Me_2$	1.579	10
trans-$B_2H_4Me_2$	1.581	10
$B_2H_2Me_4$	1.590	11
$MeBF_2$	1.60	2

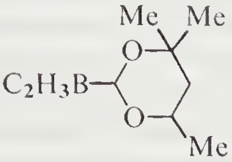
1. K. P. Coffin and S. H. Bauer, *J. Phys. Chem.*, 1955, **59**, 193.
2. S. H. Bauer and J. M. Hastings, *J. Am. Chem. Soc.*, 1942, **64**, 2686.
3. S. Lindoy, H. M. Seip and R. Seip, *Acta Chem. Scand., Ser. A*, 1976, **30**, 54.
4. H. M. Seip, R. Seip and W. Siebert, *Acta Chem. Scand.*, 1973, **27**, 15.
5. S. H. Bauer and J. Y. Beach, *J. Am. Chem. Soc.*, 1941, **63**, 1394.
6. K. Brendhaugen, E. W. Nilssen and H. M. Seip, *Acta Chem. Scand.*, 1973, **27**, 2965.
7. G. Gundersen and H. Vahrenkamp, *J. Mol. Struct.*, 1976, **33**, 97.
8. R. Johansen, H. M. Seip and W. Siebert, *Acta Chem. Scand., Ser. A*, 1975, **29**, 644.
9. L. S. Bartell and B. L. Carroll, *J. Chem. Phys.*, 1965, **42**, 3076.
10. L. Hedberg, K. Hedberg, D. A. Kohler, D. M. Ritter and V. Schomaker, *J. Am. Chem. Soc.*, 1980, **102**, 3430.
11. B. L. Caroll and L. S. Bartell, *Inorg. Chem.*, 1968, **7**, 219.

5.1.1.8 Electronic Spectra

Reported results of electronic transitions in organoboron compounds have appeared to be at times anomalous, but an extensive discussion and compilation of experimental results[57] has resulted in a clearer picture of the electronic spectra of organoboranes. Some transitions which have been reported are almost certainly not transitions due to the organoborane but instead due to the presence of oxidation products when oxygen was not rigorously excluded. For example, the peak of 260 nm ($\epsilon = 6000$) which was originally assigned[58] to $B(CH_3)_3$ can better be assigned to a ⟮B—O—O⟯ moiety,[59] although it was at one time reassigned to the B—O chromaphore.[60] Trialkylboranes in general exhibit absorption maxima in the region 215–230 nm. This is illustrated by two studies[61,62] of *n*-, *s*- and iso-tributylborane, all of which exhibit maxima near 215 nm ($\log \epsilon = 2.4$) which are essentially independent of the nature of the butyl group. This transition reportedly progresses regularly to higher energy in trialkylboranes as the ionization potential of the alkyl substituent increases, *i.e.* Bu < Pr < Et < Me.[63] A description of this transition as an intramolecular charge transfer (CT) transition from a hydrocarbon delocalized 'σ' orbital of π symmetry to the 2*p* boron atomic orbital of the same symmetry has been advanced.[63] A second, weaker band system ($\log \epsilon < 2$) is observed in trialkylboranes as the alkylborane CT band moves to higher energy. An assignment of these transitions as resulting from promotion of an electron from a boron–carbon bond to the boron empty *p*-orbital has been proposed.[63]

As expected, vinyl-, alkynyl- and aryl-boranes have received the lion's share of attention. The vinylboranes exhibit one or more relatively strong absorptions ($\epsilon \approx 10^4$) in the range 185–234 nm (Table 8) which presumably arise from intramolecular CT transitions from the alkene MO to boron.[64]

Table 8 Vinylboranes Studied by Ultraviolet Spectroscopy

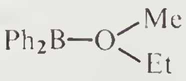
Organoborane	λ_{max} (nm)	*Ref.*
$B(C_2H_3)_3$	234	1
$(C_2H_3)_2BMe$	220	1
$C_2H_3BMe_2$	196	1
$(C_2H_3)_2BCl$	222	1
C_2H_3BMeCl	206	1
$CH_2{=}C(Me)B(OH)_2$	only end adsorption down to 205 nm	2
$C_2H_3B(OBu)_2$	185	3
	198	4
$C_2H_3B(NMe_2)_2$	218	5
$C_2H_3B(Br)(NMe_2)$	223	5

1. C. D. Good and D. M. Ritter, *J. Am. Chem. Soc.*, 1962, **384,** 1162.
2. D. S. Matteson, *J. Am. Chem. Soc.*, 1960, **82,** 4228; this reference also draws attention to the fact that the reported λ_{max} = 223 nm for $Me_2C{=}CHB(OH)_2$ appears anomalous.
3. A. N. Kikitina, V. A. Petukhov, A. F. Galkin, N. S. Fedotov, Y. N. Bubnov and P. M. Aronovich, *Opt. Spektrosk.*, 1964, **16,** 976.
4. W. G. Woods, I. S. Bengelsdorf and D. L. Hunter, *J. Org. Chem.*, 1966, **31,** 2766.
5. K. Niedenzu, J. W. Dawson, G. A. Neece, W. Sawodny, D. Squire and W. Weber, *Inorg. Chem.*, 1966, **5,** 2161.

Several classes of alkynylboranes have been studied by UV spectroscopy including compounds of the type $R_2N{-}B(C{\equiv}C{-}C{\equiv}C{-}R)_2$,[65] pyridine complexes of $Ph(aryl)BC{\equiv}CR$[66] and $(aryl)B(C{\equiv}CR)_2$,[66] $RC{\equiv}CB(OR')_2$,[67] $RC{\equiv}CB(NR'_2)_2$[67] and $RR'BNR''_2$ (where R = $MeC{\equiv}C{-}$ or $CH_2{=}C(Me)C{\equiv}C{-}$ and R′ = R or Bu^n).[67] In addition, studies of $HC{\equiv}CB(OH)_2$ and $HC{\equiv}CB(OMe)_2$ have been reported.[68]

The UV spectra of triarylboranes exhibit broad, intense ($\epsilon > 10^4$) λ_{max} in the range 280–360 nm which are thought to arise from intramolecular CT transitions from the aromatic ring to the boron empty *p*-orbital.[64,69-71] A series of mono- and di-arylboranes in which the remaining substituents are mainly amino, hydroxy and alkoxy groups have been studied.[72,73] These compounds appear to exhibit several bands but a maximum between 210–250 nm ($\epsilon \approx 0.5\text{–}1 \times 10^4$) for phenylboranes and at longer wavelengths for naphthylboranes presumably corresponds to the intramolecular CT transition mentioned above for triarylboranes.

The absorption spectrum of tetraphenylborate, BPh_4^-, exhibits maxima at 265 and 274 nm,[74] which is very similar to that of tetraphenylmethane (λ_{max}, 210, 253, 262, 272 nm).[75] Spectra of the ammonia adducts of triphenylborane[72] and tri-1-naphthylborane[69] as well as the acetonitrile adduct of triphenylborane[60] have also been studied. The UV spectrum reported[76] for the diphenylboron cation or diphenylboronium ion in ethyl methyl ether is most likely the spectrum of the trigonal boron compound (**1**) in view of NMR and conductivity studies[77] of diphenylboronium ions.



$$Ph_2B{-}O{<}^{Me}_{Et}$$

(**1**)

5.1.1.9 Nuclear Magnetic Resonance Spectra

Of all the physical tools employed in investigations of organoboron molecules, NMR has perhaps been the most widely used and important technique since a number of magnetically active nuclei are usually contained in an organoboron molecule. NMR is a non-destructive technique which can rapidly provide information concerning composition, structure and solution dynamics. Although multinuclear instrumentation and pulsed NMR methods are revolutionizing the entire field of NMR spectroscopy, boron NMR developed relatively early and results have been summarized in several review articles and books.[78–83]

Both naturally occurring boron isotopes are suitable for NMR investigations, although ^{11}B is normally observed because of its higher natural abundance (80%), its greater sensitivity to an NMR experiment (0.165 compared with $^{1}H = 1.0$) and its smaller electric quadrupole moment. The ^{11}B chemical shift range of diamagnetic compounds covers approximately 250 p.p.m. with dependence on charge, coordination number and type of substituents. Noncoordinating solvents do not seem to have a significant influence on ^{11}B shifts, but solvents which may be considered Lewis bases will normally cause a shielding of the ^{11}B resonance in trigonal compounds due to coordination. Although an overall theoretical development of boron chemical shifts has not appeared, an examination[80,81] of ^{11}B chemical shifts demonstrates that electron density at the boron nucleus plays a substantial part in determining these shifts. Trialkylboranes generally exhibit the most deshielded resonances and upfield shifts occur in trigonal compounds if the groups are capable of interacting mesomerically with the empty boron *p*-orbital. Thus unsaturated organic groups, halogens, oxygen and nitrogen substituents all cause an increase in ^{11}B chemical shifts. Also, four-coordinate boron compounds have resonances which are substantially shielded from those of analogous three-coordinate molecules. Table 9 contains ^{11}B chemical shifts of selected organoboranes which illustrate this fact.

Table 9 ^{11}B Chemical Shifts of Selected Organoboranes[1,2]

Organoborane	$\delta(^{11}B)$(p.p.m.)
BMe_3	86.6
BEt_3	86.8
$Me_2B(c\text{-}C_3H_5)$	81.8
$B(CH_2CH{=}CH_2)_3$	80.5
$B(C_2H_3)_3$	56.4
$B(C_2F_3)_3$	46.1
BPh_3	68.0
$MeBF_2$	28.2
$PhBF_2$	25.5
Me_2BF	59.0
Me_3BCl_2	61.4
$C_6F_5BCl_2$	53.0
Me_2BOMe	53.0
$MeB(OMe)_2$	29.5
Me_2BSMe	74.0
$B(SeMe)_3$	65.5
$MeB(NMe_2)_2$	33.5
$(Me_2B)_2NMe$	58.5
Me_3BPMe_3	−12.3
H_3BCO	−52
$[Me_2B(NH_3)_2]^+$	13.9
Me_4B^-	−20.7
$(C_2H_3)_4B^-$	−16.1
$(Ph)_4B^-$	−6.3
$(PhC{\equiv}C)_4B^-$	−31.0

1. Chemical shift values are taken from H. Nöth and B. Wrackmeyer, in 'NMR: Basic Principles and Progress; 14, Nuclear Magnetic Resonance Spectroscopy of Boron Compounds', ed. P. Diehl, E. Fluck and R. Kosfeld, Springer-Verlag, New York, 1978; where more than one value has been determined, the most recent value is listed.
2. All chemical shifts are referenced to $BF_3{\cdot}OEt_2 = 0$; a positive sign for $\delta(^{11}B)$ indicates a shift deshielded from the reference in accordance with the recommendation of the I.U.P.A.C. International Boron Conference, Munich and Ettal, West Germany, 1976; values in the literature previous to this time have used the opposite convention.

It is also interesting to compare the effect of various unsaturated organic groups on the boron chemical shifts of a closely related series of trigonal organoboranes. Table 10 illustrates this shielding of the boron resonance as the organic group is varied. Although these shifts undoubtedly reflect both mesomeric and inductive effects, it would appear that qualitatively the mesomeric effect of organic groups towards ^{11}B chemical shifts increases in the order ethyl < cyclopropyl < phenyl < vinyl < perfluorovinyl.[84,85]

Various correlations of ^{11}B chemical shifts with other parameters have been reported. ^{11}B chemical shifts for various *para*-substituted dihydroxyphenylboranes correlate linearly with corresponding Hammett σ-constants for the substituents.[86] Correlations with electronegativity to predict ^{11}B chemical shifts of BR_4^- (R = alkyl, vinyl, phenyl, alkynyl) appear to give satisfactory agreement with experiment.[83,87] Also, ^{11}B chemical shifts of triorganylboranes correlate with ^{13}C chemical shifts of corresponding triorganomethyl cations[88] and pairwise additivity parameters have been used to calculate chemical shifts.[88]

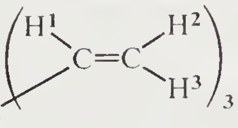
In general, proton NMR spectra of organoboranes have not been used and investigated as extensively as ^{11}B spectra. Substitution of boron for carbon in a saturated organic moiety usually results in a shielding of approximately 0.5 p.p.m.[84,89–92] Typical ^{1}H chemical shifts of organoboranes are shown in Table 11.

Table 10 ^{11}B Chemical Shifts of Organoboranes[1,2]

Formula	*Ethyl*	*Cyclopropyl*[4]	*Phenyl*	*Vinyl*	*Perfluorovinyl*
R_3B	86.8	70.3	68.0	56.4	46.1
R_2BF	59.6	54.9	47.4	42.4	—
RBF_2	28.7	28.5	25.5	22.6	21.8
R_2BCl	78.4	71.0	61.0	56.7	49.9
$RBCl_2$	63.5	60.1	55.4	53.5	31.3
R_2BBr	82.9	—	66.7	60.1	57.0
$RBBr_2$	65.6	60.2	57.7	54.7	49.6
R_2BMe	86.2[3]	—	70.6	64.4	57.8
$RBMe_2$	86.1[3]	81.7	77.6	74.5	72.7

1. Chemical shift values are taken from H. Nöth and B. Wrackmeyer, in 'NMR: Basic Principles and Progress; 14, Nuclear Magnetic Resonance Spectroscopy of Boron Compounds', ed. P. Diehl, E. Fluck and R. Kosfeld, Springer-Verlag, New York, 1978; where more than one value has been determined, the most recent value is listed.
2. All chemical shifts are referenced to $BF_3{\cdot}OEt_2 = 0$ p.p.m.; a positive sign for $\delta(^{11}B)$ indicates a shift deshielded from the reference in accordance with the recommendation of the I.U.P.A.C. International Boron Conference, Munich and Ettal, West Germany, 1976; values in the literature previous to this time have used the opposite convention.
3. E. J. Stampf and J. D. Odom, *J. Organomet. Chem.*, 1977, **131**, 171.
4. J. D. Odom and Z. Szafran, unpublished results, Univ. of South Carolina, 1980.

Table 11 Proton Chemical Shifts of Selected Organoboranes[1,2]

Organoborane	$\delta(^{1}H)$ (*TMS* = 0 p.p.m.)	J_{HH} (Hz)
BMe_3	0.8	—
BEt_3	α, 1.2; β, 0.9	6.7
	H^1, 6.7 H^2, 6.1 H^3, 6.2	$J_{12} = 13.3$ $J_{13} = 19.4$ $J_{23} = 4.1$
Me_3BNMe_3	0.3	—
Et_3BNMe_3	α, 0.3; β, 0.8	7.3
$(C_2H_3)_3BNMe_3$[3]	H^1, 6.2 H^2, 5.6 H^3, 5.3	$J_{12} = 13.3$ $J_{13} = 19.4$ $J_{2,3} = 4.9$
BMe_4^-	−0.5	—
BEt_4^-	α, −0.2; β, −0.6	7.5

1. Positive shifts are deshielded from TMS.
2. Unless otherwise designated, chemical shift and coupling constant data are from H. Nöth and H. Vahrenkamp, *J. Organomet. Chem.*, 1968, **12**, 23.
3. L. W. Hall, J. D. Odom and P. D. Ellis, *J. Organomet. Chem.*, 1975, **97**, 145.

Extensive ^{1}H NMR studies of methyl- and ethyl-boranes have been reported and conclusions have been reached concerning the electronegativity of boron in these compounds as well as inductive effects, π-bonding and anisotropy effects of various substituents.[14,93] Rotational barriers about the B—N bond in aminoorganoboranes have also been studied by ^{1}H NMR spectroscopy,[94-100] as has the conformation of phenyl rings in *B*-phenyl borazines.[92] Proton chemical shifts of adducts of trimethylborane have been correlated[101] with dissociation enthalpies,[102] although the success of this method is not general.[103] B—C π-bonding in alkenylboranes[104,105] and borylbenzenes[106] has also been studied by ^{1}H NMR spectroscopy, as has the energetics of rearrangement in alkylboranes.[107]

The advent of pulsed Fourier transform NMR spectroscopy has demonstrated that ^{13}C NMR data of organoboranes can be extremely useful.[108] Carbon-13 NMR of boron compounds has been used principally to determine ^{13}C chemical shifts, to study boron–carbon coupling constants and to investigate the question of boron–carbon π-bonding by determining the ^{13}C chemical shifts of carbon atoms not directly bonded to boron. Carbon chemical shifts have been determined for a wide variety of organoboron compounds.[108] Although there appears to be some correlation between ^{11}B chemical shifts of trigonal boranes and ^{13}C chemical shifts of carbenium ions,[109-111] a comparison of ^{13}C data of tetralkylborates and isoelectronic alkanes does not lead to a consistent correlation. However, an approximately linear relationship is obtained between $\delta(^{13}\mathrm{C})$ of a series of methylboranes and $\delta(^{11}\mathrm{B})$.[112] Typical ^{13}C chemical shift values of organoboranes are shown in Table 12.

Table 12 ^{13}C Chemical Shifts of Selected Organoboranes[1,2]

Organoborane	$\delta(^{13}C)$ (p.p.m.)	J_{BC} (Hz)
BMe_3	13.8	46.7
BEt_3	19.8 (CH_2); 8.5 (CH_3)	<52.0
BPr^n_3	31.7 (BCH_2); 18.4 (CH_2); 17.8 (CH_3)	—
$B(C_2H_3)_3$	141.7 (CH); 138.0 (CH_2)	<65.0
Me_2BNMe_2	3.0 (BCH_3); 39.2 (NCH_3)	54.0
Me_2BOMe	6.3 (BCH_3); 52.9 (OCH_3)	64.0
Me_2BSMe	9.9 (BCH_3); 12.1 (SCH_3)	50.0
$MeB(SeMe)_2$	9.2 (BCH_3); 3.6 ($SeCH_3$)	54.0
$(HC{\equiv}C)_2BNEt_2$	89.0 (BC); 94.4 (CH)	132
Me_2BBr	15.5	—
H_3BCO	156.8	30.2
BMe_4^-	6.2	39.4[3]

1. Chemical shift and coupling constant values are taken from B. Wrackmeyer, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1979, **12**, 227.
2. All chemical shifts are referenced to TMS = 0 p.p.m.; a positive sign indicates a shift deshielded from the reference.
3. The value listed in ref. 1 is incorrect; the correct value is 39.4 Hz.[4,5]
4. M. Yanagisawa and O. Yamamoto, *Org. Magn. Reson.*, 1980, **14**, 76.
5. A. J. Zozulin, H. J. Jakobsen, T. F. Moore, A. R. Garber and J. D. Odom, *J. Magn. Reson.*, 1980, **41**, 458.

For many organoboranes the resonance of the directly bonded carbon atom is not observable under normal conditions. The use of neat samples,[113] low temperatures[114,115] or ^{11}B decoupling has been reported to alleviate this problem.[116] Resonances of carbon atoms not directly bonded to boron are easily observable and a study of ^{13}C chemical shifts of these atoms has been of great utility in studying B—C π-bonding in alkenylboranes,[117-119] phenylboranes[106,116] and boron-substituted aromatic hterocycles.[116] In all cases, ^{13}C NMR appears to be a very sensitive tool to detect mesomeric B—C interactions.

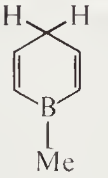
Boron–carbon coupling constants have also been determined for a wide range of compounds[108] and typical values are listed in Table 12. When boron is four-coordinate, the low electric field gradient at the boron nucleus allows easy observation of J_{BC}. In fact, in the BPh_4^- ion, coupling constant values have been determined[120,121] for all four carbon atoms ($^{1}J_{BC} = 49.4$; $^{2}J_{BC} = 1.5$; $^{3}J_{BC} = 2.7$; $^{4}J_{BC} = 0.5$ Hz). Spin-spin coupling data in triorganylboranes have been determined in a number of cases[122-127] although, as mentioned above, the directly bonded carbon resonance is not always observed. INDO MO calculations[126] of J_{BC} values give good agreement with experimentally determined values but do not support earlier work which found a good correlation between $^{1}J_{BC}$ and the amount of *s*-character in the B—C bond.[124] In all cases the sign of $^{1}J_{BC}$ has been reported to be positive relative to $^{1}J_{CH}$, which is known to have an absolute positive sign.

It should also be mentioned that ^{14}N,[128–132] ^{19}F[133–136] and ^{17}O[137] NMR spectroscopy has been used in studies of organoboron molecules.

5.1.1.10 Mass, Ion Cyclotron Resonance and Photoelectron Spectra

A mass spectral study of compounds of the type BR_3, BRR'_2 and $BRR'R''$ demonstrated that the compounds could be differentiated since molecular ions of each compound could be observed.[138,139] However, the most predominant peak in almost every case is the *m/e* 41 peak, which could correspond to $B(CH_3)_2^+$, $HB(C_2H_5)^+$ or $HB(CH_2)(CH_3)^+$. Trimethyl compounds of Group IIIA display molecular ion abundances in the order $AlMe_3 > BMe_3 > GaMe_3 > InMe_3 > TlMe_3$.[140] Methyl migration does not occur in BMe_3 under a variety of experimental conditions[141] and a $^{10}B/^{11}B$ abundance ratio has been determined from isotopically labeled trimethylborane molecules. Appearance potentials for positive ion fragments of trimethyl- and triethyl-boranes have been reported.[142,143] As mentioned previously (Section 5.1.1.3), mass spectra of organodifluoroboranes have been used to obtain ionization potentials and B—C bond dissociation energies. Fragmentation of BH_3CO in a molecular beam produces ions of the type BH_xC^+, BH_xCO^+ and BH_x^+.[144]

Ion cyclotron resonance spectroscopy has been used to study tri-*n*-butylborane and there is an almost total lack of boron-containing species,[145] in contrast to the conventional mass spectrum.[138,139] The ion–molecule reactions of BMe_3, both alone and in mixtures with other molecules, have been investigated by ICR spectroscopy.[146] The gas phase Brønsted acidity of BMe_3, proton affinity of $[Me_2B{=}CH_2^-]$, is 1527 ± 21 kJ mol^{-1}. The gas phase base strength was not determined because of failure to observe protonated BMe_3.[146] Formation of Lewis acid–base adducts R_3BF^- and R_2FBF^- in reactions of SF_5^- and SF_6^- with neutral boranes BR_3 have established the Lewis acidity order $BF_3 > FBPr^i_2 > BPr^i_3 > FBEt_2 > BEt_3 > FBMe_2 > BMe_3 > SF_4$ in the gas phase with F^- as the reference base.[147] Quantitive estimates of thermodynamic parameters of R_3BF^- adducts were also derived.[147] ICR techniques have also been employed to determine the gas phase Brønsted and Lewis acidities and Brønsted basicity of 1-methyl-1,4-dihydroborabenzene (**2**).[148] Surprisingly, the Lewis acidity, proton affinity and ion chemistry of (**2**) indicate little or no interaction of the diene π-system with boron.



(**2**)

A comparison of the photoelectron spectra of trivinylborane and triethylborane has been interpreted[149] as implying a lack of mesomeric interaction in $B(C_2H_3)_3$, although this is at variance with other spectroscopic techniques. Boron 1*s* electron binding energies of a series of gaseous boron compounds, including BMe_3 and BH_3CO, have been measured by photoelectron spectroscopy[150] and shown to be linearly related to boron atom charges estimated by Pauling,[151] CNDO[152] and extended Hückel[153] methods.

5.1.1.11 Molecular Orbital Calculations

Hyperconjugation in BMe_3 has been studied by both *ab initio* (SCF-MO) and semi-empirical (INDO) calculations and found to be unimportant.[154] However, extended Hückel calculations suggest that the π-bond character of BMe_3 is about nine times that of $AlMe_3$.[155] Electron densities calculated by the extended Hückel method show that as H is displaced by R groups (R = *n*-alkyl or *s*-alkyl) in trigonal boron compounds the positive charge on boron increases, as does the negative charge on hydrogen.[156]

As expected, vinylboranes and phenylboranes have received theoretical attention with regard to B—C π-bonding. Vinylboranes as well as vinylmethylboranes have been reported to have some π-charge on the boron atom.[157–161] The unknown vinylborane molecule, $C_2H_3BH_2$, has also been considered[161–163] and a barrier to rotation about the B—C bond found[163] to be 31.8 kJ mol^{-1}.

Pariser–Parr–Pople SCF calculations have been used to treat triphenyl- and tri-*p*-tolyl-borane[164] as well as diphenylboranes,[165] dihalophenylboranes[166] and phenylboronic acids.[167] In general, very good agreement between calculated energies and observed electronic transition energies are obtained.

Heats of formation, molecular geometries, ionization potentials and dipoles have been calculated by the MNDO method for a variety of organoboranes.[168] Self-consistent perturbation theory and a basis set consisting of gauge-invariant atomic orbitals have been used to calculate boron chemical shifts in a variey of boron compounds, including several organoboranes.[169] Finally, B—C rotational barriers and preferred geometries have been examined by *ab initio* calculations in the molecules H_2BCH_2Y, $H_2BCH_2BH_2$ and $EtBH_2$.[170]

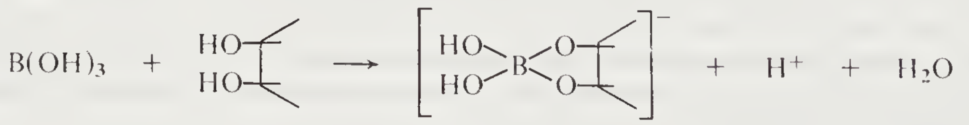
5.1.1.12 Handling, Toxicity and Analysis

The boron–carbon bond is unusually stable to water, aqueous bases and aqueous mineral acids. Trialkylboranes are particularly noteworthy in this respect in that they require relatively stringent conditions to undergo hydrolysis or protonolysis. However, organoboron compounds are sensitive to oxygen and the more volatile compounds [BMe_3, BEt_3, $B(C_2H_3)_3$] are spontaneously flammable on contact with air. Boron–halogen bonds in organoboranes, of course, are much more susceptible to hydrolysis and the handling of any organoboron compound must be adapted to the chemical and physical characteristics of that particular compound. In general, organoboranes are handled on vacuum systems, in Schlenk-type apparatus, inert atmosphere boxes or by using specialized bench-top methods. All of the techniques have been thoroughly described elsewhere.[5,171]

The toxicity of a wide range of organoboranes has apparently not been studied in an extensive and systematic manner, but boron–carbon compounds do not appear to be particularly toxic.[172] However, due to the lack of detailed studies, organoboron compounds should be treated as toxic unless data to the contrary have been reported.

The analysis of volatile organoboranes can be achieved by vapor phase chromatography provided that inert liquid and stationary phases are used, protic sites are converted to trimethylsilyl groups and injection port temperatures are regulated such that thermal degradation of the molecules does not occur. As a general rule of thumb, the retention time of an organoborane on a nonpolar column is similar to that of the corresponding hydrocarbon.

The success of analytical determinations of boron and carbon in organoboranes depends upon complete cleavage of all boron–carbon bonds. This normally is achieved by various means of oxidation and a variety of reagents have been used and described. These reagents include but are not limited to various carboxylic acids,[173,174] including F_3CCO_2H,[175,176] alkaline hydrogen peroxide,[175,177–180] NaOH,[175] H_2SO_4,[175] Me_3NO,[181–184] oxygen,[185,186] alkaline potassium persulfate[187] and ammoniacal silver ion.[180,188,189] Boron is normally converted to boric acid, $B(OH)_3$, which is a weak acid and yields a poor endpoint when titrated with base. However, the addition of mannitol enables boric acid to act as a stronger acid (equation 1) which may be titrated with standard base to methyl red endpoint.[175]



(1)

It also appears that some boronic acids, $RB(OH)_2$, can be titrated by NaOH in the presence of mannitol using phenolphthalein as an indicator.[190] Borinic acids, R_2BOH, suffer from the same problem as $B(OH)_3$ in that they give a poor endpoint. The problem can be alleviated to some extent by briefly heating the solution before titration.[190]

5.1.2 PREPARATIVE METHODS OF THREE-COORDINATE NON-CYCLIC ORGANOBORANES

5.1.2.1 General Discussion

As will become evident, the methods of preparation of organoboranes are wide and varied. Many of these approaches have been critically reviewed.[6,7,191] In general the same methods are applicable for the synthesis of symmetrical triorganylboranes (BR_3), unsymmetrical triorganylboranes

($BR^1R^2R^3$), diorganylboranes (R_2BX) and monoorganylboranes (RBX_2). The characteristics of major synthetic methods will be covered and an attempt will be made to point out differences which occur in various types of organoboranes. Cyclic organoboranes, of course, will not be treated (see Chapters 5.2 and 5.3) The two most popular and widely used methods, transmetallation and hydroboration, will be discussed first. The better method for the preparation of a particular compound will generally depend upon whether one is an organic or inorganic chemist. Although transmetallation is the most widely used and most general procedure, hydroboration is normally the method of choice for organic chemists since it is experimentally a more simple method and, more importantly, extensive studies regarding the scope and limitations have been reported.[2,3,5] A further benefit of hydroboration is that because of its stereospecificity, the stereochemistry of the organoboron product can be readily defined. However, the discussion of hydroboration in this chapter will be limited because it will be covered in detail in separate chapters (Chapter 45.2–45.5).

5.1.2.2 Transmetallation

A transmetallation reaction, for our purposes, can be defined as a reaction in which an alkyl, alkenyl, alkynyl or aryl group is transferred from a metal to boron by the reaction of an organometallic compound with a suitable boron compound (Scheme 1). The popularity of this method derives primarily from the wide range of organic groups which can be introduced. A variety of metals can be used and the boron-bound groups X can also be a number of different substituents. However, good yields of pure compounds require the correct choice of both the metal and the X group. Metals which have been used most extensively are Li, Na and K in Group IA, Mg in Group IIA, Al in Group IIIA, Si, Sn and Pb in Group IVA and Zn, Cd and Hg in Group IIB. The group on boron which is usually replaced includes other organic groups, halogens, hydrogen, OR, SR and NR_2. Typical transmetallation reactions are shown in equations (2)–(9)[193–198,31,199] and Table 13 lists organometallic reagents and boron-bonded substituents which have been used in combination with one another. In most cases the reference listed is a recent reference and a much more complete listing can be found in refs. 6 and 7.

$$\begin{tikzcd} BX_3 + MR \arrow[r] & RBX_2 + MX \arrow[d, "MR"] \\ R_3B + MX & R_2BX + MX \arrow[l, "MR"'] \end{tikzcd}$$

Scheme 1

$$BF_3 + 3RMgBr \longrightarrow BR_3 + 3MgBrF \qquad (2)$$

$$4B_2H_6 + Al_2Me_6 \longrightarrow 2BMe_3 + 2Al(BH_4)_3 \qquad (3)$$

$$B(OR)_3 + HC{\equiv}CMgBr \longrightarrow HC{\equiv}CB(OR)_2 \qquad (4)$$

$$B(OBu)_3 + (C_3H_5)_3Al_2Br_3 \longrightarrow B(C_3H_5)_3 + AlBr_3 + Al(OBu)_3 \qquad (5)$$

$$4BCl_3 + (CH_2{=}CH)_4Sn \longrightarrow Cl_2BCH{=}CH_2 + SnCl_4 \qquad (6)$$

$$BCl_3 + 3Me_4Pb \longrightarrow BMe_3 + 3Me_3PbCl \qquad (7)$$

$$2BF_3 + (CH_2{=}CH)_2Zn \longrightarrow 2F_2BCH{=}CH_2 + ZnF_2 \qquad (8)$$

$$BBr_3 + PhHgBr \longrightarrow PhBBr_2 + HgBr_2 \qquad (9)$$

All factors which influence the course of transmetallation reactions have not been properly and thoroughly investigated but the available evidence does provide a relatively large number of generalizations which can be made. Also, some specific reactions have been studied in detail. When a metal in the organometallic reagents is substantially more electropositive than boron

Table 13 Typical Transmetallation Reagents

Organometallic reagent	*Boron substituent replaced*	*Ref.*
RLi	H	1
	F	2
	Cl	3
	Br	4
	R′	5
	OR′	6
	SR′	7
RNa	H	8
	F	9
	Cl	9
	Br	10
RK	H	8
	OR′	11
R_2Mg	H	12
	F	13
RMgX	H	14
	F	15
	Cl	16
	Br	17
	I	18
	R′	19
	OR′	20
R_3Al	H	21
	F	22
	Cl	22
	Br	22
	I	22
R_2AlX	F	23
	Cl	24
	OR′	25
$RAlX_2$	F	23
	Cl	24
	OR′	25
R_4Si	Cl	26
	NR_2	27
R_4Sn	F	28
	Cl	29
	Br	30
	I	31
R_4Pb	H	32
	Cl	33
R_2Zn	F	34
	Cl	35
	R′	36
	OR′	37
R_2Hg	F	38
	Cl	20
RHgX	H	39
	Cl	40
	Br	17

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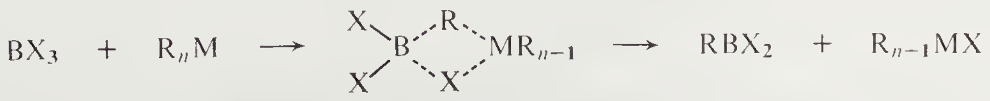
and the boron-bonded substituent X is a halogen, the yield of organoborane is normally excellent since the equilibrium heavily favors production of the borane and the metal halide.[200] Although the same is probably true for X = OR, it is not clear what the situation is for other X substituents.[191] When the metal and boron are comparable in electronegativity, the sensitivity to other factors appears to become more important and in fact the direction of transmetallation may be reversed.

For a given boron compound, two studies have suggested reactivities of various metals. With $B(OBu)_3$, phenyl derivatives of metals react in the order Mg > Cd > Zn > Hg.[201] In a second investigation[202] the order of Zn and Cd is reversed towards $B(NMe_2)_3$, with methyl and ethyl compounds of the following metals demonstrating an order of Al > Zn > Cd > Sn. Further, it has been suggested[191] that, in general, the more electropositive the metal the more reactive will be the organometallic reagent towards a particular boron substrate, *i.e.* K, Na > Li > Mg > Al > Zn, Cd > Pb, Hg, Sn.

With regard to various boron substituents, organolithium or Grignard reagents displace the X group in the order Cl > OR > NR_2.[203] Perhaps the most careful study has been an investigation with triethylalane and halogenoboranes.[204] Triethylalane reacts with the boron trihalides in the order F > Cl > Br > I. In the same study[204] it was reported that the order of reactivity toward $AlEt_3$ was $BX_3 > RBX_2 > R_2BX$ and this order is generally accepted towards any given organometallic reagents, although this has not been demonstrated conclusively in a large number of cases. In fact, in the $AlEt_3$ study[205] the results for X = F were not conclusive and the order may even be reversed. Finally, vinyl and phenyl groups seem to be readily transferred from tin reagents, much more so than saturated organic groups.[31] Few studies have been reported which dealt with the mechanism(s) of transmetallation. Two general routes which must be considered[205] are shown in equations (10) and (11). However, more work is required to determine which, if either, or if both mechanisms are operable and under what conditions.

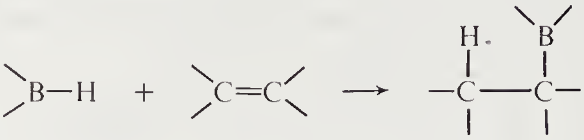


$$BX_3 + R_nM \longrightarrow \begin{array}{ccc} X & & R \\ & B & & MR_{n-1} \\ X & & X \end{array} \longrightarrow RBX_2 + R_{n-1}MX \qquad (10)$$

$$BX_3 + R_nM \longrightarrow [RBX_3]^-[R_{n-1}M]^+ \longrightarrow RBX_2 + R_{n-1}MX \qquad (11)$$

5.1.2.3 Hydroboration

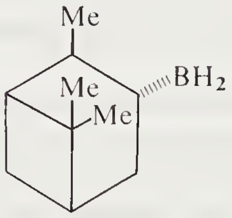
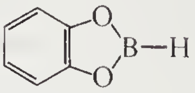
As previously mentioned, the hydroboration reaction (equation 12) will be extensively discussed in Chapters 45.2–45.5 and thus only a brief summary will be given here. This reaction has been thoroughly studied and although it is a more recent method for preparing B—C bonds than transmetallation, it is much better understood. Critical reviews, carefully pointing out the scope and limitations of this reaction, have been published.[1–3,206]



(12)

Since a detailed discussion of hydroboration will appear later, an attempt will be made at this point to emphasize major advantages and disadvantages of the method. In addition, Table 14 lists most of the reagents which can be used as hydroborating agents and a relatively recent reference. A more complete listing, particularly of references, can be found in refs. 6 and 7.

Table 14 Hydroboration Reagents

Reagent	*Ref.*
BH_3	1
BH_3·THF	2
$BH_3·SMe_2$	3, 4
$BH_3·NR_3$	5
RBH_2·amine	6
BH_2Cl	7
$BHCl_2$	8
BH_2Cl·amine	9
BH_2Cl·etherate	10–12
$BHCl_2$·etherate	13
$BHCl_2$·etherate, BCl_3	14
$BH_2Cl·SMe_2$	15
$BHCl_2·SMe_2$	15, 16
$BH_2Br·SMe_2$	17
$BHBr_2·SMe_2$	16, 18, 19
$BHI_2·SMe_2$	16
9-BBN	20–23
	24
B_2H_6	25, 26
$LiBH_4$	27
$NaBH_4$	27, 28
KBH_4	27
$LiAlH_4$	27, 29
LiH	27
NaH	27
$Al(BH_4)_3$	30
$Na(BHEt_3)$	31
$(Et_2NBH_2)_2$	32
R_2NBH_2	33
$[(BuS)_2BH]_2$	34
$(EtS)_3B_2H_3$	35
$R_4B_2H_2$	36
$R_3B_2H_3$	37
$R_2B_2H_4$	38
	39

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A major advantage of the hydroboration reaction is its experimental simplicity. As illustrated in Table 14, a wide variety of hydroborating agents can be employed, but when $THF{\cdot}BH_3$ or $Me_2S{\cdot}BH_3$ (both of which are commercially available) are used, problem by-products are avoided. Also, with the agents above, as is so many times the case with hydroboration, the product solution can be utilized directly for further reaction of the organoborane. Other advantages include the fact that hydroboration is, in many cases, highly regiospecific and since the reaction involves a stereospecific *cis* addition of B—H across the double or triple bond, the stereochemistry of the reaction is highly defined.

Perhaps the greatest disadvantage in using the hydroboration reaction to prepare organoboranes is that the reaction is limited to the preparation of only those compounds which contain aliphatic β-hydrogen atoms (equation 12). This means, of course, that molecules such as BMe_3, $B(CH_2Ph)_3$ and trineopentylborane are not available *via* hydroboration.

Further, although the boron could possibly add to either carbon of a double bond, hydroboration is usually highly selective. Thus one of the possible products is readily prepared but the other possible compound can then not be prepared by hydroboration. For example, hydroboration of 2-methylpropene quantitatively produces an isobutylborane but yields no *t*-butyl derivative.

In the opposite sense, if a double bond is unsymmetrically substituted with substituents having similar steric and electronic requirements, both carbon atoms may be attacked by boron, producing a mixture of compounds which may prove difficult or impossible to separate. This has been illustrated in the reaction of oct-1-ene with $THF{\cdot}BH_3$.[8]

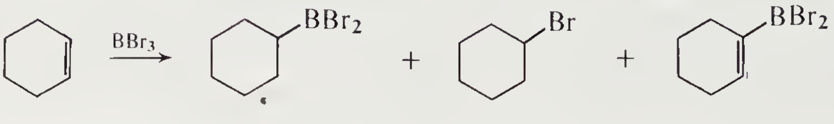
In the final analysis the hydroboration reaction is one of tremendous chemical significance and utility and should be carefully considered when preparing organoboranes.

5.1.2.4 Haloboration

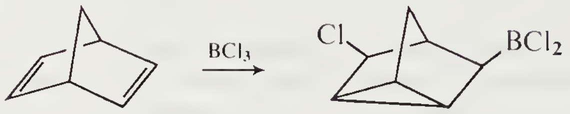
Haloboration refers to the reaction of a trihaloborane BX_3 or other haloborane, RBX_2 or R_2BX, with an unsaturated organic moiety to afford organoboranes (Scheme 2).[207] Boron tribromide appears to be more reactive than BCl_3 but secondary reaction products may occur,[208] *e.g.* equation (13).[2] Other typical haloboration reactions with alkenes are shown in equations (14)–(17).[207–209]

$$\mathrm{RC{\equiv}CR' + YBX_2 \longrightarrow RC(Y){=}C(R')BX_2}$$
$$\mathrm{+\ RC(BX_2){=}CR'X}$$

Scheme 2



(13)



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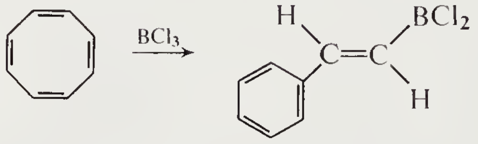

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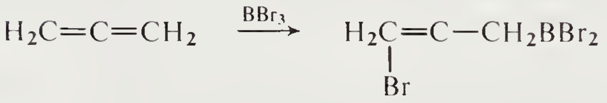
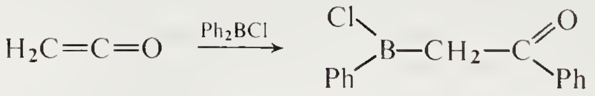
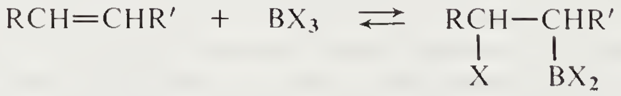


$$\mathrm{H_2C{=}C{=}CH_2 \xrightarrow{BBr_3} H_2C{=}\underset{Br}{C}{-}CH_2BBr_2} \qquad (16)$$

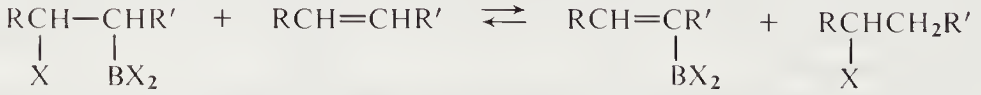


$$\mathrm{H_2C{=}C{=}O \xrightarrow{Ph_2BCl} (Cl)(Ph)B{-}CH_2{-}C({=}O)Ph} \qquad (17)$$

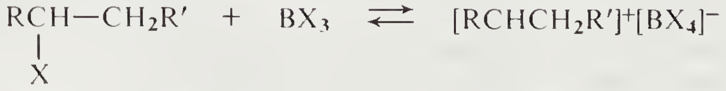
The haloboration reaction with alkenes is more complicated than the hydroboration reaction and it suffers from several problems that limit its preparative applicability. A tentative mechanism has been proposed[210] and is shown in equations (18)–(21). An alternative to equation (19) may be equations (22) and (23).



$$\mathrm{RCH{=}CHR' + BX_3 \rightleftharpoons \underset{X}{RCH}{-}\underset{BX_2}{CHR'}} \qquad (18)$$

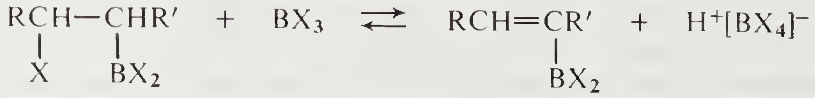


$$\mathrm{\underset{X}{RCH}{-}\underset{BX_2}{CHR'} + RCH{=}CHR' \rightleftharpoons RCH{=}\underset{BX_2}{CR'} + \underset{X}{RCHCH_2R'}} \qquad (19)$$

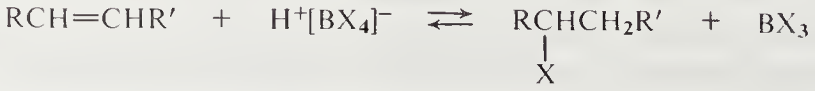


$$\mathrm{\underset{X}{RCH}{-}CH_2R' + BX_3 \rightleftharpoons [RCHCH_2R']^+[BX_4]^-} \qquad (20)$$

$$\mathrm{[RCHCH_2R']^+[BX_4]^- \longrightarrow \underset{BX_2}{RCHCH_2R} + X_2} \qquad (21)$$



$$\mathrm{\underset{X}{RCH}{-}\underset{BX_2}{CHR'} + BX_3 \rightleftharpoons RCH{=}\underset{BX_2}{CR'} + H^+[BX_4]^-} \qquad (22)$$



$$\mathrm{RCH{=}CHR' + H^+[BX_4]^- \rightleftharpoons \underset{X}{RCHCH_2R'} + BX_3} \qquad (23)$$

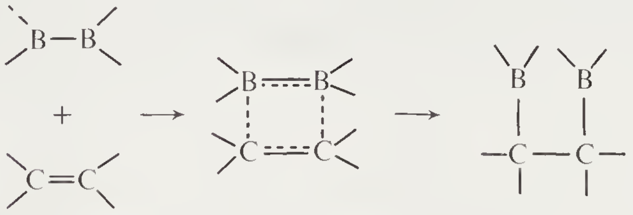
A detailed study[211] of the haloboration of alkynes has revealed several major differences between this reaction and the hydroboration reaction. For example, haloboration occurs with Markownikov addition and the stereochemistry is not always the same. In addition, as the alkyne basicity increases the rate of reaction increases and there is a reactivity dependence on the Lewis acidity of the haloborane.

5.1.2.5 Diboration

The term 'diboration' was coined[212] to describe the very interesting and characteristic reaction of the diboron tetrahalides, B_2X_4, in their facile addition across carbon–carbon double and triple bonds to yield vicinal bis(dihaloboryl) organic compounds (equations 24 and 25).[213] Although at least three different mechanisms of addition can be envisioned, stereochemical investigations strongly implicate a four-center transition state. With but one exception[214] it has been shown that *cis* addition occurs with both double and triple bonds.[215–217] Presumably the π-system of the organic moiety interacts with the two vacant boron p-orbitals, producing the postulated transition state and finally resulting in homolytic cleavage of the boron–boron bond (equation 26). Alkenes and alkynes react under relatively mild conditions. Substituents on the unsaturated carbon (*e.g.* alkyl, halogen, dichloroboryl) decrease the reactivity of the unsaturated molecule towards B_2Cl_4.[218–220]

$$R_2C{=}CR_2 \quad + \quad B_2X_4 \quad \longrightarrow \quad X_2BCR_2CR_2BX_2 \tag{24}$$

$$RC{\equiv}CR \quad + \quad B_2X_4 \quad \longrightarrow \quad RC(BX_2){=}C(BX_2)R \tag{25}$$



(26)

Cyclopropene is cleaved to give a 1,3 disubstituted propane, while vinyl chloride reacts with B_2Cl_4 to yield a triboryl molecule[221] according to Scheme 3. Cyclic unsaturated systems (*e.g.* cyclopropene,[222] cyclobutene[222] and cyclohexene[223]) all react readily with B_2X_4 molecules.

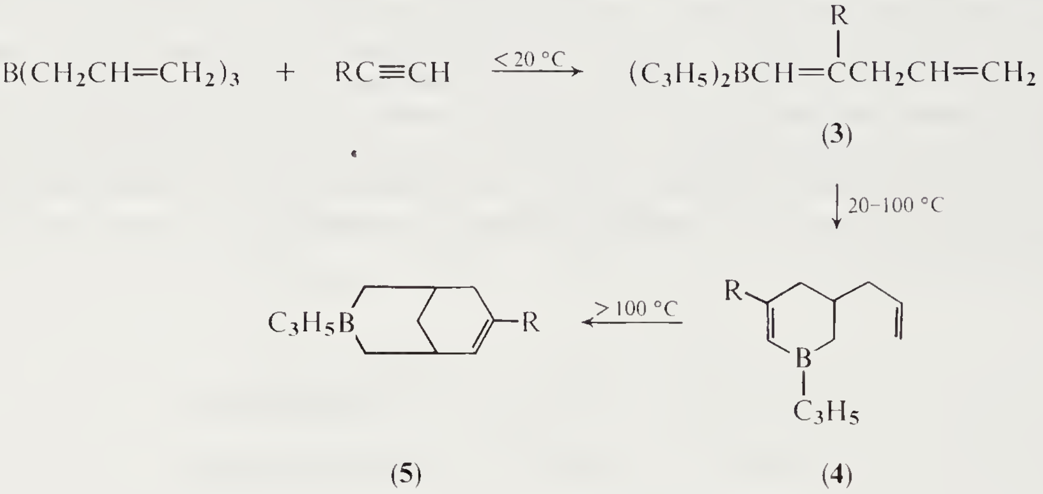
$$\begin{tikzcd}
H_2C{=}CHCl \quad + \quad B_2Cl_4 \arrow[r] & H_2C(BCl_2)CHClBCl_2 \arrow[d, "-BCl_3"] \\
Cl_2BCH_2CH(BCl_2)_2 & H_2C{=}CH(BCl_2) \arrow[l, "B_2Cl_4"']
\end{tikzcd}$$

Scheme 3

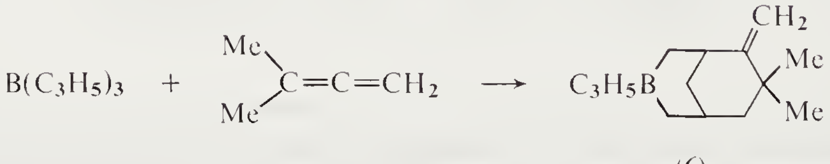
A significant limitation of the diboration reaction is the availability of B_2X_4 molecules. Diboron tetrachloride is not simple to prepare and B_2F_4 and B_2Br_4 are both normally prepared from the tetrachloride.[213] Thus until better preparative methods for these compounds become available, the diboration reaction will remain limited in scope.

5.1.2.6 Allylboration

In contrast to other classes of organoboranes, allylboranes are highly reactive, analogous to the more usual organometallic reagents.[107] Allylboranes react under mild conditions with nucleophilic reagents containing a labile hydrogen (*e.g.* H_2O, alcohols, thiols), with nitriles and with carbonyl compounds (aldehydes, ketones and quinones). Most important for our purposes here is that allylboranes react with various kinds of unsaturated organic compounds to yield new organoboranes through the formation of new B—C bonds. For example, triallylborane reacts with acetylene and substituted acetylenes (RC≡CH) in three consecutive steps (Scheme 4) to produce the substituted diallyl(penta-1,4-dien-1-yl)borane (**3**), 5-diallyl-1-boracyclohex-2-ene (**4**) and 3-allyl-3-borabicyclo[3.3.1]non-6-ene (**5**). Substituents on acetylene have included alkyl, alkenyl, phenyl, alkoxy, trimethylsilyl, trimethylsilylmethyl and chloromethyl.[107] Additionally, allylboration reactions with allenes yield allyl compounds of 3-borabicyclo[3.3.1]nonane.[224] For example, the reaction of triallylborane with 3-methylbuta-1,2-diene affords the compound (**6**) shown in equation (27).



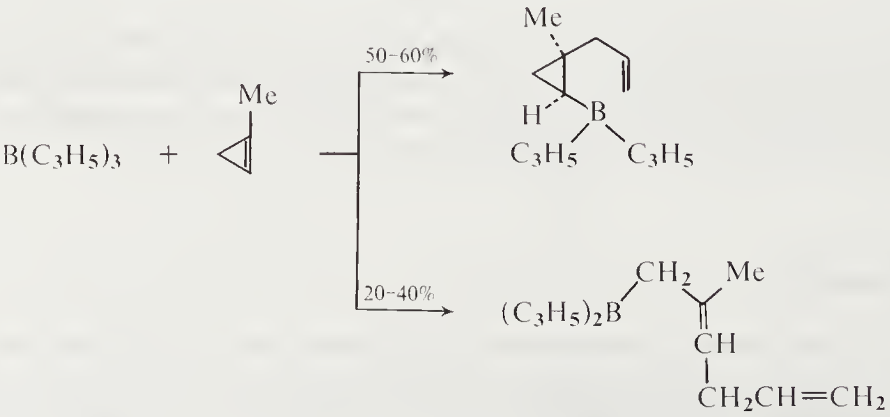
Scheme 4



(**6**)

(27)

Finally, triallylborane allylborates cyclopropenic molecules to give diallyl(hexa-2,5-dien-1-yl)boranes and borallylic cyclopropanes.[225] An example is shown in Scheme 5 of the allylboration of 1-methylcyclopropene.



Scheme 5

5.1.2.7 Friedel–Crafts Type

This reaction is useful in certain instances when it is necessary to introduce a boron-containing group on to an aromatic hydrocarbon to produce an arylborane (equation 28).[226–229] The reaction is catalyzed by Friedel–Crafts type catalysts and all of the boron trihalides can be used except BF_3. Diboron tetrachloride also reacts with benzene but not with polynuclear aromatics.[213] Major limitations of this reaction include potential problems with diboronation, which the organoborane may undergo in the presence of hydrogen halide,[226,230] and the fact that substituted benzenes may yield a mixture of products some of which involve rearrangement of substituents about the ring. Aryl iodides react with BI_3 to give the aryldiiodoborane with the $—BI_2$ group attached specifically where the iodine was placed originally.[231] However, traces of moisture and extended periods of heating can cause isomerization problems in this reaction.

$$\mathrm{ArH} + \mathrm{BX_3} \longrightarrow \mathrm{ArBX_2} + \mathrm{HX} \qquad (28)$$

A wide variety of cyclic heteroaromatic boron compounds have been prepared by this method.[232–238] but these will not be discussed in this chapter.

5.1.2.8 Redistribution and Exchange

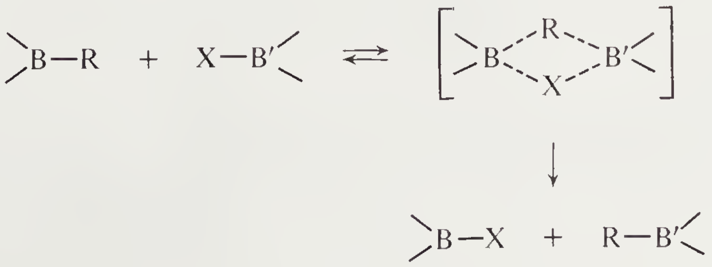
Redistribution and exchange reactions are extremely common in boron chemistry, particularly three-coordinate boron compounds, because of the availability of the empty p-orbital on boron. These reactions can be between two triorganylboranes (equation 29), between a triorganyl- and a trihalo-borane (equation 30) or from a disubstituted organoborane (equation 31). These types of reactions can be very useful in the preparation of organohaloboranes and other three-coordinate boron compounds which are partially substituted with organic compounds. However, these reactions can also work in opposition to the preparation of pure unsymmetrical organoboranes.

$$\mathrm{BR_3} + \mathrm{BR'_3} \rightleftharpoons \mathrm{R_2BR'} + \mathrm{RBR'_2} \qquad (29)$$

$$\mathrm{BR_3} + \mathrm{BX_3} \rightleftharpoons \mathrm{RBX_2} + \mathrm{R_2BX} \qquad (30)$$

$$2\mathrm{R_2BX} \rightleftharpoons \mathrm{BR_3} + \mathrm{RBX_2} \qquad (31)$$

Because this area has received so much attention from a large number of researchers, organoboron redistributions and exchanges have been critically reviewed.[6,7,191,239] In general the R group in these reactions can be alkyl, alkenyl or aryl and the X group can be a wide variety of substituents including H, alkyl, aryl, F, Cl, Br, I, NR_2, OR and SR.[6] As expected, this type of reaction is impeded or prevented by large, bulky groups bonded to boron,[240–242] by the presence of alkenyl[31,133,243,244] or phenyl[245] groups bound to boron and by the presence of boron–fluorine bonds.[246,247] As discussed earlier, alkenyl and phenyl groups have been shown by several studies to participate in boron–carbon π-bonding by means of the empty p-orbital on boron. Fluorine is also generally considered to be a good mesomeric 'back-bonder' to boron. Thus these redistribution reactions have been postulated to occur *via* a bridged transition state,[243,246–249] as shown in equation (32). Consistent with this postulate is the fact that an exchange reaction also appears to be slowed when the formation of an intramolecular dative bond can occur to render boron four-coordinate.[250,251] In addition, the relative rate of exchange of BR_3 molecules with alkoxyboranes is $R_2BOR' > RB(OR')_2 > B(OR')_3$ and B—O π-bonding has been postulated to account for this order.[6,252]



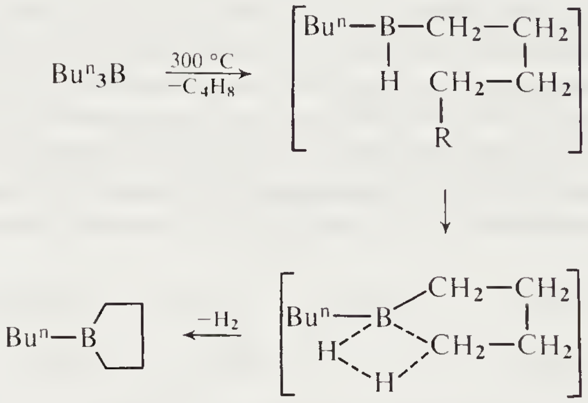
(32)

Further support for a bridged transition state comes from the fact that these reactions are catalyzed by >B—H compounds[248,253–255] and accelerated when the X group can easily participate in bridge bonding.[256] The catalytic effect of >B—H is easily explained since H is small, can readily form bridges and does not participate in back-bonding.

The disproportionation reaction shown in equation (31) is probably endothermic, *i.e.* enthalpy forms the mixed compound. However, experimentally the equilibrium can be pulled towards the $BR_3 + RBX_2$ molecules by continuous removal of the most volatile component of the equilibrium mixture.

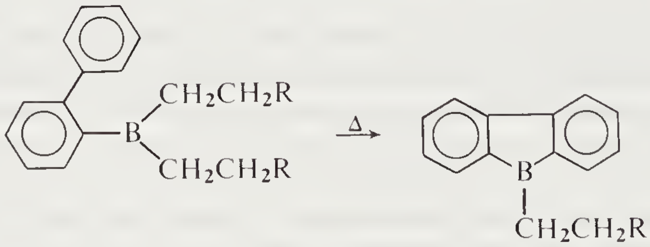
5.1.2.9 Thermal

Thermally induced reactions of organoboranes include redistribution reactions, cyclization reactions and isomerizations. Redistribution and exchange processes were discussed in Section 5.1.2.8 and cyclization reactions will be mentioned only briefly. At pyrolysis temperatures greater than approximately 200 °C, trialkylboranes can eliminate hydrogen and/or alkene to afford organoboron heterocycles. Five- and six-membered boron-containing rings appear to predominate and a four-center transition state has been proposed[257] in the mechanism of formation of the B—C bond (Scheme 6). Consistent with this postulated mechanism is the fact that if the BR_3 molecule is equilibrated prior to pyrolysis with diborane the intermediate >B—H species are formed and the reaction is facilitated.[260]

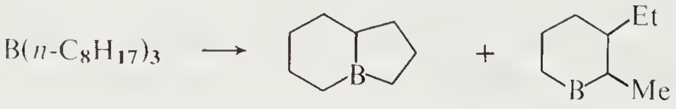


Scheme 6

Conditions which are not quite so harsh have been reported to cyclize aromatic organoboranes (equation 33).[261] Other typical examples of thermal cyclization reactions are shown in equations (34)-(36).[262–264]

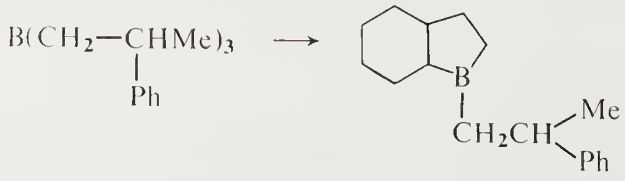


(33)



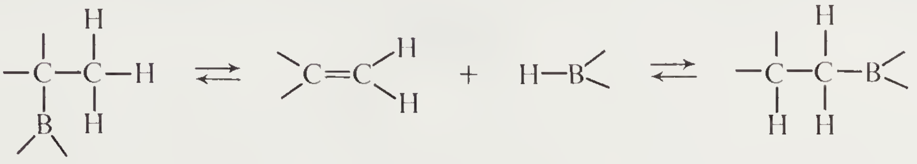
(34)

(35)



(36)

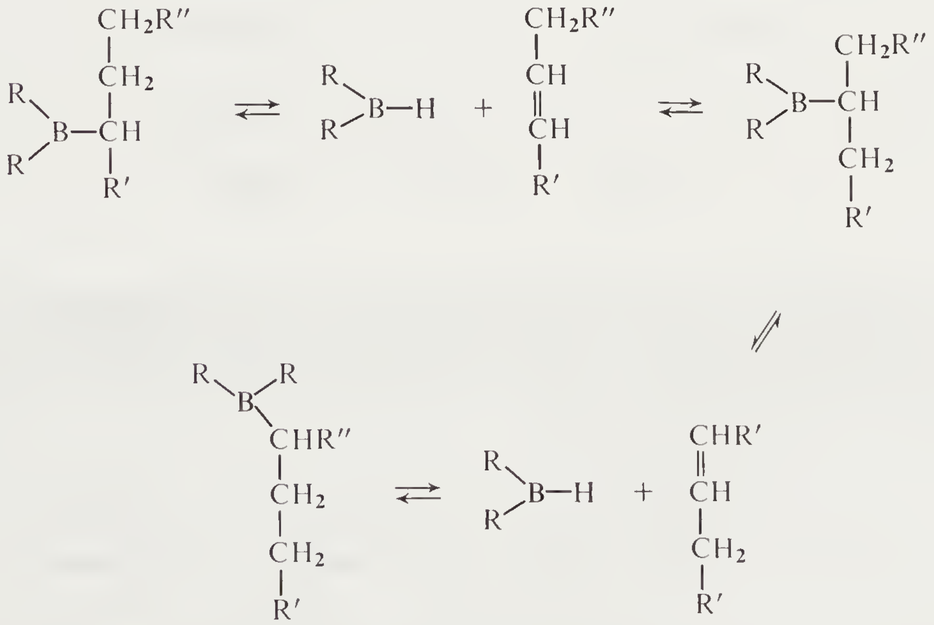
Isomerization or rearrangement reactions are very common in organoboron chemistry and are usually thermally induced. In this section, reactions in which the number of B—C bonds is equal to or greater than that of the reactant will be considered. Obviously isomerization reactions could also lead to cleavage of B—C bonds and this will be discussed in a later section. A considerable number of studies have been reported in this area and these kinds of reactions have been reviewed in several articles. The thermal rearrangement of saturated organoboranes (equation 37) has been reviewed[6,265] with regard to the synthetic utility of hydroboration. In addition, allylic[107] rearrangements of boron as well as a general survey[266] of rearrangements of unsaturated organoboron compounds have been treated.



(37)

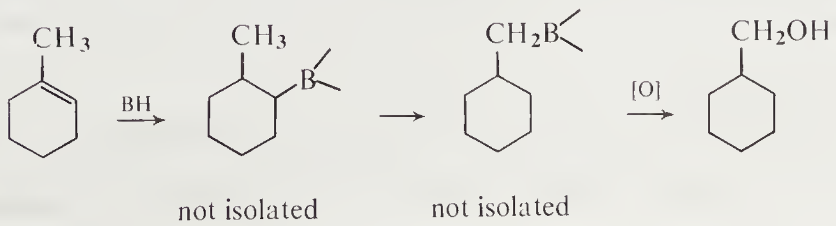
Organoborane isomerizations have been classified[7] into four types as follows: (1) branched-chain acyclic ⇄ straight-chain acyclic; (2) acyclic ⇄ cyclic; (3) ring contraction and expansion; (4) *cis* ⇄ *trans*. Alkylboranes isomerize above approximately 130 °C and $>$B—H bonds appear to catalyze these reactions. This point should be remembered during hydroboration reactions and heating should be avoided whenever possible. Tertiary alkylboranes isomerize especially easy, as shown in equation (38).[241] Data accumulated thus far suggest thermodynamic control of isomerization with steric effects is dominant, although other effects must also have a significant impact on these reactions. The mechanism certainly is some kind of reverse hydroboration–rehydroboration equilibrium (Scheme 7).[191] The reverse hydroboration step is probably the rate determining step and the postulated mechanism accounts for the observation that it is easier for a boron atom to move past a single alkyl branch than through a double branch and also accounts for the fact that an excess of alkene inhibits the reaction.[2,7] Isomerizations can also take place during transmetallation reactions and, as mentioned previously during hydroboration reactions, as shown in equations (39)[267,268] and (40).[269]

$$BBu^i_2Bu^t \longrightarrow BBu^i_3 \qquad (38)$$



Scheme 7

$$Bu^tMgBr + BF_3{\cdot}OEt_2 \longrightarrow BBu^i_3 + BBu^i_2Bu^t \qquad (39)$$



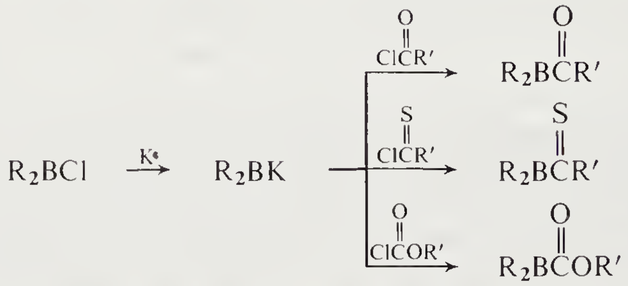
(40)

5.1.2.10 Miscellaneous

There are many other reactions which have been used to prepare organoboranes other than the general methods described in preceding sections and some of these will be shown here. The action of metals on boron halides and subsequent reactions with organic molecules can be used to form B—C bonds (Scheme 8). Examples of these reactions are shown in equations (41)–(43).[270,271,229]

$$R_2BX + 2M \longrightarrow R_2BM + MX \xrightarrow{R'X} R_2BR' + MX$$

Scheme 8


(41)

$$4(MeO)_2BCl + 8Li + CCl_4 \xrightarrow{THF} C[B(OMe)_2]_4 + 8LiCl \quad (42)$$

$$B(OR)_3 + 2Al + 3R'X \longrightarrow BR_3 + Al(OR)_3 + AlX_3 \quad (43)$$

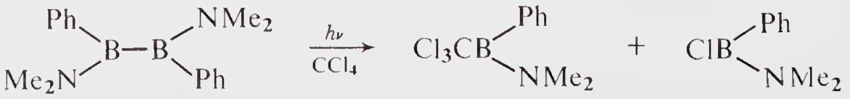
Organoboranes with perfluorinated saturated organic groups are not very common in organoboron chemistry, presumably because of the tendency of fluorine to migrate from carbon to boron. However, one method[272,273] which has been used to prepare these compounds uses an amine adduct of a diorganoboron potassium compound (equation 44). Equation (45) also demonstrates[272] the preparation of a trifluoromethylborane.

$$KBBu^n{}_2\cdot NEt_3 + CF_3I \longrightarrow CF_3BBu^n{}_2\cdot NEt_3 \quad (44)$$

$$CF_3BBu^n{}_2 \xleftarrow{HCl}$$

$$B_2H_6 + CF_3SCl \longrightarrow CF_3BF_2 \quad (45)$$

Photolysis reactions have been employed to some extent in other preparations of organoboranes. For example, photolysis of benzene and either BBr_3 or BI_3 yields the phenyldihaloborane $PhBX_2$.[274] The preparation of one of the few examples of a trichloromethyl organoborane also uses photolytic conditions (equation 46).[275]


(46)

In a more esoteric vein, the cocondensation of carbon vapor and BCl_3 or B_2Cl_4 yields dichloroboryl organic species (equations 47 and 48).[276] A similar reaction with Me_2NBH_2 and vaporized carbon yields Me_2NBHMe as the major product.[277] A cocondensation reaction involving BF (from elemental boron and BF_3)[278] and acetylene affords the $FB(CH{=}CHBF_2)_2$ molecule.[279]

$$BCl_3 + C(g) \xrightarrow{\text{cocondense}} Cl(BCl_2)C{=}C(BCl_2)Cl + (Cl_2B)_3CCl + (Cl_2B_2)CCl_2 \quad (47)$$

$$B_2Cl_4 + C(g) \xrightarrow{\text{cocondense}} C(BCl_2)_4 + (Cl_2B)_3CCl + (Cl_2B)_2CCl_2 \quad (48)$$

5.1.2.11 Conclusion

From the above discussion it is obvious that there are many, many ways to prepare three-coordinate non-cyclic organoboranes. The method of choice will depend on a number of factors, including the availability of starting materials, the experimental facilities which are available and the amounts of materials which are required. It is always dangerous to generalize but some attempt to discuss in a relatively comprehensive manner the best method for the preparation of various classes of organoboranes covered in the section should be made.

Symmetrical triorganylboranes, BR_3, are easily prepared and hydroboration and transmetallation should be the method of choice. There are two classes of non-cyclic unsymmetrical triorganylboranes, partially 'mixed' R_2BR' molecules and totally 'mixed' $BBR'R''$ molecules. Again hydroboration and transmetallation should be strongly considered but redistribution and/or rearrangement reactions could also be important methods for these molecules.

With some constraints, stepwise hydroboration offers an excellent route to the partially mixed molecules *via* 'RBH_2' or 'R_2BH' precursors. If the borane is available as RBX_2 or R_2BX, then reduction of these molecules in the presence of alkene should afford the desired product without redistribution. This can be used for mixed trialkylboranes, dialkylalkenylboranes and alkyldialkylboranes from hydroboration of alkynes[280] or, in some cases, allenes.[281,282] Exchange reactions could be used to prepare R_2BR' by using BR_3 and a large excess of BR'_3 if the latter is readily available in large quantity. The reaction of monoorgano- and diorgano-boranes, RBX_2 and R_2BX, with organometallic reagents R′M can be an excellent way to prepare alkylboranes, arylboranes, alkylallylboranes,[283] dialkylalkenylboranes[284] and dialkylcyclopentadienylboranes.[285] Alkoxy groups[286] and halogens appear to be the best X groups. Metals have included Na, Li, Mg[287] and Hg.[288] Redistribution represents a potential problem and can be avoided by rapid experimental work-up procedures.

Completely mixed organoboranes $BRR'R''$ can be difficult to prepare. At this time there is no general 'best' method for these molecules. Grignard reagents have been used,[289] as shown in equation (49) for the preparation of totally mixed triarylboranes, but yields are poor. Thexyldialkenylboranes and thexyldialkylboranes have been prepared[280,290] by stepwise hydroboration, but the reaction is not general. The preparation of these kinds of molecules certainly deserves further study.

$$XBRR' + R''M \longrightarrow BRR'R'' + MX \tag{49}$$

It has been suggested[191] that there are three principal approaches to the preparation of compounds of the type RBX_2: (1) double dealkylation of BR_3; (2) redistribution with BR_3 and BX_3; (3) direct synthesis of the one B—C bond. For alkylboron compounds, hydroboration is an appealing method but a major problem is halting the reaction at the monoalkyl stage. Alkyldichloroboranes are especially valuable as precursors for conversions to other molecules of the type RBX_2. Transmetallation is a possibility and reactions of Grignard reagents with $B(OR)_3$ molecules have been reported,[291] as have reactions of SnR_4 molecules with BCl_3.[204] Triethylaluminum and BX_3 molecules (not BF_3) appear to react[204] to give ethyldihaloboranes in good yield and this reaction should be tested for its generality. Monoalkenylboranes can be best prepared by hydroboration of alkynes[292,293] or from transmetallation with the corresponding tin compounds.[31,294] Monoarylboranes are probably best prepared by transmetallation with organolithium, Grignard[190] or tin reagents.[295] Friedel–Crafts type reactions should also be considered.

For diorganoboranes the three approaches listed for the monoorgano molecules should be considered. For two identical R groups, hydroboration to the dialkyl stage of transmetallation are probably the preferred routes. Again $AlEt_3$ reacts with BX_3 under the proper conditions[204] to give good yields of Et_2BX. For two different R groups, stepwise hydroboration does not provide a general route.[280,290] Transmetallation reactions using organolithium and Grignard reagents[190] with alkoxyboron compounds have been used but redistribution reactions can be a problem. Rearrangement reactions have also been used with some success.[290,296,297]

5.1.3 REACTIONS OF THREE-COORDINATED ORGANOBORANES

5.1.3.1 Transmetallation

Just as transmetallation can be an effective method for the preparation of organoboranes (Section 5.1.2.1), so can certain reactions of organoboranes be used to transfer an organic group to other metals. These types of reactions can readily be divided into metathesis reactions (equation 50) and the reaction of organoboranes with metal salts (equation 51).

$$>\!B{-}R \quad + \quad MR' \quad \longrightarrow \quad >\!B{-}R' \quad + \quad MR \qquad (50)$$

$$>\!B{-}R \quad + \quad MX \quad \longrightarrow \quad >\!B{-}X \quad + \quad MR \qquad (51)$$

Reactions of the metathesis type have been reported often using Grignard reagents,[242,298,299] diorganomagnesium reagents[300] and organoaluminum compounds.[301,302] Typical reactions are shown in equations (52)–(54).[303,304,301] It has been suggested[7] that these reactions probably involve a four-coordinate borane intermediate due to the formation of electron deficient organo-bridged dinuclear structures.

$$BPr^n_3 \quad + \quad BeEt_2 \quad \longrightarrow \quad BePr^n_2 \qquad (52)$$

$$BBu^n_3 \quad + \quad EtMgBr \quad \longrightarrow \quad MgBu^n_2 \qquad (53)$$

$$BEt_3 \quad + \quad AlBu^n_3 \quad \longrightarrow \quad AlEt_3 \qquad (54)$$

Reactions of organoboranes with metal salts are well known to give boron–carbon bond cleavage products.[305] Table 15 lists some metal salts whose reactions with organoboron compounds have been investigated. The most extensive investigations have been conducted with the reactions of organoboron compounds with Hg(II) salts to yield organomercurials. Arylmercury(II) salts are readily synthesized (equation 55) from the corresponding boronic acid and mercury(II) chloride,[306–308] mercury(II) bromide,[308,309] mercury(II) acetate[310] and mercury(II) hydroxide.[311] Symmetrical diarylmercurials are obtained ty the reaction of arylboronic acids with mercury(II) oxide,[311] arylmercury(II) nitrate[312] and arylmercury(II) perchlorate,[312] while asymmetrical organomercurials can be prepared in a similar manner (equation 56).[313]

$$ArB(OH)_2 \quad + \quad HgX_2 \quad \xrightarrow{H_2O} \quad ArHgX \quad + \quad B(OH)_3 \quad + \quad HX \qquad (55)$$

$$ArB(OH)_2 \quad + \quad RHgX \quad \longrightarrow \quad RHgAr \qquad (56)$$

Trialkylboranes react with $Hg(OAc)_2$ to form dialkylmercury compounds. It has been found[314] that the reactivity of various tri-*s*-alkylboranes towards mercury(II) benzoate decreases in the following order: cyclopentyl > cyclohexyl > cyclooctyl > *s*-butyl > norbornyl.

Stereochemical investigations have shown that the transfer of organic groups from boron to mercury can occur by either retention[314–316] or inversion of configuration,[317–319] while mechanistic studies favor boron–mercury exchange *via* electrophilic attack by mercury(II) cations.[308]

Salts of many other metals react with organoboranes and examples are listed in Table 15. Summaries of these reactions have also appeared.[7,305]

Amino derivatives of metals, while not strictly salts, are many times useful transmetallation reagents. For example, organoboranes do not react with $AlCl_3$ but tris(dimethylamino)alane reacts readily[320] (equation 57). Dimethylaminotrimethylstannane has also been used to prepare trimethylorganotin compounds.[321]

$$2BR_3 \quad + \quad Al(NMe_2)_3 \quad \longrightarrow \quad 2R_2BNMe_2 \quad + \quad R_2AlNMe_2 \qquad (57)$$

Table 15 Reactions of Organoboranes with Metal Salts

Metal Salt	*Organoborane*	*Ref.*
$HgCl_2$	$RB(OH)_2$	1–11
$HgCl_2$	$RB(OR')_2$	12–16
$HgCl_2$	R_2BOR'	17, 18
$HgCl_2$	BR_3	19, 20
$HgBr_2$	$RB(OH)_2$	21, 22
$Hg(OAc)_2$	$RB(OH)_2$	17, 22
$Hg(OAc)_2$	$RB(OR')_2$	23
$Hg(OAc)_2$	R_2BOR'	17, 18
$Hg(OAc)_2$	BR_3	20, 24, 25
$Hg(OH)_2$	$RB(OH)_2$	26
$Hg(OMe)_2$	BR_3	16
HgO	$RB(OH)_2$	26
$Hg(NO_3)_2$	$RB(OH)_2$	27
$Hg(ClO_4)_2$	$RB(OH)_2$	27
TlX_3 (X = halide)	$RB(OH)_2$	8, 9, 26, 28
$Ag(NH_3)_2^+$	$RB(OH)_2$	1, 2, 4, 5, 29–35
$AgOH$	BR_3	36
CuX_2 (X = halide)	$RB(OH)_2$	2, 4–6, 21
$Cu(OAc)_2$	$RB(OH)_2$	5, 37, 38
$CuSO_4$	$RB(OH)_2$	21
CuX_2 (X = halide)	BR_3	39
PbO	BR_3	20
$Pb(OAc)_4$	BR_3	40
$ZnCl_2$	$RB(OH)_2$	4–6, 21, 28, 30, 35
CdX_2 (X = halide)	$RB(OH)_2$	21, 28, 30, 35
$ZnCl_2$	BR_3	41
VCl_4	BR_3	42
$FeCl_2$	BR_3	43
$FeCl_3$	BR_3	40

1. A. Michaelis and P. Becker, *Ber.*, 1882, **15**, 180.
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6. A. N. Nesmeyanov, V. A. Sazonova, V. N. Drozd and L. A. Nikonova, *Proc. Acad. Sci. USSR* (*Engl. Transl.*), 1960, **131**, 369.
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19. G. Wittig, G. Keicher, A. Rueckert and P. Raff, *Liebigs Ann. Chem.*, 1949, **563**, 110.
20. J. B. Honeycutt, Jr. and J. M. Riddle, *J. Am. Chem. Soc.*, 1960, **82**, 3051.
21. A. D. Ainley and F. Challenger, *J. Chem. Soc.*, 1930, 2171.
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27. D. S. Matteson, J. O. Waldbillig and S. W. Peterson, *J. Am. Chem. Soc.*, 1964, **86**, 3781.
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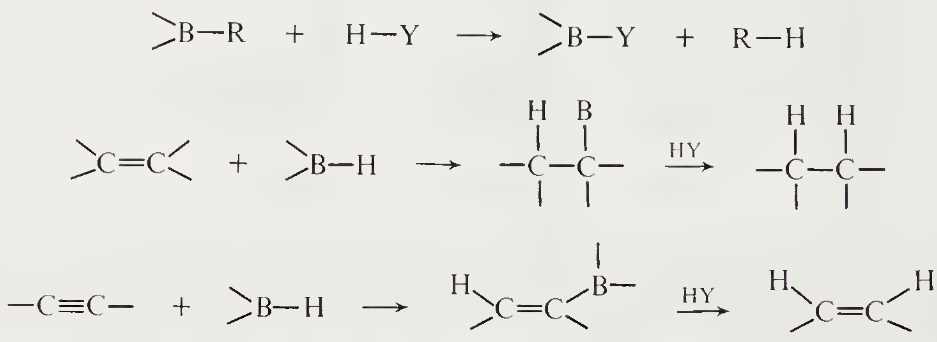
Finally, it should be mentioned that in a few cases organoboranes react directly with a metal to afford the organometallic reagent.[322]

5.1.3.2 Protodeboronation

Protodeboronation refers to a reaction in which the B—C bond is cleaved by a protic reagent HY (equation 58). Examples of protodeboronation reagents are shown in Table 16 and a recent reference is given. A more complete listing of reagents (*e.g.* those which lead to a cyclic boron compounds) and references can be found in refs. 6 and 7. A most important application of this reaction occurs in the synthesis of saturated hydrocarbons and *cis*-alkenes after the hydroboration of alkenes and alkynes, respectively (equations 59 and 60).



(58)

(59)

(60)

Table 16 Protodeboronation Reagents

Reagent	*Ref.*	*Reagent*	*Ref.*
H^+(aq.)	1	H_2S	10
H_2O	2	RSH	11
OH^-(aq.)	3	NH_3	12
HF	4	RNH_2 or R_2NH	13
HCl	5	N_2H_4	14
HBr	6	$RNHNH_2$	14
ROH	7	$RCONH_2$	15
OR^-	8	$Ph_3P{=}NH$	16
RCOOH	9	RSO_3H	17
		$ZnCl_2$(aq.)	18

1. B. F. Spielvogel, R. F. Bratton and C. G. Moreland, *J. Am. Chem. Soc.*, 1972, **94**, 8597.
2. H. C. Brown, E. Negishi and P. L. Burke, *J. Am. Chem. Soc.*, 1970, **92**, 6649.
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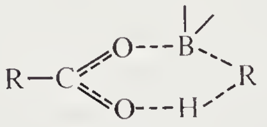
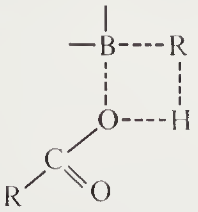
Inorganic acids, *e.g.* hydrohalic acids, do not seem to be as effective in protodeboronation as carboxylic acids and this has been attributed[7] to the ease with which a carboxylic acid could form a cyclic transition state such as (**7**) with the organoborane. Alternatively, a four-center transition state (**8**) can also account for observed experimental results.[225,323]



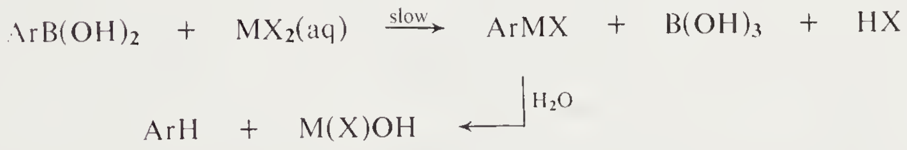
(**7**)



(**8**)

When carboxylic acids are used as protodeboronation reagents, the ease with which this occurs is $BR_3 > R'CO_2BR_2 > (R'CO_2)_2BR$. This, of course, would support a mechanism in which the initial step is a coordination between the borane Lewis acid and the organic acid acting as a Lewis base and would parallel the Lewis acidity of the boron atom.[324–326] In fact, stepwise cleavage of organoboranes can occur by stoichiometric control of the amount of HY, *i.e.* one can prepare R_2BY, RBY_2 or BY_3 from R_3B.[327,328]

Other factors which have been found to be important in these reactions are steric effects in which tertiary organic groups react more sluggishly than primary or secondary groups[329] and the fact that trimesitylborane is not nearly so reactive towards water as triphenyl- and trinaphthyl-borane.[330] Catalytic effects also seem to be important in that a large number of metals catalyze protodeboration of arylboronic acids[180,189,331] in which transmetallation (Section 5.1.3.1) is followed by hydrolysis (Scheme 9). Catalytic amounts of thiols have been shown to catalyze cleavage of the B—C bond with alcohols[332–334] and amines,[335] while peroxides appear to catalyze protodeboronation reactions with thiols.[336] Methoxide ion[271] and pivalic acid[337] are also catalysts in certain protodeboronation reactions.



Scheme 9

Finally it should be mentioned that there are several examples of thermally induced intramolecular protodeboronations, examples of which are shown in equations (61)–(63).[338,339]

$$Et_3BNH_3 \xrightarrow{450\ °C} \tfrac{1}{3}(EtBNH)_3 + 2C_2H_6 \tag{61}$$

$$PhB(OH)_2 \xrightarrow{200\ °C} HBO_2 + C_6H_6 \tag{62}$$

$$Ph_2BOH \xrightarrow{175\ °C} \tfrac{1}{3}(PhBO)_3 + C_6H_6 \tag{63}$$

5.1.3.3 Oxidation Reactions

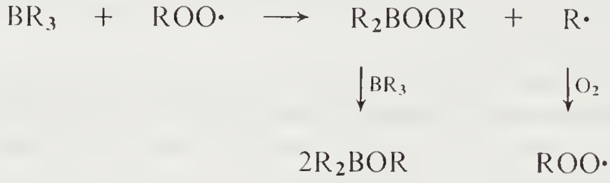
Oxidation reactions of organoboranes can be divided into three categories: (1) reactions with oxygen (autooxidation); (2) reactions with peroxides and related compounds; and (3) reactions with other oxidizing agents.

The autooxidation of organoboranes produces alkoxyboranes, and, in general, the reaction stops at the dialkoxyborane stage[330,340–347] (equation 64) but will, in the presence of solvent, proceed to the trialkoxyborane.[348] Subsequent treatment of the alkoxyborane with water affords alcohols and, in conjunction with hydroboration, alcohols can be synthesized readily from alkenes.

$$BR_3 + O_2 \longrightarrow RB(OR)_2 \tag{64}$$

Reactivity trends have been investigated extensively and it is clear that an empty boron *p*-orbital is required for oxidation as Lewis bases (*e.g.* amines and water) inhibit the reaction,[349] as do groups attached to boron which are capable *via* unshared electron pairs of mesomeric interaction with the empty boron orbital. Thus the following reactivity trends have been established in a number of studies:[244,350–353] $BR_3 > R_2BOR > RB(OR)_2$; $BR_3 > R_2BCl > RBCl_2$; $BR_3 > R_2BOH > RB(OH)_2$; alkylboranes > vinylboranes; $BMe_3 > 1,1\text{-}Me_2B_2H_4$ and $Me_4B_2H_2$.

The generally accepted mechanism of autooxidation involves a radical chain process[350,354] in which an alkylperoxy radical attacks boron to form a peroxide (or diperoxide) and an organic radical. The organic radical then reacts with oxygen, propagating the chain by formation of the alkylperoxy radical. The borane peroxide reacts with a second oxygen or undergoes an intermolecular reaction[355] to yield an alkoxyborane (Scheme 10). Consistent with this mechanism are experiments which demonstrate that radical scavengers[343,350,354] inhibit the reaction, radical generators initiate the reaction[342,356] and formation of the peroxyborane results in stereoisomeric organic groups losing their stereospecificity.[357] Further, an observed reactivity[350] of *t*-alkylborane > *s*-alkylborane > *n*-alkylborane > methylborane is rationalized on the basis of stabilizing effects on the alkyl radical in the transition state and the activated complex of the propagation step.

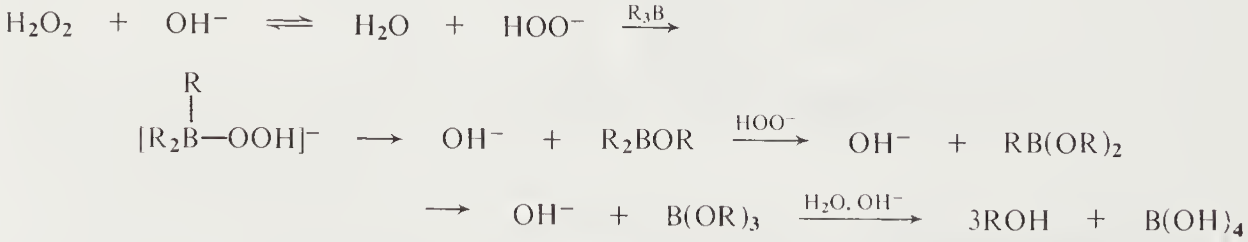


$$\begin{tikzcd} BR_3 + ROO\cdot \arrow[r] & R_2BOOR \arrow[d, "BR_3"] & + & R\cdot \arrow[d, "O_2"] \\ & 2R_2BOR & & ROO\cdot \end{tikzcd}$$

Scheme 10

Based on available data the initiation step is probably a R_2BO_2 complex and increased steric bulk of the organic groups bonded to boron increases the induction period.[358]

Alkaline hydrogen peroxide and related compounds also cleave the B—C bond and normally all B—C bonds in the organoborane react. Again, as in the reaction with oxygen, if the Lewis acidity of the boron is decreased by a bonded group possessing an unshared pair adjacent to the boron atom, the reactivity diminishes in the order $BR_3 > XBR_2 > X_2BR$ where X is halogen, OH or OR.[178] Peroxidation is frequently used in conjunction with hydroboration to produce alcohols from alkenes, aldehydes or ketones from vinylboranes and phenols from phenylboranes. In general the reaction is stereospecific, proceeding with retention of configuration.[359,360] The reaction appears to be very general and the mechanism is postulated[361–363] to be that shown in Scheme 11. Note that radicals do not appear to be involved. However, one study involving the use of Fenton's reagent (Fe^{2+}, H_2O_2) may involve radical reactions[364] and the formation of radicals has been proposed in the oxidation of BPh_3 with organic hydroperoxides.[365]



$$H_2O_2 + OH^- \rightleftharpoons H_2O + HOO^- \xrightarrow{R_3B}$$
$$[R_2\overset{\displaystyle R}{\overset{|}{B}}\text{—}OOH]^- \longrightarrow OH^- + R_2BOR \xrightarrow{HOO^-} OH^- + RB(OR)_2$$
$$\longrightarrow OH^- + B(OR)_3 \xrightarrow{H_2O,\ OH^-} 3ROH + B(OH)_4^-$$

Scheme 11

It should be noted that, in additon to alkaline conditions, acidic[366,367] and neutral conditions have also been utilized for the oxidation of organoboranes. However, under neutral conditions radical coupling normally occurs.[8]

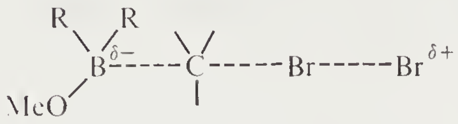
Other oxidative agents which have been employed in the oxidation of organoboranes are chromic acid,[368] elemental sulfur,[369] selenium,[370] *n*-butyl nitrite,[371] nitric oxide,[371] nitrosocyclohexane,[372] trimethylamine oxide,[182,183] anodic oxidation,[373,374] chromyl trichloroacetate,[375] trifluoroacetic acid[178,376] and a mixture of RuO_4, $NaIO_4$ and sodium acetate.[377]

5.1.3.4 Halodeboronation

Reaction of organoboranes with chlorine, bromine or iodine results in cleavage of the B—C bond to yield a haloboron compound and an organic halide (equation 65).[378–381] Two different mechanisms, one ionic and one radical, appear to be operable in these reactions.

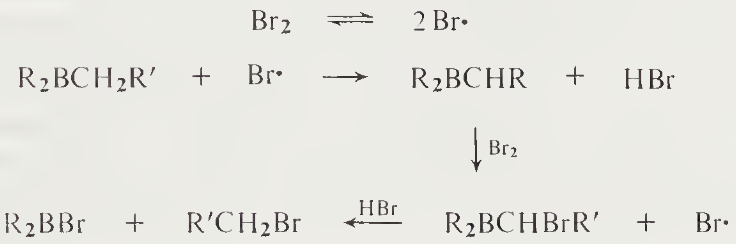

(65)

In the ionic reaction, nucleophiles (*e.g.* OH^- or OMe^-) are required and the reaction proceeds with stereochemical inversion.[382–384] The proposed transition state (**9**) explains this inversion. This reaction appears to occur mainly with the less reactive halogens.



(**9**)

The free radical reaction does not occur with iodine but with bromine and chlorine and the organoborane must contain at least one α-C—H bond. Hydrogen abstraction occurs and the proposed mechanism[385] is shown in Scheme 12.

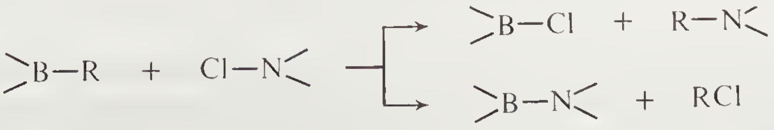


Scheme 12

Relative rates for halodeboronation are $Br_3 > XBR_2 > X_2BR$, where X = halogen, OH or OR.[178] Rate studies have been reported on the brominolysis of several arylboronic acids and the reactions are first order in both boronic acid and bromine. Further, the reactions display a positive salt effect, inhibition by acids, catalysis by bases and an aromatic electrophilic displacement mechanism is postulated.[386–388]

Related reactions should also be discussed in this section. First, the pseudohalogen $(SCN)_2$ reacts with organoboranes[389] as shown in equation (66). Similar reactions occur with KSCN[390] and KSeCN.[391,392] Second, related primarily by the fact that boron–halogen compounds are obtained by B—C bond cleavage is the reaction of *N*-chloroamines with alkylboranes.[393–395] Actually boron–nitrogen compounds have also been observed in this reaction (Scheme 13). The chloroborane is obtained when $ClNH_2$ is used in basic THF solution and apparently occurs by a polar 1,2-rearrangement.[395] The reaction to yield the aminoborane (as well as the chloroborane) can occur with *N*-chlorodialkylamines in chlorobenzene or isopentane and proceeds *via* a radical mechanism.[394] The radical reaction can be inhibited by addition of galvinoxyl.[394] Chlorophosphines react in a similar manner.[396]

$$BR_3 + (SCN)_2 \longrightarrow R_2BSCN + RSCN \qquad (66)$$



Scheme 13

5.1.3.5 Hydrogenolysis

The reaction of trialkyl- or triaryl-boranes with hydrogen requires conditions of heat and/or pressure and produces diborane or alkylboron hydrides (equation 67).[301,397,398] Metals, metal hydrides and tertiary amines have all been used as catalysts. Related reactions are shown in equations (68)–(70).[399,400]

$$BR_3 + H_2 \xrightarrow[\text{pressure}]{\text{heat}} \tfrac{1}{2}B_2H_6 + 3RH \qquad (67)$$

$$BR_3 + H_2 \xrightarrow[\text{discharge}]{\text{silent electric}} R_4B_2H_2 \qquad (68)$$

$$BEt_3 + 3H_2 + NEt_3 \xrightarrow{\Delta} H_3BNEt_3 + 3C_2H_6 \qquad (69)$$

$$2BR_3 + 7H_2 \xrightarrow{\text{alkali metal}} 2MBH_4 + 6RH \qquad (70)$$

5.1.3.6 Radical Reactions

Reactions of this type have previously been discussed in connection with oxidation reactions (Section 5.1.3.3) with oxygen and peroxides as well as halogenolysis reactions (Sections 5.1.3.4). In this connection it should be noted that trialkylboranes do not add to carbonyl groups of aldehydes and ketones in the same way as organolithium and organomagnesium reagents since they are much less reactive. However, organoboranes react rapidly with some α,β-unsaturated carbonyl compounds (*e.g.* acrolein[401] and methyl vinyl ketone[402]) to give a 1,4-addition reaction (equation 71). The organoborane products can then be hydrolyzed to produce aldehydes or ketones, thus providing an easy homologation route to a chain lengthening of three or more carbons. This reaction has been extended to a wide range of organic structures including acyclic, cyclic and bicyclic.[403] Mechanistic investigations have revealed the reaction involves organoborane free radicals and a catalytic amount of oxygen added in a controlled manner speeds up the reaction (Scheme 14).

$$BR_3 + H_2C{=}CH{-}CHO \xrightarrow[\text{THF}]{25\ ^\circ\text{C}} RCH_2CH{=}CH{-}OBR_2 \qquad (71)$$

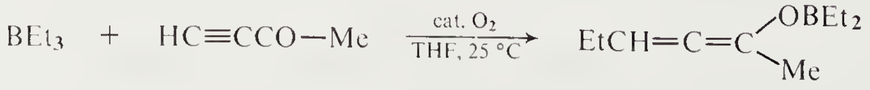
$$BR_3 + O_2 \longrightarrow R\cdot + R_2BO_2\cdot$$

$$R\cdot + H_2C{=}CH{-}CHO \longrightarrow RCH_2\dot{C}H{-}CHO \longleftrightarrow RCH_2CH{=}CHO\cdot$$

$$R\cdot + RCH_2CH{=}CHOBR_2 \xleftarrow{BR_3}$$

Scheme 14

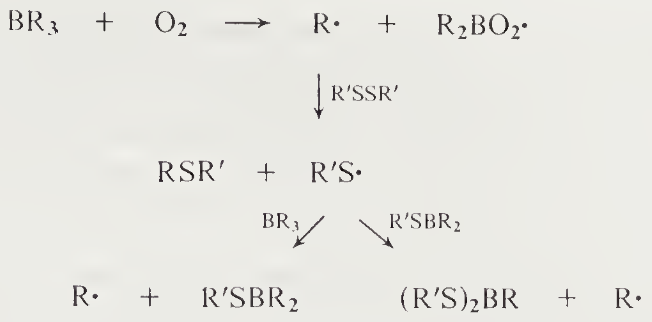
Compounds like acetylacetylene[404] (equation 72) and acrylonitrile (equation 73) react similarly and this area has been thoroughly investigated and critically reviewed.[403]



$$BEt_3 + HC{\equiv}CCO{-}Me \xrightarrow[\text{THF, 25 °C}]{\text{cat. }O_2} EtCH{=}C{=}C\begin{smallmatrix}\diagup OBEt_2\\ \diagdown Me\end{smallmatrix} \qquad (72)$$

$$BEt_3 + H_2C{=}CH{-}CN \longrightarrow Me(CH_2)_2{-}CH{=}C{=}N{-}BEt_2 \qquad (73)$$

In general, organoboranes react slowly or not at all with disulfides. However, addition of air or irradiation with UV light produces the organic sulfide in excellent yield.[405] The reaction is inhibited by iodine and is also thought to involve free radical reaction by initial production of an organoborane free radical and an organic free radical (Scheme 15).



Scheme 15

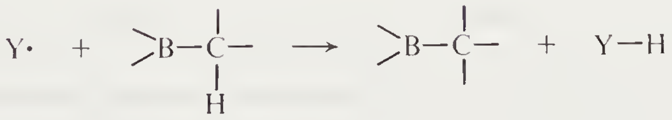
In terms of radical reactions in which the radical attacks the organoborane, there are essentially two types of processes which occur. The first, which is the reaction we have considered extensively in autooxidation, reactions with peroxides, reactions with the lower halogens and 1,4-addition reactions, is a reaction in which a free radical cleaves the B—C bond and produces an organic radical (equation 74). A reaction which has not been mentioned is the reaction with dimethylamino radicals,[394,406] *e.g.* equations (75) and (76). As mentioned earlier, factors which affect the rate of these reactions include steric effects (both the organoborane and the attacking radical), mesomeric effects (*i.e.* the availability of the boron empty orbital) and the stability of the radical which is cleaved from the borane.[350,407] These factors appear to be closely interrelated and relative contributions and their importance vary from reaction to reaction.

$$\mathrm{Y\cdot} + \mathrm{{>}B{-}R} \longrightarrow \mathrm{Y{-}B{<}} + \mathrm{R\cdot} \qquad (74)$$

$$\mathrm{Me_2N{-}N{=}N{-}NMe_2} \xrightarrow{h\nu} \mathrm{2Me_2N\cdot} + \mathrm{N_2} \qquad (75)$$

$$\mathrm{Me_2N\cdot} + \mathrm{BBu_3} \longrightarrow \mathrm{Bu_2BNMe_2} + \mathrm{Bu\cdot} \qquad (76)$$

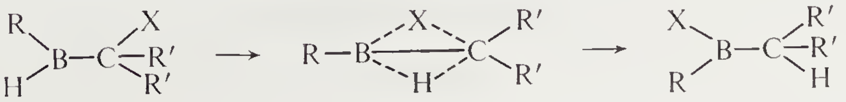
Bromine radicals attack the α-H of an organoborane instead of initially effecting B—C cleavage (equation 77).[408–410] Both reactions (equations 74 and 77) occur when organoboranes are attacked by methyl,[411–413] trifluoromethyl[411] and trichloromethyl[414,415] radicals. Pyridine adducts of diorganohaloboranes are apparently dehalogenated by alkali metals to form $R_2\dot{B}$—pyridine radicals[416,417] while γ-irradiation of trimethylborane and ammonia–trimethylborane produces the radicals $Me_2B{-}\dot{C}H_2$ and $H_3N(Me_2)B{-}\dot{C}H_2$, respectively.[418]



$$\mathrm{Y\cdot} + \mathrm{{>}B{-}\underset{H}{\overset{|}{C}}{-}} \longrightarrow \mathrm{{>}B{-}\underset{|}{\overset{|}{\dot{C}}}{-}} + \mathrm{Y{-}H} \qquad (77)$$

5.1.3.7 Migration Reactions

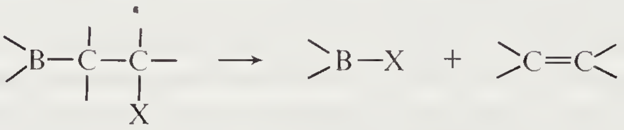
These reactions can be conveniently divided into reactions in which a halogen atom migrates from carbon to boron and a reaction in which a boron bonded organic group migrates to an adjacent atom which has a good leaving group attached to it. There are a large number of examples of the former reaction.[6] Organoboranes containing a halogen on the α-carbon are thought to proceed[419–421] *via* an intramolecular bridged intermediate shown in equation (78). Kinetic studies are also consistent with a bridged intermediate and intramolecular transfer.[421]



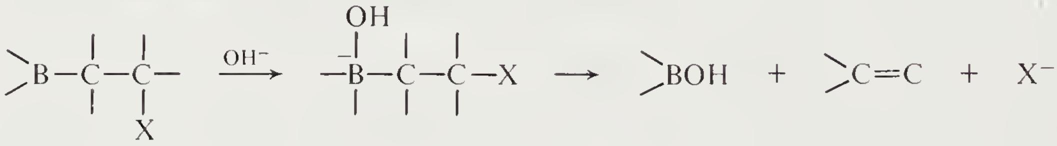
(78)

The difficulty in preparing various perfluoroorganoboranes, $R_FB\!<$, may be traced to the fact that they are unstable with respect to the corresponding $FB\!<$ compounds.[188,272,422–425] Support for this hypothesis comes from the stability of perfluorovinyl-[422,426] and perfluorophenyl-boranes[427] compared with perfluoroalkylboranes. The vinyl and phenyl compounds mesomerically interact with the empty boron *p*-orbital, inhibiting the formation of the bridged intermediate shown in equation (78), while no such interaction occurs with the alkyl compounds. Four-coordinate perfluoroorganoboranes are also quite stable, lending further support to the above hypothesis.

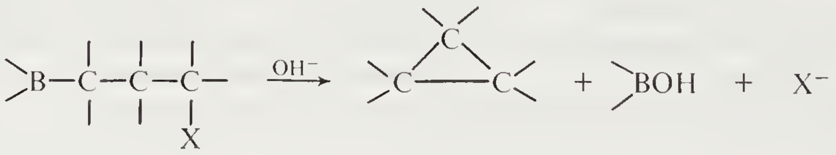
When a halogen atom is attached to the β-carbon of an organoborane, halogen transfer again occurs to the boron atom but an elimination reaction to liberate an alkene (or alkyne) also occurs (equation 79). This reaction is sometimes termed dehaloboronation and can be accomplished by pyrolysis *in vacuo* and in some cases by the use of a Lewis base to trap the haloborane (equation 80).[211,428] Hydroboration of vinyl chloride and 3-chlorocyclohexene presumably leads to unstable products because of subsequent dehaloboronation reactions,[429,430] and β-fluorine transfer has been found to occur in reactions of fluoroalkenes with several boranes.[188,424,425,431] In some cases a nucleophile is required to effect elimination and a haloborane is not formed (*e.g.* equation 81).[429,432,433]


(79)


(80)

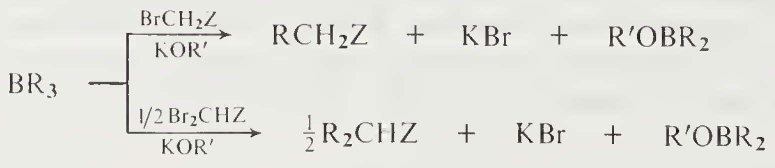

(81)

A halogen substituent on the γ-carbon in an organoborane will undergo a displacement under nucleophilic conditions to produce cyclopropanes (equation 82).[429,430,434–436]


(82)

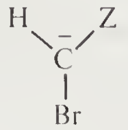
In the migration of a boron attached organic group to a neighboring atom, an intramolecular alkylation or arylation occurs providing a means in many instances of forming a new C—C bond. The borane portion of the molecule can then be cleaved, providing routes to longer organic chains. The alkyl or aryl rearrangement occurs with retention of configuration at the migrating carbon atom and the rearrangement is accelerated by a developing positive charge on the neighboring atom to which migration occurs, as well as by increasing negative charge on the boron atom.

Triorganoboranes react with halogenated organic compounds of the type shown in Scheme 16 to effect C—C bond formation.[437–440] Alkoxide is required in these reactions and the preferred base is 2,6-di-*t*-butylphenoxide.[437] The reaction is thought to proceed *via* an α-halo carbanion (**10**) generated by the base, which then attacks the organoborane followed by a rapid migration of the organic group. Rearrangement also occurs when triorganoboranes react with ylides,[441–443]



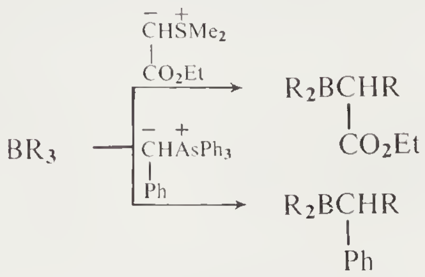
$Z = CO_2Et$, halogen, nitrile, COR, $CH{=}CHCO_2Et$

Scheme 16

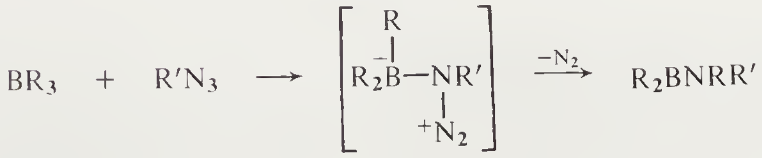


(10)

as illustrated in Scheme 17. An example of a migration other than to a carbon atom is provided by the reaction of organoboranes with organic azides to produce aminoboranes and subsequently, if desired, secondary amines (equation 83). Alkyldichloroboranes and dialkylchloroboranes react more rapidly than trialkylboranes, which is attributed to their greater Lewis acidity.[444–446] This entire area of migrations has been well summarized.[6]



Scheme 17



$$BR_3 + R'N_3 \longrightarrow \left[\begin{array}{c} R \\ R_2\overset{-}{B}\text{—}NR' \\ {}^{+}N_2 \end{array}\right] \xrightarrow{-N_2} R_2BNRR' \qquad (83)$$

5.1.3.8 Reaction with Alkali Metals

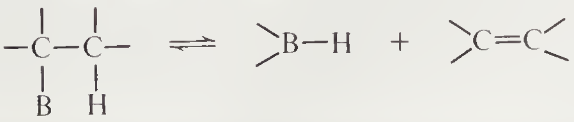
This reaction is exclusive for arylboron compounds and the products are one-electron reductions (equation 84).[330,447] Physical studies of these compounds indicate that a monomer–dimer equilibrium exists in these compounds which is dependent upon steric effects and solvent. Thus $NaBPh_3$ is dimeric and diamagnetic, sodium trimesitylborane and tri-β-methylnaphthylborane are monomeric and paramagnetic and sodium tri-α-naphthylborane is monomeric in THF but dimeric in diethyl ether.[417,448–450]

$$BAr_3 + M \rightleftharpoons MBAr_3 \qquad (84)$$

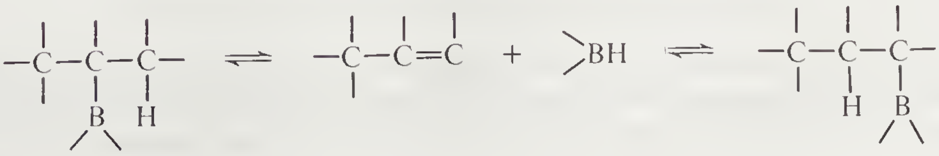
Although alkali metal is consumed when exposed to trialkylboranes, no reaction is evident and no ESR signals are observed.[450]

5.1.3.9 Dehydroboration

The dehydroboration reaction (equation 85) normally requires elevated temperatures and not only has direct dehydroboration been observed and studied[451–454] but the reaction almost certainly occurs in alkyl isomerization reactions (equation 86).[455–458] In the isomerization reaction the

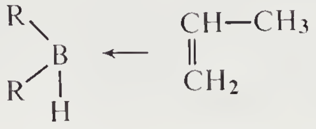


(85)

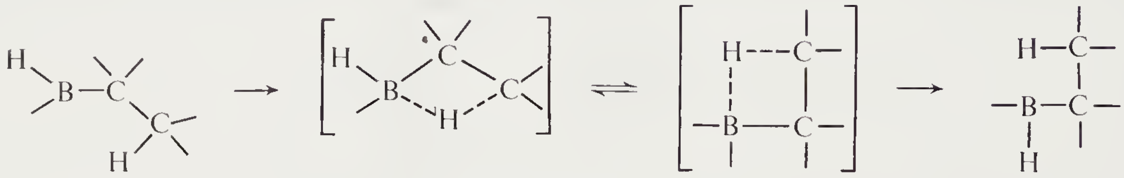


(86)

end product results from movement of the boron to the carbon which is least sterically hindered and is postulated to occur *via* the dehydroboration–hydroboration sequence shown in equation (86). Thorough studies of the thermal isomerization of propyl- and butyl-boranes indicate essentially complete dissociation of the alkyl group (as the alkene) in most cases.[459,460] However, for secondary triorganoboranes only partial dissociation and rotational inversion of a π-complex (**11**) is implied.[460] Several studies have reported that ethers and B—H compounds catalyze these isomerization reactions.[455,456,461] and an alternative mechanism which does not involve dehydroboration involves a bridged intermediate (Scheme 18).



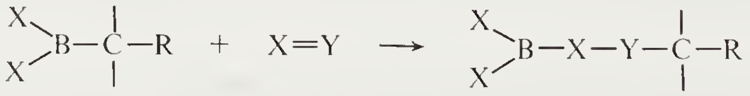
(**11**)



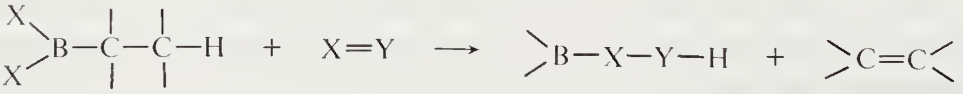
Scheme 18

5.1.3.10 Reactions with Unsaturated Molecules

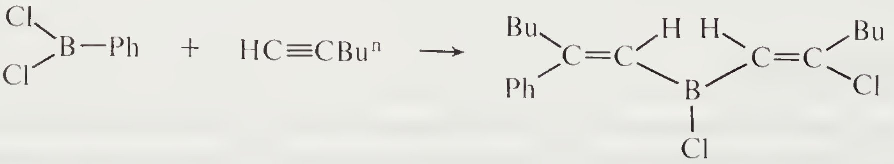
Boron–carbon bonds can be cleaved in many cases by reaction with compounds containing multiple bonds. These reactions can occur by insertion of the multiply bonded system to give an addition reaction (equation 87) or the multiply bonded system can insert and displace an alkene from the organoborane (equation 88). The addition reaction has already been discussed with regard to the 1,4-addition of an organoborane to an α,β-unsaturated carbonyl compound (Section 5.1.3.6) and this particular reaction will not be discussed further. There are a large number of examples of the addition reaction other than carbonyl compounds and the area has been reviewed.[6–8] The reaction also occurs with alkenes,[225,462,463] alkynes,[211,464,465] vinyl ethers,[466] nitriles,[467] isocyanate[468,469] and carbodiimide.[470] With alkynes, *cis* addition occurs[211] as demonstrated in equation (89).



$$X_2B-\overset{|}{\underset{|}{C}}-R \;+\; X{=}Y \longrightarrow X_2B-X-Y-\overset{|}{\underset{|}{C}}-R \qquad (87)$$



$$X_2B-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-H \;+\; X{=}Y \longrightarrow {>}B-X-Y-H \;+\; {>}C{=}C{<} \qquad (88)$$

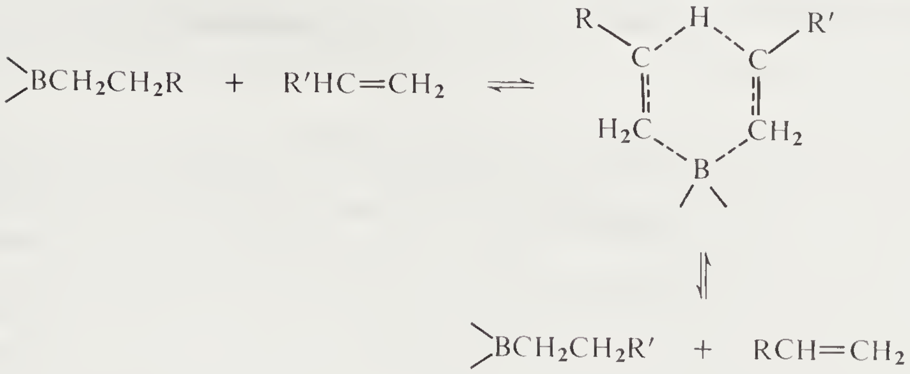


(89)

The displacement reaction (equation 88) has been carried out both in the presence of and absence of ether solvent.[455,471] The identity of the other substituents, X, on boron (equation 88) reportedly influences the ease with which an alkene is displaced and the following order has been established for the X group:

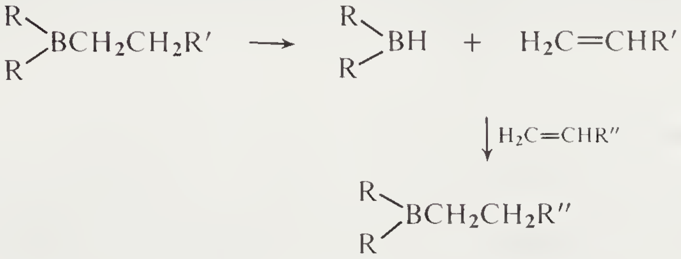
$$\mathrm{Bu^i} > \text{boracyclopentyl} > \mathrm{Br} > \mathrm{Cl} > \mathrm{SR} > \mathrm{OR} \approx \mathrm{NR_2}$$

Two different mechanisms have been postulated for the displacement reaction. One involves a cyclic six-membered transition state (Scheme 19) and is consistent with rate studies and isomer product distribution.[472,473] The second mechanism which has been advanced for displacement



Scheme 19

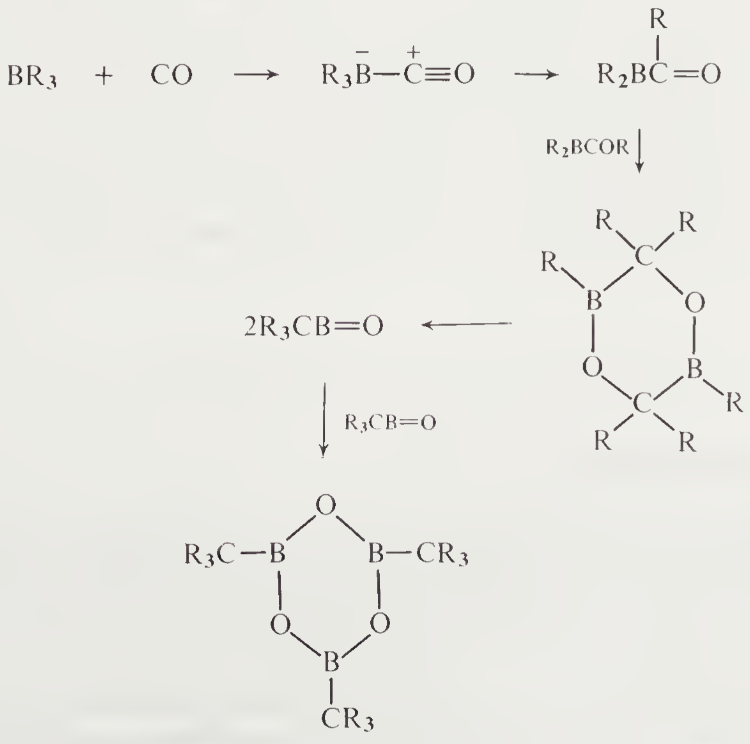
reactions (Scheme 20) involves a dehydroboration to produce a dialkylborane which then hydroborates the unsaturated substrate.[455,461]



Scheme 20

The 'carbonylation' reaction is also a reaction of organoboranes with an unsaturated system, carbon monoxide. This reaction has been reviewed in detail.[3,8,474,475] This reaction is a useful synthetic method for transferring more than one group from a single boron to a single carbon and as such has been extensively studied. However, it has given way in recent years to the cyanoborate reaction,[476] which is experimentally simpler.

The carbonylation reaction is catalyzed by borohydride ion in ether[477] and proceeds stereospecifically in that the organic group which migrates from boron to the CO carbon does so with retention of configuration.[478] Although it has not been studied in great detail, a mechanism which is consistent with experimental results[27] is that shown in Scheme 21. The mechanism is in the absence of any other added reagents. However, synthetic methods allow the carbonylation reaction in the presence of additional reagents to provide alcohols, aldehydes, ketones, borodioxolanes and cyclic esters of boronic acid.



Scheme 21

5.1.4 FOUR-COORDINATE NON-CYCLIC ORGANOBORANES

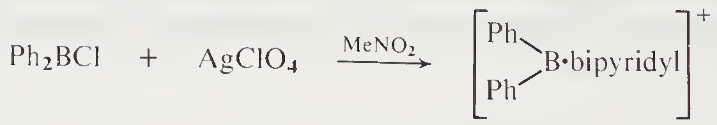
5.1.4.1 General Discussion

Four-coordinated organoboranes can be divided into three major categories: cationic, anionic and neutral Lewis acid–Lewis base adducts. The cationic compounds are the organoboronium ions which consist of one or two organic groups and two Lewis base molecules bonded to boron to form a molecule of the type $RR'BL_2$ where L is Lewis base. The anionic compounds are, of course, derivatives of the borohydride ion, BH_4^-, and have found extensive use in organic synthesis. The discussion of these compounds in this chapter will focus on the synthesis of these molecules and on some of their reactions, although most of their chemistry which is concerned with the synthesis of organic molecules will be covered in separate chapters (45.1–45.11). The Lewis acid–Lewis base adducts formed by organoboranes and Lewis bases having donor atoms from Groups VA and VIA are an extensively and widely studied class of molecules. Most of the compounds are boron–nitrogen, boron–phosphorus and boron–oxygen adducts, although arsenic, sulfur and selenium bases have also been used. Our discussion here will focus on the synthesis and properties of some of these molecules.

5.1.4.2 Organoboronium Ions

Boron cations are formed when there are less than three 'negative' groups bound to a boron(III) atom. Thus, possibilities of organoboron cations containing four-coordinate boron and having general formulae $R_2BL_2^+$ and RBL_3^{2+} are possible. In reality, boron cations have been most extensively studied[479–481] when boron is bonded to hydrogen (*i.e.* $BH_2L_2^+$) and the area of organoboron cations has not received much attention.

In general, compounds which have been prepared contain either two identical organic groups, $R_2BL_2^+$ (R = Me,[482] Pr,[483] Bu[484–486] phenyl,[483,487–491] cyclohexyl[492]), an organic group and a hydrogen, $R(H)BL_2^+$ (R = Me_3SiCH_2,[493] phenyl,[494,495] cyclohexyl[492,495]), or an organic group and a halogen, $R(X)BL_2^+$ (R = Me, X = Cl;[496] R = Me, X = Br;[496] R = Ph, X = Cl[497]). In almost all cases the Lewis bases are amines and include ammonia, trialkylamines, hydrazine, acetonitrile, pyridine and bipyridyl. Examples of the preparation of organoboronium ions are shown in equations (90)–(93).[488,490,492,482]



$$Ph_2BCl + AgClO_4 \xrightarrow{MeNO_2} [Ph_2B\cdot bipyridyl]^+ \qquad (90)$$

$$2Ph_2BCl + SnCl_4 \xrightarrow{EtNH_2} [Ph_2B(EtNH_2)_2]^+ \qquad (91)$$

$$2(cyclohexyl)_2BH\cdot pyridine + I_2 \xrightarrow{pyridine} 2[(cyclohexyl)_2B(pyridine)_2]^+ \qquad (92)$$

$$Me_2BH_2BMe_2 + 2NH_3 \longrightarrow [Me_2B(NH_3)_2]^+ \qquad (93)$$

5.1.4.3 Anionic Organoboranes

A large number of four-coordinate anionic complexes containing B—C bonds are known. At one time the most extensively studied anion was the tetraphenylboron anion, BPh_4^-, because of interest in the analytical applications of various tetraphenylboron salts.[498,499] However, more recent studies have concentrated on triorganoborohydride anions, BR_3H^-, because of their extensive synthetic utility in organic[500] and organometallic chemistry.[501]

In general these anionic molecules are synthesized from an anion and a three-coordinate borane. The boranes can range from a boron trihalide to a triorganoboron compound and the anion can be generated from a number of sources. One of the most effective methods seems to be analogous to the transmetallation reaction. Representative examples of the synthesis of anionic organoboranes are shown in equations (94)–(108).[502–516]

$$\mathrm{BMe_3 + LiH \xrightarrow{Et_2O,\ 0\ ^\circ C} LiMe_3BH} \qquad (94)$$

$$\mathrm{BEt_3 + NaH \longrightarrow NaEt_3BH} \qquad (95)$$

$$\mathrm{BBu_3 + MH \xrightarrow{THF} MBu_3BH} \qquad (96)$$

$$\mathrm{M = Li, Na}$$

$$\mathrm{2BMe_3 + LiH \xrightarrow{THF,\ 0\ ^\circ C} Li[Me_3BHBMe_3]} \qquad (97)$$

$$\mathrm{BR_3 + LiBu^t \xrightarrow{THF,\ -78\ ^\circ C} LiBu^t{}_3BH} \qquad (98)$$

$$\mathrm{BR_3 + Li(MeO)_3AlH \longrightarrow LiR_3BH + Al(OMe)_3} \qquad (99)$$

$$\mathrm{B_2H_6 + 2LiPh \longrightarrow 2LiPhBH_3} \qquad (100)$$

$$\mathrm{BR_3 + BH_4^- \longrightarrow R_3BHBH_3^-} \qquad (101)$$

$$\mathrm{B_2H_6 + MgR_2 \longrightarrow Mg(RBH_3)_2} \qquad (102)$$

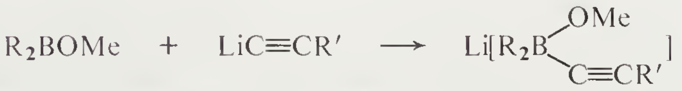
$$\mathrm{B_2H_6 + 2Ph_3P{=}CH_2 \longrightarrow 2Ph_3\overset{+}{P}CH_2BH_3^-} \qquad (103)$$

$$\mathrm{BF_3 + Me_3SnCF_3 \longrightarrow CF_3BF_3^-} \qquad (104)$$

$$\mathrm{BMe_3 + LiMe \longrightarrow LiBMe_4} \qquad (105)$$

$$\mathrm{BR_3 + LiC{\equiv}CH \longrightarrow Li[R_3BC{\equiv}CH]} \qquad (106)$$

$$\mathrm{BR_3 + LiCH{=}CH_2 \longrightarrow Li[R_3BCH{=}CH_2]} \qquad (107)$$



$$\mathrm{R_2BOMe + LiC{\equiv}CR' \longrightarrow Li\left[R_2B\begin{matrix}\diagup OMe\\ \diagdown C{\equiv}CR'\end{matrix}\right]} \qquad (108)$$

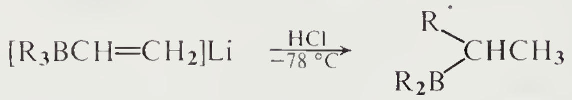
Only in the case of the reactions of trialkylboranes with alkali metal hydrides have systematic studies been conducted with regard to steric effects, solvent effects, *etc.* in the synthesis of anionic organoboranes. For example, the reaction in THF of LiH and NaH with trialkylboranes of varying steric requirements was examined and found to be strongly influenced by the steric requirements of the BR_3 molecule.[503] At 25 °C the order of reactivity with LiH was $BEt_3 > BBu^n_3 > BBu^i_3 \gg BBu^s_3$, whereas NaH was much more reactive. Highly hindered organoboranes [*e.g.* trisiamylborane and tris(*trans*-2-methylcyclopentyl)borane] were inert towards both hydrides even at 65 °C. A very general and quantitative route to a large number of lithium trialkylborohydrides is available through the reaction of $LiBu^t$ with trialkylboranes.[505] Even highly hindered organoboranes react and the formation of the products appears to be due to kinetic rather than thermodynamic factors. Solvent effects also appear to be important in the formation of alkali metal trialkylborohydrides.[502,504]

Many of the reactions of anionic organoboranes are used, as stated previously, in synthetic organic chemistry and these will be discussed only briefly in this chapter since they will be covered in detail in other chapters (45.1–45.11). The reactions of these molecules can be classified into several major groups, including reactions in which the molecule serves as a hydride source, reactions with protic sources, exchange reactions, migration reactions and oxidative reactions.

In reactions where anionic organoboranes function as hydride sources the trialkylborohydrides are the most extensively investigated. These molecules are well established as potent hydride donors towards a variety of organic electrophiles in serving as chemo-, regio- and stereo-selective reducing agents,[517–522] as reagents in new carbon–carbon bond forming reactions,[523,524] as reagents in the synthesis of transition metal carbonyl compounds[525–532] and in other synthetic transformations.[533,534] These areas have been reviewed.[500,507,517]

It might be expected that tetracoordinate anionic organoboranes would add H^+ to form a molecular HBR_4 species. However, only one instance of this has been reported,[535] $HB(C{\equiv}CH)_4$, and the structure of this molecule is unknown. Lithium ethynyl- and ethenyl-trialkylborates react with concentrated HCl (equations 109 and 110) at low temperature to produce the Markownikov tricoordinate alkenyl and alkyl-borane[515] with regiochemistry opposite from that which is obtained from hydroboration of terminal alkynes[536] or alkenes.[2,3,5]

(109)



(110)

Triethylborohydride is hydrolyzed selectively at the B—H bond to yield BEt_3,[537] while hydrolysis of BR_4^- ions with 20% acetic acid rapidly produces an alkane followed by hydrolysis of the organoborane at a slower rate.[538] The tetraphenylborate anion is decomposed in strong acid to $B(OH)_3$[539] or Ph_2BOH.[540,541] At elevated temperatures an alkylammonium ion can furnish a proton to effect B—C bond cleavage in BPh_4^- to produce an amineborane which loses a second molecule of benzene to give an aminoborane.[542]

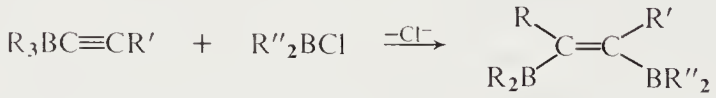
In reactions analogous to transmetallation and exchange reactions among tricoordinate boranes, anionic four-coordinate organoborohydride molecules will also exchange organic groups. Representative examples are shown in equations (111)–(113).[543–545]

$$BPh_4^- + RHgCl \longrightarrow RHgBPh_4 \longrightarrow BPh_3 + RHgPh \quad (111)$$

$$2BEt_4^- + HgCl_2 \longrightarrow 2BEt_3 + Et_2Hg \quad (112)$$

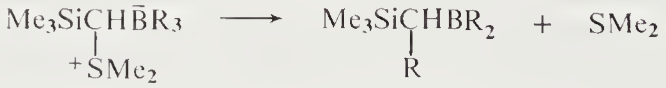
$$BPh_4^- + 2PhBI_2 \longrightarrow 3Ph_2BI \quad (113)$$

In the discussion of migration reactions of three-coordinate organoboranes (Section 5.1.3.7), it was pointed out that migration was enhanced by a build-up of negative charge on the boron atom. Four-coordinate anionic organoboranes should be expected to undergo the same type of reaction with the formal negative charge promoting migration. Examples of such reactions are shown in equations (114)–(116).[546–548]



(114)

$$3Ph_3\overset{+}{P}CH_2BR_3^- \xrightarrow{\Delta} B(CH_2R)_3 + 2Ph_3PBR_3 + PPh_3 \quad (115)$$



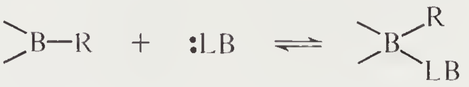
(116)

$$\underset{^+SMe_2}{Me_3Si\underset{|}{C}H\bar{B}R_3} \longrightarrow \underset{R}{Me_3Si\underset{|}{C}HBR_2} + SMe_2 \quad (116)$$

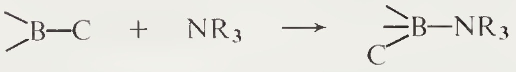
Oxidation studies of four-coordinate anions have centered mainly on tetraarylborate salts. Iron(III) ion oxidizes BPh_4^- to biphenyl,[549] as does hexachloroiridate(IV), $IrCl_6^{2-}$.[550] Electrochemical oxidation of BPh_4^- also yields biphenyl as well as Ph_2BOH.[551] Photochemically, BPh_4^- decomposes in the absence of oxygen to yield Ph_2BOH and phenylcyclohexadienes, while biphenyl is produced as well when oxygen is present.[552,553]

5.1.4.4 Organoborane Lewis Acid–Lewis Base Adducts

The propensity of trivalent boron to share electrons with suitable donor molecules in order to complete its octet and thus produce the most favorable electronic configuration has led to an extremely large and varied class of borane adducts. Lewis bases from Groups VA and VIA react with tricoordinate boron compounds in a 1 : 1 manner to produce compounds which have tetrahedral (or nearly so) geometry about the boron atom. When the borane is a strong acceptor and the base is a strong donor, then the reaction in equation (117) goes to completion and a stable adduct is formed. Of course, in many cases an adduct is not stable and an equilibrium is established or the adduct is completely dissociated depending upon acid and base strength, conditions of stoichiometry, temperature and pressure. It is very difficult to generalize concerning relative acid strengths of organoboranes since their acceptor strengths may vary depending upon the Lewis base. However, it has been stated[6] that a general trend for BY_3 molecules which form adducts with simple bases shows an acceptor strength for Y as follows: $I > Br > Cl > H > CF_3 > C_6F_5 > F >$ aryl $>$ alkyl $>$ OR.[102,134,272,554–562] An examination of these groups and the studies which have been conducted concerning adduct stabilities demonstrate that the major factors which determine borane acceptor strengths must be (1) inductive effects of Y, (2) mesomeric effects of Y, (3) steric effects of Y and (4) reorganization energy of the borane. Properties of the Lewis base which influence the stability of an adduct are primarily steric and electronic.[3]


(117)

The elements of Group VA (N, P) have been the most extensively studied donor atoms in organoborane Lewis base adducts. In trimethyl-Group III molecules it has been determined[563–565] that Lewis acidity towards amines decreases in the order $Me_3Al > Me_3Ga > Me_3In > Me_3B > Me_3Tl$. Such a vast number of amine–organoborane adducts have been prepared that no attempt will be made here to list them. Tables cataloging these compounds and some of their properties can be found elsewhere.[554,566–568] In addition, an extensive listing of ^{11}B and ^{14}N chemical shifts of amine–boranes (mono-, di- and tri-organo) has appeared.[81] The great majority of these compounds can be prepared by simple mixing of the amine and organoborane in the absence or presence of solvent (equation 118). However, other methods have been employed and they have been outlined elsewhere.[568] Examples of these methods are shown in equations (119)–(123).[569–572,562,573]


(118)

$$Li[MeBH_3] + [Me_3NH]Cl \xrightarrow{Et_2O} H_2(Me)BNMe_3 \tag{119}$$

$$(—BR—O—)_3 + 3NR'_3 \xrightarrow{LiAlH_4,\ Et_2O} 3H_2(R)BNR'_3 \tag{120}$$

$$H_3BNH_3 + Pb(C_2H_3)_4 \longrightarrow H_2(C_2H_3)BNH_3 + HPb(C_2H_3)_3 \tag{121}$$

$$B_2H_2Me_4 + 2NMe_3 \longrightarrow 2H(Me)_2BNMe_3 \tag{122}$$

$$HOBAr_2 + Me_2NH \xrightarrow{LiAlH_4} H(Ar)_2BNMe_2H \tag{123}$$

Since such a large number of amine–organoboranes have been synthesized, their chemistry has been more extensively studied than any other class of organoborane–Lewis base adducts. Most of these studies have involved displacements or exchange reactions, although one of the most important reactions of amine–organoboranes is their pyrolysis to form organoaminoboranes (equation 124).

$$R_3NBR'_3 \xrightarrow{\Delta} R_2NBR'_2 + R—R' \tag{124}$$

Most exchange reactions probably proceed by a dissociative mechanism. For example, in the exchange between Me_3BNMe_3 and BMe_3 and Me_3BNMe_3 and NMe_3, careful concentration dependence studies and a determination of energies and entropies of activation determined that a dissociative mechanism is involved.[574] Similarly, the reaction between Me_3BPMe_3 and PMe_3 in toluene proceeds by the same type mechanism.[575] The ylide (**12**) is able to displace amines from organoboranes (equation 125) with a qualitative order of reactivity of *t*-butyl > s-butyl > methyl.[511] Organothioboranes can be prepared[576,577] from trimethylamine–alkylboranes as shown in equation (126). Acids or heat will free triarylboranes from their amine complexes (equation 127).[578] Finally, kinetic studies have been reported for the hydrolysis of pyridine–diphenylborane[579] and the hydrolysis of arylborane–amine adducts.[579,580]

$$\underset{(\mathbf{12})}{Ph_3P{=}CH_2} + H_2(R)BNMe_3 \xrightarrow[80\ ^\circ C]{C_6H_6} Ph_3\overset{+}{P}CH_2\overset{-}{B}H_2R + NMe_3 \qquad (125)$$

$$RH_2BNMe_3 + 2R'SH \longrightarrow RB(SR')_2 + NMe_3 + H_2 \qquad (126)$$

$$Ar_3BNR_3 + HCl \longrightarrow BAr_3 + [NR_3H]Cl \qquad (127)$$

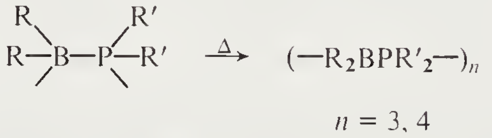
Phosphine–organoborane adducts are generally synthesized by mixing the phosphine and organoborane at low temperature in the presence or absence of a solvent. Surprisingly, relatively few phosphine–organoborane complexes have been prepared and completely characterized. A complete lising of compounds can be found elsewhere,[581,582] as can their ^{11}B chemical shifts.[81] In general, phosphine–organoboranes are not as stable as phosphine–BH_3 complexes. Trimethylborane does not form an adduct with PH_3 or $MePH_2$ in the vapor phase, while Me_2PHBMe_3 is 92% dissociated in the vapor phase at 39 °C.[102] Trimethylphosphine does form a stable adduct with BMe_3 which is not 100% dissociated in the vapor phase until 125 °C.[583] The following order of basicities of phosphines towards BMe_3 has been determined:[583]

$$EtMe_2P > Me_3P > C_2H_3PMe_2 \gg Et_3P > (C_2H_3)_3P$$

Using BEt_3 as a reference acid it has been established that the following basicities hold:[584]

$$Me_3P > Me_3N$$
$$Me_2PNMe_2 > MeP(NMe_2)_2 > P(NMe_2)_3;$$

The most important reactions of phosphine–organoboranes is their smooth pyrolysis to yield cyclic phosphinoboranes (equation 128).[581]



(128)

Although arsinoorganoboranes have been reported, there does not appear to be any reference to arsine–organoboranes in the literature.

Organoborane adducts with Group VIA donors have been studied much less extensively than their Group VA counterparts. This can certainly be attributed, in part, to the weaker basicity of oxygen, sulfur and selenium molecules. Table 17 is a listing of some oxygen adducts with organoboranes.

Table 17 Organoborane Adducts with Oxygen Lewis Bases

Compound	*Ref.*
$Me_3B{\cdot}OMe_2$	8
$(PhC{\equiv}C)_3B{\cdot}THF$	6
$Ph_2BCl{\cdot}OR_2$	7
$PhBCl_2{\cdot}OEt_2$	4
$Ph_2BBr{\cdot}OEt_2$	1
$(\alpha\text{-naphthyl})_2BCl{\cdot}OR_2$	7
$PhB(\alpha\text{-naphthyl})Cl{\cdot}OR_2$	7
$PhB(p\text{-Tol})Cl{\cdot}OR_2$	7
$ClCH_2CH_2BCl_2{\cdot}OMe_2$	5
$FcBCl_2{\cdot}OR_2$	3
$Et_3B{\cdot}O{=}CHNMe_2$	2

1. C. S. Cundy and H. Nöth, *J. Organomet. Chem.*, 1971, **30**, 135.
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An examination of the literature reveals that just as much work has been reported concerning organoborane–sulfur adducts as organoborane–oxygen adducts. However, many of these adducts are not very stable. For example, BR_3 molecules react with H_2S and thiols, R′SH, to form not the adducts $R_3B{\cdot}SHR$ but instead R_2BSH or R_2BSR'.[582] Dimethyl sulfide and BMe_3 form a solid adduct at −78 °C which is fully dissociated at 20 °C.[585] Triphenylborane forms stable adducts with Me_2S and Pr^i_2S which are prepared[586] from sulfonium salts as shown in equation (129). Table 18 lists some sulfide–organoborane complexes which have been reported.

$$(Me_2SBr)^+Br^- \quad + \quad NaBPh_4 \quad \longrightarrow \quad Ph_3BSMe_2 \quad + \quad PhBr \qquad (129)$$

Table 18 Sulfide–Organoborane Adducts[1]

Adduct	*Melting point*
$PhBCl_2{\cdot}SMe_2$	37–38
$MeBBr_2{\cdot}SMe_2$	72–74
$PhBBr_2{\cdot}SMe_2$	liquid
$MeBI_2{\cdot}SMe_2$	39–41
$BuBI_2{\cdot}SMe_2$	27–29
$PhBI_2{\cdot}SMe_2$	93–94
$MeC_6H_4BI_2{\cdot}SMe_2$	138–140
$PhBI_2{\cdot}SEt_2$	65–67
$PhBI_2{\cdot}SPr_2$	30–32
$PhBI_2{\cdot}SBu_2$	−39 to −41
$Me_2BBr{\cdot}SMe_2$	28–29
$Me_2BI{\cdot}SMe_2$	34–36
$Ph_2BI{\cdot}SMe_2$	106–107

1. All data are taken from W. Siebert and F. Riegel, *Chem. Ber.*, 1975, **108**, 724, and M. Schmidt and F. R. Rittig, *Chem. Ber.*, 1970, **103**, 3343.

A relatively small number of selenide–organoborane adducts have been prepared. Dimethyl selenide reacts with dimethylhaloboranes and methyldihaloboranes to form stable 1 : 1 adducts which are colorless to yellow solids.[582,587] Diphenyl selenide reacts only with $MeBI_2$ to form an adduct.[587] Table 19 lists adducts which have been reported for selenides with organoboranes. It should also be mentioned that, analogous to the sulfur case, stoichiometric quantities of BMe_3 and Me_2Se react at −78 °C to form a colorless solid which at 25 °C is completely dissociated.[585]

Table 19 Selenide–Organoborane Adducts[1]

Adduct	*Melting point*
$Me_2BBr{\cdot}SeMe_2$	21–22
$Me_2BI{\cdot}SeMe_2$	26–27
$MeBBr_2{\cdot}SeMe_2$	73–75
$MeBI_2{\cdot}SeMe_2$	47–49
$Ph_2BI{\cdot}SeMe_2$	79–81
$PhBI_2{\cdot}SeMe_2$	84–86
$MeBI_2{\cdot}SePh_2$	51–52

1. All data taken from W. Siebert and F. Riegel, *Chem. Ber.*, 1975, **108**, 724.

Finally, borane carbonyl, H_3BCO, should be mentioned as a molecule containing a boron–carbon bond and four-coordinate boron. The molecule can be prepared from B_2H_6 and CO at elevated pressures[588] or from boroxine, $H_3B_3O_3$, and CO.[589] Borane carbonyl will decompose at ambient temperature and equilibrium is attained at 100 °C.[588,590] In an interesting reaction[591] the B—H bonds in BH_3CO add to C_2H_4, as shown in equation (130).

$$H_3BCO \quad + \quad 3C_2H_4 \quad \longrightarrow \quad BEt_3 \quad + \quad CO \qquad (130)$$

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5.2

Boron in Ring Systems

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5.2.1 INTRODUCTION

5.2.1.1 Historical Perspective and Scope

Although organoboranes have been known for over a century,[1] the possibility of incorporating boron into ring systems has only developed since the chemical nature of its hydrides was first systematically investigated by Stock.[2] The first report of a boron–carbon heterocycle was relatively recent,[3] although since then the field has expanded dramatically.

Cyclic derivatives of boron have been observed in systems comprising boron bonded to saturated carbon atoms, in which the boron atom (or atoms) is in its group coordination of three, with a formally vacant *p*-orbital. The chemical properties and reactivities of such systems are related to the availability of the vacant orbital, which is governed primarily by steric factors. The normally low activation energy pathway to attack at boron by nucleophilic species results in properties similar to non-cyclic organoboranes; however, incorporation of boron into a ring system often results in increased stability towards isomerization over the non-cyclic analogues. The boron in such rings is also able to act as a Lewis acid, and acquire an extra pair of electrons from suitable neutral or anionic Lewis bases to form ring complexes in which the boron reaches its coordination saturation of four. These complexes have chemical properties and stability which reflect the resultant poorer availability of low activation energy pathways to chemical attack.

Early in the development of cyclic boron compounds the possibility of interaction of the vacant 2*p*-orbital of boron with π-systems and thus the formation of a more delocalized π-system was realized. The formation of cyclic systems in which one or more alkenes were directly bonded to boron, and extension of π-involvement to aromatic and antiaromatic systems, has been a fruitful area of interest. The properties of such systems are related to the probable aromatic or antiaromatic nature. For example, borole derivatives have proved to be extremely reactive, whereas the borabenzene anion is relatively stable and gives rise to metal complexes analogous to benzene.

The isoelectronic and isoorbital relationship of a BN unit with a CC unit has also been a fruitful concept in the design of ring systems. Much effort has been expended on studying BN analogues of many organic cyclic systems, and there are many heterocycles in which BN bonds form integral components of rings. The BN bonding may take the form of the formal coordinate two-electron bond, N→B, analogous to the isoelectronic C—C single bond, and thus give rise to saturated rings. Many examples will be found in this chapter of such interaction, although the structures have been presented in such a way as to avoid the electron-origin formalism, and bonding has been indicated by a simple covalent N—B bond. The bonding may also take the form of a σ,π interaction of the type $N\rightleftharpoons B$, analogous to the C═C double bond. Since the extent of π-interaction in such

NB systems in many instances is still speculative, structures of heterocycles involving such bonds have mostly been presented in the form $>$N—B$<$ unless there is evidence to suggest that extensive p_π–p_π interaction occurs.

A number of heterocycles have been described in which boron interacts with other potential π-donor atoms, for example O, S or P. In common with N, rings may be formed in which the boron bonds to one or two other heteroatoms and these may be the same or different atoms. These atoms may also occur in the ring in positions not adjacent to the boron atom. There are also a number of heterocycles which contain heteroatoms which do not interact with the boron through π-bonding, for example Si and Sn; these may bond directly to the boron, or may be elsewhere in the ring. Rings containing heteroatoms other than boron will normally have organic functional groups attached to the boron or the other heteroatoms, or both.

5.2.1.2 Preparative Methods for Rings in which Boron is Bonded to Carbon Atoms Only

Rings derived from carbon and boron only have been prepared by a number of general methods: (a) elimination of metal salt from a difunctional organometallic species, such as a dilithio reagent, di-Grignard reagent or organotin compound, with a boron derivative of the type RBX_2; (b) hydroboration of a di- or poly-alkene; (c) thermal rearrangement, elimination or pyrolytic methods involving alkene–BH equilibria in organoboranes; (d) co-condensation of transient species such as BF with alkynes; (e) boron insertion into an η-ring of an organometallic compound, and subsequent displacement of the new boron ring by a stronger ligand; (f) ring closure in aromatic or unsaturated systems by elimination of small, thermodynamically stable molecules such as HCl; (g) cyclization of alkenes or alkynes with allylboranes. Similar methods may also be used to form heterocycles containing other heteroatoms in positions non-adjacent to the boron atom.

5.2.1.3 Preparative Methods for Rings in which Boron is Bonded to Other Heteroatoms

The methods for preparing derivatives in which one or more other heteroatoms are bonded to boron in heterocyclic systems include: (a) hydroboration; (b) nucleophilic displacement of an electronegative functional group (e.g. —Cl, —OR, $>$S, $>$NR) attached to boron of an organoborane derivative; these reactions often involve protolysis of the functional group, and the elimination of the HX moiety; (c) donor–acceptor bond formation; (d) Friedel–Crafts cyclic dehydrohalogenation; (e) elimination of thermodynamically stable small molecules, for example R_3SiCl from $R_3SiNR'_2$ and a boron halide derivative; (f) insertion of an unsaturated species into a B—R bond; (g) elimination of metal halide from elemento-metal derivatives and boron halide derivatives; (h) cyclic polymerization, or cyclic addition of unsaturated intermediates such as boron imines.

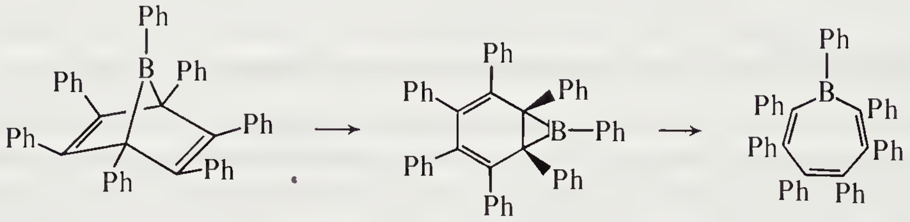
5.2.1.4 Literature Reviews

Various aspects of the chemistry of boron in ring systems have been reviewed previously either as specific reviews devoted to ring systems or in a more general area of boron chemistry, and it is appropriate to summarize these at this stage. Probably the most comprehensive compilation is that in Gmelin's Boron supplement (1954), the Boron Compounds parts 1, 3, 4, 5, 13 and 17 (1974–1978), and Boron in Biology, Medicine and Pharmacy (1980).[4] A number of books on boron chemistry contain relevant chapters,[5–18] and reference will be made to these where appropriate. In addition, numerous review articles of the early literature on various aspects have appeared in review journals,[19–39] and reference will also be made to these where pertinent. Cyclic compounds appear as part of an overview of organoboron chemistry, and reviews in this field should also be consulted.[40–54] Summaries of data on the NMR of boron compounds contain references to many boron heterocycles, and are valuable sources of data.[55–57] More recent reviews of relevant organoborane chemistry include allylboron compounds,[58,59] organoborane chemistry,[60,61] organoborane heterocycles *via* cyclic hydroboration,[62,63] organometallic benzo heterocycles,[64] aromatic boron-containing heterocycles,[65] the borabenzene anion and its metal complexes,[66] 1,3-diaza-2-boracycloalkanes,[67] boraaza aromatic compounds,[68] triple layered complexes with boron heterocycles as ligands,[69] borazines,[70] and the synthesis of diamond-like systems using allylboranes.[71]

5.2.2 RINGS INVOLVING BORON IN SUBSTITUTED CYCLOALKANES (C—B—C RINGS)

5.2.2.1 Classification

The rings may be classified as single-ring compounds according to ring size, as polycyclic compounds with boron involved in one ring or with boron as a bridgehead atom, and as ring compounds containing other heteroatoms not directly bonded to boron. The smallest saturated ring that is observed as a stable entity is the subsituted cyclopentane, although a three-membered ring has been proposed as an intermediate in the rearrangement process (1).[72] A mass spectrometric 'identification' of a three-membered ring has also been reported.[275]



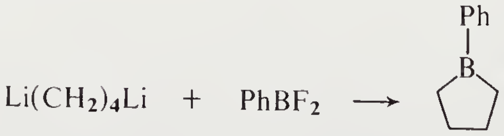
(1)

There has been no indication of a four-membered ring even from rearrangement reactions, although addition of methylborylene to an alkene gives a possible compound.[275]

5.2.2.2 Borolane (Boracyclopentane) and its Derivatives

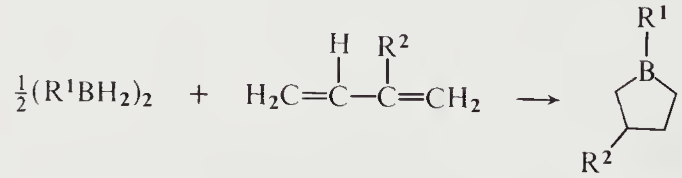
The earliest report[3] of an organoboron heterocycle was the phenyl-substituted compound (**1**), obtained from a bismetallo intermediate. Di-Grignard reagents have also been used to synthesize analogous compounds.[5b]

Derivatives of the borolane ring have been synthesized by hydroboration of dienes,[63] although some of the early studies led to erroneous conclusions. Thus substituted diboranes $(RBH_2)_2$ or their amine adducts react with buta-1,3-diene or its substituted derivatives to form (**1**) and its substituted analogues,[5] as in equation (3). By this method, compounds (**1**), (**2**), (**3**) and (**4**) have been reported.[5,63]



(**1**)

(2)



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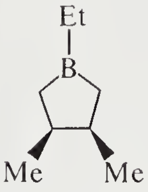
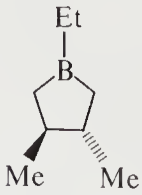
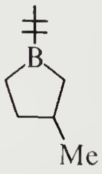


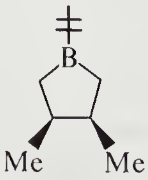
(**2a**)



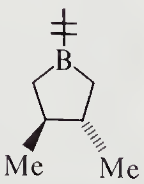
(**2b**)



(**3**)

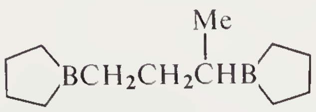


(**4a**)

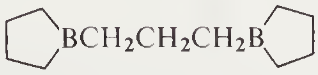


(**4b**)

Considerable work has been expended on the hydroboration of dienes with diborane, borane in ether solutions, or substituted boranes. The products depend on the molecular ratio of the reagents and also on the thermal history of the reaction mixture, since rearrangement processes are extremely facile; furthermore, regioselectivity of the hydroboration steps by partly alkylated borane intermediates can also influence the observed products.[63] Thus the stoichiometric hydroboration of buta-1,3-diene by $BH_3{\cdot}THF$ at 0 °C produces 70:30 of the dumbbell organoboranes (**5**) and (**6**).

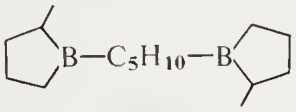


(5)

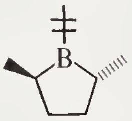


(6)

Hydroboration of penta-1,4-diene can lead to the substituted ring system (**7**) through B—H induced isomerization, and higher dienes behave similarly to give, for example, (**8**). Pyrolysis of BR_3, hydroboration in the presence of AlR_3 or BR_3 through catalysed alkyl exchange and displacement reactions between dienes and boron trialkyls all result in 1-alkylborolanes (see refs. 5 and 63 for a detailed discussion).



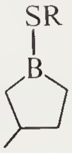
(7)



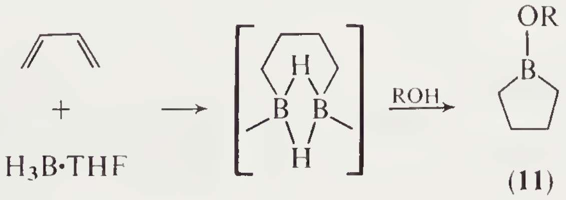
(**8**)

Compounds with functional substituents at boron may be obtained by hydroboration of butadiene or isoprene, *e.g.* with $ClBH_2{\cdot}Et_2O$ to yield (**9**)[63] or with $(RSBH_2)_x$ to yield (**10**).[73] Reactions of intermediate bridged partial hydroboration products with alcohols lead to *B*-alkoxy substituted derivatives (**11**).[63] Reactions on these derivatives can then lead to a variety of boron-substituted borolanes (equations 5–14).[59,63,74–80]

(**9**)

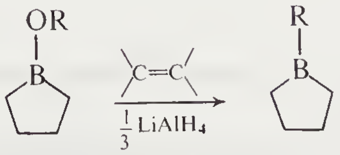


(**10**)



(**11**)

(4)



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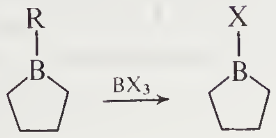

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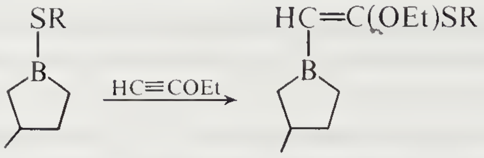
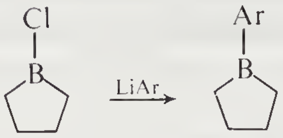


(7)



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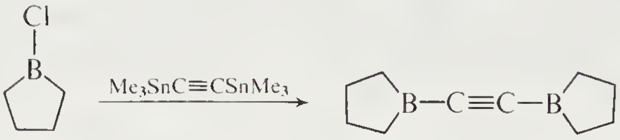

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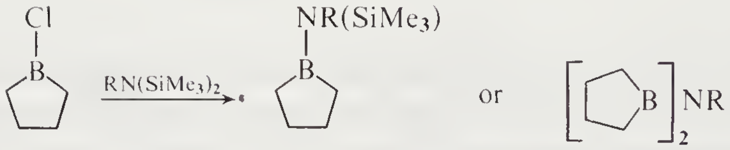

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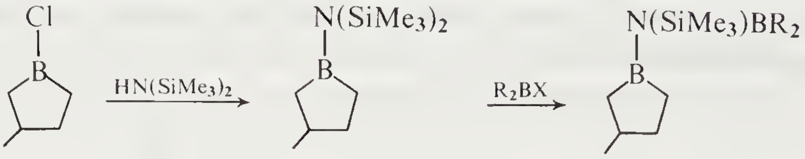

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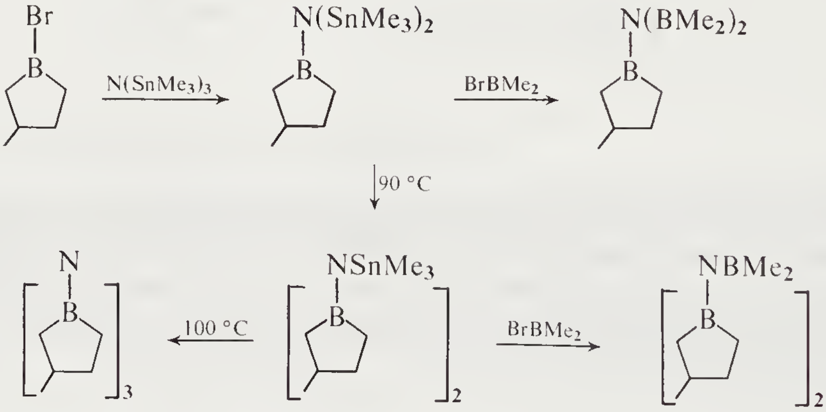

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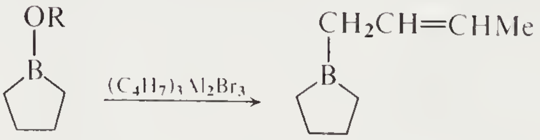
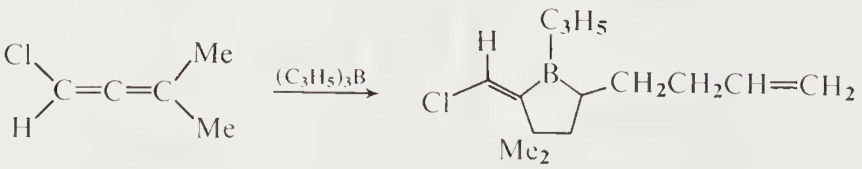


(14)

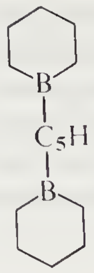
The reaction of triallylborane with 1-chloro-3-methylbuta-1,2-diene also results in a five-membered ring (equation 15).[59]



(15)

5.2.2.3 Borinane (Boracyclohexane), Borepane (Boracycloheptane) and their Derivatives

Hydroboration of penta-1,4-diene and hexa-1,5-diene with borane–THF also produces dumbbell molecules of structures (**7**), (**12**), (**13**) and (**14**), although the proportion of polymeric products is higher than with buta-1,3-diene. Hydroboration of 2,5-dimethylhexa-1,5-diene with ethyldiborane gave *cis* and *trans* isomers, (**15**) and (**16**), and these isomerize to five-membered rings on heating.[5]



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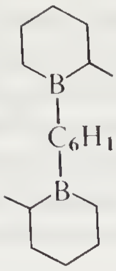

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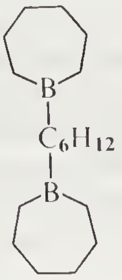

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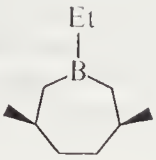

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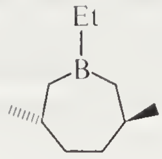
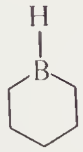
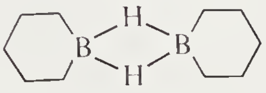


(16)

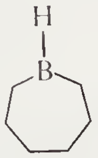
The *exo* boron–alkyl bond in the six- and seven-membered ring compounds is cleaved with $BH_3 \cdot THF$ more easily than in the borolane ring system to give compounds of the type (**17**) and (**18**) as dimers. The stability of these compounds is higher than that of the borolane.[63] An alternative route to the six-membered ring system has been described by the ring expansion shown in equation (16).[81]



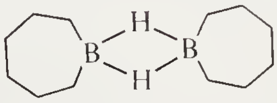
(17a)



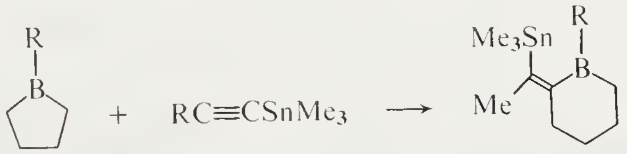
(17b)



(18a)



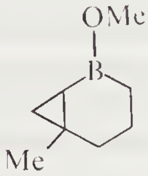
(18b)



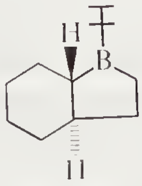
(16)

5.2.2.4 Polycyclic Compounds with Non-bridgehead Boron Atoms

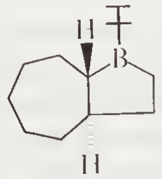
The six-membered ring derivative (**19**) has been reported[82] from 1-methylcyclopropene and triallylborane, *via* hydroboration of an intermediate in the presence of methylborate.[59] The highly hindered 1,1,2-trimethylpropylborane reacted with a series of dienes to give (**20**)–(**25**) in a completely stereoselective manner.[63]



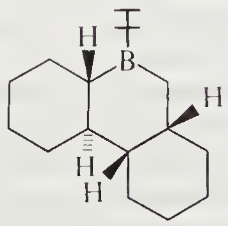
(19)



(20)



(21)



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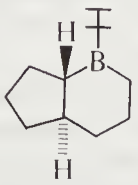
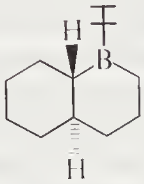
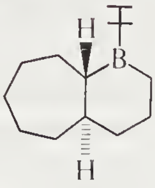


(23)

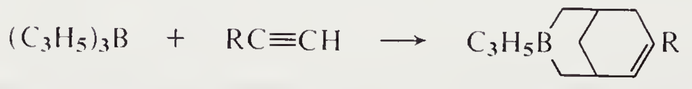


(24)



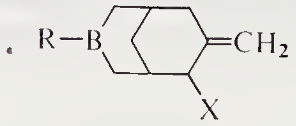
(25)

Interaction of triallylborane with substituted acetylenes or allene at elevated temperatures (130–180 °C) yields 7-substituted 3-allyl-3-borabicyclo[3.3.1]non-6-enes (**26**). Tris(2-methylallyl)borane reacts in a similar manner. Some of the products are subject to rearrangement reactions at elevated temperatures, *e.g.* propargyl chloride and propargyl bromide, from which derivatives of the type (**27**) can be obtained. The products from cyclohexenylacetylene undergo Diels–Alder addition with maleic anhydride (equations 18 and 19). Intermediates in the reactions of triallylborane with acetylenes are the boracyclohex-2-ene and boracyclohexane rings, as in equation (20).

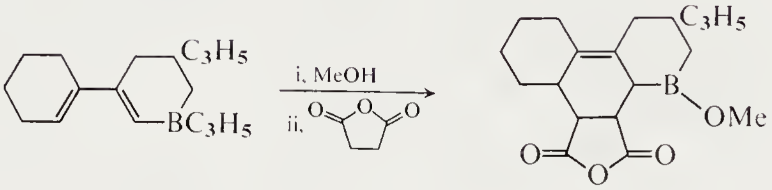


(17)

(**26**)

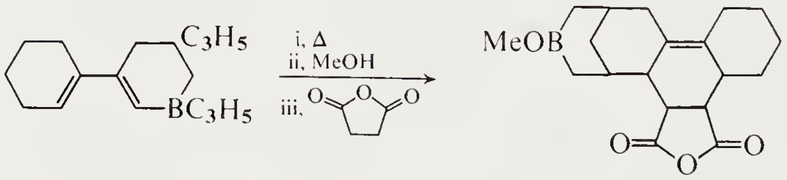


(**27**)



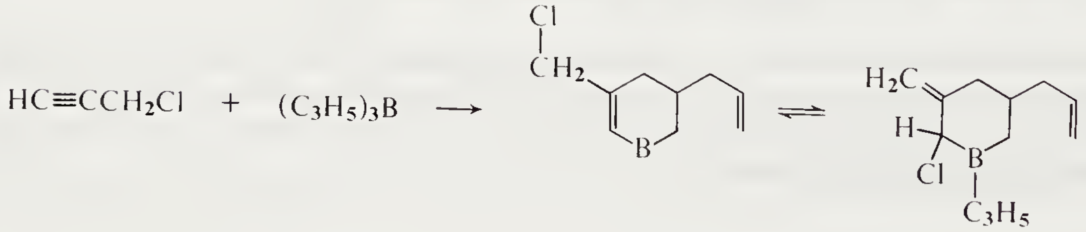
(18)

(**28**)



(19)

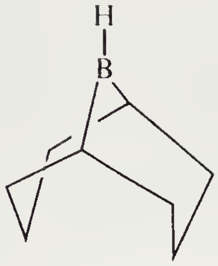
(**29**)

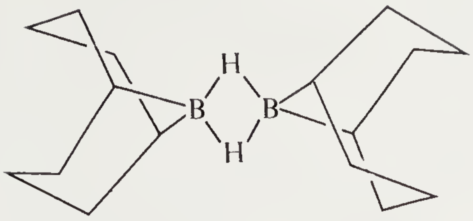


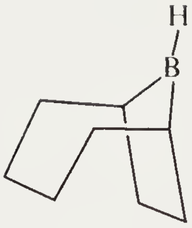
(20)

A variety of functional derivatives of these systems can be obtained. Thus methanol readily cleaves the B—allyl bond to give propene and B—OMe. The double bond in some derivatives of (**26**) can be reduced by H_2/Raney Ni, whereas others require $H_2/Pd/SrCO_3$. The double bond will also undergo alcohol addition under acid conditions. The *B*-allyl substituent in some compounds can be reduced to BPr^n by H_2/Pt.

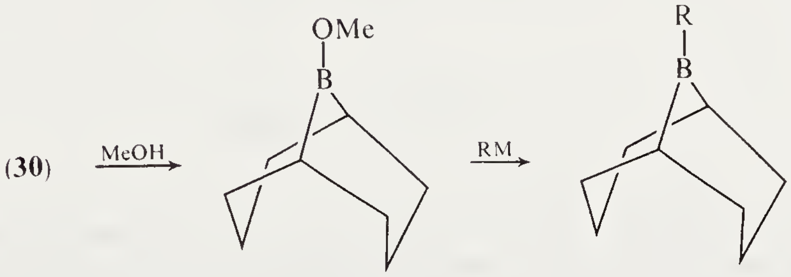
Considerable effort has been expended on the study of 9-borabicyclo[3.3.1]nonane (9-BBN) and its derivatives. The parent compound (**30**), which normally exists in the dimeric form (**31**), is readily prepared, along with its [4.2.1] isomer (**32**) by hydroboration of cycloocta-1,5-diene with BH_3·THF.[63,88] *B*-Alkylated derivatives are similarly prepared by hydroboration of cyclooctadiene with tetraalkyldiboranes, or by pyrolysis, *e.g.* of tricyclooctylborane.[5,83] 9-BBN has proved to be a useful reagent because of the ready availability of the starting diene, the ease of preparation, and its remarkable thermal stability. Crystalline 9-BBN can be stored under dry nitrogen at room temperature indefinitely, and is relatively stable to air and moisture. It is also conveniently soluble in a number of common organic solvents. It is also commercially available.


(**30**)

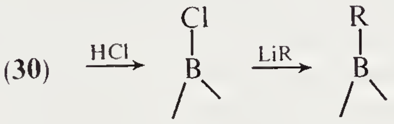

(**31**)


(**32**)

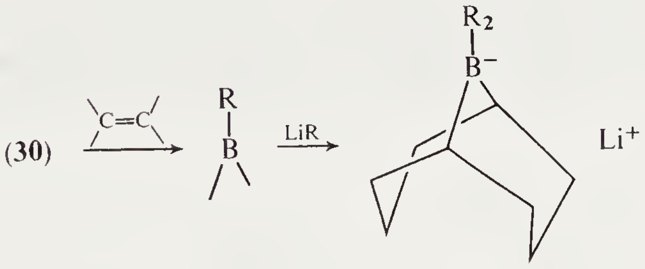
B-Substituted derivatives are readily obtained from 9-BBN. Methanolysis yields *B*-methoxy-BBN which in turn may be alkylated with organometallic reagents containing Li, Mg or Al. Hydroboration of alkenes with 9-BBN occurs quantitatively, except for highly hindered or highly unreactive alkenes; the reaction also shows considerable regioselectivity. Some of its reactions are summarized in equations (21)–(23), in which the reactive species is the dissociated (monomeric) form.[63]



(21)



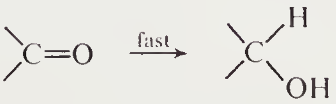
$$(\mathbf{30}) \xrightarrow{\text{HCl}} \overset{\text{Cl}}{\underset{/\ \backslash}{\overset{|}{\text{B}}}} \xrightarrow{\text{LiR}} \overset{\text{R}}{\underset{/\ \backslash}{\overset{|}{\text{B}}}} \qquad (22)$$



(23)

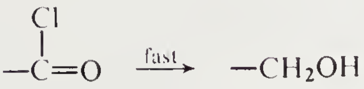
(**33**)

9-BBN has been used extensively as a selective reducing agent and examples of its behaviour are summarized in equations (24)–(32).[63,84]



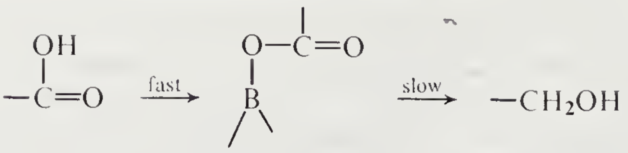
$$\rangle \text{C}{=}\text{O} \xrightarrow{\text{fast}} \rangle \text{C}\langle^{\text{H}}_{\text{OH}} \qquad (24)$$

$$\rangle \text{C}{=}\overset{|}{\text{C}}{-}\overset{|}{\text{C}}{=}\text{O} \xrightarrow{\text{fast}} \rangle \text{C}{=}\overset{|}{\text{C}}{-}\overset{|}{\text{C}}\langle^{\text{H}}_{\text{OH}} \qquad (25)$$



$$-\overset{\text{Cl}}{\overset{|}{\text{C}}}{=}\text{O} \xrightarrow{\text{fast}} -\text{CH}_2\text{OH} \qquad (26)$$

$$-\overset{\text{OR}}{\overset{|}{\text{C}}}{=}\text{O} \longrightarrow -\text{CH}_2\text{OH} \qquad (27)$$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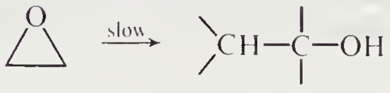
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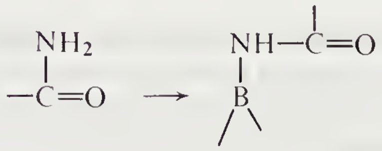
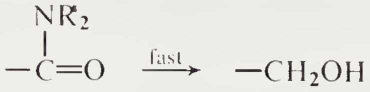
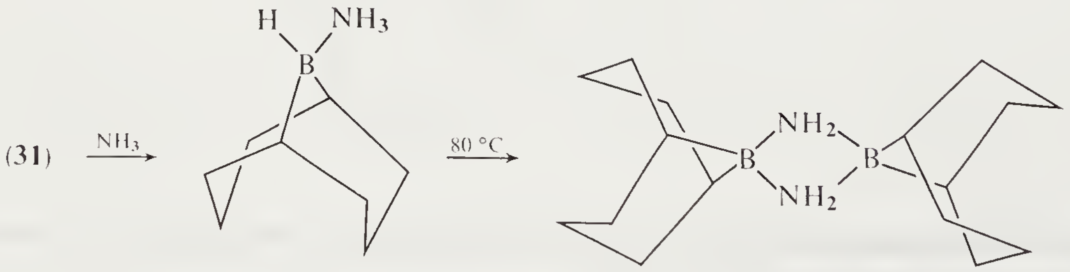

(30)


(31)

$$\overset{NR_2}{\overset{|}{-C=O}} \xrightarrow{fast} -CH_2OH \qquad (31)$$

$$-CN \xrightarrow{slow} -CH_2NH_2 \qquad (32)$$

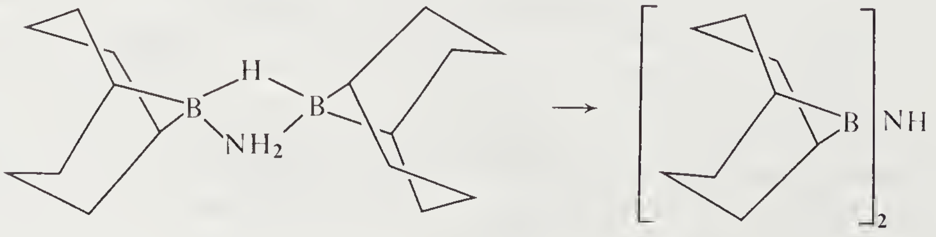
In its reactions with protonic species, the first slow step of the reaction is dissociation of the 9-BBN dimer into the monomeric form, which then rapidly reacts. Examples of protonic reactions have been given in equations (21) and (23), but protonic reactions are general.[84] Protonic reactions occur with alcohols, phenols, amines, thiols, amides, acids and probably occur with initial formation of 9-BBN adducts. It has been shown that 9-BBN forms stable complexes with the small, strong donors such as Me_3N, py and γ-pic, but those with larger and weaker donors such as Et_3N, TMEDA and Me_2S exist in dynamic equilibrium with 9-BBN and donor.[85] Thus 9-BBN reacts with ammonia to give an initial adduct which then eliminates hydrogen to yield (**35**), which can serve as a precursor for a variety of nitrogen derivatives of 9-BBN (equations 33–38).[86] 9-BBN also reacts with BBr_3 to give the B—Br derivative, which cleaves ethers.[87]



(33)

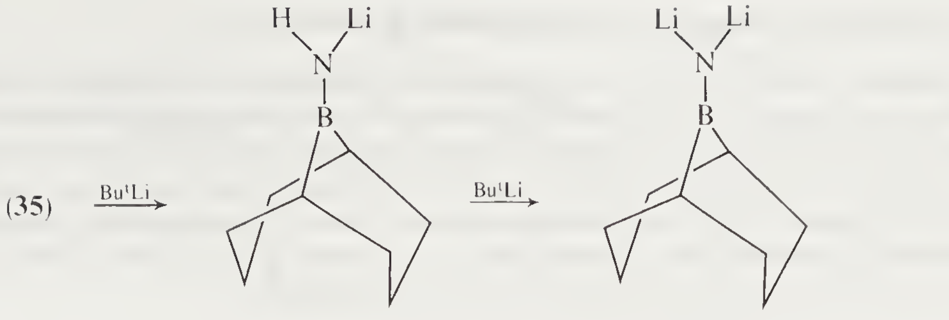
(**34**) (**35**)

(**31**) + (**35**) ⟶



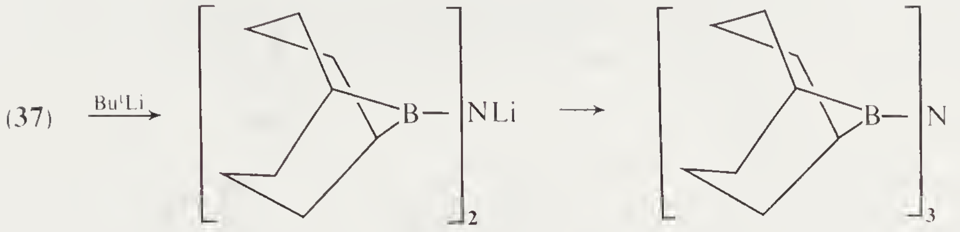
(34)

(**36**) (**37**)



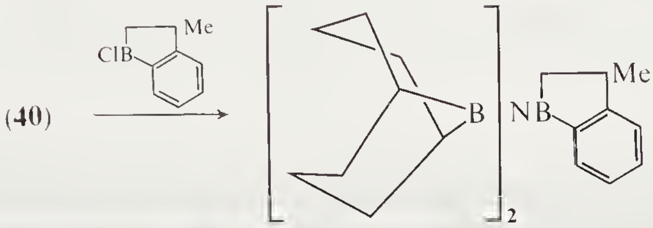
(38) **(39)**

(35)



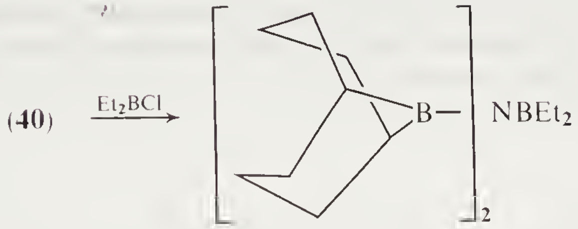
(40) **(41)**

(36)



(42)

(37)



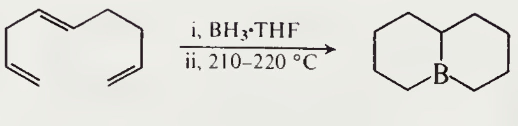
(43)

(38)

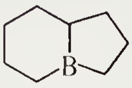
In addition to acting as a selective hydroborating agent and as a selective reducing agent, 9-BBN will also act as a non-participating blocking group in organic synthesis. Its application in carbonylation reactions, alkylation reactions, bromination reactions, cyclopropane synthesis, and alkene synthesis *via* iodination has been discussed.[63] Other organic applications and properties of 9-BBN include its preparation and reducing properties,[89] specifically D-labelled 9-BBN,[90] the preparation of the *B*-allyl derivative from the B—OMe compound and allylaluminium,[91] the preparation of *B*-alk-1-ynes through alkyne isomerization,[92] *cis*-addition to alkenes,[93] high regioselectivity in the hydroboration of but-3-enyl derivatives,[94] reactions of cyclic alkenes, non-conjugated dienes, conjugated dienes, and alkynes,[95–99] reactions of aldehydes and ketones,[100] reduction of phenalone to phenalene,[101] reactions of aryl sulphones,[102] and regioselectivity in the hydroboration of vinyltrimethylsilane.[103] Reactions of its derivatives which have also been studied include the mechanism and reaction course of the interaction of *B*-alkyl derivatives with Br_2,[104] reaction of *B*-alkyl derivatives with *N*-substituted 2-lithioindoles,[105] a cyclic pathway for the reduction of benzaldehyde to benzyl alcohol with *B*-alkyl derivatives,[106,107] and reduction of functionalized aldehydes by *B*-siamyl derivatives.[108] The pyridine adduct of 9-BBN reduces aldehydes and ketones,[109] and the Li^+ salt of the *B*-dialkyl anion **(33)** reacts with acetyl chloride to give *cis*-bicyclo[3.3.0]oct-1-yldialkylboranes.[110,111]

5.2.2.5 Polycyclic Compounds with Bridgehead Boron Atoms

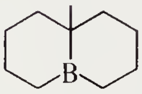
Hydroboration of polyenes has led to polycyclic compounds with bridgehead boron atoms. Thus hydroboration of nona-1,4,8-triene leads initially to a polymeric material which is thermally depolymerized, and 9-boradecalin (**44**)[5,63] may be distilled from the reaction mixture. Pyrolysis of $B(n\text{-}C_9H_{19})_3$ also leads to the same product.[5] Similarly, pyrolysis of tri-*n*-octylborane leads to 8-borahydrindane (**45**),[5] and hydroboration of octa-1,4,7-triene also gives this compound. Furthermore, hydroboration of 5-methylnona-1,4,8-triene gives isomers of the compounds (**46**), which can be carbonylated and converted to the alcohol (**47**).



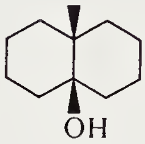
(**44**) (39)



(**45**)

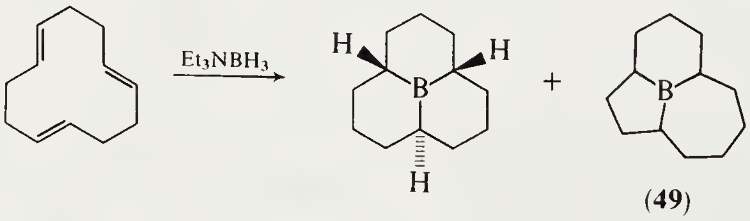


(**46**)

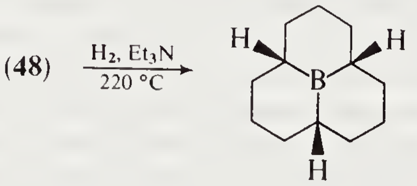


(**47**)

There have been a number of studies on the hydroboration of cyclododeca-1,5,9-triene, and the isomeric constitution of the eventual products has been the subject of some dispute.[5,63,112] *trans,trans,cis*-Cyclododecatriene reacts with Et_3NBH_3 to form *cis,cis,trans*-perhydro-9b-boraphenalene (**48**) and a second isomer believed to be (**49**). Thermal treatment of the product at 200 °C converts the mixture to pure (**48**). *trans,trans,trans*-Cyclododecatriene also produced (**48**) predominantly. It is possible to isomerize (**48**) to a second isomer (**50**) by heating with hydrogen in the presence of NEt_3, or with LiH.

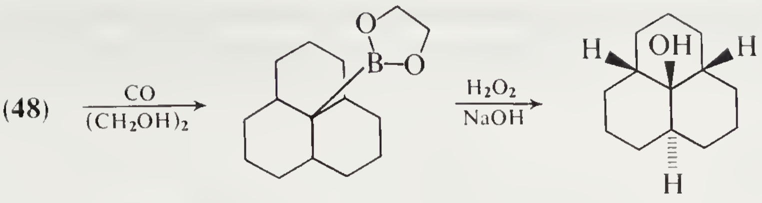


(**48**) (**49**) (40)



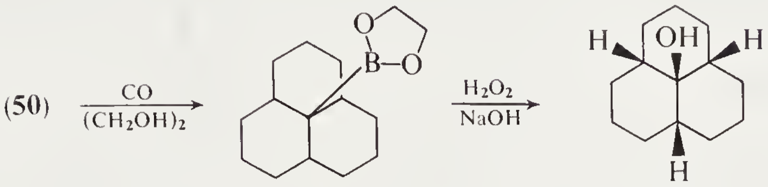
(**50**) (41)

The structural assignment of these isomers has been supported by spectroscopic and chemical data. Thus carbonylation with CO at high pressure is thought to proceed with retention of configuration, and the ultimate perhydro-9b-phenalenols obtained from (**48**) and (**50**) have been shown to be (**51**) and (**52**), respectively.[113,114] If (**50**) is treated with KCN and $(CF_3CO)_2O$ instead of the carbonylation, then a different isomeric perhydro-9b-phenalenol (**53**) is formed, whereas (**48**) still yields (**51**).[115]



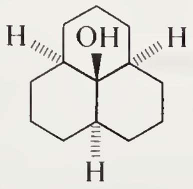
(51)

(42)



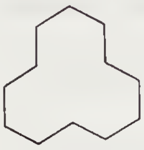
(52)

(43)

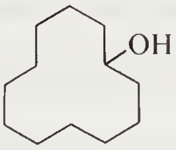


(53)

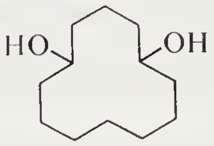
The perhydro-9b-boraphenalenes will also serve as precursors for a range of organic derivatives. Protonolysis with propionic acid led to a variety of products, depending on the conditions. Ultimate cleavage of B—C bonds led to cyclododecane (**54**), but partial protonolysis followed by peroxide hydrolysis led to mixtures of alcohols (**55**) and (**56**), whose isomer constitution was not established.[116,117] Peroxide hydrolysis of perhydroboraphenalene leads to the triol (**57**). UV-induced bromination led to (**58**), which was converted to the alcohol (**59**) on peroxide hydrolysis.[118] Oxidation of (**48**) also gave the ketone (**60**), which could be converted into the amine (**61**).[119] Alternatively, the isomeric amine (**62**) was formed by the reaction sequence (45).[120] The perhydroboraphenalenes form adducts with ammonia, pyridine and piperidine, but vapour pressure



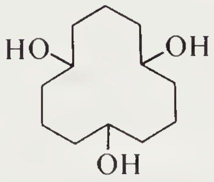
(54)



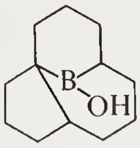
(55)



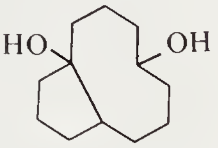
(56)



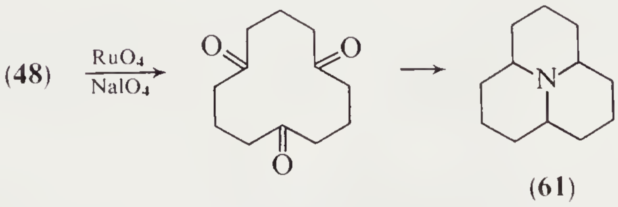
(57)



(58)

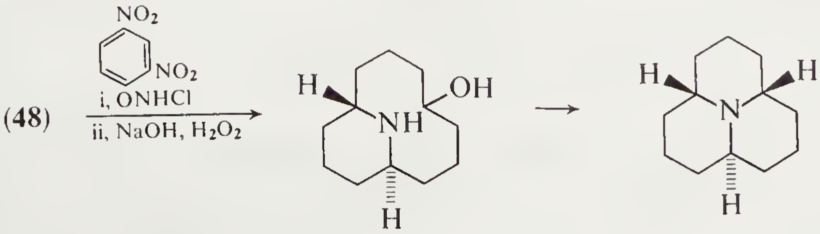


(59)



(60) (61)

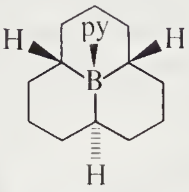
(44)



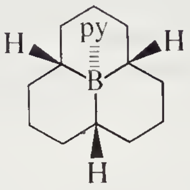
(62)

(45)

measurements failed to detect complexes with THF, water and triethylamine.[116] The structures of the pyridine adducts have been suggested on the basis of the shifts of the methine protons in (**63**) and (**64**).[63]



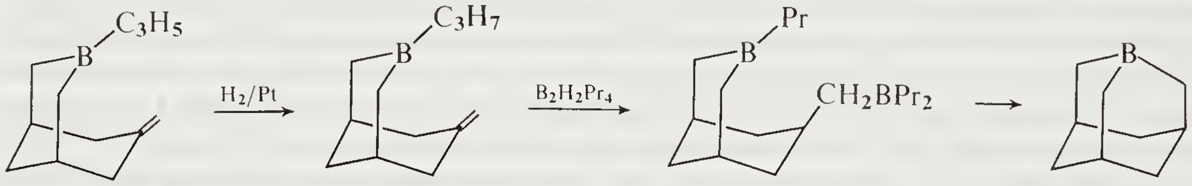
(**63**)



(**64**)

5.2.2.6 Boraadamantanes

When triallylborane is treated with allene, the initial product is 3-borabicyclo[3.3.1]nonane with a methylene group in the 7-position (compounds of type **27**). Hydrogenation of the *B*-allyl substituent and hydroboration of the methylene group gives rise to a dibora compound which will cyclize to 1-boratricyclo[3.3.1.$1^{3,7}$]decane (1-boraadamantane) (**65**).[58,59,71] Similarly, hydroboration of 3-methoxy-7-methylene-3-borabicyclo[3.3.1]nonane, which is more easily synthesized, also leads to (**65**).

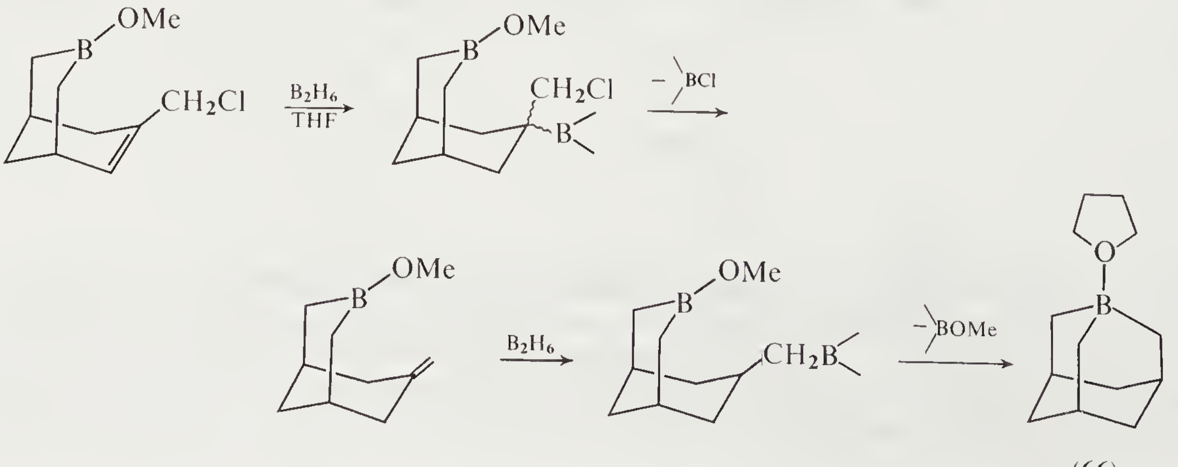


(46)

(**65**)

The boron in this system is a particularly good acceptor because of the steric requirements of the adamantane structure, which force it to be pyramidal, and the compound is normally isolated as a donor–acceptor complex with a ligand such as pyridine or ether. The ether adduct has been used to synthesize other, more thermally stable, complexes by a simple ligand-displacement reaction.

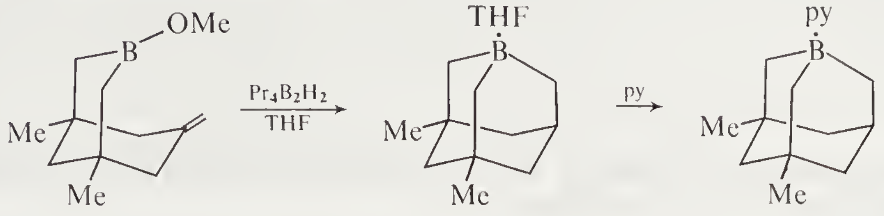
1-Boraadamantane has also been prepared from the reaction between triallylborane and propargyl chloride,[121] *via* the reaction scheme shown in equation (47). Methods similar to these have



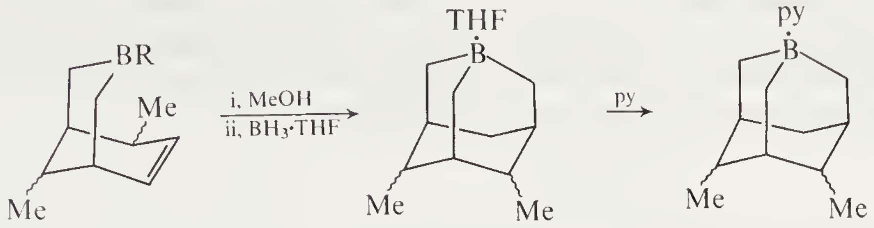
(47)

(**66**)

been used to prepare functionally substituted 1-boraadamantanes, *e.g.* from 3-methoxy-1,5-dimethyl-7-methylene-3-borabicyclo[3.3.1]nonane (equation 48), and cyclization of $(MeCH{=}CHCH_2)_3B$ with $MeOCH_2C{\equiv}CH$ (equation 49).[122]

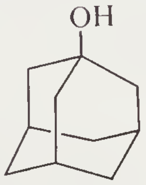


(67) **(68)** (48)



(69) **(70)** (49)

As with other boron heterocycles, carbonylation of the 1-boraadamantane system led to replacement of the boron by carbon and, hence, the synthesis of adamantane derivatives. Thus, ether or tetrahydrofuran complexes have led to the products **(71)**–**(73)**.



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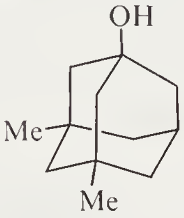

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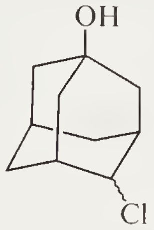
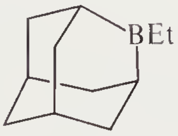


(73)

The isomeric 2-boraadamantane has been prepared by treating bicyclo[3.3.1]nona-2,6-diene with organoboranes.[123,124] By this route, compounds **(74)** and **(75)** were obtained.



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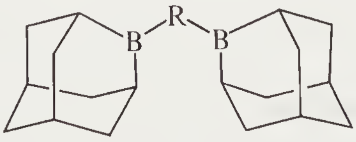
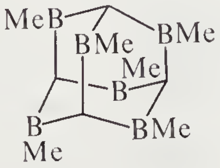
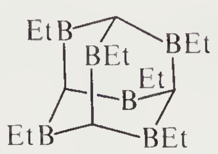


(75)

Hexaboraadamantanes have been obtained by several methods. The sealed-tube pyrolysis of BMe_3 led to $(MeB)_6(CH)_4$ **(76)**.[125–127] The derivative $(EtB)_6(CH)_4$ **(77)** was obtained from reaction (50) as a minor product.[128] The halogen-substituted derivative **(78)** was obtained by thermal degradation of $Cl_2BCH_2CH_2BCl_2$.[129]



(76)



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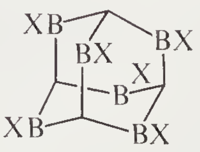
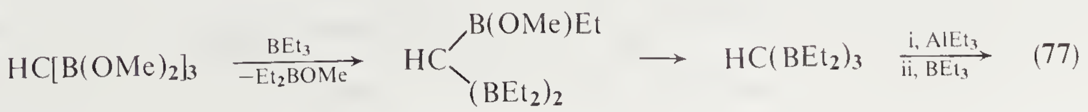


(78)



$$\mathrm{HC[B(OMe)_2]_3 \xrightarrow[-Et_2BOMe]{BEt_3} HC\begin{matrix}\diagup B(OMe)Et \\ \diagdown (BEt_2)_2\end{matrix} \longrightarrow HC(BEt_2)_3 \xrightarrow[ii,\ BEt_3]{i,\ AlEt_3} (77)} \qquad (50)$$

The structure of 2,4,6,8,9,10-hexamethyl-2,4,6,8,9,10-hexaboraadamantane (**76**) was established by an X-ray diffraction study.[130] In its chemical properties, it was shown to form weak complexes with NMe_3, PMe_3 and PMe_2Ph, but was a weaker acceptor than BMe_3.

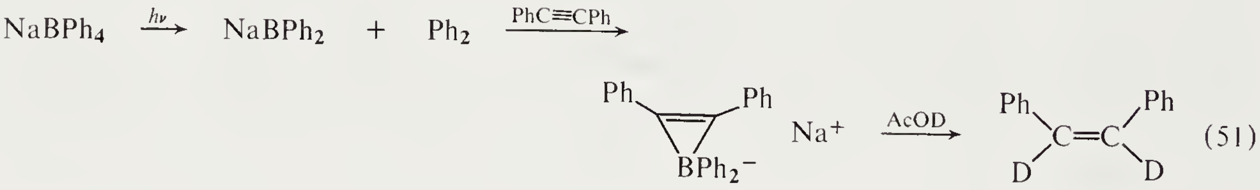
5.2.3 RINGS INVOLVING BORON IN SUBSTITUTED CYCLOALKENES AND BORA AROMATICS (C—B—C RINGS)

5.2.3.1 Introduction

A number of systems have been described in which boron is incorporated into a cycloalkene such that the π-system of the double bond or bonds is able to interact with the vacant p-orbital on boron. Similarly, the π-delocalization of an aromatic ring system may also interact with an adjacent boron atom, incorporated into a suitable ring.

5.2.3.2 Three-membered Rings

A three-membered ring system (**79**) was suggested as a result of the addition of diphenylacetylene to the photolysis product of sodium tetraphenylborate, on the basis of the isolation of a *cis*-diphenylethylene on cleavage with acetic acid (equation 51).[131]

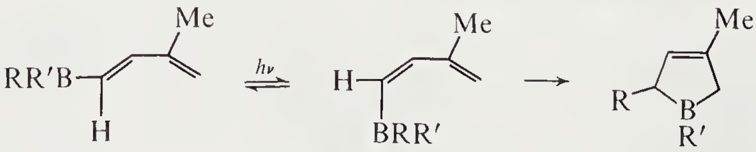


(**79**)

(51)

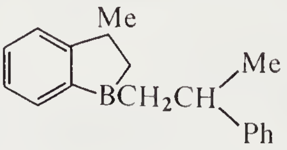
5.2.3.3 Five-membered Rings

Photolysis and ring closure of dialkyl-1,3-dienylboranes led to boracyclopent-3-enes (**80**) (equation 52). Pyrolytic ring closure of aralkylboranes has been used to prepare a number of ring systems in which a boron atom is adjacent to an aromatic ring, for example the boraindanes.[5] Thus pyrolysis of $B(CH_2CHMePh)_3$ or $B(CH_2CH_2Ph)_3$ leads to, respectively, (**81**) or (**82**).

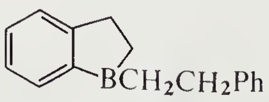


(**80**)

(52)

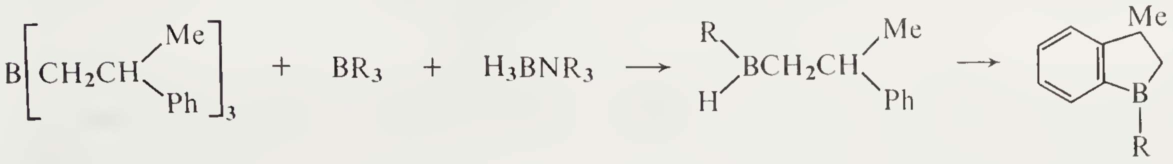


(**81**)



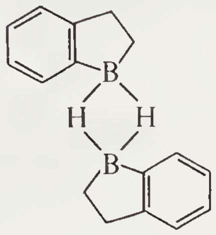
(**82**)

The reactions are catalyzed by the presence of compounds containing B—H bonds; mixtures of trialkylboranes and triaralkylboranes can be used to yield other B—R derivatives, and these reactions are also catalyzed by B—H compounds (equation 53). The substituent at boron may often be changed, for example from alkyl to hydrogen, through reaction with hydrogen or diborane, leading to bridged compounds of the type (**84**) and (**85**) or from alkyl to halogen through reactions with boron halides to give compounds of the type (**86**), or with alkylborates to give the analogous alkoxy derivatives. The *B*-alkoxyboraindanes react further with ethanolamine or 2-aminophenol to give *trans*-esterified derivatives with four-coordinate boron (*e.g.* **87**).

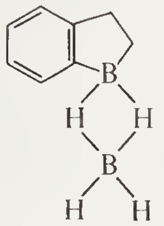


(53)

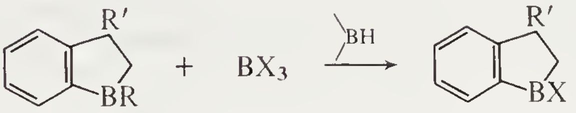
(**83**)



(**84**)

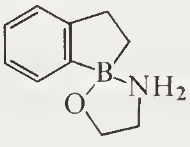


(**85**)



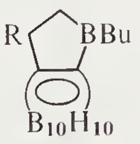
(54)

(**86**)

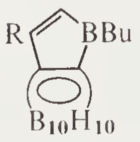


(**87**)

A carborane nucleus will also serve as a suitable 'aromatic' system, and thermal decomposition of (2-alkyl-*o*-carboran-1-yl)dibutylborane or [2-(1-alkenyl)-*o*-carboran-1-yl]dibutylborane leads to ring closure and formation of the ring systems (**88**) and (**89**), respectively.[132]

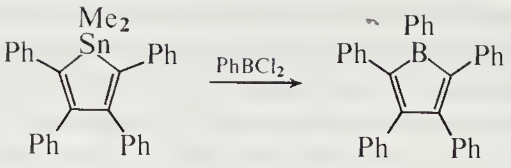


(**88**)

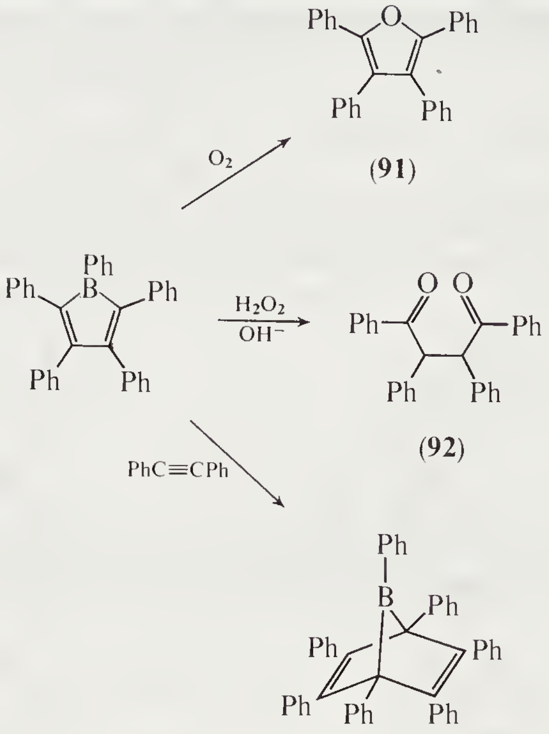


(**89**)

Interest has centred on the borole ring system, with its possible antiaromatic character. Although a compound, claimed to be pentaphenylborole, was prepared from phenylboron dichloride and dilithiotetraphenylbutadiene,[133] the properties were such as to throw doubt on its nature. Later work showed that a highly reactive, green compound (**90**) could be prepared either by the original method or, more efficiently, by a transmetallation reaction on an organotin starting material (equation 54).[134] The compound was shown to undergo ready oxidation to tetraphenylfuran (**91**) or, with peroxide, to the diketone (**92**). It was also a powerful reagent for Diels–Alder addition of alkynes, giving 7-borabicyclo[2.2.1]heptadiene (**93**).[72] The latter system underwent two skeletal rearrangements: (a) a facile degenerate net twofold [1,3] suprafacial sigmatropic migration of the 7-substituted boro group, and (b) a non-degenerate anionic [1,2] aryl shift from C to B, converting the 7,7-dimethylborate salt of (**93**) to an aryl(dimethyl)pentaarylborate salt.[135]

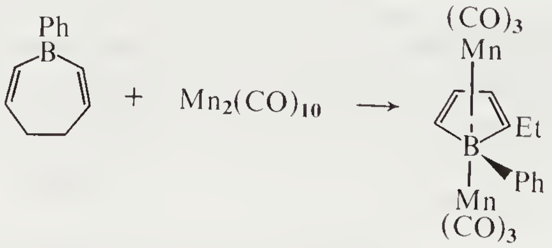

(54)

(90)

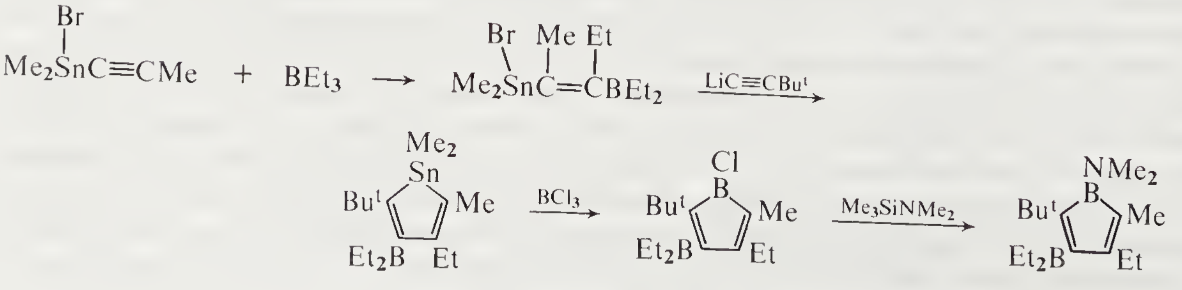

(91) **(92)** **(93)**

(55)

A metallo derivative of the borole ring system (**94**) has also been prepared (as a triple-decker sandwich compound) by an unusual rearrangement reaction of a borepin (equation 56).[136] A transmetallation reaction on an organotin heterocycle has also led to the borole ring system (**95**) *via* the reaction sequence shown in equation (57). Compound (**95**) was an extremely oxygen-sensitive, deep-red coloured liquid, and it reacted with Me_3SiNMe_2 or Me_3SiOMe to produce the B—NMe_2 or B—OMe derivatives.[137]

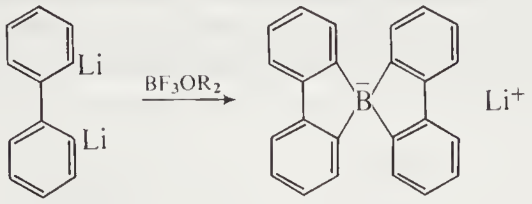

(56)

(94)


(57)

(95)

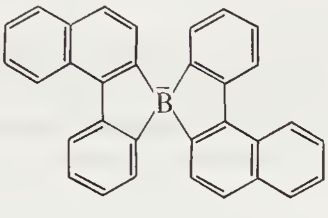
Reaction of a boron halide with a dilithio reagent has long been known to give rise to heterocyclic systems,[5] and this method has been used to prepare *spiro*-heterocyclic anions **(96)**.



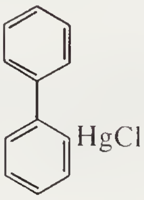
(58)

(96)

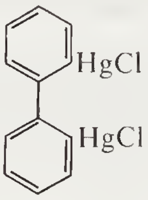
It has proved possible to separate optical isomers of the anion **(97)** using an optically active ammonium salt. The anions undergo cleavage reactions, the natures of which are dependent on conditions. When **(96)** is treated with acidic acetone in the presence of mercury(II) chloride, biphenylmercury chloride **(98)** is obtained, whereas alkaline acetone in the presence of mercury(II) chloride yields the bis-mercury derivative **(99)**.



(97)

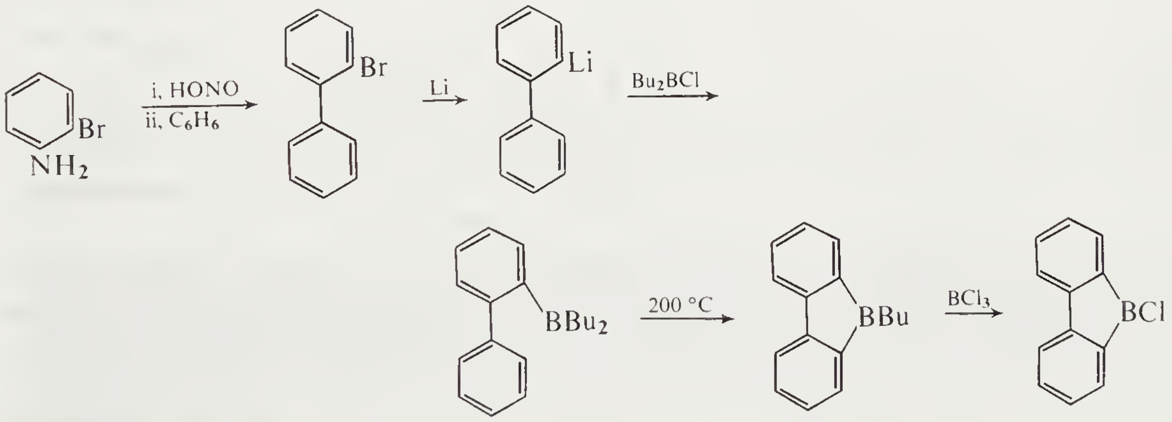


(98)



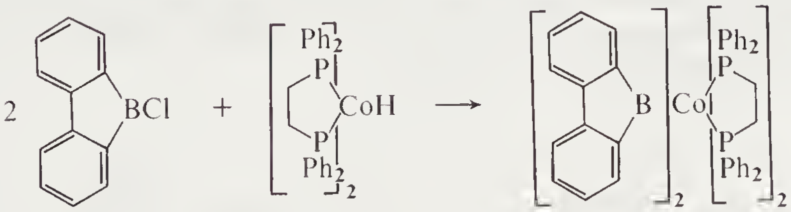
(99)

The reaction scheme shown in equation (59) has led[138] to the neutral derivatives **(100)** and **(101)**. Compound **(101)** has then been used as a precursor for the σ-bonded boron–transition metal derivative **(102)** (equation 60) and compound **(103)** was similarly prepared.[139]



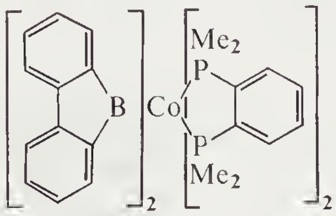
(59)

(100) **(101)**



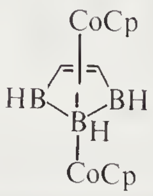
(60)

(102)

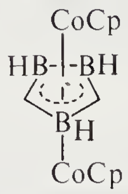


(103)

A triple-decker sandwich complex of a C_2B_3 ring system (**104**) has been obtained from the reaction between the carborane 2,3-$C_2B_4H_8$ and $CoCl_2$ in the presence of NaC_5H_5 and $Na/C_{10}H_8$ after oxidative work-up.[140] Compound (**104**) and its *C*-methyl derivative are subject to thermal rearrangement, leading eventually to the isomeric species (**105**),[141] and the nuclear magnetic relaxation properties of these and related metallocarboranes have been discussed.[142]



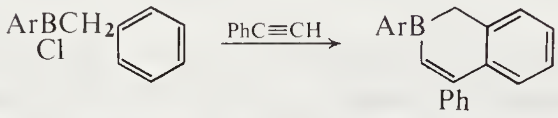
(**104**)



(**105**)

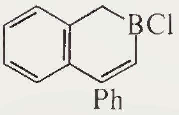
5.2.3.4 Six-membered Rings

A six-membered alkenyl-aromatic ring system (**106**) has been obtained from reactions between chlorobenzylboranes and phenylacetylene.[143] Similar reactions lead to the B—Cl and B—Ph compounds (**107**) and (**108**). These compounds were not reduced to the aromatic boranaphthalene anion by alkali metals, although alkyllithium reagents led to the system (**109**).

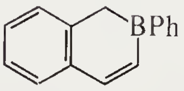


(**106**)

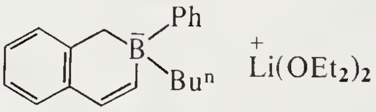
(61)



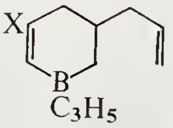
(**107**)



(**108**)



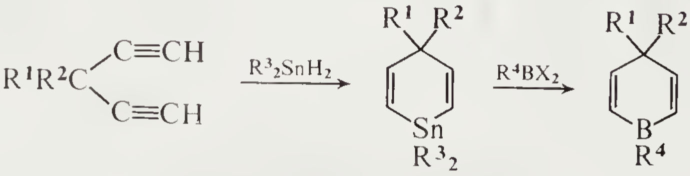
(**109**)



(**110**)

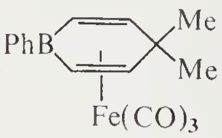
Reactions of triallylboranes with acetylenic derivatives give rise initially to diallyl(penta-1,4-dien-1-yl)boranes, which can undergo intramolecular cyclization reactions to substituted 1-boracyclohex-2-enes (**110**), and a large number of related derivatives have been prepared.[59]

A number of derivatives of boracyclohexadiene (**111**) have been described. The hydrostannation of dialkynes led to the formation of stannacyclohexadienes which were the starting materials of transmetallation reactions.[144–146] These cyclic dienes are of particular interest as precursors to metal complexes of diene-ring compounds, and the borabenzene (triene) anionic ring and its metal complexes.[147] Thus photochemical reaction with $Fe(CO)_5$ and $(\eta\text{-}C_5H_5)Co(CO)_2$ led to the derivatives (**112**) and (**113**). Reaction of (**111**; R^1, R^2 = H, R^4 = Ph) with $LiBu^t$ led to deprotonation and formation of the borabenzene anion (**114**).

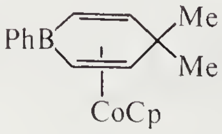


(**111**)

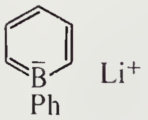
(62)



(**112**)



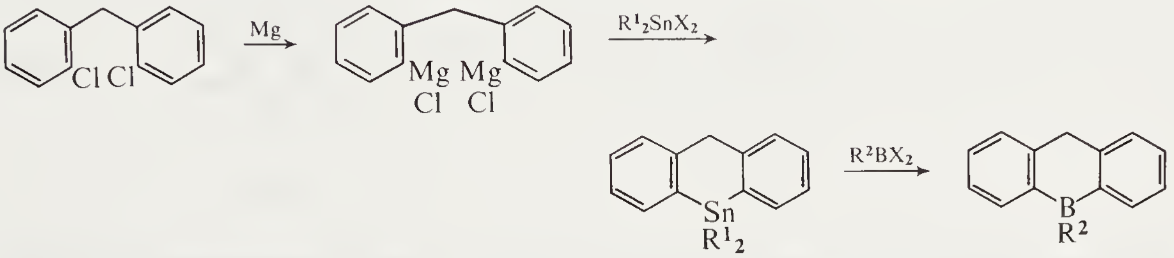
(**113**)



(**114**)

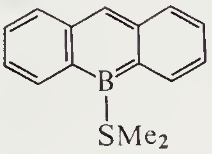
A number of derivatives of the dibenzo analogues of the diene ring system have also been prepared either through a di-Grignard route[148] to the corresponding tin heterocycle which is then subjected to a transmetallation reaction, or from ring closure through thermal elimination of hydrogen or alkane from an aromatic organoborane.[64,149]

In earlier work, evidence for deprotonation to the corresponding 9-boraanthracene anion was based on UV evidence,[150] and it was suggested that the neutral system could be obtained as an unstable dimethylsulphane adduct (**116**).[151] It was later shown that (**115**) was deprotonated to (**117**) by $LiBu^t$ in the presence of a polar solvent. In hexane, a very reactive crystalline adduct (**118**) formed.[152] It was further shown that if a bulky mesityl group was substituted at boron (position 9), there was no evidence for adducts of type (**118**) with organolithium reagents in benzene or ether solvents, but deprotonation of carbon atom 10 occurred. The corresponding 9-mesityl anion was converted to a variety of 10-substituted derivatives (**119**) by electrophilic reagents.[153]

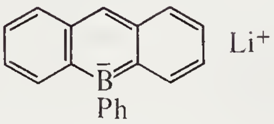


(**115**)

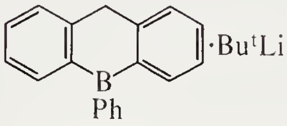
(63)



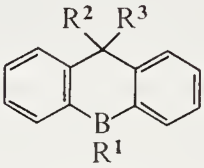
(**116**)



(**117**)

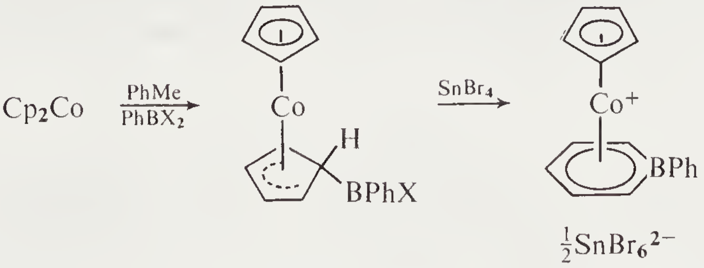


(**118**)



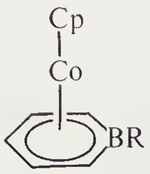
(**119**)

The borabenzene anion and its transition metal derivatives have been the subject of a recent review.[66] The system was first prepared as a cobalt complex in a ring-expansion reaction of bis(cyclopentadiene)cobalt. Hydrolysis of the cationic complex (**120**) led to the neutral complexes (**121**) and (**122**).[154] The cobalt complex (**122**) was then used as a precursor for a range of borabenzene–metal derivatives, through reactions with metal carbonyls and other reagents.[155,156] It was also possible to generate alkali metal derivatives of the borabenzene anion from the cobalt complex by treatment with a metal cyanide (equation 65), and the resulting sodium or potassium salts were useful intermediates for the metathetical synthesis of a range of transition metal derivatives.[145,157,158]

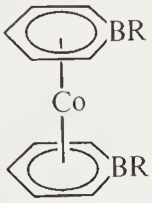


(**120**)

(64)



(**121**)



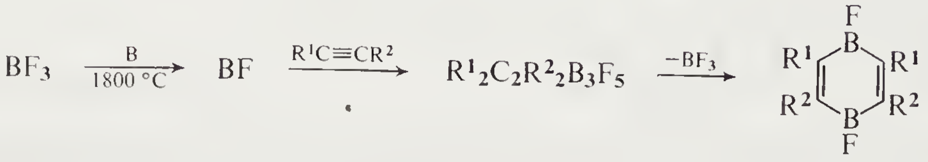
(**122**)

$$Co(C_5H_5BR)_2 \xrightarrow{MCN} 2M(C_5H_5BR) \qquad (65)$$

In addition, the main group derivatives $Tl(C_5H_5BR)$ (R = Me, Ph) have been prepared by metathesis on alkali metal borinates using TlCl in acetonitrile; the properties of the ring system are more easily studied in the thallium derivatives and mass spectral and detailed NMR parameters have been obtained.[159] The data on the borabenzene anion and its derivatives are consistent with a system of considerable π-delocalization. It has been described as a delocalized π-system perturbed by the difference in boron and carbon orbital electronegativities.

5.2.3.5 Six-membered Rings with Two Heterocyclic Boron Atoms

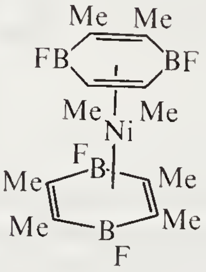
The first synthesis of the 3,6-diboracyclohexa-1,4-diene ring system was reported from the condensation of boron monofluoride with alkynes (equation 66).[160]



(66)

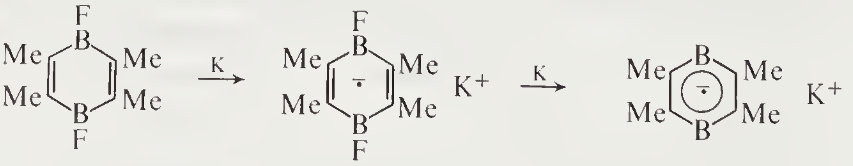
(**123**)

The ring system (**123**; R^1, R^2 = Me) reacted rapidly with $Ni(CO)_4$ to displace two molecules of CO and give $C_4Me_4B_2F_2Ni(CO)_2$, from which two further molecules of CO could be displaced on UV irradiation to give (**124**).[161]



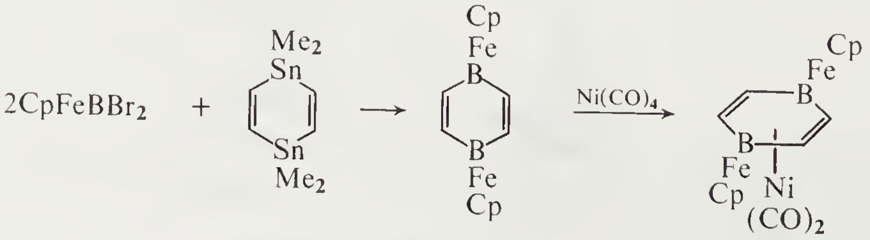
(**124**)

Compound (**123**; R^1, R^2 = Me) was reduced in two steps by potassium in dimethoxyethane; the first step produced an unstable radical anion, which subsequently underwent further reduction with removal of the fluorine substituents and yielded a second radical anion, tetramethyl-1,4-diborine (**126**).[162] A second route to the 3,6-diboracyclohexa-1,4-diene ring system involved a transmetallation reaction on the analogous di-tin ring. Compound (**127**) also displaced CO from $Ni(CO)_4$ to give a metalla complex (**128**).[163]



(67)

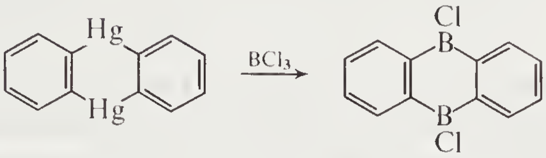
(**125**) (**126**)



(68)

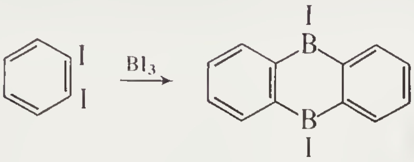
(**127**) (**128**)

The related dibenzo heterocyclic system (**129a**) has been prepared by treating the corresponding mercury compound with boron halide. In reactions with protonic reagents, a variety of 3-substituted derivatives were obtained.[164] An alternative route to the related system (**129b**) has been as a by-product in the reactions to prepare Ph_2BI from either $PhBI_2$ with Ph_3B or $PhBI_2$ with $NaBPh_4$. The compound results from intramolecular elimination of HI from $PhBI_2$.[165] Similarly, the compound has also been obtained from reaction (70).[166]



(69)

(129a)

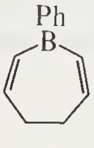


(70)

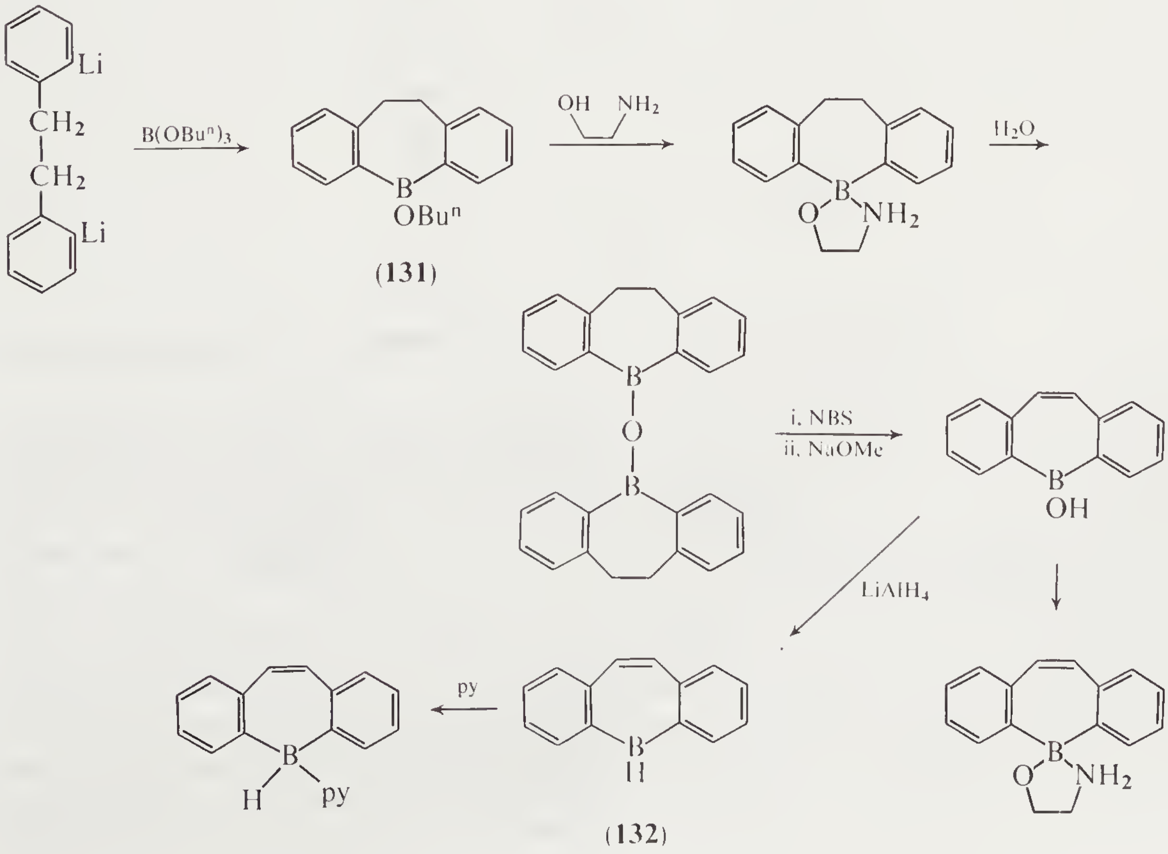
(129b)

5.2.3.6 Seven-membered Rings

Addition of dimethylstannane to hexa-1,5-diyne followed by treatment of the resulting tin heterocycle with phenylboron dihalide, in a manner analogous to reaction (62), led to the boracycloheptadiene (**130**),[146] which will also serve as a precursor for a number of metal complexes.[136,167] The analogous dibenzo derivative (**131**) was one of the earliest boron heterocycles to be studied,[5,168] and its preparation and reactions are summarized in the reaction scheme shown in equation (71).

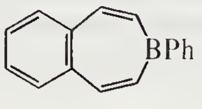


(**130**)

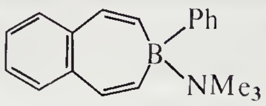


(71)

Studies on the dibenzoborepin system (**132**) and the related benzoborepin (**133**) have indicated that the compounds are, essentially, aromatic[5,169] but that aromatic character is lost when the vacant orbital on boron is involved in donor–acceptor complexes of the type (**134**).

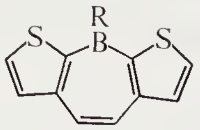


(**133**)

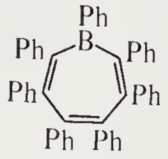


(**134**)

The synthesis of derivatives of borepinodithiophene (**135**) has been reported[170] and a comparison of the physical properties made with LCI-SCF-MO (PPP) calculations for some derivatives. In particular, π-electron densities were correlated with ^{1}H and ^{11}B chemical shift measurements.[171] The phenyl-substituted borepin (**136**) has been obtained from the thermal rearrangement of a Diels–Alder addition product (**93**) of pentaphenylborole (**90**) and diphenylacetylene.[72,135]



(**135**)

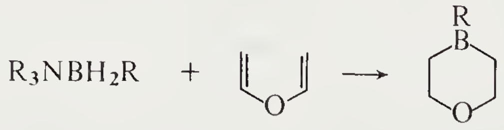


(**136**)

5.2.4 RINGS CONTAINING OTHER HETEROELEMENTS IN ADDITION TO BORON IN POSITIONS NOT ADJACENT TO BORON (C—B—C RINGS)

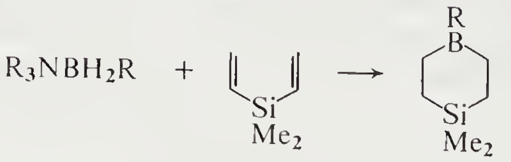
5.2.4.1 Cycloalkane Analogues

Two routes have been used to synthesize systems containing boron and a second heteroatom. Hydroboration of divinyl derivatives of oxygen and silicon has led to the six-membered rings (**137**) and (**138**). Addition of H_2S to divinylboron derivatives has also led to six-membered rings (equation 74).[5]



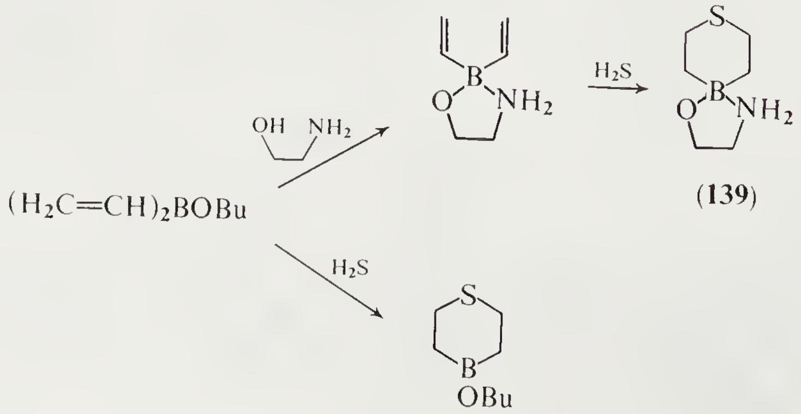
(**137**)

(72)



(**138**)

(73)



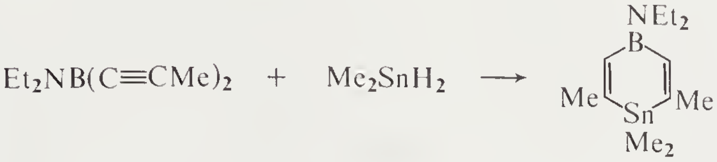
(**139**)

(**140**)

(74)

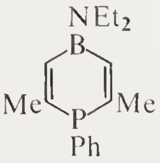
5.2.4.2 Cycloalkene Analogues

Hydrostannation of bis-acetylene derivatives has led to the boron–tin cyclohexadiene derivative (**141**),[172] and an analogous radical-initiated addition of phenylphosphine to a bis(alkyne)borane led to the corresponding boron–phosphorus cyclohexadiene derivative (**142**).[173] The NMR parameters of a number of derivatives related to compounds (**141**) and (**142**) have been quoted from unpublished data.[55] The reaction of the di-tin heterocycle with phenylboron dichloride has also led to derivatives similar to (**141**), from which metal complexes may be obtained.[146] The addition of trialkylborane to a bis(alkyne)tin derivative led primarily to a tin heterocycle, although a small amount of a compound related to (**141**) was obtained.[174,175]



(75)

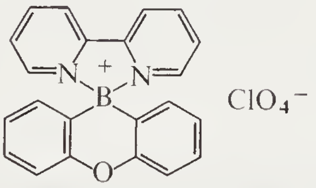
(**141**)



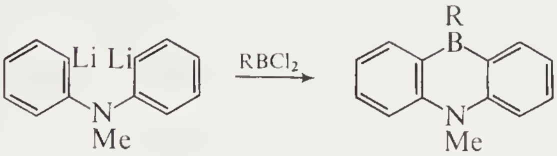
(**142**)

5.2.4.3 Aromatic Systems

Early studies[5] on the synthesis of aromatic boron compounds led to the isolation of ring systems (**143**) and (**144**).



(**143**)

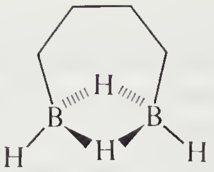


(76)

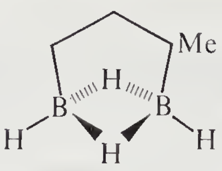
(**144**)

5.2.5 RINGS DERIVED FROM HYDROGEN-BRIDGED SPECIES

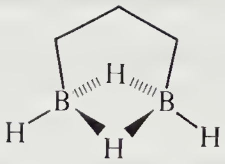
Although the hydroboration of dienes has been described as a route to cyclic organoboranes, as described in Section 5.2.2, it has also been shown that the reactions involve cyclic intermediates in which the bridge B—H—B system is important. These early studies of the gaseous reaction between butadiene and diborane at 100 °C led to the identification of the 1 : 1 product as primarily 1,2-tetramethylenediborane (**145**), with a trace of 1,2-(1′-methyltrimethylene)diborane (**146**).[63,176] Hydroboration of allene also led to a similar product (**147**),[177] and the NMR spectra of these and related products were investigated. These compounds were later synthesized in solution reactions, and the 1 : 2 diborane–butadiene reaction product was found to be 1,2-bis(tetramethylene)diborane (**148**), whose structure was established on the basis of the molecular weight of its amine addition compounds, the ten-membered heterocycles (**149**) and (**150**).[178] Compound (**148**) reacts with potassium hydride to form the singly hydrogen-bridged anion (**151**) and a similar reaction with the stoichiometric (1 : 3) products (**6**) of B_2H_6 and butadiene led to the anions (**152**) and (**153**).[179]



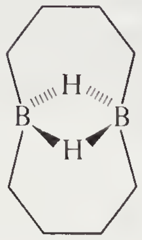
(145)



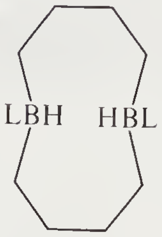
(146)



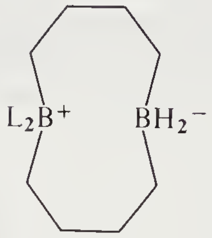
(147)



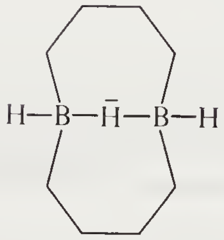
(148)



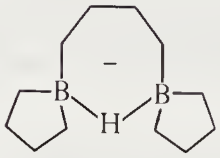
(149)



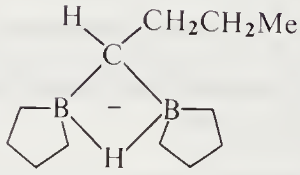
(150)



(151)

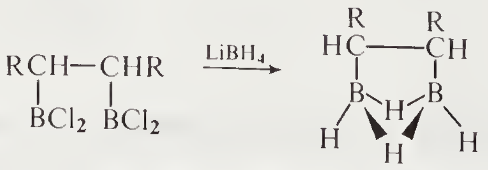


(152)



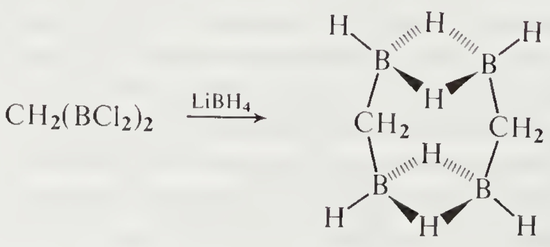
(153)

An alternative synthetic route to the related ring system (**154**) was through the reduction of a bis(dichloroboryl)alkane.[180,181] A more complex ring system (**155**) was similarly prepared.[182] Aromatic derivatives of related structure have been prepared by the reaction scheme shown in equation (79).[183]



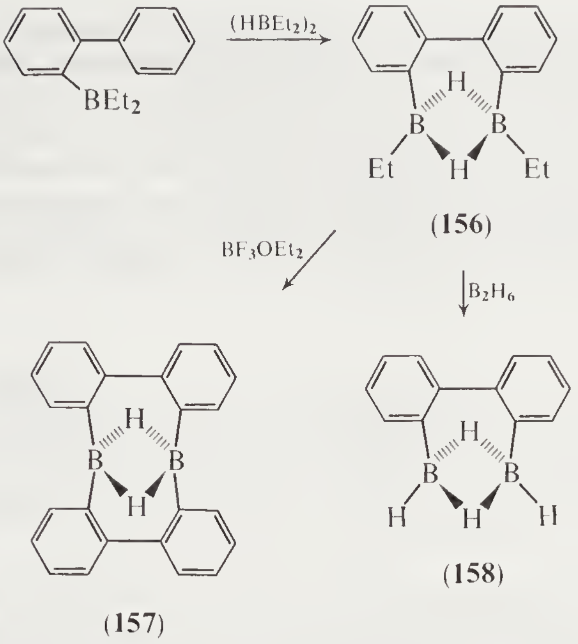
(154)

(77)



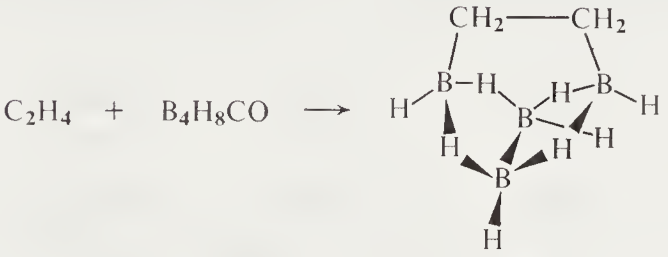
(155)

(78)



(79)

Alkenes react with tetraborane carbonyl to form a complex ring system (**159**).[184]



(**159**)

(80)

5.2.6 RINGS INVOLVING A NITROGEN HETEROATOM BONDED TO BORON, IN ADDITION TO A BORON–CARBON RING BOND (C—B—N RINGS)

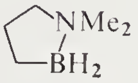
5.2.6.1 Boron–Nitrogen Analogues of Cycloalkanes

It has long been realized that a boron atom and a nitrogen atom together were isoorbital and isoelectronic with two carbon atoms, although the detailed charge distribution in a B—N system would be different from that in the C—C analogue. In formal terms, bonding between tricovalent nitrogen and tricovalent boron results from donor–acceptor interactions, and this may occur to give rise to cyclic compounds as well as non-cyclic species.[5] Although the three-membered ring analogue of cyclopropane was suggested as a metastable product of the catalytic reduction of the azide derived from Me_2BCH_2Cl, later work showed this to be incorrect and the product was the alkyl-rearrangement species $H_2NB(Me)Et$. The four-membered ring (**160**) has been described from the reaction of ethylenimine and diborane, generated *in situ*; however, in the light of the non-existence of the three-membered ring, this product would merit re-investigation.

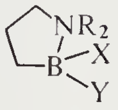
(**160**)

(81)

The five-membered ring system 1,1-dimethyl-1,2-azaborolidine (**161**) is well established and was originally prepared by hydroboration of *N*,*N*-dimethylallylamine with $H_3B{\cdot}NMe_3$. Other routes to derivatives of the same general type (**162**) have been reported by a number of workers (see refs. 5, 185–187 and references quoted therein). The compounds have been of interest in respect of the possibility of an equilibrium between cyclic and open-chain forms, and IR and NMR spectroscopic and dipole moment measurements have been determined and correlated with the structure.[188] The synthetic methods have included the addition of reagents to 1,2-azaborolidines, and exchange reactions with species such as BX_3, $B(SR)_3$, ROH, *etc.*

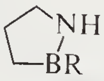


(**161**)



(**162**)

The 2-alkyl-1,2-azaborolidine (**163**), 1-alkyl-1,2-azaborolidine (**164**) and 1,2-dialkyl derivatives (**165**) have been extensively investigated. The 1-substituted derivatives were prepared by hydroboration of a secondary allylamine or allylimine with triethylamineborane (equations 82 and 83).[189] The compounds are stable to the atmosphere and to hydrolysis at room temperature, and are dimeric in solution. The monomer–dimer characteristics (equation 84) have been investigated by NMR and other spectroscopic techniques.[190] Reactions with protonic species occur readily on gentle heating, and B—X substituted derivatives (X = OR, SR) result.

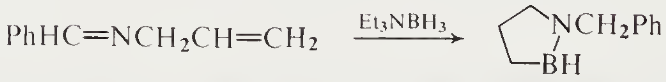


(**163**)

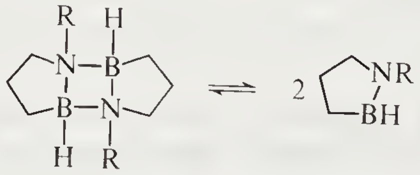
(**164**)

(**165**)

(82)



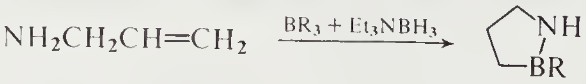
(83)



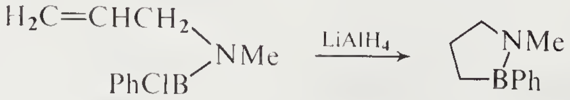
(**166**)

(84)

The 2-substituted derivatives have been obtained by treating allylamine with a mixture of trialkylborane and triethylamineborane (equation 85), and their degree of association studied by ^{11}B NMR spectroscopy.[191] The 1,2-dialkyl derivatives of the 1,2-azaborolidine system (**165**) were early derivatives of the ring to be described, and were prepared by two methods, both involving allylic derivatives (equations 86, 87).[192] The ring system was also found as a major product in the synthesis of 1-aza-5-borabicyclo[3.3.0]octanes (**168**)[193,194] and also by utilizing the reaction of $CH_2{=}CHCH_2NHR$ with trialkylborane and triethylamineborane; their monomer–dimer equilibria have also been studied by ^{11}B NMR and IR spectroscopy.[195] A general mechanism



(85)

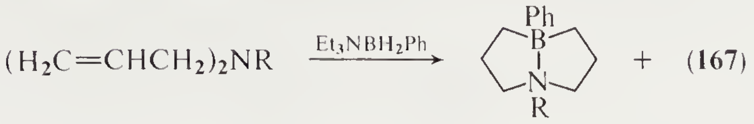


(**167**)

(86)

$$H_2C{=}CHCH_2NHMe \xrightarrow{Me_3NBH_2Ph} (\mathbf{167}) \qquad (87)$$

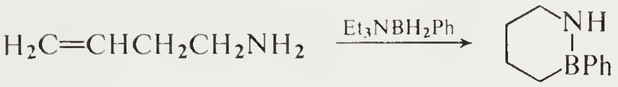
for the formation of 1-methyl-2-phenyl-1,2-azaborolidine from reaction (88) was proposed to involve the elimination of propene through a concerted process involving a six-centred transition state.[196]



(88)

(168)

The six-membered ring 2-phenyl-1,2-azaboracyclohexane (**169**) was obtained from 3-butenylamine and $PhBH_2{\cdot}NEt_3$.[192] An alternative route involved the reaction between (haloalkyl)-boranes and amines, and high yields were obtained from borinic esters (equation 90). The method was extended to the preparation of seven-membered rings (equations 91 and 92).[197] The B—N bond of the seven-membered ring was found to add protonic reagents in a manner analogous to the 1,2-azaborolidines.



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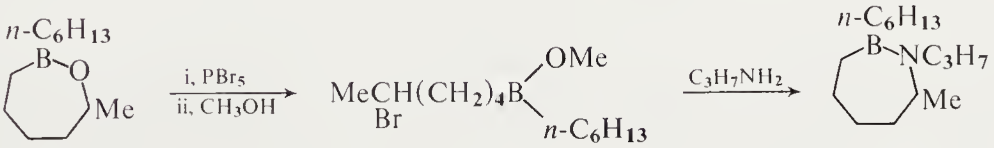

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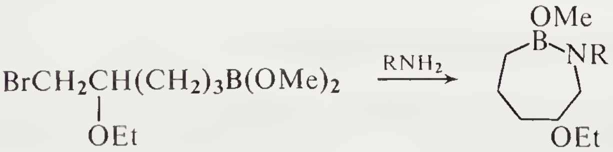
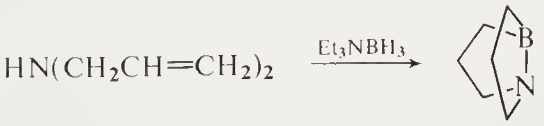


(92)

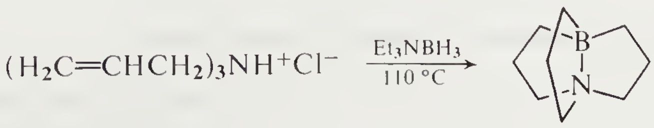
The 1,5-substituted bicyclic compounds 1-aza-5-borabicyclo[3.3.0]octane (**168**) have already been described from the hydroboration of a diallylamine (reaction 88). The compounds were shown to be air-stable white solids.[194] The unsubstituted 1-aza-5-borabicyclo[3.3.0]octane (**171**) has also been described through a hydroboration reaction.[198] Its photoelectron spectrum was correlated with a monomeric form in the gas phase, whereas the crystalline form was dimeric.[199]



(93)

(171)

A stable, tricyclic compound, 1-aza-5-boratricyclo[3.3.3.$0^{1,5}$]undecane (**172**), was also prepared through a hydroboration reaction, although in order to obtain a good yield of the monomeric compound the triallylamine was present as the hydrochloride.[200] The compound was stable to air and aqueous hydrolysis, and could be steam-distilled from the reaction mixture.



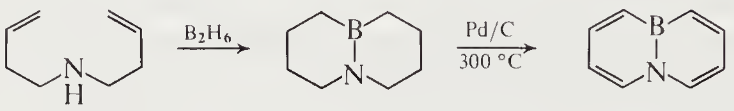
(94)

(172)

Calculations on the related hypothetical system 1-aza-4-boratricyclo[2.2.2.0^{1,4}]octane (**173**) have been carried out to ascertain the possibility of bond stretch isomerism. The calculations suggest that the closed and open forms lie in individual potential wells, with only a small barrier separating them, and that the open form is more stable.[201,202]

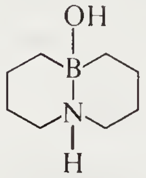
(**173**)

As part of a systematic survey of the chemistry of aromatic boron–nitrogen compounds, 9-aza-10-boradecalin (**174**) was prepared by hydroboration of dibut-3-enylamine, and the product was dehydrogenated to 9,10-azaboranapthalene. The physical and spectroscopic properties of both compounds have been studied, together with those of the hydrate (**176**).[5a,203]



(**174**) (**175**)

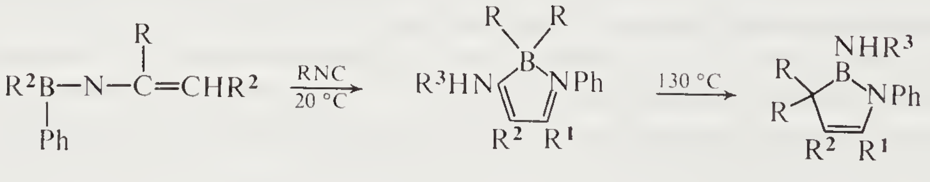
(95)



(**176**)

5.2.6.2 Boron–Nitrogen Analogues of Cycloalkenes

Enaminodialkylboranes react with *t*-butyl isocyanide to form complexes which rearrange upon heating to yield 1,2-azaborolines (**177**).[204] The NMR spectra of the related compounds (**178**)–(**180**) have been reported.[55,205]



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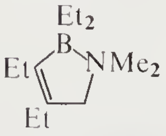
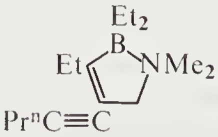
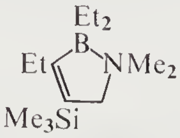
(**177**)



(**178**)



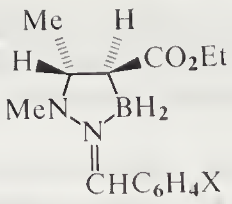
(**179**)



(**180**)

5.2.6.3 Boron–Nitrogen Analogues of Nitrogen Heterocycles

The hydroboration of enehydrazones led to derivatives of the ring system (**181**); the crystal structure indicated a B—N bond distance of 1.600 Å. The compounds could be reduced to derivatives (**182**).[246]



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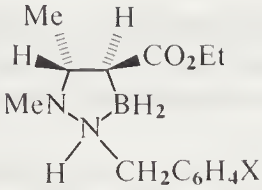
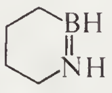


(182)

5.2.6.4 Boron–Nitrogen Analogues of Aromatic Hydrocarbons

In view of the analogy of a BN unit with a CC unit, and the possibility of π-interaction between the atoms, much effort has been expended on the synthesis of BN analogues of aromatic hydrocarbons; comparisons are then drawn between the two systems, and the extent of aromatic delocalization has been the subject of much theoretical speculation and experimental investigation. A recent review on the field has been published,[68] in addition to earlier reviews.[5]

The benzene analogue 1,2-azaborine, and its *N*-substituted derivatives, have been the subject of investigations. Attempts to make the starting compound **(183)** by treating but-3-enylamine with hydroboration reagents such as $Me_3N{\cdot}BH_3$ or chloroboranes resulted only in the formation of borazenes, whereas *N*-methylbut-3-enylamine or *N*-phenylbut-3-enylamine with $Me_3N{\cdot}BH_3$ led to the substituted ring **(184)**, with some dimeric side-products.[206]



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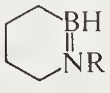
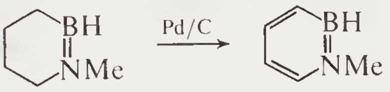


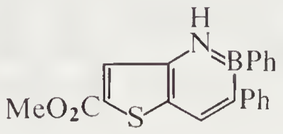
(184)

The *N*-methyl derivative could be dehydrogenated to yield the highly reactive *N*-methyl-2,1-borazarene **(185)**, which was identified only by its mass and IR spectra.[207] The compound is subject to rapid polymerization. Its behaviour is much more like polarized butadiene than benzene, resulting from the electronegativity difference between boron and nitrogen.



(185) (97)

Earlier routes[68] to the 1,2-azaborabenzene ring involved condensation of methyl-2-styryl-3-aminothiophene-5-carboxylate with phenylboron dichloride giving **(186)**, which could be desulphurized to **(187)**. Condensation of 4-aminobut-1-ene with diborane followed by dehydration, and decomposition of the borazine analogue of triphenylene **(188)**, also led to azaborabenzene derivatives.



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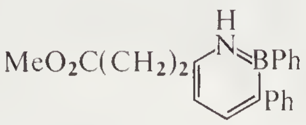

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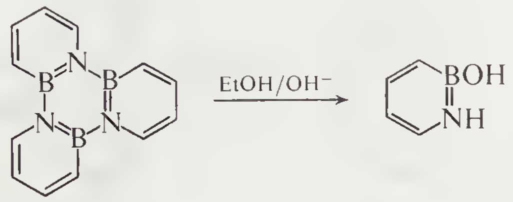
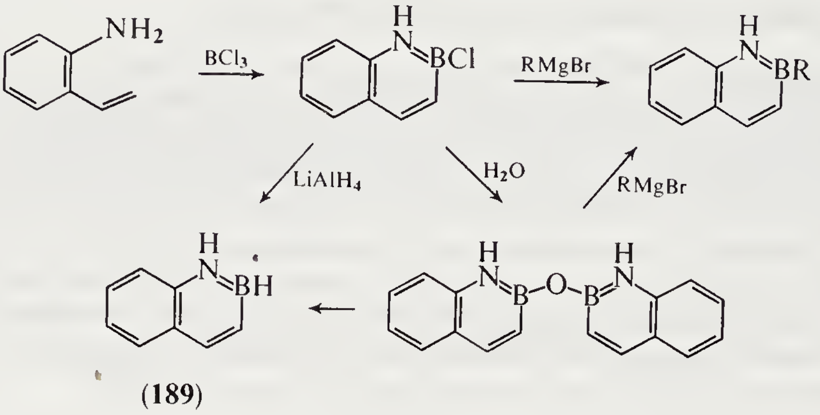


(188) (98)

9,10-Azaboranaphthalene (**175**) has already been described as the dehydrogenation product of 9-aza-10-boradecalin (reaction 95). The chemical shifts of the ^{11}B NMR signals of (**175**) and its 4-bromo derivative have been quoted as evidence of aromatic character of the ring system.[208]

A number of derivatives of 1-aza-2-boranaphthalene (**189**) were first reported by reactions (99)–(101).[5] An alternative synthetic method to 1-aza-2-boranaphthalene involved the cycloaddition of an aryne to an aminoborane (equation 102).[209] The ^{11}B NMR spectra of a number of derivatives have been reported.[55]



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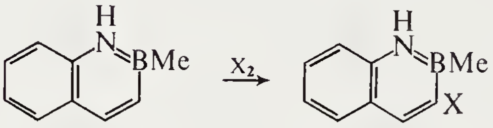

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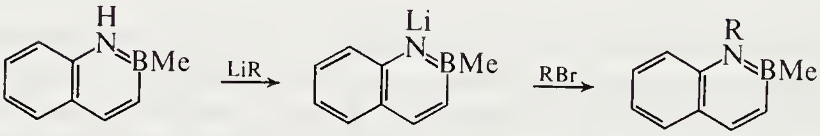

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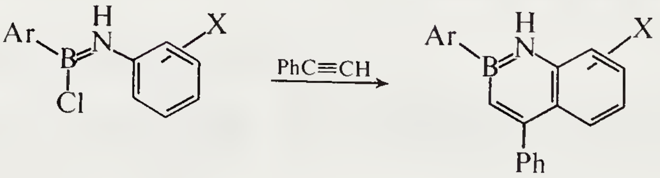
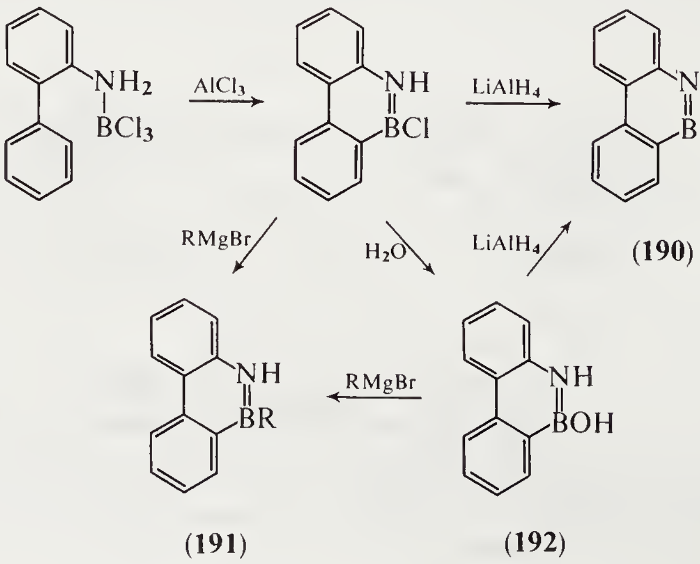


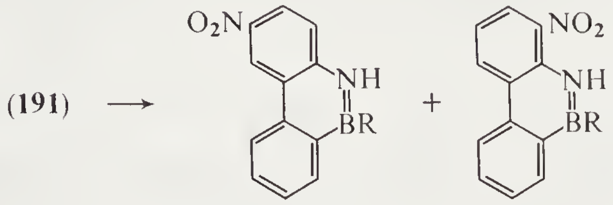
(102)

9-Aza-10-boraphenanthrene (**190**) and a number of its derivatives[5a,68] were first synthesized through a Friedel–Crafts ring closure reaction (equation 103).[210] A similar reaction between



(103)

2-aminobiphenyl and KBF_4 with $AlCl_3$ led to (**192**).[211] Aromatic substituted derivatives were obtained through nitration (equation 104),[212] and *N*-substituted derivatives have been obtained through N—Li intermediates[213,214] which can be further lithiated to give the reduced ring system (**193**).



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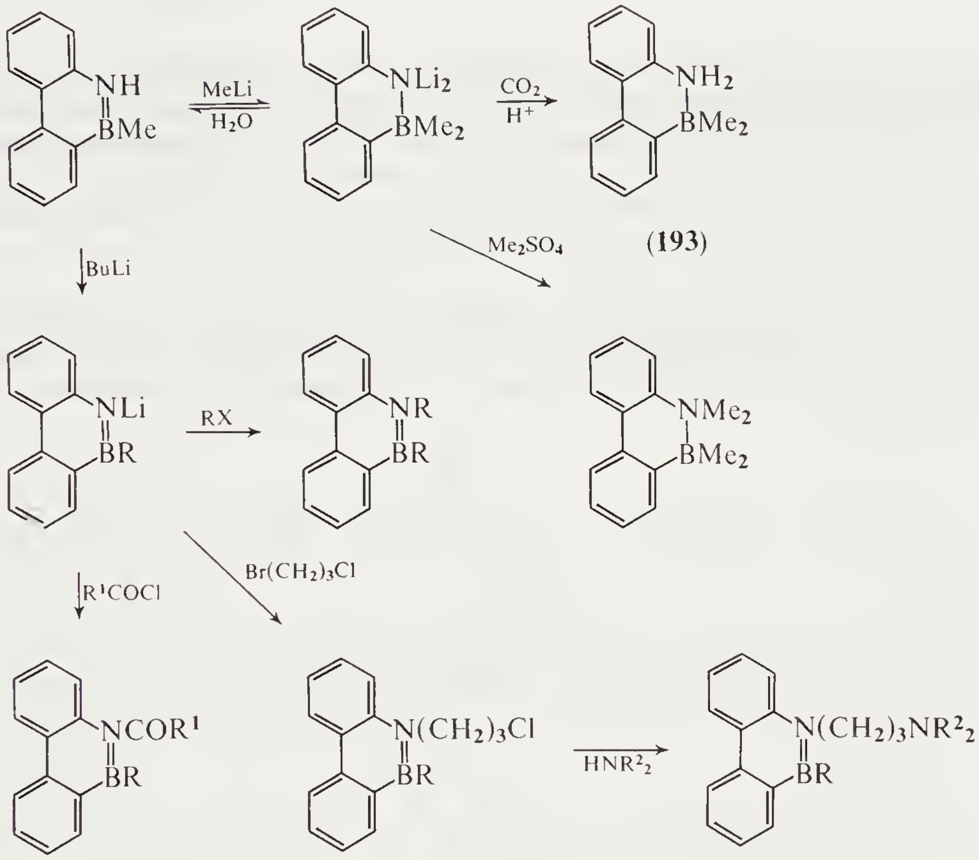
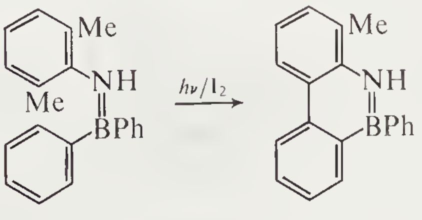


(105)

An alternative route to the 9,10-azaboraphenanthrene ring system has been through oxidative photocyclization of anilinodiphenylboranes substituted in the anilino ring.[215,216] Thus the 2,6-dimethyl derivative (**194**) eliminated methane to give (**195**), whereas anilinodimesitylborane yielded mainly derivative (**196**) by a 1,2-methyl migration.[217] In a similar reaction, 10-phenyl-8,9-diaza-10-boraphenanthrene (**197**) was obtained from a photochemical reaction between 2-aminopyridine and diphenylboron chloride.[218]



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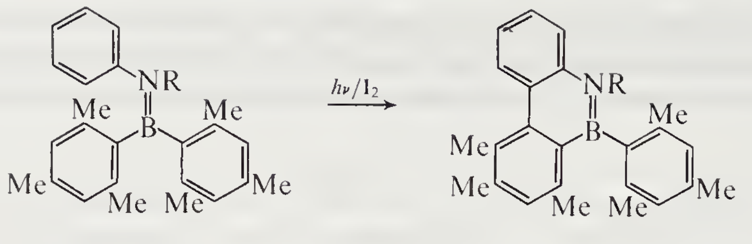
(**194**) (**195**)



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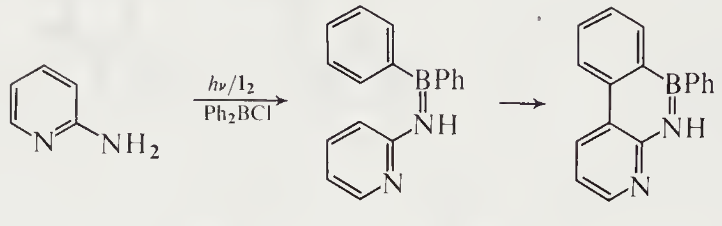
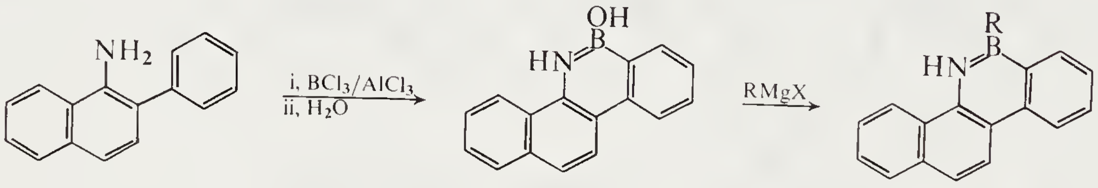


(197)

(108)

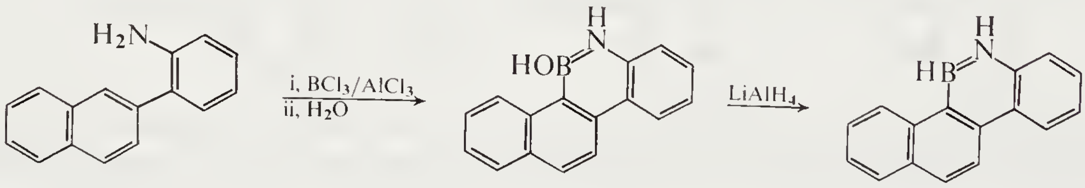
The dipole moment of (**191**; R = Me) was reported,[219] and calculations of π-electron density by the Hückel method indicated 'aromatic character', whereas studies of ^{11}B shifts indicated the absence of resonance stabilization, suggesting rather that the B—N bonds are closely similar to those in acyclic compounds. Furthermore, the formation of salts[220] from 10-hydroxy-9-aza-10-boraphenanthrene (**192**) and the ready formation of the tetramethylammonium salt of 10,10-dihydroxy-9-aza-10-boraphenanthrene suggest that the aromatic nature of the ring system is, at best, tenuous.[221]

A number of other related polycyclic aromatic systems have also been synthesized by ring-closure reactions. 11-Aza-12-borachrysene and 12-aza-11-borachrysene derivatives have been made by reactions (109) and (110).[222] Other related systems are summarized by reactions (111)-(114).[223,224]



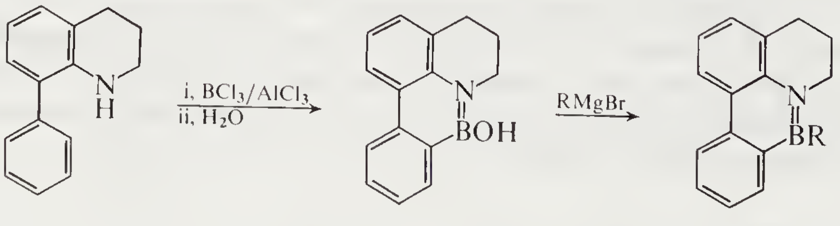
(198) **(199)**

(109)



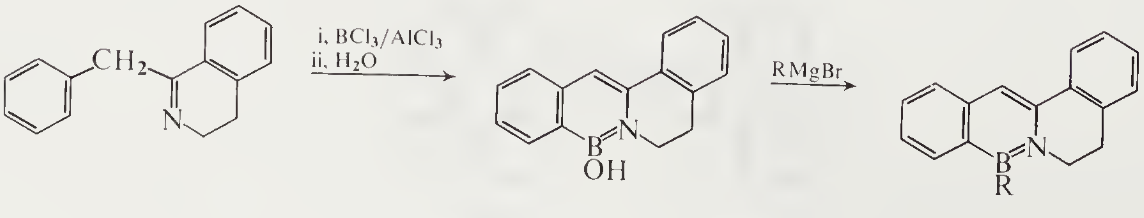
(200) **(201)**

(110)



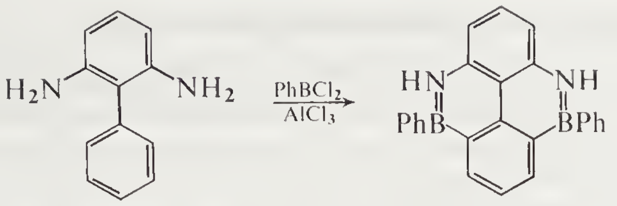
(202) **(203)**

(111)



(204) **(205)**

(112)



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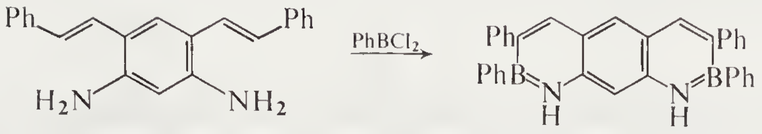
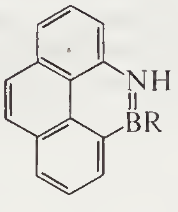


(207)

(114)

Friedel–Crafts cyclization of 4-aminophenanthrene and boron trichloride gave (**208**) with difficulty, and an alternative route involving reduction of 4-nitro-9,10-dihydrophenanthrene followed by cyclization led to (**209**).[68]



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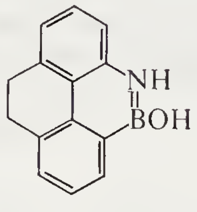
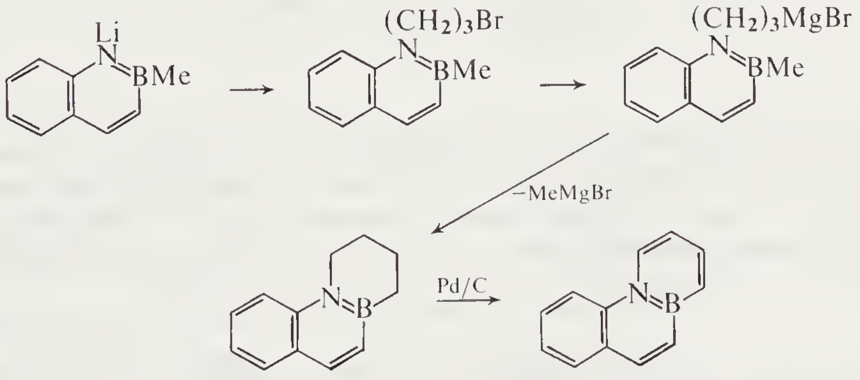


(209)

A ring-closure scheme involving elimination of a Grignard reagent has been used to prepare (**210**) and similar reactions led to (**211**) and (**212**).[68] Some doubt has been cast on the reported existence of the 11,12-azaboraphenalenenium cation (**213**), on the basis of UV spectra.[68]



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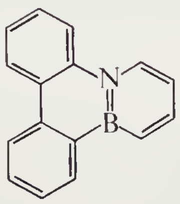

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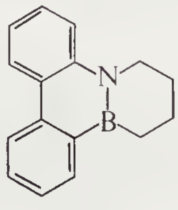

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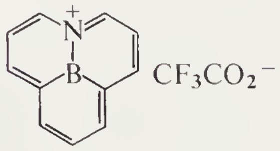
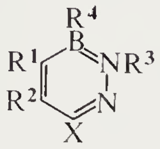


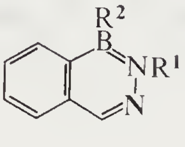
(213)

5.2.6.5 Boron–Nitrogen Analogues of Aromatic Heterocycles

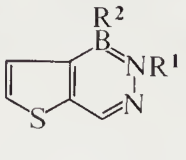
The 2,3-azaborapyridine ring system (**214**), the related fused rings 3,4-azaboraisoquinoline (**215**) and the isomeric azaborathienopyridines (**216**)–(**218**) show considerable chemical stability.[68] Derivatives of the 2,3-azaborapyridine ring have been prepared by desulphurization of various azaborathienopyridines,[225–227] usually with Raney nickel. The compound (**214**; R^1 = Et; R^2, X = H; R^3, R^4 = Me) brominates readily at the 6-position; the derivative (R^1, X = H; R^2 = Et; R^3, R^4 = Me) undergoes ready bromination at positions 4 and 6. Nitration also occurs at positions 4 and 6 in these derivatives.[228,229]



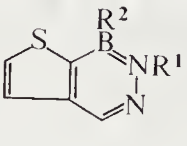
(**214**)



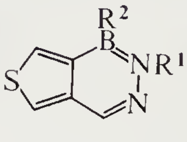
(**215**)



(**216**)

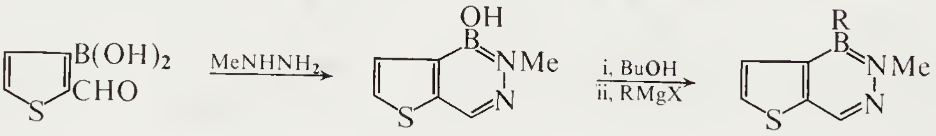


(**217**)



(**218**)

The azaborathienopyridines have been prepared from formylthiopheneboronic acids and hydrazine derivatives, as in equations (116)–(118).[230–231] A number of derivatives of these systems have been examined for their effectiveness against bacteria. The ring system (**218**) was the least stable of the azaborathienopyridines. A number of substitution reactions have been studied.[68] Derivatives of (**216**) and (**217**) where R^2 = H have been prepared by reduction of the R^2 = OH compounds with $LiAlH_4$.[232] Investigation of the rates of deuteria-deprotonation on R^2 = OH derivatives of (**216**) and (**217**) occurred mainly in the 3-position, and that the similarity of the rates to those of the heterocyclic analogues indicated the aromaticity of the B—N ring system.[233] The X-ray structure of (**217**; R^2 = OH, R^1 = Me) confirmed the planarity of the system, and the B—N bond distance of 1.435 Å was similar to that in borazine.[234]



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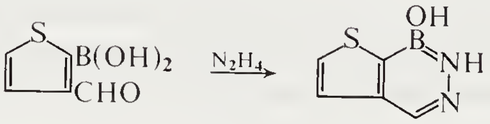
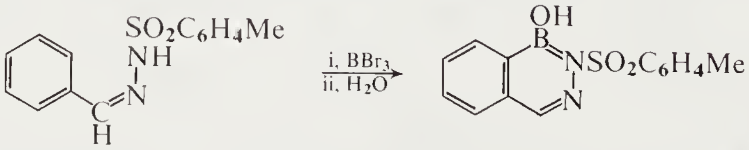


(117)

(118)

The 3,4-azaboraisoquinoline ring system (**215**) has been prepared by treating *o*-formylboronic acid with hydrazine and its derivatives,[235] or more recently by ring closure reactions on arenesulphonylhydrazones with boron halides (equation 119).[236,237] The same route can be used to synthesize the azaborathienopyridines, and the extended ring system (**219**), and these also are of potential antibacterial interest.[238]



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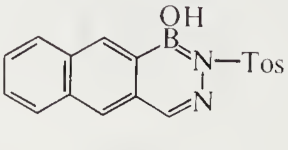
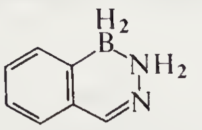
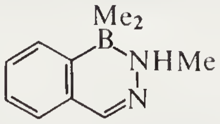


(**219**)

The B—N bond of (**215**; $R^1 = H$, $R^2 = \frac{1}{2}O$) was reduced with $LiAlH_4$ to 1,2,3,4-tetrahydro-3,4-azaboraisoquinoline (**220**); the crystal structure of (**221**) indicated a half-chair ring with the B—N bond lengthened to 1.645 Å.[239]

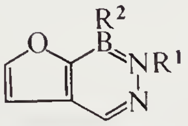


(**220**)

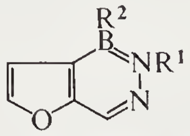


(**221**)

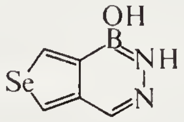
Reactions of formylfuranboronic acids with hydrazines led to derivatives of the type (**222**) and (**223**),[240,241] and these also were compounds of biological interest, having antibacterial properties.[242] A similar route led to the selenium derivative (**224**).[243]



(**222**)

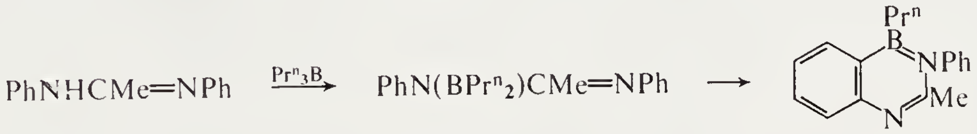


(**223**)



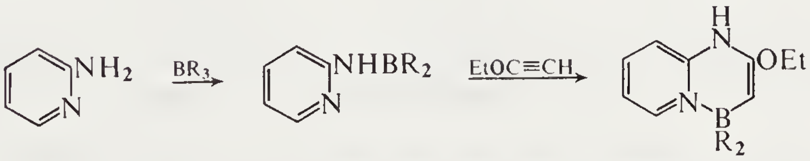
(**224**)

Pyrolytic ring closure of an organoborane adduct of an imine led to derivatives of the 3-aza-4-boraquinoline ring system (**225**).[244] The ring system (**226**) was derived from 2-aminopyridine by reaction (121).[245]



(120)

(**225**)

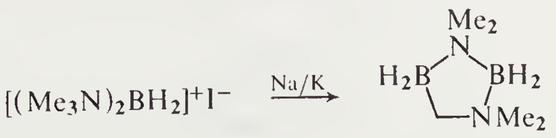


(121)

(**226**)

5.2.6.6 Boron–Nitrogen Derivatives with More than One Boron Atom

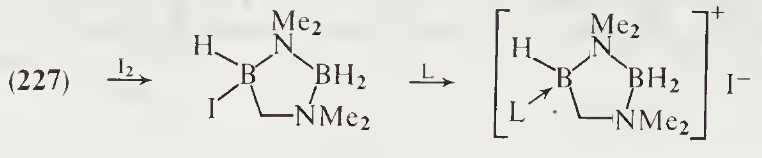
When bis(trimethylamine)dihydroboronium iodide was reduced, 1,1,3,3-tetramethyl-1,3-diazonia-2,4-diboratocyclopentane (**227**) was formed.[246,247] The compound could be halogenated with halogens or hydrogen halides to yield monohalogenated derivatives with the substituent in

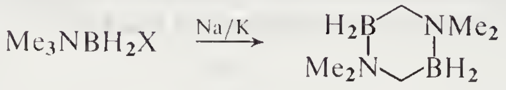


(122)

(**227**)

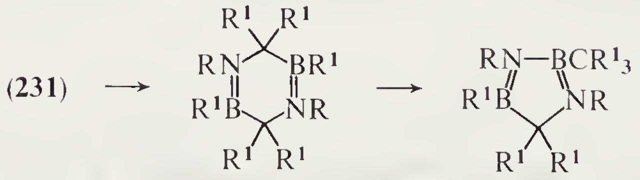
the 4-position, and also polyhalogenated species. The iodo derivative (**228**) reacted with Lewis bases to form cationic ring derivatives (**229**).[248] The related six-membered ring 1,1,4,4-tetramethyl-1,4-diazonia-2,5-diboratocyclohexane (**230**) was obtained from the reaction between trimethylaminemonohaloboranes and Na/K alloy. Its crystal structure confirmed the nature of the ring.[249,250]


(**228**) (**229**) (123)

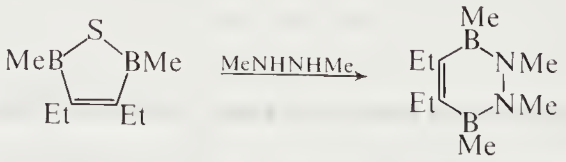

(**230**) (124)

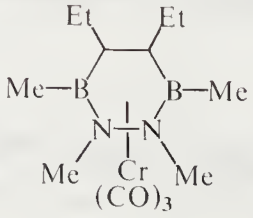
Two related ring systems were obtained from the reactions between organoboranes and isocyanides.[251–257] The reaction initially yields an adduct which is thermodynamically unstable with respect to the dimer ring (**231**); these undergo rearrangement on heating to yield the isomeric structure (**232**), certain derivatives of which undergo ring contraction on heating further to give the ring system (**233**).


(**231**) (125)

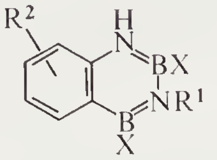

(**232**) (**233**) (126)

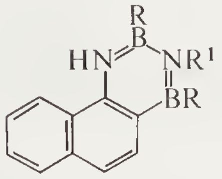
A compound (**234**) analogous to benzene, but with two B—N units, has been synthesized as an air-sensitive liquid by treating 3,4-diethyl-2,5-dimethyl-1,2,5-thiadiborolene with *N*,*N*′-dimethylhydrazine.[258] The compound behaves as a six-electron donor and reacts with tris(acetonitrile)tricarbonylchromium to give the *hexahapto* complex (**235**).


(**234**) (127)

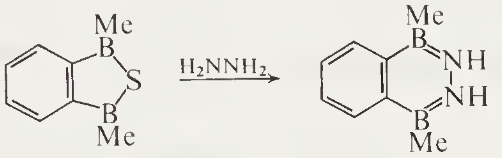

(**235**)

The elimination of hydrogen halide from adducts of arylamines with boron halide derivatives, in particular the triiodide, led to compounds of the type (**236**), derivatives of 1,3-diaza-2,4-diboranaphthalene.[259,260] Halogen exchange could be effected at the 2,4-positions on treatment with suitable metal halides. A similar reaction with α-naphthylamine led to the derivatives (**237**).[261–265]


(**236**)


(**237**)

Two-boron/two-nitrogen ring systems (**238**) and (**239**) have been derived from the corresponding two-boron/sulphur system by treatment with hydrazine derivatives.[266] Derivatives of (**238**) have been shown to form complexes with Cr, Mo and W through the benzo ring, and these are more stable than the corresponding benzene complexes.[267]


(128)

(**238**)


(129)

(**239**)

5.2.7 RINGS INVOLVING AN OXYGEN HETEROATOM BONDED TO BORON, IN ADDITION TO A BORON–CARBON RING BOND (C—B—O RINGS)

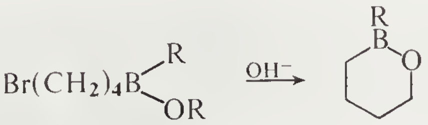
5.2.7.1 Boron–Oxygen Analogues of Cycloalkanes and Cycloalkenes

The simple five-membered ring compounds 1,2-oxaborolanes (**240**) have been prepared by the hydroboration reaction,[268] and a study of the association has been made by ^1H and ^{11}B NMR spectroscopy.[269] Similarly, the action of allyl alcohol on trialkylboranes has also been used as a preparative route. 2-Alkoxy-1,2-oxaborolanes were prepared by the action of tributylborate on the products of hydroboration of triallylborate or allyl alcohol.


(130)

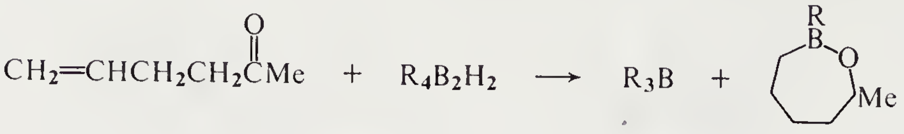
(**240**)

The six-membered heterocycles, (2-alkyl-1,2-oxaborinanes) (**241**) were synthesized by the hydrolysis of methyl alkyl(4-bromobutyl)borinates.[270]

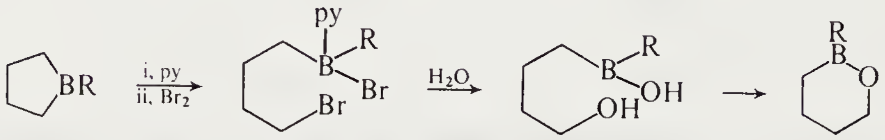

(131)

(**241**)

Hydroboration of 5-hexen-2-one or 5-hexen-2-ol with tetraalkyldiboranes led to the seven-membered 1,2-oxaborepane (equation 132).[271] The boron reacts with OH^- or amine ligands. Alternatively, the six- and seven-membered rings can be prepared by the ring expansion reactions,[272,273] as in equations (133) and (134).

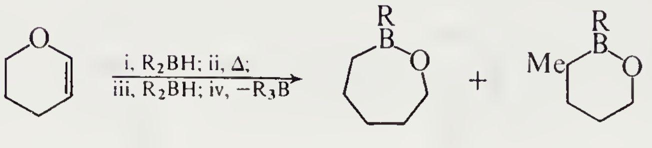


(132)



(133)

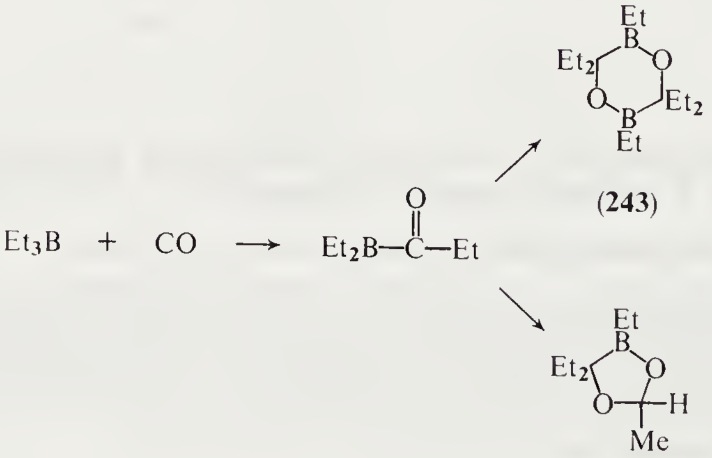
(**241**)



(134)

(**242**)

The interaction of trialkylboranes and carbon monoxide leads to CO insertion into a boron–carbon bond, and the intermediate subsequently can give either five- or six-membered rings (equation 135).[274]

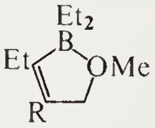


(**243**)

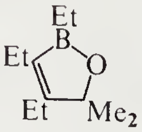
(135)

(**244**)

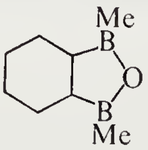
The NMR spectra of a number of derivatives of the ring systems (**245**) and (**246**) have been described.[205] The interaction of [MeB], generated from $MeBBr_2$ and NaK_5, with cyclohexene gave a number of products, one of which was 'identified' by GLC–MS as (**247**).[275] Boron–oxygen rings have also been obtained from the reactions of acetylenic derivatives with triallylborane.[276,277]



(**245**)

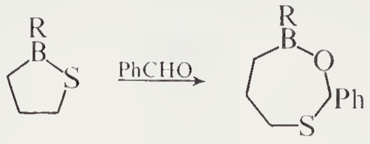


(**246**)



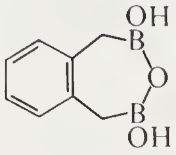
(**247**)

Insertion of aldehydes and ketones into a thiaborolane ring also yields boron–oxygen ring derivatives (**248**), although in some instances the reaction was reversible.[278] Other systems which have been reported include compounds (**249**) and (**250**).[279,280]

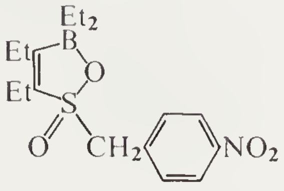


(136)

(**248**)



(**249**)



(**250**)

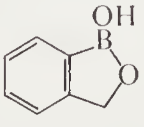
5.2.7.2 Aromatic Boron–Oxygen Rings

The delocalization of electrons from π-interaction of a boron–oxygen linkage with an aromatic system has been the subject of a number of investigations by analogy with the boron–nitrogen systems described in Section 5.2.6.[68] In general, the boron–oxygen ring systems are much less 'aromatic' than their boron–nitrogen analogues.

Preparation of a boron–oxygen analogue of the benzene ring has been described by equation (137).[281] The internal ester of *o*-hydroxymethyl phenylboronic acid (**252**) is stable to nitration, although the stability probably arises as a result of its cyclic nature rather than its aromatic character.[282,283] The compound can also be diazotized.[284]

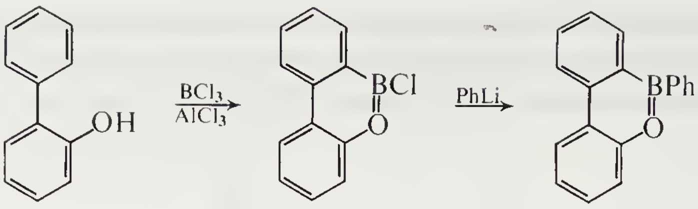
(137)

(**251**)



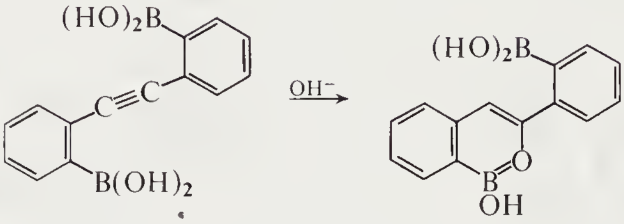
(**252**)

The boraoxa aromatic systems (**253**)–(**256**) have been obtained from ring-closure reactions as in equations (138) and (139).[5a,68] Derivatives of (**257**) have found use as antioxidants for white oil,[285] and its salts have analgesic, anticonvulsive, antiserotonin and antioxytocin properties.[286] Boraoxabenz[*a*]anthracenes (**258**) have also been obtained from the nitrogen analogues, but are much less aromatic.[68]



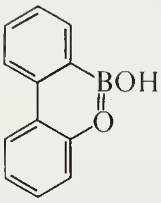
(253) **(254)**

(138)



(255)

(139)



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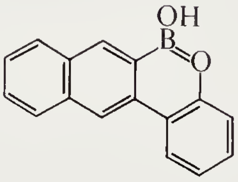

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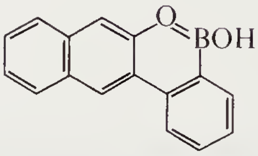
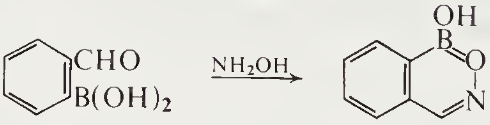


(258)

Heterocyclic analogues have been described by methods analogous to the boron–nitrogen systems (equations 140–142).

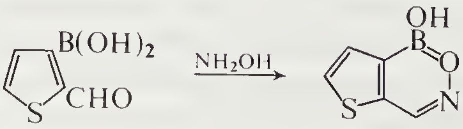


(259)

(140)

(260)

(141)

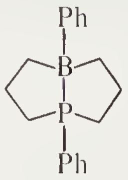


(261)

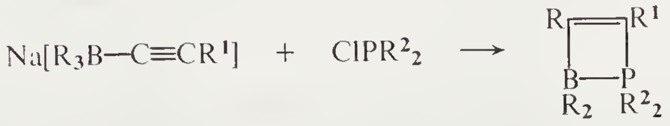
(142)

5.2.8 RINGS INVOLVING PHOSPHORUS, SULPHUR OR OTHER HETEROATOMS BONDED TO BORON (C—B—P AND C—B—S RINGS)

When diallylphenylphosphine was hydroborated with triethylaminephenylborane, a thermally very stable compound (**262**) was obtained.[287] Sodium trialkyl-1-alkynylborates react with chlorodiorganophosphines to give organo-1,2-phosphaboret-3-enes (equation 143).[288,289]



(**262**)



(**263**)

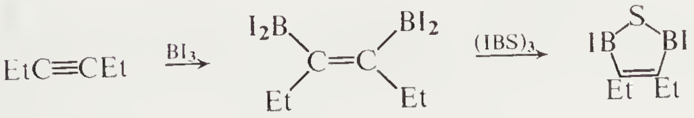
(143)

When Me_2BCH_2Cl was treated with Me_2PH, a compound of empirical formula $Me_2BCH_2PMe_2$ resulted. This compound was monomeric at 125 °C but gave a dimeric molecular ion. Similar associated species were obtained with Me_2AsH and MeSH.[290]

Hydroboration of allylthiol with 1,2-dibutyldiborane led to the 2-butyl-1,2-thiaborolane (**264**).[278,291]

(**264**)

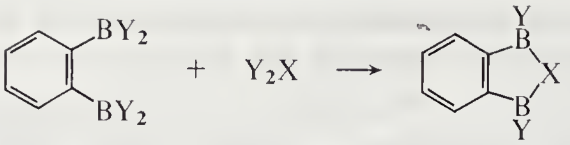
The delocalized ring system Δ^3-1,2,5-thiadiborolene (**265**) has been made from hex-3-yne, by adding BI_3 and then inserting sulphur from $(IBS)_3$,[292] and a number of 2,5-substituted derivatives obtained by substitution reactions.[293] The crystal structure indicates two planar molecules associated in the unit cell such that boron–sulphur interactions occur, forming a four-membered B—S ring.[294] The sulphur in the ring can be replaced by the nitrogens of a hydrazine (reaction 127). The ring also acts as a ligand in a number of metal complexes, and multidecker sandwich complexes with Fe, Mn and Ni have been described.[295–297]



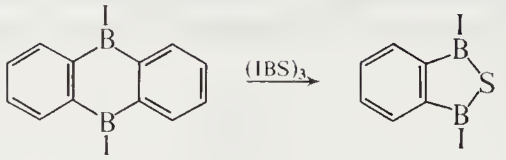
(**265**)

(144)

Aromatic thiadiborolene rings have also been synthesized by several routes (equations 145–148).[266] These rings also will form metallo complexes.[298] A related selenadiborolene ring has been obtained by the ring-closure reaction (149).[299]



(145)



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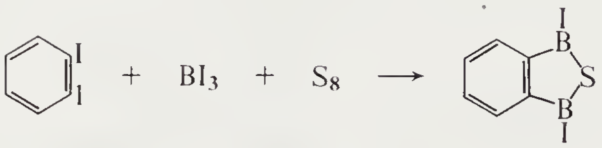

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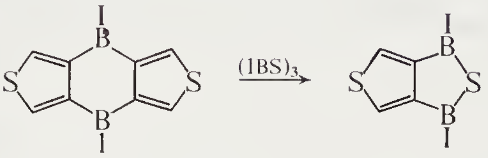
(266)



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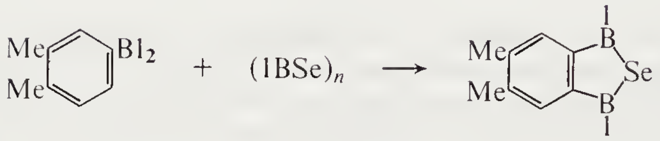
(267)



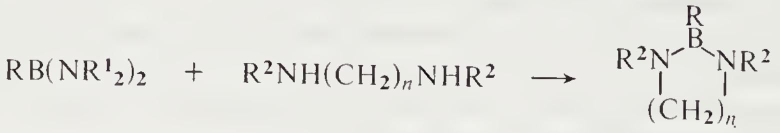
(149)

(268)

5.2.9 RINGS INVOLVING TWO NITROGEN ATOMS BONDED TO BORON (N—B—N RINGS CONTAINING CARBON)

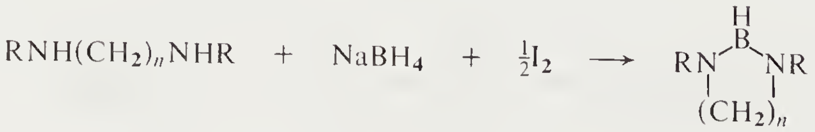
5.2.9.1 1,3-Diaza-2-boracycloalkanes

A series of rings of general structure (**269**) have been described, and their chemical and physical properties investigated during the last quarter century. The methods of synthesis have included transamination reactions of alkylaminoboranes with α,ω-diamines,[300] as in equation (150), or alternatively by treating the diamine with diborane (reaction 151) or an amine–borane (reaction 152).[67,301] The elimination of hydrogen halide from *N*,*N*-diphenyldiaminoborane and alkylboron dihalide has also given the five-membered ring system, as in equation (153).[302]



(150)

(269)



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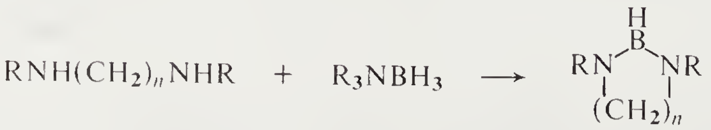

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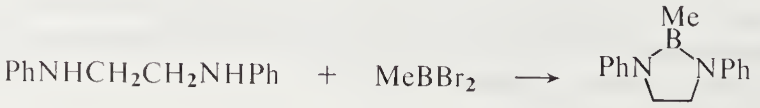
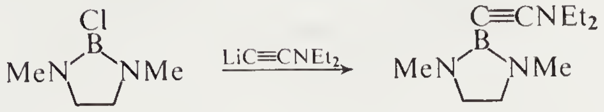


(153)

Numerous derivatives of the rings have been prepared with organic and inorganic substituents at boron. For example, organometallic reagents react readily with boron–halogen derivatives, as in equation (154) and (155).[77,303,304]

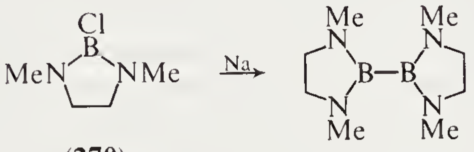


(270)

(154)

(155)

Boron-boron coupled rings can be prepared by 'Wurtz' type reactions on 2-chloro-1,3-diaza-2-boracycloalkanes, or by treating diboron tetrachloride with diamines (reactions 156 and 157).[305]

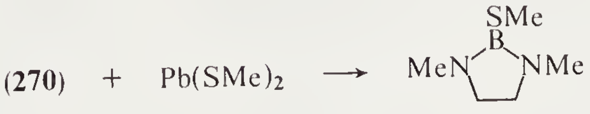


(270) **(271)**

(156)

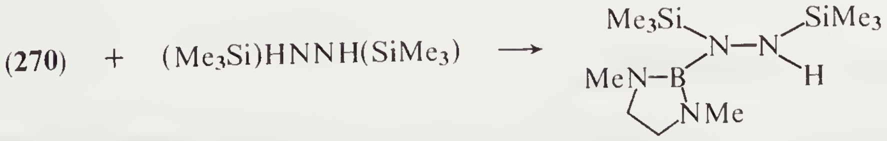
$$B_2Cl_4 + MeNHCH_2CH_2NHMe \longrightarrow \textbf{(271)} \qquad (157)$$

Various hydrazino substituted diazaboracycloalkanes have been obtained from 2-chloro-1,3-diaza-2-boracycloalkanes (**270**) and partially substituted hydrazines; alternatively, 2-alkylthio-1,3-diaza-2-boracycloalkanes (**272**) have been used as starting materials.[306,307] Examples of such reactions are given in equations (158)–(161).



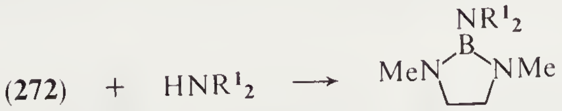
(272)

(158)



(273)

(159)



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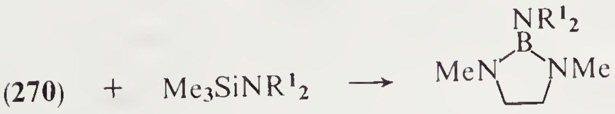
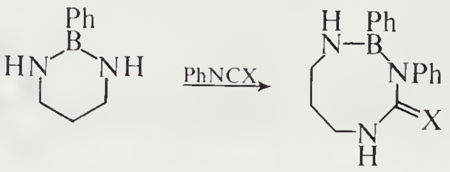


(161)

The 1,3-diaza-2-boracycloalkane ring system also undergoes the ring insertion reactions (162) and (163) with 1,3-dipolar reagents such as isocyanates, and the extended ring systems (**274**) and (**275**) are formed.[308-311]



(162)

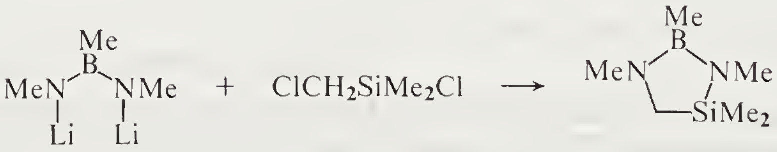
(**274**)

(163)

(**275**)

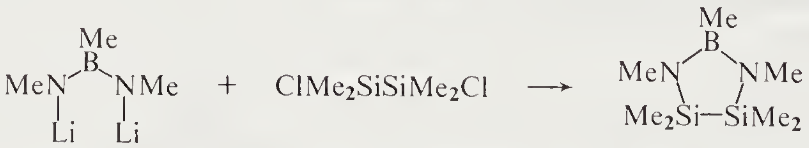
Many studies of the NMR spectroscopic properties of diazaboracycloalkanes have been made.[77,312-322] These have included the nuclei ^{1}H, ^{11}B, ^{13}C and ^{14}N, and have concerned aspects such as conformational studies in ring systems, correlations of chemical shift with electron delocalization and p–p π-bonding, and transmission of substituent effects. Mass spectral studies have indicated gaseous borenium cations, BX_2^+, which arise with cleavage of exocyclic groups.[323]

Derivatives of diazaboracyclopentane, (**276**) and (**277**), in which one or both of the carbons were replaced by silicon have been prepared from *N*-lithio derivatives of aminoboranes by treatment with chlorosilane derivatives.[324] ^{11}B NMR indicated significant N—B π-bonding in the compounds.



(164)

(**276**)

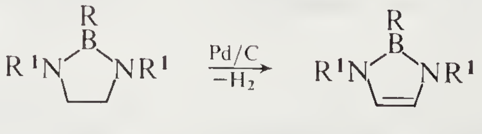


(165)

(**277**)

5.2.9.2 1,3-Diaza-2-boracycloalkenes

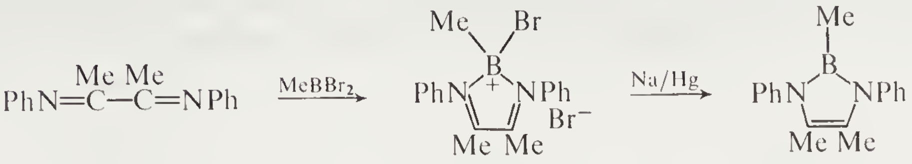
It has proved possible to dehydrogenate 1,3-diaza-2-boracyclopentane derivatives with palladium/charcoal (reaction 166); the resulting diazaboracyclopentenes (**278**) show significant electron delocalization in their experimental and spectroscopic properties, and MO calculations also support this.[325,326]



(166)

(**278**)

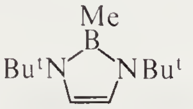
An alternative route to the 1,3-diaza-2-boracyclopentene ring system (**280**) has been the reaction between an α,β-diimine and an alkylboron dihalide. The intermediate cationic ring compound (**279**) was reduced with sodium amalgam (reaction 167).[327,328] The compounds, however, are unstable and rapidly decompose, although the spectroscopic properties of a number of derivatives have been reported.



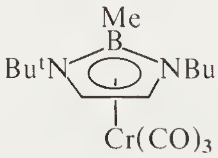
(**279**) (**280**)

(167)

Further evidence for a delocalized 6π-electron ring system came from the isolation of a tricarbonylchromium complex (**282**) from $(MeCN)_3Cr(CO)_3$ and (**281**).[329]



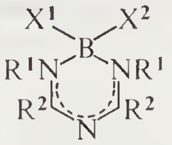
(**281**)



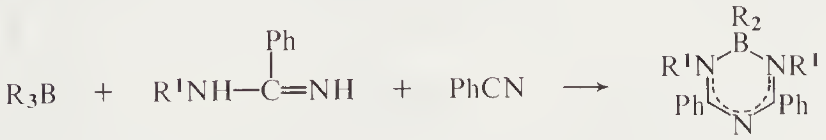
(**282**)

5.2.9.3 Other Monocyclic Compounds

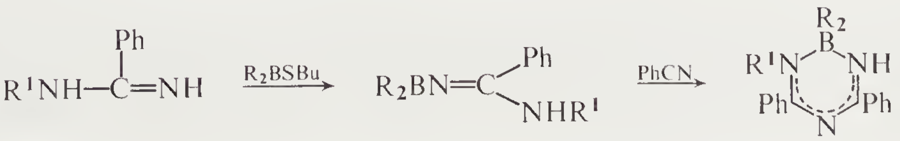
Biguanide was shown to react with aminoboranes and boron acids to give heterocycles containing four-coordinate boron (**283**).[330] The ring was more stable to hydrolysis than the 9,10-azaboraphenanthrene system. Similar compounds were also prepared by heating a mixture of benzamidine, benzonitrile and trialkylborane.[331] Other reactions leading to the ring system are summarized in equations (168) and (169).[332] A related ring system (**284**) was prepared by treating the adduct of acetamidine and tripropylborane with two moles of aminodipropylborane (equation 170).[333]



(**283**)



(168)



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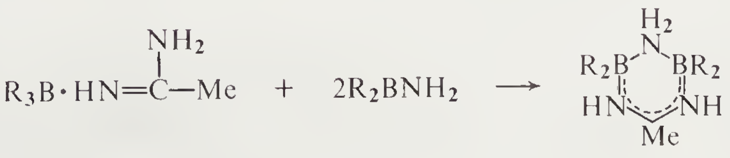
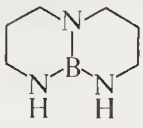


(170)

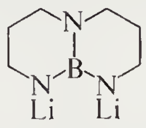
(**284**)

5.2.9.4 Polycyclic Compounds including Aromatic Derivatives

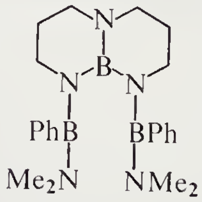
The transamination reaction between 3,3-diaminodipropylamine and tris(dimethylamino)-borane gave 1,8,10,9-triazaboradecalin (**285**) in good yield.[334] The compound was readily metallated at the 1,8-positions with lithium alkyls, and the dilithio derivative (**286**) was a useful precursor to a number of derivatives (**287**–**289**).[335] Unsymmetrically substituted derivatives were also prepared by transamination reactions.[336] In common with the diazaboracycloalkanes, insertion reactions with 1,3-dipolar reagents led to ring expansion, and products of the type (**290**)–(**292**).



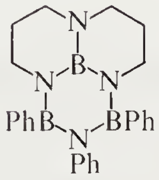
(**285**)



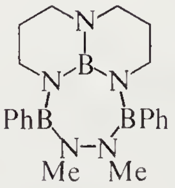
(**286**)



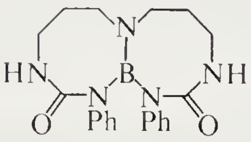
(**287**)



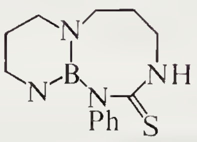
(**288**)



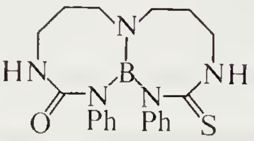
(**289**)



(**290**)



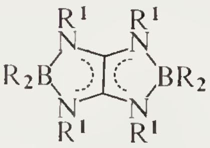
(**291**)



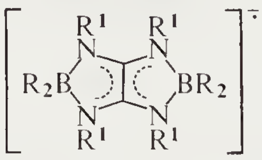
(**292**)

Transamination reactions on tris(aminoalkyl)amines by tris(dimethylamino)borane did not easily lead to the expected tryptic derivatives, but gave polymeric materials instead.[337]

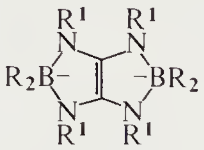
The reaction between *sym*-tetraethyloxamidine and trialkylborane gave the highly stable ring system (**293**) in high yield.[338] The compound was reduced in two stages by potassium metal; initially, a green radical anion (**294**) formed, and subsequently a red dianion (**295**) resulted.



(**293**)

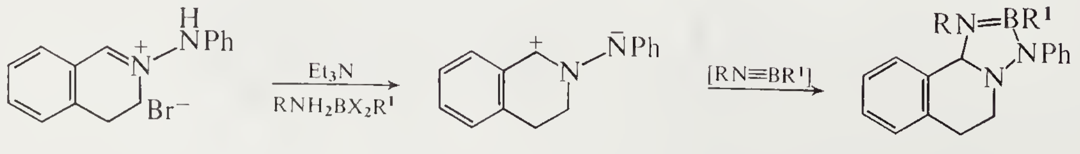


(**294**)



(**295**)

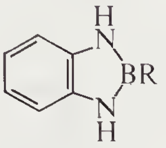
1,3-Dipolar cycloaddition reactions have led to a number of boron heterocycles. Thus the intermediate boron imide, produced from dehydrohalogenation of the adduct of a primary amine with an organoboron dihalide, reacted with the dipolar compound (**296**) according to equation (171) to give the heterocycle (**297**).[339]



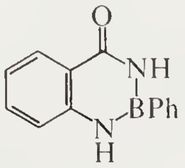
(171)

(**296**) (**297**)

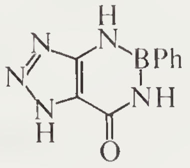
Elimination reactions of boron halide or boronic acid derivatives with amine derivatives have led to a number of heterocycles. Thus $PhBCl_2$ or $PhB(OH)_2$ with *o*-phenylenediamine led to (**298**),[340,341] and many derivatives behave similarly.[342,343] Related reactions occur with other diamines, and heterocycles of the types (**299**)–(**303**) result.[344–346] The carbonyl group in (**299**) was converted to an amino group by successive reactions with $POCl_3$, EtOH and NH_3,[347] resulting in the compound (**304**). Compounds of type (**298**) have also been obtained from *o*-phenylenediamine and trialkylboranes,[348,349] and the *N*,*N*′-bis(trimethylsilyl) derivative of *o*-phenylenediamine reacted with tris(dimethylamino)borane, or methylbis(methylthio)borane, to give derivatives of the same system.[350]



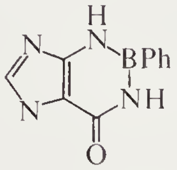
(**298**)



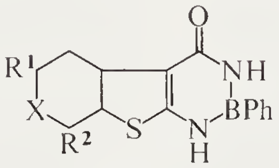
(**299**)



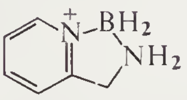
(**300**)



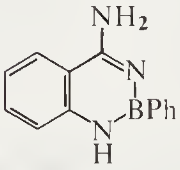
(**301**)



(**302**)

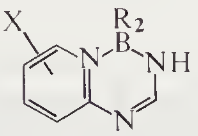


(**303**)

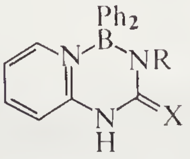


(**304**)

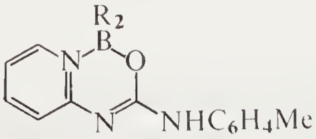
Condensation of 2-pyridylaminodialkylboranes with formamide gave the cyclic coordination compound (**305**);[351] the related system (**306**) resulted from the cyclic condensation of RNCX with 2-pyridylaminodiphenylborane.[352] Derivatives of the type (**306**) were also obtained from the reaction of *N*-(*o*-tolyl)-*N*′-(2-pyridyl)urea with butylthio(diphenyl)borane; the reaction also yielded the O—B—N ring system (**307**), which was thermally isomerized to (**306**).[353] Other systems which have been described are compounds (**308**) and (**309**).[354]



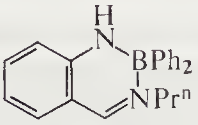
(**305**)



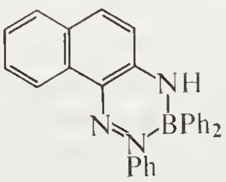
(**306**)



(**307**)

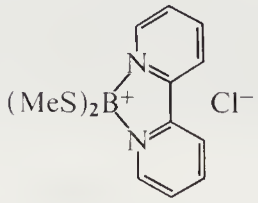


(**308**)

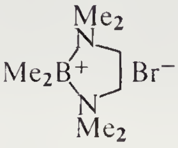


(**309**)

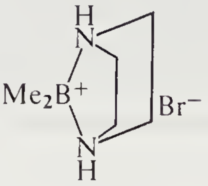
In addition to the cationic ring system (**303**), other cationic ring derivatives have been reported. $(MeS)_3B$ reacted with bipyridyl in the presence of CH_2Cl_2 to give the bipyridylboronium complex (**310**).[355] Other related boronium complexes are compounds (**311**)–(**318**).[356]



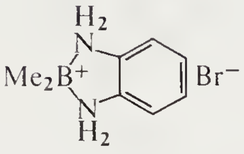
(**310**)



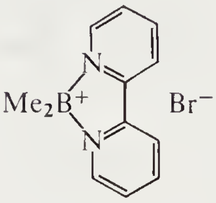
(**311**)



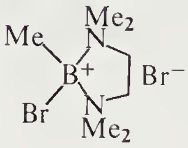
(**312**)



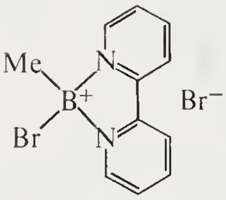
(**313**)



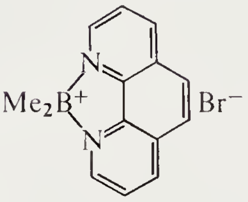
(**314**)



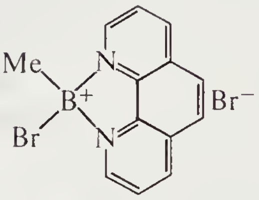
(**315**)



(**316**)

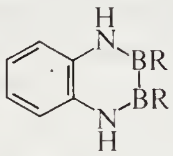


(**317**)

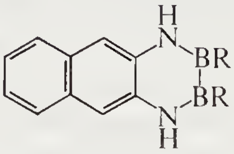


(**318**)

Three ring systems, (**319**), (**320**) and (**321**) which are related to the N—B—N rings but which contain N—B—B—N bonds, have been obtained from *o*-phenylenediamine or the corresponding naphthalenediamine, by utilizing a transamination reaction on bis(dimethylamino)dialkyldiboron derivatives.[357,358]



(319)



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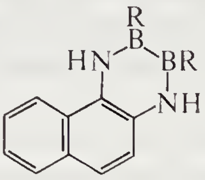
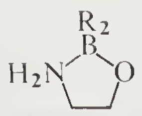


(321)

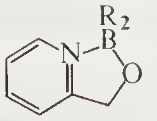
5.2.10 RINGS INVOLVING A NITROGEN ATOM AND ANOTHER HETEROATOM BONDED TO BORON (N—B—O, N—B—S AND RELATED RINGS CONTAINING CARBON)

5.2.10.1 Derivatives of Amino Alcohols and Amino Acids; Saturated Monocyclic Systems

It has long been known that amino alcohols form stable derivatives with boronic and borinic acids.[5c] Examples have already been described in earlier sections, including compounds (**87**) and (**139**) and reaction (71). In general, aminoethanol reacts with R_2BOH to yield compounds of general structure (**322**). The crystal structures (R = *p*-tolyl or phenyl) of some derivatives have been described.[359] Derivatives with chiral boron atoms have been made by reaction (172).[360] Compounds of the type (**324**) have also been described.[361]



(**322**)

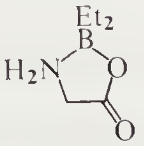


(**324**)

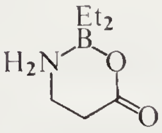
(**323**)

(172)

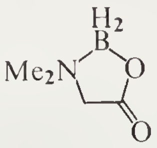
When trialkylboranes were treated with amino acids, stable five- or six-membered rings, (**325**) and (**326**), resulted.[362] Similar compounds (**327**)–(**329**) were obtained as intermediates in the hydrolysis of the (ethyldimethylglycine)trimethylamineboron(1+) cation, by displacement reactions of glycine derivatives on Me_3NBH_2I, and by substitution reactions on (**327**). The chemistry of the system led to the strong base (**330**).[363]



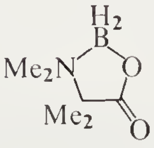
(**325**)



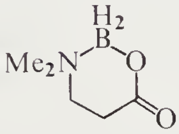
(**326**)



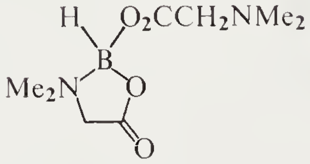
(**327**)



(**328**)

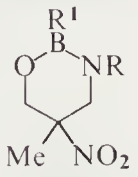


(**329**)

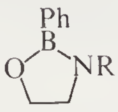


(**330**)

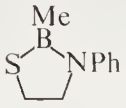
The reaction between $(O_2N)RNHMeCCH_2OH$ and $R'B(OH)_2$ led to the ring (**331**),[364] whereas that between $PhB(SEt)_2$ and $RNHCH_2CH_2OH$ gave (**332**).[365] A related N—B—S ring (**333**) has also been reported.[366]



(**331**)



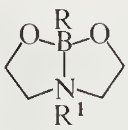
(**332**)



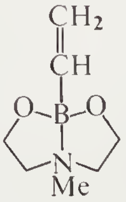
(**333**)

5.2.10.2 Saturated Polycyclic Systems

A number of early workers have reported the reaction between diethanolamines and organoboron derivatives as a route to the stable ring system (**334**).[367–369] The vinyl derivative (**335**) failed to be subject to oxidative polymerization.[370]



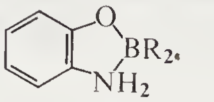
(**334**)



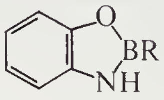
(**335**)

5.2.10.3 Unsaturated and Aromatic Systems

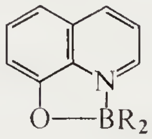
Much early work (see, for example, refs. 5a, 5c, 5g and 6b) was carried out on the reactions of 2-aminophenols with organoboranes, organoboron dihalides and similar compounds[371] to form the ring systems (**336**) and (**337**). The physical properties of these compounds have been studied, including ^{11}B NMR[372] and electrochemical properties.[373] Compounds of type (**337**) have also been prepared by the reaction between diborane and benzoxazole derivatives. The reaction proceeds through an intermediate borane complex.[374] The reaction between 8-hydroxyquinoline and trialkylboranes led to systems of the type (**338**),[375,376] whereas 2,5-bis(alkylamino)-1,4-benzoquinones and trialkylboranes gave the air-stable symmetric heterocycles (**339**).[377] Several diphenylboron chelates derived from azomethines (**340**) have been prepared by reactions of salicylaldehyde with primary amines, hydrazines or ammonia, and diphenylboronic acid anhydride.[378] Their mass spectral properties have been examined as a function of the substituent, R.[379]



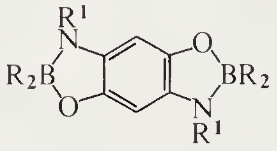
(**336**)



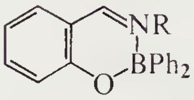
(**337**)



(**338**)

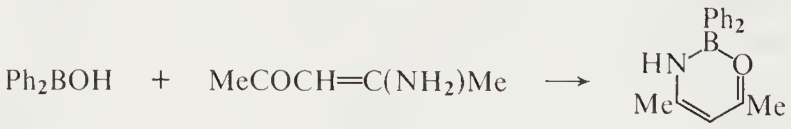


(**339**)



(**340**)

The heterocycle (**341**) was prepared by reaction (172),[380] and two related systems (**342**) and (**343**) were obtained by reactions (173) and (174) respectively.[381,382] The reactions between 2-pyridylamino-dialkyl- or -diaryl-boranes with aldehydes and ketones have been shown to give rise to the chelate rings of the type (**344**).[383,384] 2-Pyridylaminodiphenylborane also reacted with carbon dioxide to give (**345**), and (**346**) arose when oxygen was bubbled through a warm benzene suspension of the same starting compound, or by its partial hydrolysis and thermal breakdown.[385] Cleavage reactions of 2-amino- and 2-hydroxy-pyridine with dipropyl- or dibutyl-boric anhydride gave rise to the systems (**346**), (**347**) and (**348**).[386]

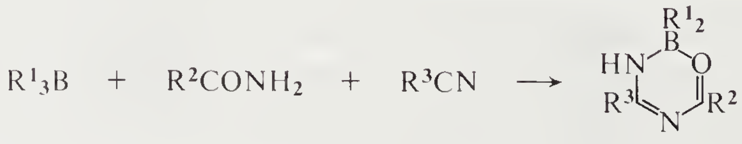


(**341**)

(172)

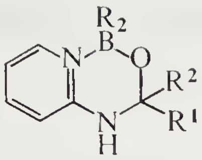
(**342**)

(173)



(**343**)

(174)



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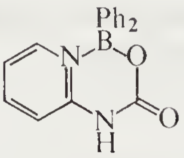

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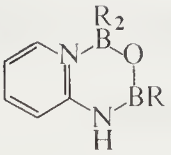

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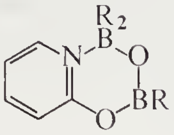

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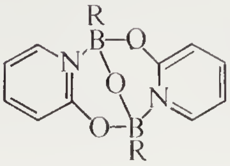


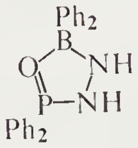
(348)

5.2.10.4 Other Rings with N—B—O Units

The ring (**349**) was prepared by reaction (175), and its spectroscopic and chemical properties studied.[387] Compound (**350**) was prepared by an analogous method. Ammonium pivalate reacted with two moles of triethylborane to give the ring system (**351**).[388] Dimeric amidoboranes of ring structure (**352**) were obtained by treating *N*-substituted trifluoroacetamides with boron trihalide.[389,390] The ring system (**353**) was obtained from reaction (176).[391] An X-ray study of spiro-9*H*-borepino[2,3-*b*:7,6-*b*′]dithiophene-9,2′-[1.3.2]oxazaborolidine showed that the seven-membered ring was in the boat form, and the oxazaborolidine ring was in the half-chair form.[392] The crystal structure of 4-methyl-2-phenyl-3*H*-1,3,5,2-oxadiazaboroline (**354**) showed both rings planar, with a dihedral angle of 4.5°.[393]

(175)

(349)



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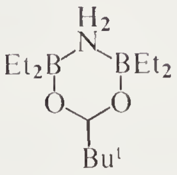

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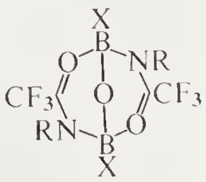

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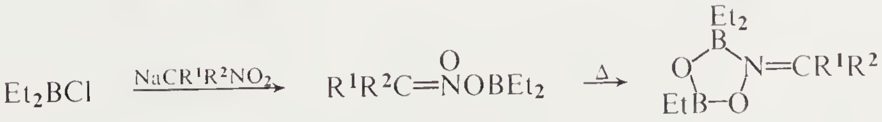

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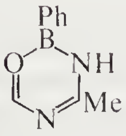
(353)



(354)

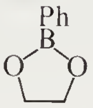
5.2.11 RINGS INVOLVING TWO OXYGEN ATOMS BONDED TO BORON (O—B—O RINGS CONTAINING CARBON)

5.2.11.1 Introduction

It would be totally inappropriate to try to cover exhaustively all the ring systems which involve the O—B—O unit, since it has long been known that polyhydric alcohols and related systems form stable chelates with boric acid and its derivatives. An extensive review of many of these systems is included in ref. 6a. Thus diols and polyols with units such as —CH(OH)—CH_2—CH(OH)— or —CH(OH)—CH(OH)—, catechol, hydroxy acids and dibasic acids are just a few of the many organic compounds that form neutral or anionic systems containing the O—B—O unit. Therefore just a few representative examples are included in this section.

5.2.11.2 Saturated Systems

Saturated systems, *e.g.* **(355)**, **(356)** and their substituted derivatives, have been extensively studied, and have been prepared by azeotropic removal of water from a mixture of a diol and phenylboronic anhydride in toluene; in some systems a direct reaction of diol and phenylboronic anhydride liberated water which could be mechanically separated.[394] Alternatively,[395] trimethylborane reacted directly with a diol to give the ring system **(357)**. The preparation, spectroscopic properties and chemical reactions of *B*-vinyl and *B*-ethynyl derivatives have been described.[5d,396] The ring systems based on **(355)**–**(358)** have also been obtained from photolysis of trialkylboranes in primary alcohols,[397] and by electrolysing trialkylboranes in acetone in the presence of tetraalkylammonium halides.[398] Alkyl derivatives of type **(358)** have also been prepared cleanly by a general redistribution reaction of trialkylboranes and trimethyleneborate, and the products examined for their ease of halogenation; the resulting α-bromoalkylboronate esters were potential synthetic intermediates.[399] Oligomeric rings were obtained from $RB(OH)_2$ and $HO(CH_2)_nOH$.[400] A number of studies of the NMR parameters of the rings have been made,[57,319] including line width and adduct formation,[401] association[269] and conformational studies.[315,402] The reaction between alkane diols and activated triethylborane leads to a number of rings and their derivatives.[403,404] Xylitol and mannitol react with activated triethylborane to give the polycyclic systems **(359)** and **(360)**.[405,406] Ring systems based on thio sugars have also been investigated.[407,408]



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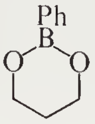

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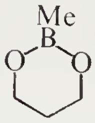

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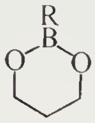

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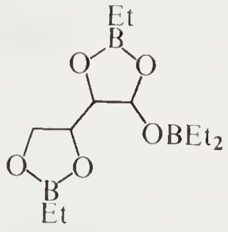

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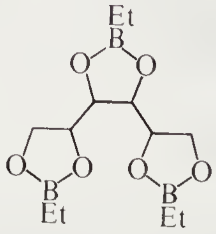
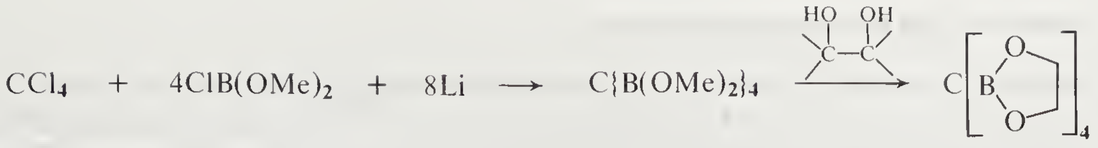


(360)

The formation of O—B—O ring systems has been used to stabilize borate esters in which a number of borons are bonded to the same carbon atom. For example, the reaction between carbon tetrachloride, dimethoxyboron chloride and lithium gives rise to $C\{B(OMe)_2\}_4$, which will exchange alkoxy functions with diols such as ethylene glycol, pinacol or catechol. These derivatives then serve as precursors for a range of boron-substituted carbanions by reaction with organometallic reagents, and thus are synthetically useful intermediates (see equations 177–184).[409–418]

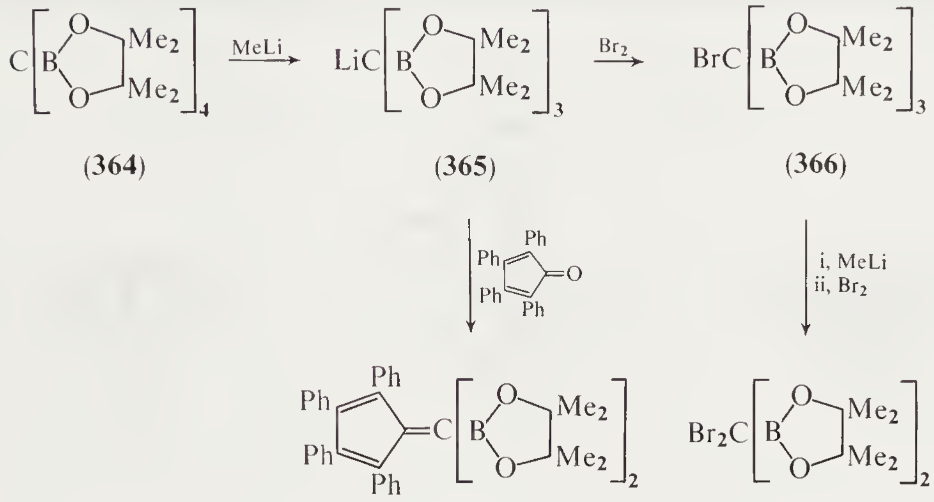


(361)

(177)

(362) **(363)**

(178)



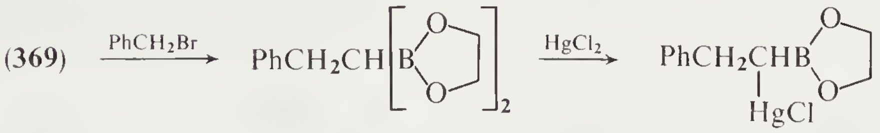
(364) **(365)** **(366)**

(179)

(367) **(368)**

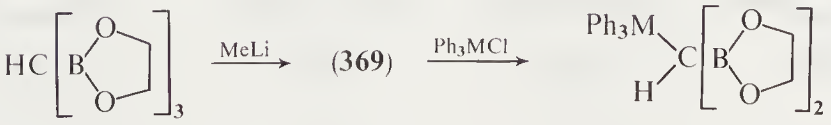
(369) **(370)**

(180)



(371) **(372)**

(181)



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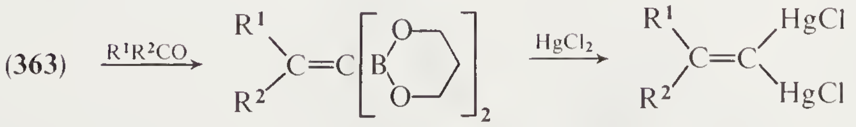

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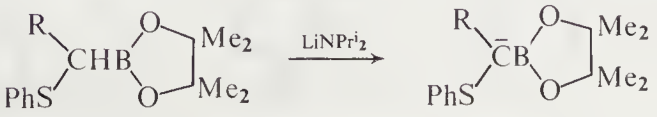


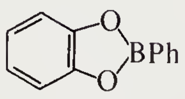
(375) **(376)**

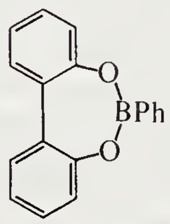
(184)

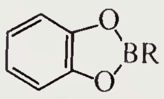
5.2.11.3 Aromatic and Unsaturated Systems

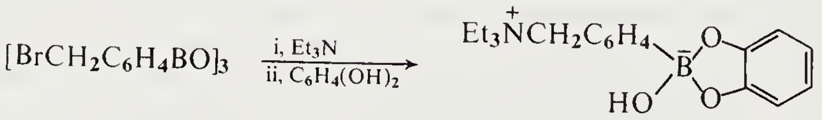
There have been a number of derivatives of catechol and other aromatic diols prepared by routes analogous to those already described for saturated systems.[5c,419,420] The ring systems (**377**) and (**378**) have been investigated for their antioxidant properties.[5d] Derivatives of the type (**379**) react with Grignard reagents to give unsymmetric triorganoboranes.[421] The neutral benzeneboronic acid esters of diols are usually rapidly hydrolysed in aqueous solutions.[422] However, compound (**380**), prepared by reaction (185), is stable to water from which it can be crystallized.[423]

β-Diketones and β-ketoesters have also long been known to react with boronic acid and its derivatives to give compounds of the types (**381**) and (**382**).[5c,424,425] Compounds of type (**381**) undergo cleavage with carboxylic acids and boron-substituted derivatives (**383**) are obtained.[426] Cleavage with perchloric acid gave the cationic species (**384**).[427] Compounds (**385**)–(**387**) were prepared by treating $Ph_2BOCH_2CH_2NH_2$ with $Ac_2CHCHAc_2$, $Ac_2CHCH_2CHAc_2$ or Bz_2CH_2, respectively.[428]


(**377**)

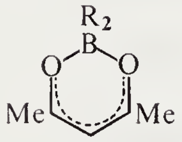

(**378**)

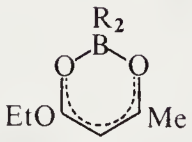

(**379**)

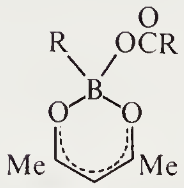


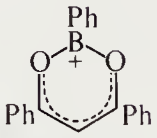
(**380**)

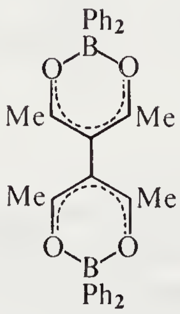
(185)

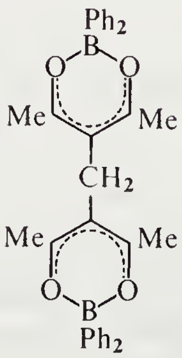

(**381**)

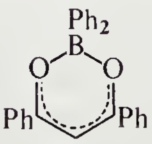

(**382**)


(**383**)

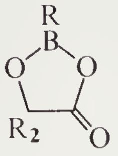

(**384**)


(**385**)

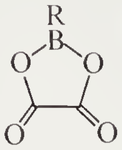

(**386**)


(**387**)

Dihalgenoorganoboranes react with α-hydroxycarboxylic acids to give 2,5,5-triorgano-1,3,2-dioxaborolan-4-ones (**388**),[429] which are much weaker Lewis acids than the 2-organo-1,3,2-dioxaborolane-4,5-diones (**389**). The latter give 1 : 1 adducts with a number of bases. The NMR of a number of these derivatives have been reported.[55] The NMR parameters of the related six-membered ring (**390**) have also been described.[55] The insertion of carbon dioxide or carbon disulphide into the B—N bonds of dimethylaminodiborane(4) derivatives gave rise to the bicyclic derivatives (**391**) and their thio analogues (**392**).[430] Oxybis[(acyloxy)alkylboranes] have been shown by IR spectroscopy and cryoscopy to adopt the bicyclic structure (**393**).[431]



(**388**)



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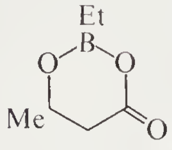

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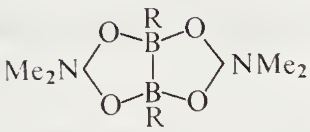

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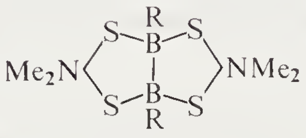

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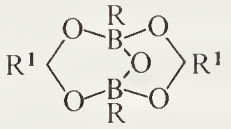
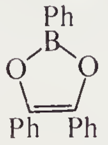


(**393**)

The interaction of benzoin with phenylboronic acid led to the ring system (**394**), whereas in the presence of aniline the same reagents yielded (**395**).[432] Chloral hydrate and phenylboronic acid gave (**396**). Other related compounds have also been described.[433] The B,N-betaine type of boron chelates (**397**) result from *N*-(2-hydroxyalkyl) nitrones and diphenylboron halide,[434a,434b] and the parent hydroxyaminoalkanols yield the ring system (**398**). Crystal structures of these and the related derivative (**399**) have been reported.[435,436] The mass spectra of a number of boron chelates have been described and the effect of the boron substituents compared. Fragmentation involving the cleavage of B—Ph groups was important. Compounds studied included derivatives of types (**338**), (**340**) and (**399**)–(**402**).[437,438]



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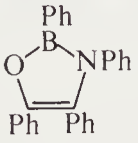

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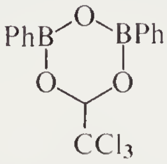

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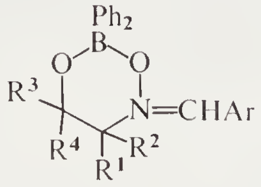

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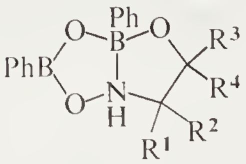

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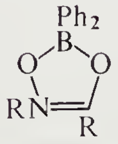
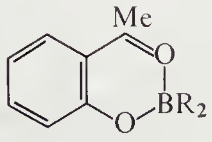
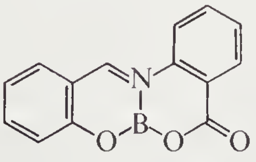


(**399**)



(**400**)



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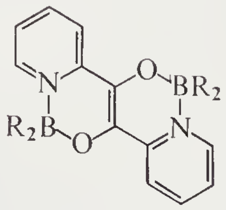
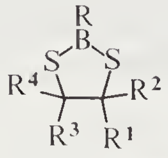


(**402**)

5.2.12 RINGS INVOLVING SULPHUR (O—B—S AND S—B—S RINGS)

Derivatives of the type (**403**) and (**404**) are readily synthesized by protolytic reactions of dithiols on R'_3NBH_2R[439] or RBX_2.[440,441] It was also prepared from the B—Cl analogue by methylation with MeLi[442] or from the B—H analogue by hydroboration of alkenes or alkynes.[443] The 1,3,2-dithiaborolanes are subject to association in the solid state, and are better Lewis acids than the oxygen analogues, forming stable complexes with Me_3N. Similar protolytic reactions between $PhB(SEt)_2$ and $HSCH_2CH_2OH$ gave (**405**),[444] and *o*-$C_6H_4(OH)(SH)$ and RBX_2 gave (**406**).[445]



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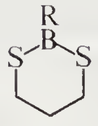

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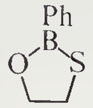

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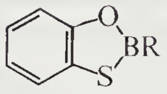


(406)

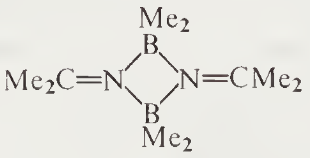
5.2.13 RINGS DERIVED FROM BORON AND ATOMS OTHER THAN CARBON

5.2.13.1 Introduction

There have been many ring systems described which perhaps only just come under the classification of cyclic organoboron compounds, but without some mention of which, any description of cyclic boron compounds would be incomplete. However, the extent of the available literature and its adequate review elsewhere of compounds such as borazines[70] and boroxines makes a comprehensive coverage of these systems inappropriate for this work. Other areas which have received extensive coverage elsewhere include boron–nitrogen heterocycles,[24] and only cursory attention will be given in this review.

5.2.13.2 Boron–Nitrogen Rings

Four-membered ring systems have been obtained as dimers of aminoboranes and ketiminoboranes. For example, *N*-chloro-2-propanimine reacts with trimethylborane to give (**407**).[446] The analogous triphenylphosphineiminoborane (**408**) was obtained from $Ph_3P{=}NSiMe_3$ and R_2BX, although the product was monomeric in the gas phase.[447] Doubt has been cast on the true nature of compounds earlier reported to be of the type (**409**). These are probably only stable as four-membered rings, when R′ is a group with a π-donor atom bonding directly to the boron,[24] although derivatives with R = Bu^t, which are extremely oxidatively and hydrolytically sensitive, have been obtained by reaction (185).



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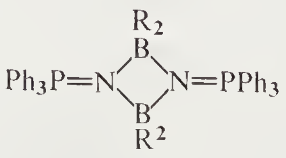

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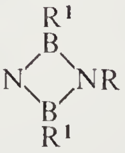

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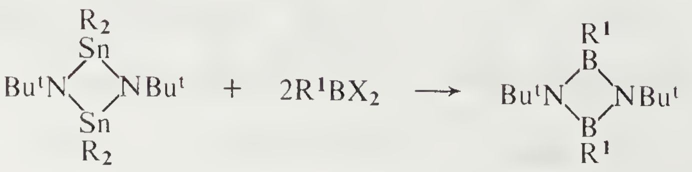
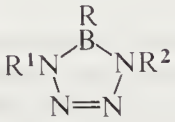
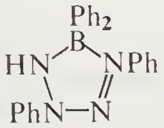
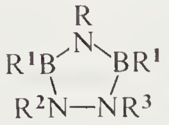


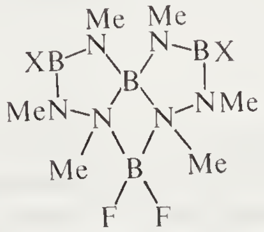
(185)

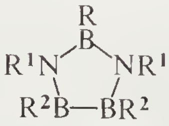
In the five-membered ring series, interaction of organic azides with incipient boron imines resulted in derivatives of the type (**410**).[24] The NMR spectra of a number of derivatives have been reported.[55] 2,4-Diphenyltetrazene was able to displace aminoethanol from β-aminoethyldiphenylborinate to give the cyclic chelate (**411**).[24] There have been a number of derivatives (**412**) of 1,3,4-triaza-2,5-diborolidine described from transamination reactions[24,448] or elimination reactions involving boron–sulphur derivatives.[449,450] Most of these are monomeric rings, but the derivative (R^1 = F) is dimeric,[451] through N→B coordination of adjacent molecules, with associated fluoride migration resulting in structure (**413**). The NMR parameters of a number of derivatives have also been described.[55] Derivatives of 1,3-diaza-2,4,5-triborolidine (**414**) have been obtained from *N*-lithiated derivatives of (diamino)alkylboranes and derivatives of B_2Cl_4.[24] Other five-membered rings have been reported from the association of aminoborane and hydrazinoborane monomer units.


(**410**)

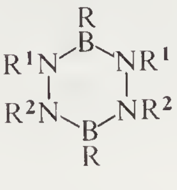

(**411**)


(**412**)


(**413**)

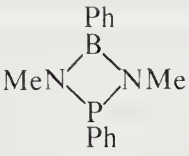

(**414**)

In the six-membered ring series, the most studied system is undoubtedly that of the borazines, which are beyond the scope of this review. The dimers of hydrazinoboranes have been shown to be cyclic compounds through N→B coordination. Related compounds, the pyrazaboles, were obtained from reactions between pyrazole and boron compounds with protolytic groups. The compounds are particularly stable, and have been reviewed.[24] The condensation of aminoboranes or organothioboranes with hydrazines readily yields the ring system (**415**), of which a number of *B*-functional derivatives have been described. Depending on the functional substituent, the ring system may exist in the monomeric form or else associate to form, principally, dimers. In addition, the exchange of boron functional substituents may occur through associative equilibria.[449,452–457]


(**415**)

5.2.13.3 Boron–Nitrogen Rings Containing Other Heteroatoms

A number of four-, five- and six-membered rings containing boron, nitrogen and phosphorus have been obtained by reactions involving elimination of Me_3SiX from P—N—Si derivatives with organoboron halides. Thus $PhP\{NMe(SiMe_3)\}_2$ with $PhBBr_2$ gave 1,3,2,4-diazaphosphaboretidine (**416**), whereas with $Cl(Me_2N)BB(NMe_2)Cl$, a derivative of 1,3,2,4,5-diazaphosphadiborolidine (**417**) resulted.[458] Most of the (phosphineamino)boranes, obtained from (silylamino)phosphines and boron halide derivatives, were monomeric, although a few dimerized at low temperatures to the six-membered ring system (**418**). Alternatively, thermolysis of borylaminophosphorus and borylaminosilicon derivatives gave rise to ring systems (**419**)–(**421**) and the analogous silicon derivative (**422**).[459] A derivative of thiadiazaboretidine (**423**) resulted from the interaction of bis(dimethylamino)phenylborane and sulphonyl diisocyanate.[460]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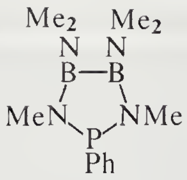
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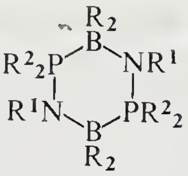
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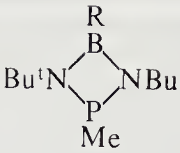
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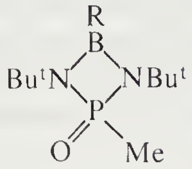
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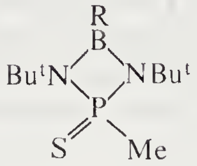
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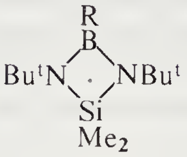
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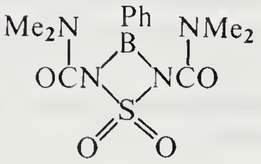
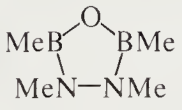

(423)

Elimination reactions on boron–sulphur derivatives, which led to the formation of ring system (**412**), can also be used to prepare rings containing other heteroatoms. The reaction products of $MeB(SMe)_2$ and substituted hydrazines gave intermediates such as MeSB(Me)NMeNMeB(Me)SMe, which eliminated further methanethiol on treatment with H_2O or H_2S to give the ring systems (**424**) and (**425**); a mixture of hydrazine and primary amine with $MeB(SMe)_2$ gave (**426**).[461] The reaction of lithiated 1,2-dimethylhydrazine with $Br(Me)BNMeSi(Me)_2Br$ or the analogous phosphorus derivative gave the ring systems (**427**) and (**428**);[462,463] further reaction of (**427**) with boron halides led to unsymmetrically substituted derivatives of (**412**). Five-membered rings containing two silicon atoms (**429**) have been obtained from elimination reactions between a diamino(alkyl)borane and a halogenated disilane, or the alternative organoboron dihalide and a 1,2-diaminodisilane.[464,465] Ring systems (**430**)–(**433**) have also been reported.[466]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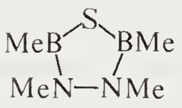
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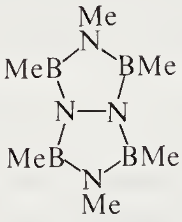
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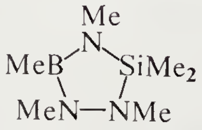
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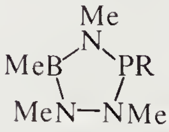
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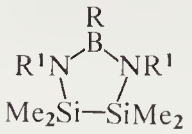
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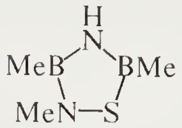
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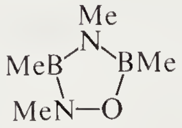
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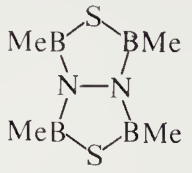
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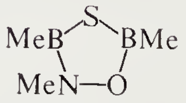
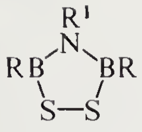

(433)

The He(I) photoelectron spectra of isoelectronic 6π-electron, five-membered ring compounds have been examined. Derivatives of (**412**), (**424**), (**425**), (**431**), (**433**), (**434**) and (**435**) showed that the cyclic π-conjugation decreased on successive exchange of N atoms by S atoms in the ring.[467] Derivatives of the trithiadiborolane (**435**) undergo ring opening and intramolecular cyclocondensation when treated with primary amines, resulting in rings (**434**), (**436**) and borazines.[466,468] Other derivatives of borazines have been prepared by reactions of $MeB(NMeLi)_2$ with Ph_2SiCl_2,[469] or by treating cyclotrisilazane with phenylboron dichloride,[470] to yield the ring systems (**437**) and (**438**). Ring systems (**439**)–(**442**) have also been described.[463] Two further nitrogen-containing heterocycles are (**443**)[5g] and (**444**).[471]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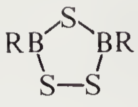
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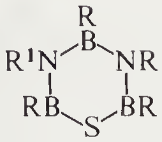
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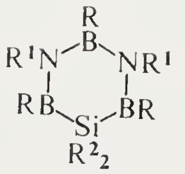
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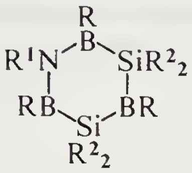
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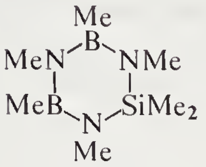
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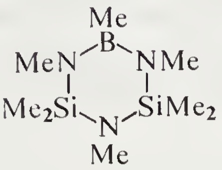
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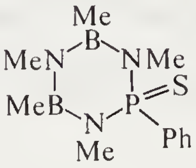
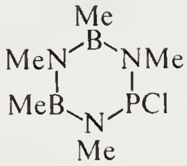
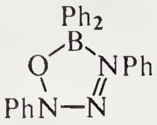
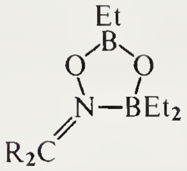

(441)

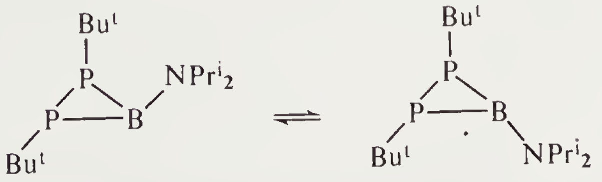

(442)


(443)


(444)

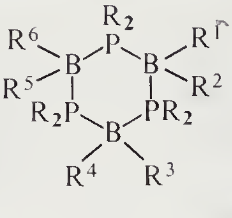
5.2.13.4 Boron–Phosphorus and Boron–Silicon Rings

The first well-defined three-membered heterocycle (**445**) was formed from KBu^{t}PPBu^{t}K and $Pr^i_2NBCl_2$. The compound was stable under inert conditions, and its physical and spectroscopic properties were consistent with a monomer in which little π-interaction occurred between the P and B atoms. Rapid inversion of the two geometric isomers occurred above −100 °C.[472]


(445a) **(445b)**

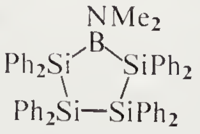
(186)

The phosphorus analogues of trimeric aminoboranes have been known for many years. Recently, *B*-organo-substituted derivatives of 1,2,3,4,5,6-hexahydrotriboraphosphanes have been prepared by replacement of *B*-halogen substituents using organometallic reagents (compounds **446**).[473] A number of the NMR parameters of trimeric and tetrameric boraphosphanes have been described.[474]

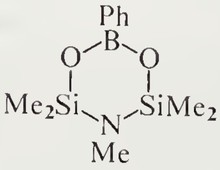


(**446**)

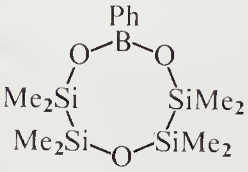
Cleavage by lithium of a Si—Si bond in the four-membered ring compound $(Ph_2Si)_4$, followed by treatment with Me_2NBCl_2, resulted in the Si_4B ring (**447**), in which no delocalization of electrons between boron and silicon was apparent.[475] The interaction of phenylboronic acid with either chloro-silazanes or -disilanes resulted in the rings (**448**) or (**449**).[476]



(**447**)



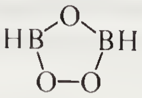
(**448**)



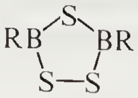
(**449**)

5.2.13.5 Boron–Oxygen, Boron–Sulphur and Boron–Selenium Rings

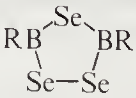
The chemistry of boroxines (anhydrides of boronic acids) lies beyond the scope of this review. A product of partial oxidation of pentaborane(9) was shown to be the five-membered ring (**450**).[477] Organic derivatives were obtained from controlled oxidations of alkyldiboranes.[478,479] The reaction of hydrogen polysulphide with boron tribromide yielded an analogous sulphur ring compound with bromine at boron, from which alkyl derivatives (**451**) could be obtained. Alternatively, these derivatives were prepared by treating RBI_2 with S_8.[480,481] The compounds were useful synthetic reagents for other heterocycles and metal complexes. The sulphur compounds and their seleno analogues (**452**) have also been obtained from reactions of organoboranes with sulphur or selenium.[482] NMR data on a range of derivatives of type (**452**) have been reported.[55]



(**450**)



(**451**)

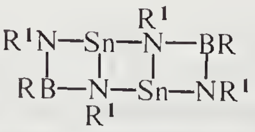


(**452**)

5.2.14 POSTSCRIPT

Two recent reviews have appeared, containing sections on heterocyclic boron compounds.[483,484] Ring systems discussed and not otherwise mentioned in this review include (**453**) and (**454**).

(**453**)



(**454**)

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5.3

Boron Ring Systems as Ligands to Metals

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5.3.1 GENERAL ASPECTS

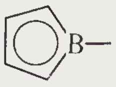
The first transition metal complexes of boron-containing ring ligands were discovered in 1967. Since then syntheses for an increasing number of these ligands which with few exceptions are bound to metals of the *d*-block have been developed, and many new structures and unexpected reactions have been found. By now this unfolding new area of boron chemistry between the field of metallocarboranes and the classical metallocenes has gained sharper contours and to some extent generalizations have become possible.

A review on 'Heterocyclic π-Complexes of the Transition Metals' in general is available.[1] There are specialized accounts on 'Metal Sandwich Complexes of Cyclic Planar and Pyramidal Ligands Containing Boron'[2] and on 'Boron Heterocycles as Ligands in Transition-Metal Chemistry'.[3]

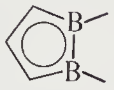
5.3.1.1 The Ligands

The ligands to be considered here may conveniently be grouped in five classes:
(i) conjugated boron–carbon ligands, (**1**)–(**9**);
(ii) non-conjugated boron–carbon ligands, *e.g.* (**10**)–(**12**);
(iii) boron–nitrogen ligands, (**13**) and (**14**);

(iv) boron–carbon–nitrogen ligands, (**15**)–(**18**);
(v) boron–carbon–sulphur ligands, (**19**) and (**20**).

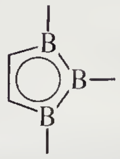


(**1**) π^4



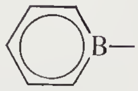
(**2**) π^3

(**3**) π^3

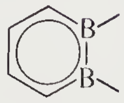


(**4**) π^2

(**5**) π^2



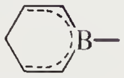
(**6**) π^5



(**7**) π^4

(**8**) π^4

(**9**) π^4



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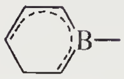
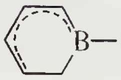
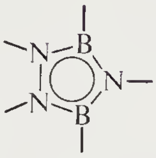


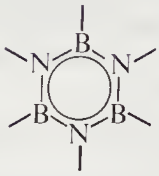
(**11**) π^4



(**12**) π^4

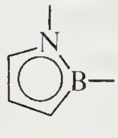


(**13**) π^6

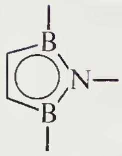


(**14**) π^6

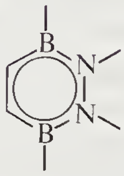
(**15**) π^5



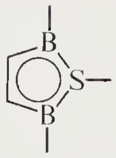
(**16**) π^5



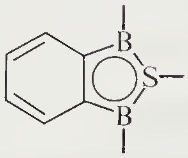
(**17**) π^4



(**18**) π^6



(**19**) π^4



(**20**) π^4

Some of these ligands are totally unknown ((**2**), (**7**), (**8**), (**11**)); others only exist in transition metal complexes ((**3**), (**4**), (**5**), (**6**), (**12**), (**16**)). The classes (ii)–(v) comprise large varieties of ligands. For class (ii) quite arbitrary examples are given while for the classes (iii)–(v) all systems are shown that are known as ligands in transition metal complexes.

Useful analogies with the more familiar hydrocarbon systems may be noted by counting numbers of π-electrons. In this sense the four-electron ligands (**1**) and (**9**) are analogues of the cyclobutadiene ligand.

Another relationship is specially useful for boron–carbon ligands. Formal substitution of carbon with boron in an unsaturated hydrocarbon generates boron–carbon systems with qualitatively predictable changes in the MO diagrams. Thus, in going from benzene to borabenzene derivatives (**6**) and 1,4-diboracyclohexa-2,5-dienes (**9**), the HOMO of benzene is raised in energy and becomes a low-lying LUMO in (**9**).

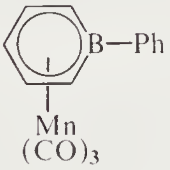
Generalization: All boron–carbon systems possess low-lying MOs which are half-occupied in odd-electron systems (such as (**3**) and (**6**)) and empty in even-electron systems (such as (**1**), (**5**) and (**9**)).

As a consequence, the free, uncharged even-electron systems are strong Lewis acids provided that the substituent at boron does not allow for strong π-interaction. It is also expected that all boron–carbon systems may be reduced to anions. This has been verified in a few cases, the observation of six-π-electron anions of type (**1**)$^{2-}$,[4] (**6**)$^{-}$ [5,6] and (**9**)$^{2-}$ [7] being notable examples. In binding to transition metals the donor–acceptor properties of all boron–carbon systems are of predominant acceptor character.

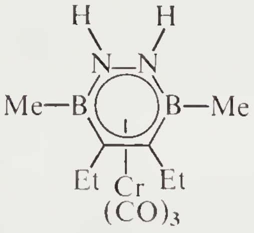
In boron–nitrogen and boron–carbon–nitrogen systems π-interaction between boron and nitrogen results in an internal compensation of Lewis acidity from the B atoms and Lewis basicity from the N atoms. In binding to transition metals the donor–acceptor properties of (**15**),[8] (**14**)[9] and (**17**)[10] seem close to those of pyrrole, benzene and borole ligands respectively. The boron–carbon–sulphur systems (**19**)[11] and (**20**)[12] are strong Lewis acids if free, and are strong acceptors when acting as donor–acceptor ligands to transition metals.

5.3.1.2 Structure and Bonding in Sandwich-type Complexes

The vast majority of complexes to be considered here obey the 18-electron rule. A large body of X-ray structural studies demonstrate that boron in these compounds is within bonding distance of the metal. However, the metal tends to slip away from the boron towards the more electronegative ring atoms C, N and S and thus the differences between *d*(M—B), *d*(M—C), *etc.* are usually larger than expected considering differences between the respective covalent radii of boron, carbon, *etc.* alone. This is accompanied by small out-of-plane distortions of inherently planar ligands and considerable slip distortions of the metal with respect to the ring centre whenever possible by symmetry. For instance, in the borabenzene derivative (**21**)[13] (Mn—B = 238.5, Mn—C(2) = 225.0, Mn—C(3) = 217.5, Mn—C(4) = 215.5 pm), the borabenzene ring is essentially planar, but the projection of the Mn atom onto the C_5B plane is 34 pm closer to C(4) than to the B atom. In the 1,2-diaza-3,6-diboracyclohex-4-ene derivative (**22**)[14] (Cr—B = 236, Cr—C = 230.2, Cr—N = 214.5 pm), the heterocycle is folded along the B—B axis by 12° and the Cr atom is shifted considerably towards the N ring atoms.



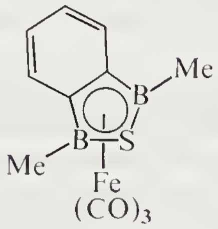
(**21**)



(**22**)

The effects of complexation to a transition metal on intra-ring bond distances are most unambiguously seen in cases where the geometries of both a free ligand as well as of the same ligand complexed to a metal are known. Such a situation exists in systems derived from (**9**),[15] (**14**),[16] (**18**)[14] and (**19**).[17] The data foster the idea that changes of intra-ring bond distances increase with increasing back-bonding, with no significant changes in (**14**), small changes in (**18**) and considerable changes in (**9**) and (**19**). In the case of the 1,2,5-thiadiborolene complex (**23**) (with C(3)—C(4) lengthened to 144.6 pm, B—C(ring) (av.) shortened to 152.6 pm, and B—S (av.) lengthened to 187.4 pm and estimated free ligand values of 136, 159 and *ca.* 182 pm, respectively; *cf.* refs. 17 and 18), a precision electron density map actually shows π-electron density in the B—C(ring) bonds.[18]

The uneven electron density distribution in the ring ligands may cause strong conformational preferences in complexes. Thus in the hexaethylborazine complex (**24**) the carbonyl groups are oriented *trans* to the N atoms[16] and in the 1,2,5-thiadiborolene complex (**25**) the two coplanar ligands are rotated by a right angle with respect to each other showing no internal rotation on the ^{1}H NMR time scale at room temperature.[19] Obviously in these complexes, the high electron density regions of the ligand HOMO occupy the positions of CO groups in the corresponding metal carbonyls $[Cr(CO)_6]$ and $[Ni(CO)_4]$ respectively. The origin of conformational preferences and slip distortions in complexes of five-membered ring ligands has been analyzed in detail by MO methods[20] and some of the predictions made remain to be verified by experimental investigation.



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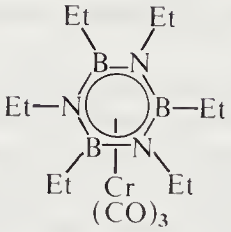

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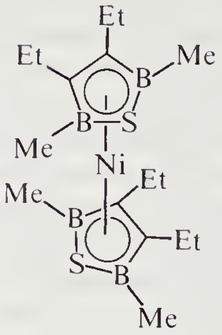


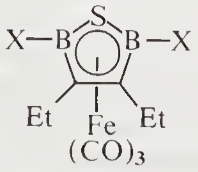
(25)

^{11}B NMR shifts are valuable as a simple test for metal–boron bonding. A vast compilation of data is available.[21] Most complexes show resonances of δ = 15–30 p.p.m. to low field from $BF_3{\cdot}OEt_2$ corresponding to upfield shifts of 0–50 p.p.m. with respect to free ligand values where existent. High upfield shifts are observed when π-interactions contribute little to the shielding of the ^{11}B nucleus in the free ligand, *i.e.* in uncharged boron–carbon ligands ((**1**), (**9**), and (**10**)) and in boron–carbon–sulphur ligands ((**19**) and (**20**)). π-Interactions with exocyclic substituents at boron, especially with Me_2N and MeO groups, greatly reduce the upfield shift on complexation mainly due to better shielding of the boron in the free ligand (for the best known example, *cf.* ref. 17). The strong endocyclic π-interactions in nitrogen-containing ring systems ((**13**)–(**18**)) reduce the upfield shift even more efficiently rendering this criterion worthless in limiting cases.

5.3.1.3 Patterns of Reactivity in Sandwich-type Complexes

Metal–boron bonding very efficiently suppresses the Lewis acidity of the boron. Most complexes are stable to hydrolysis and are not attacked at boron by nucleophiles such as amines, NaCN in acetonitrile, or often even LiMe in ether. However, in cationic complexes where the back-bonding ability of the metal is reduced, Lewis acidity at boron may become quite strong with a remarkable preference for hard Lewis bases. This type of reactivity has only been studied with cationic borabenzene derivatives and is treated in detail in Section 5.3.2.2.

Nucleophilic substitution at boron is possible when the substituent is a strongly electronegative group, *e.g.* MeO and Cl. For instance, many derivatives of type (**26**)[17] and (**27**)[7] have been made in this way (*e.g.* equation 1), often with ligands that are likely to be non-existent in the free state, *e.g.* (**26**) (X = H)[17] and (**27**) (X = H, Me).[7]



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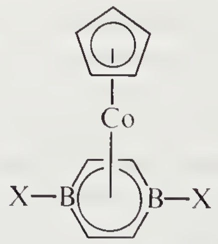


(27)

$$\underset{(\mathbf{26},\ X = I)}{[Fe(CO)_3\{Et_2C_2(BI)_2S\}]} \xrightarrow{LiBH_4} \underset{(\mathbf{26},\ X = H)}{[Fe(CO)_3\{Et_2C_2(BH)_2S\}]} \qquad (1)$$

Complexes of the more strongly back-bonding boron ring ligands often show a remarkable stability against oxidation and an equally remarkable ability to undergo reduction. Pertinent quantitative data have mainly been collected for complex borabenzene derivatives (Table 1). Formal replacement of a C_5H_5 ligand in ferrocene or cobaltocene by a C_5H_5BR ligand (**6**) results in a stabilization of the metal *d*-orbitals through improved back-bonding (for a detailed theoretical analysis see ref. 22). This is apparent as an increase of the ionization potential (0.4–0.5 eV per ring) and of all redox potentials (0.3–0.5 V per ring). Consequently complex borabenzene derivatives show a richer anion chemistry than their cyclopentadienyl counterparts and a more limited cation chemistry. A striking effect is the stabilization of species with more than 18 valence electrons such as the 19-electron system $[Fe(C_5H_5BPh)_2]^-$ (potassium salt in THF solution, stable at −10 to −40 °C for about one day)[23] and the 20-electron anion $[Co(C_5H_5BPh)_2]^-$ (isolated as $[PPh_4][Co(C_5H_5BPh)_2]$, m.p. 158–159 °C)[24] which have counterparts of only fleeting existence in cyclopentadienyl chemistry.

The phenomena described here for complex borabenzene derivatives are expected to be of more general validity. One further example is given to support this opinion: $[CpCo(MeBC_4H_4BMe)]$ (**27**) (X = Me) suffers irreversible oxidation at +1.52 V *vs.* SCE in acetonitrile whereas quasi-reversible reduction occurs at −1.50 V *vs.* SCE.[25] Again, both potentials are surprisingly anodic.

Table 1 Ionization Potentials and Redox Potentials[a] of some Metallocenes and Metallocene-type Borabenzene Derivatives

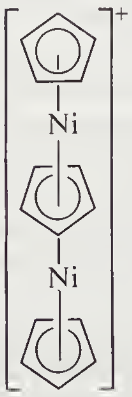
		M = Fe			M = Co	
Complex	*IP*(eV)[1,b]	$\bar{E}_{0/+}$ (V)[2,c]	$\bar{E}_{0/-}$ (V)	*IP*(eV)[3,d]	$\bar{E}_{0/+}$ (V)[4,c]	$\bar{E}_{0/-}$ (V)[4,c]
$[M(C_5H_5)_2]$	6.88	0.48	−2.93[5,e]	6.2_1	−0.95	−1.88
$[M(C_5H_5)(C_5H_5BMe)]$		0.84		6.5_6	−0.46	−1.57
$[M(C_5H_5)(C_5H_5BPh)]$		0.88		6.6_3	−0.44	−1.46
$[M(C_5H_5BMe)_2]$	7.73	1.10		7.1_5	−0.02	−1.25
$[M(C_5H_5BPh)_2]$	7.67	1.13	−1.77[2,c]	7.2_5	+0.05	−1.11

[a] *vs* SCE. [b] Measured by photoelectron spectroscopy. [c] Measured by cyclovoltammetry in CH_2Cl_2. [d] From mass spectrometry. [e] Polarographic half-wave potential measured in DMF at −30 °C.

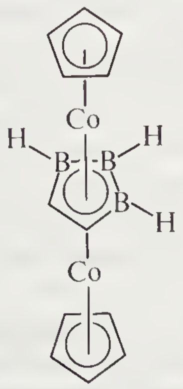
1. A. J. Ashe, III, E. Meyers, P. Shu, T. Von Lehmann and J. Bastide, *J. Am. Chem. Soc.*, 1975, **97**, 6865.
2. U. Koelle, *J. Organomet. Chem.*, 1978, **157**, 327.
3. G. E. Herberich, G. Greiss, H. F. Heil and J. Müller, *Chem. Commun.*, 1971, 1328.
4. U. Koelle, *J. Organomet. Chem.*, 1978, **152**, 225.
5. Y. Mugnier, C. Moise, J. Tirouflet and E. Laviron, *J. Organomet. Chem.*, 1980, **186**, C49.

5.3.1.4 Multiple-decked Complexes

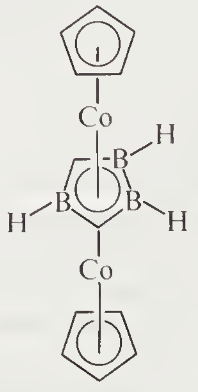
Boron-containing ring ligands show an unrivalled ability to form multiple-decked complexes. Prototypes of the triple-decked compounds are the boron-free 34-electron cation $[CpNi(\mu\text{-}Cp)NiCp]^+$ [26] (**28**) which was discovered in 1972 and the two isomeric 30-electron complexes $[CpCo(\mu\text{-}C_2B_3H_5)CoCp]$[27] (**29**) and (**30**) which were described in 1973. In these compounds two metal atoms are sandwiched between three ring ligands forming a linear stack.



(**28**)



(**29**)

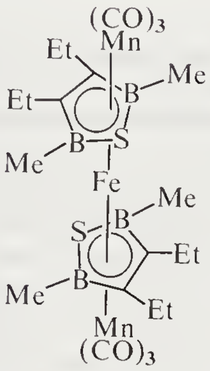


(**30**)

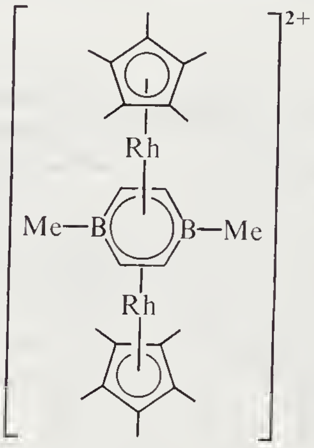
The characteristic feature of all triple-decked complexes is the *central* or *inner* bridging ring ligand which is bifacially bound to two metal centres. The metal atoms carry additional *outer* ligands such as C_5H_5 or CO groups to complete their valence shells. Systems with ring ligands as outer ligands are called triple-decked *sandwich* complexes.

Further extension of this building principle would eventually lead to a whole class of multiple-decked complexes including linear polymers of an alternating sequence of metal atoms and central rings as a limiting case. These possibilities were already envisaged in 1973[27] and in 1978 the first quadruple-decked complex (**31**) was described.[28]

The earlier history of the triple-decked complexes has been reviewed in 1977.[26] Presently, multiple-decked complexes of the five-membered ring systems (**1**), (**3**), (**4**), (**5**) and (**19**) acting as central ligands and of the first-row transition metals Mn, Fe, Co and Ni are known. The only example outside these confines is the cation $[(C_5Me_5)Rh(\mu\text{-}MeBC_4H_4BMe)Rh(C_5Me_5)]^{2+}$ [29] (**32**) which contains a six-membered central ligand and a heavier transition metal. For further individual examples and details the reader is referred to the appropriate later subsections.



(**31**)



(**32**)

The 18-electron rule may readily be adapted to multiple-decked complexes. Each central ligand gives rise to three bonding MOs. Thus six valence electrons for each central ligand contribute to the valence shells of two metal centres. Consequently the magic number of valence electrons is 30 for triple-decked compounds and 42 for quadruple-decked complexes. Moreover, in metallocenes with d^{5-8} metal centres the number of valence electrons ranges from 17 to 20. This corresponds to a range of 28 to 34 valence electrons for triple-decked complexes. Examples, either fully characterized or only observed, for this whole range of values are known[30,31] but the magic number 30 corresponds to maximal stability. The few known quadruple-decked compounds mostly have 42 valence electrons but 43- and 44-electron species with central ligands of type (**19**) have also been made.

The known triple-decked sandwich complexes may roughly be described as $\pi^6/d^{5-8}/\pi^6/d^{5-8}/\pi^6$ systems. This approximation, although being useful as a starting point for MO considerations, should not be taken too literally since it neglects the mixing between the metal and ligand orbitals. With this in mind, the essential *d*-level schemes for metallocenes and triple-decked sandwich complexes with d^{6-8} metal centres are quoted (Figure 1) from an available MO analysis.[32]

There are three low-lying *d*-orbitals for each metal atom. With the occupancy of these the magic 18- and 30-electron configurations are established. In metallocenes there is one high-lying e_1 set which by mixing with ligand orbitals becomes antibonding. In a few cases (*e.g.* $[CoCp_2]$ and $[NiCp_2]$), one or two electrons are tolerated in e_1 with concomitant weakening of the metal–ligand bond.[33] In triple-decked sandwich complexes like (**28**) there are two combinations of the individual e_1 sets. The higher of these, e_1'', through interaction with central ligand orbitals, becomes strictly antibonding, too high for occupancy. The lower one, e_1', cannot interact with central ligand orbitals and thus is essentially non-bonding with the bridging ligand and slightly antibonding with the outer rings. This e_1' set may be occupied with up to four electrons. This result[32] is often cited as the 30/34-electron rule.

Substitution of carbon with boron in the central ring generates the series $[C_5H_5]^-$, $[C_4BH_5]^{2-}$, $[C_3B_2H_5]^{3-}$, $[C_2B_3H_5]^{4-}$, *etc.* with increasing formal charges and orbital energies. In parallel with this the metal–central ring interactions become stronger, thus more and more favouring the triple-decked structures. The same argument shows that N ring atoms produce the opposite effects

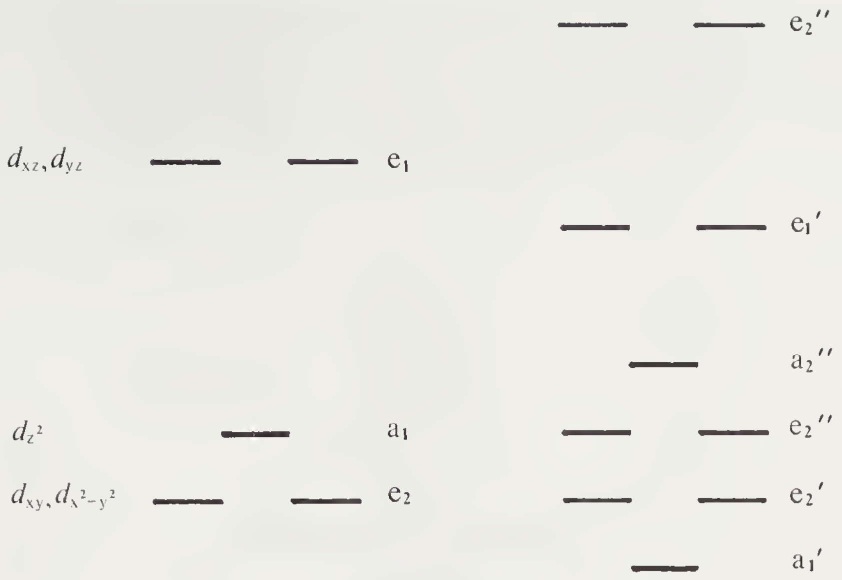


Figure 1 *d*-Level Schemes of Metallocenes (left) and Triple-Decked Sandwich Complexes (right) with d^{6-8} Metal Centres

in accord with the observation that no multiple-decked complexes are known with nitrogen-containing systems such as (**13**)–(**18**) acting as central ligands.

In an alternative description, multiple-decked complexes may be described as a special class of metallocarboranes. Thus, *e.g.* complex (**30**) is a seven-vertex cage compound with a total of 16 (2 × 2 (2 CoCp) + 2 × 3 (2 CH) + 3 × 2 (3 BH)) electrons for cluster bonding. The cluster rules[34] (see also Chapters 1, 5.4 and 5.5) correctly predict the observed *closo* structure of a pentagonal bipyramid. Obviously for a 30-electron species with a five-membered central ring the two descriptions are equivalent, and the same holds for 42-electron quadruple-decked complexes. From the viewpoint of the polyhedral cage compounds it is quite remarkable that deviations from the ideal numbers of electrons participating in cluster bonding do not result in gross changes of the cluster type as they would in boranes and carboranes[34] but are expected merely to increase the metal–ligand bond lengths. The somewhat large Ni—C distances in (**28**) (Ni—C (av.) = 208.5 and 214.5 pm for outer and central Cp ligands, respectively)[35] seem to support this expectation.

Structural investigations on multiple-decked complexes have been undertaken in many cases to ascertain the gross structures but the data are fully available only in a few cases. Generally, *all* intra-ring bond distances of a ring ligand tend to be slightly greater if acting as a central rather than as an outer ligand. The data of the quadruple-decked complex (**31**) (C(3)—C(4) (av.) = 147.7, B—C(ring) (av.) = 154.4, B—S (av.) = 192.8 pm)[28] and of the half-sandwich complex (**23**) (C(3)—C(4) = 144.6, B—C(ring) (av.) = 152.6, B—S (av.) = 187.4 pm)[18] may serve as an example. Metal-to-ring distances vary considerably and this phenomenon still awaits detailed theoretical analysis. The coordination number of boron increases from four in outer ligands to five in central ligands and this is accompanied by an upfield shift of the ^{11}B magnetic resonance, typically in the order of 10–15 p.p.m. for comparable metal–ring fragments.

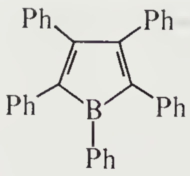
5.3.2 SYSTEMS WITH BORON–CARBON RING LIGANDS

5.3.2.1 Complexes of Five-membered Conjugated Rings

5.3.2.1.1 Complexes of 1H-borole (C_4BH_5)

1H-Borole as a conjugated four-electron ligand is expected to form similar complexes as cyclobutadiene and cyclopentadienone. Of the very few known 1H-boroles the highly reactive 1,2,3,4,5-pentaphenyl derivative (**33**) is the oldest and best characterized representative.[4,36] Both (**33**) and the corresponding dipotassium salt (**34**)[4] may be used as starting materials in conventional syntheses affording remarkably robust complexes such as [Fe(CO)$_3$·(**33**)], [CoCp·(**33**)], [Ni(CO)$_2$·(**33**)] and [Pt(cod)·(**33**)] (Scheme 1).[4,37]

A second route to complexes of 1H-borole starts from 1-phenyl-4,5-dihydro-1H-borepin (**35**). Under drastic conditions, in refluxing mesitylene, complex formation is accompanied by ring



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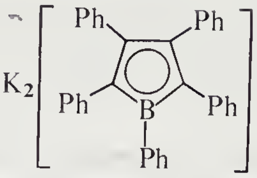

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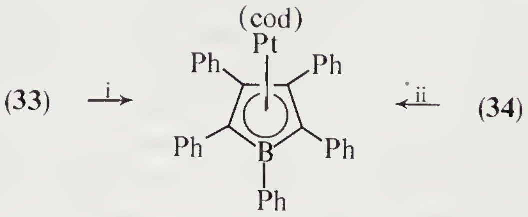
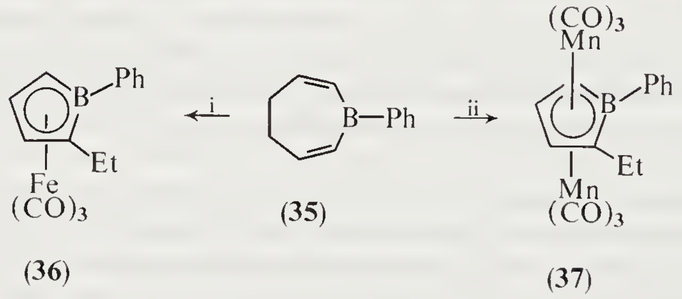


i, $[Pt(cod)_2]$; ii, $[PtCl_2(cod)]$

Scheme 1

contraction reactions leading to compounds with 2-methyl-1-phenylborinato and 2-ethyl-1-phenyl-1H-borole ligands. For instance, with $[Fe(CO)_5]$ as a source of the 14-electron fragment $Fe(CO)_3$, the 1H-borole complex **(36)**[37] is obtained (*inter alia*) whereas with $[Mn_2(CO)_{10}]$ providing the 13-electron fragment $Mn(CO)_3$ the triple-decked compound **(37)**[38] is formed in good yield (Scheme 2). These profound transformations probably involve double bond migrations and a ring-opening dehydroboration/ring-closing hydroboration sequence.

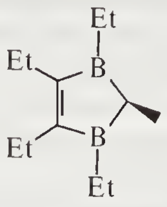


i, $[Fe(CO)_5]$, 165 °C; ii, $[Mn_2(CO)_{10}]$, 165 °C

Scheme 2

5.3.2.1.2 *Complexes with 1,3-diborolenyl ligands* ($C_3B_2H_5$)

The unsaturated organoborane **(38)** is the most easily accessible Δ^4-1,3-diborolene.[39] It serves as an ideal precursor of the ligand **(39)** and, in fact, all work on complexes of the 1,3-diborolenyl ring **(3)** is based on this approach.



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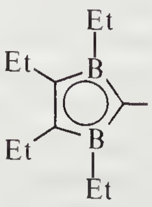
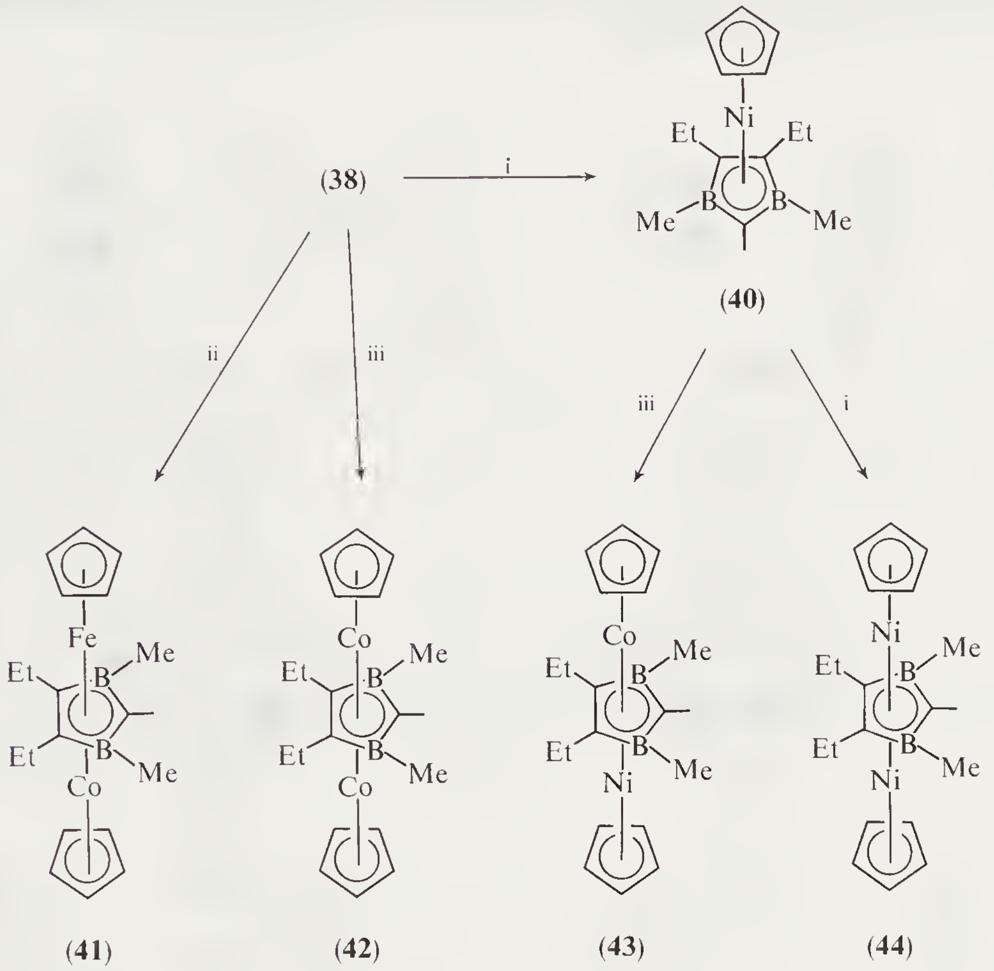


(39)

Treatment of (**38**) with [$\{Ni(CO)Cp\}_2$] at about 165 °C affords the orange-red sandwich complex (**40**) as the main product (Scheme 3).[40] The structure of (**40**) is that of an 18-electron complex with two η^5-bound ligands and all metal–carbon bond lengths are comparable to those in ferrocene rather than to those nickelocene ([$FeCp_2$]: Fe—C = 206.3 pm; [$NiCp_2$]: Ni—C = 220 pm; (**40**): Ni—C = 204–209, Ni—B = 217.5 pm).[40]



i, [$\{Ni(CO)Cp\}_2$]; ii, [$\{Fe(CO)_2Cp\}_2$], [$Co(CO)_2Cp$]; iii, [$Co(CO)_2Cp$].

Scheme 3

The remarkable series of triple-decked sandwich complexes (**41**)–(**44**) with 30–33 valence electrons (Scheme 3) is mentioned in short communications together with details about (**41**)[41] and (**44**).[30] These compounds have 0, 1, 2 and 1 unpaired electrons respectively and thus illustrate an important ramification of the 30/34-electron rule. The general strategy for the syntheses of (**41**)–(**44**) is much the same as for (**40**). The addition of a metal–ligand fragment to a stable uncharged 18-electron sandwich complex such as (**40**) to give a triple-decked complex has little precedent in earlier chemistry (*cf.* ref. 26).

The redox chemistry of (**44**) has been studied (Scheme 4). Oxidation affords a 32-electron cation (**44**)$^+$ which is isoelectronic with (**43**) and reduction yields a diamagnetic 34-electron anion.[30]

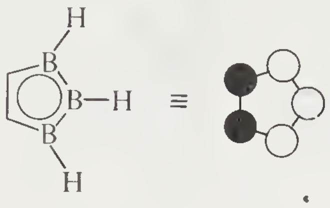
$$(\mathbf{44})^+BF_4^- \xleftarrow{i} (\mathbf{44}) \xrightarrow{ii} K^+(\mathbf{44})^-$$

i, $AgBF_4$; ii, K, THF.

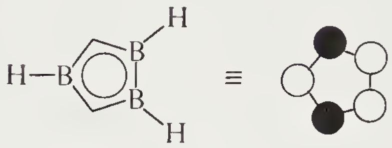
Scheme 4

5.3.2.1.3 Complexes of the isomeric planar $C_2B_3H_5$ ligands

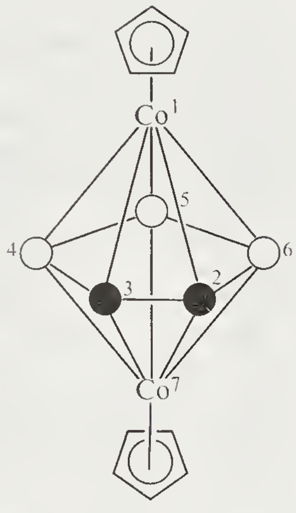
The isomeric ligands (**45**) with adjacent carbon atoms (1,2,3-triboracyclopent-4-ene) and (**46**) with non-adjacent carbon atoms (1,2,4-triboracyclopenta-3,5-diyl) have no independent existence and in a strict sense only occur in triple-decked complexes such as (**45**)·Co_2Cp_2 and (**46**)·Co_2Cp_2 which are the most studied multiple-decked complexes to date. These two compounds may either be described as complexes with bridging ligands using the representations (**29**) and (**30**) or alternatively as metallocarboranes (**47**) (shortly called 1,7,2,3-isomer) and (**48**) (1,7,2,4-isomer). Since these compounds have emerged from studies in metallocarborane chemistry the latter description is preferred in the following.



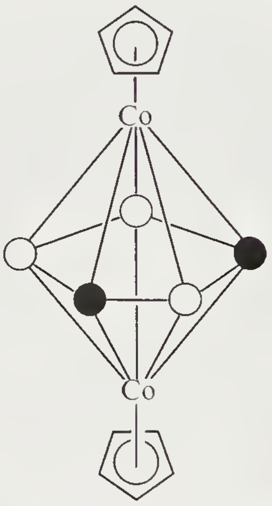
(**45**)



(**46**)

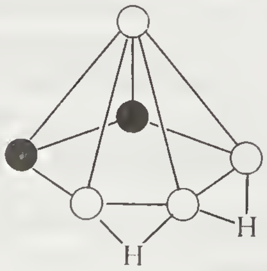


(**47**)

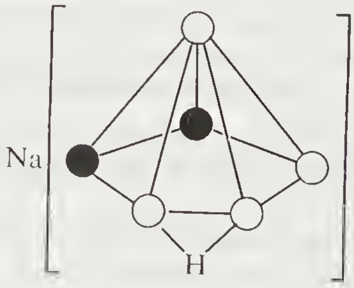


(**48**)

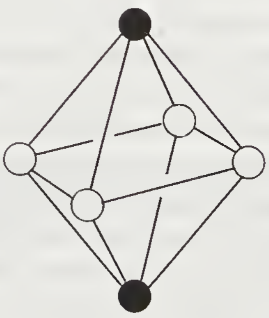
Suitable ligand precursors are *nido*-2,3-dicarbahexaborane(8) (**49**) or the corresponding bridge-deprotonated anion in (**50**) for compounds with adjacent carbon atoms, and *closo*-1,6-dicarbahexaborane(6) (**51**) for compounds with non-adjacent carbon atoms.



(**49**)



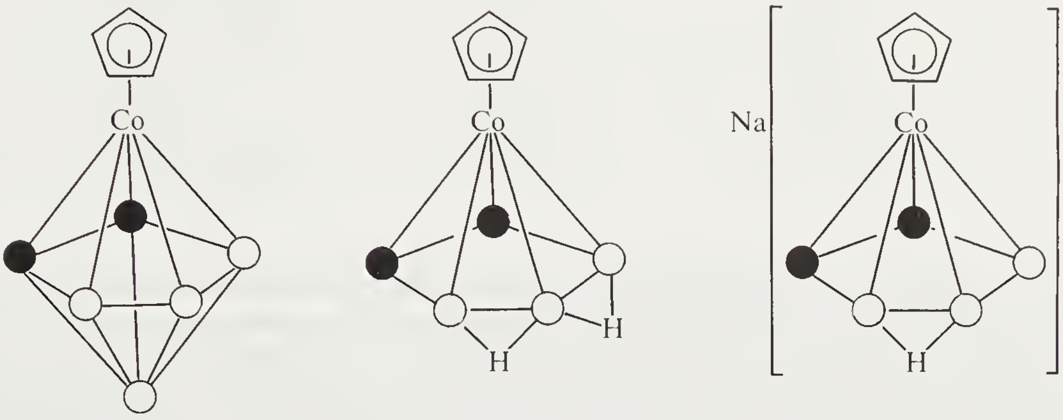
(**50**)



(**51**)

The most useful preparative strategy is a mixed-ligand synthesis reacting $CoCl_2$ with a mixture of NaCp and (**50**) or ionic species derived from (**49**) or (**51**) by treatment with $NaC_{10}H_8$ (sodium–naphthalene) in THF. The primary product mixture is then oxidized with air in the presence of water. In this procedure the triple-decked sandwich complexes are formed as by-products with maximal yields of 5% for (**47**), the red 1,7,2,3-isomer and 4% for (**48**), the green 1,7,2,4-isomer.[42]

In the system NaCp/$CoCl_2$/(**50**), compound (**52**) is the main product (63%) when acid is present during the oxidation step. When this is not the case, extensive degradation takes place and (**53**), obviously formed from (**52**) by base-induced removal of the apical BH group, becomes the main product (16%). In an independent experiment (**53**) may then be transformed into the triple-decked compound (**47**) (16%) using the same overall procedure just described (Scheme 5).[42] These details give a plausible picture of how the formation of (**47**) and similarly that of (**48**) might occur. Both isomers (**47**) and (**48**) are unreactive to water and air.[27] Above 200 °C (**47**) slowly isomerizes *via* the 1,2,4,5- and 1,2,3,5-intermediates to (**48**) (Scheme 6) which is stable to about 400 °C.[43]

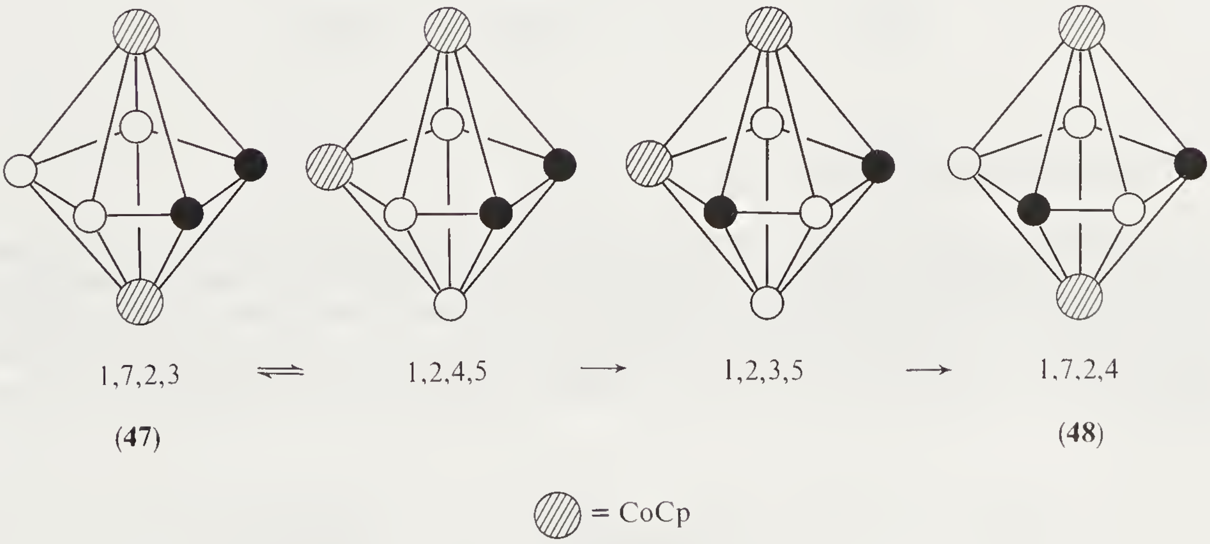


(**52**) (**53**) (**54**)

$$(\mathbf{53}) \xrightarrow{\text{i}} (\mathbf{54}) \xrightarrow{\text{ii–iv}} (\mathbf{47})$$

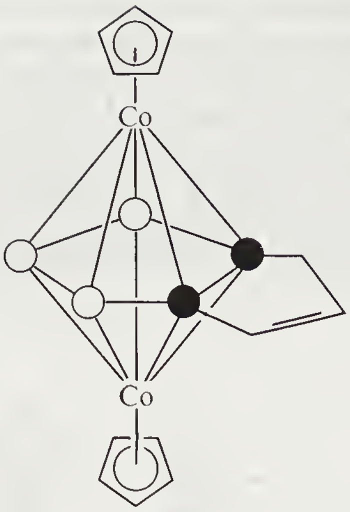
i, NaH in THF; ii, NaCp; iii, $CoCl_2$; iv, O_2/H_2O.

Scheme 5

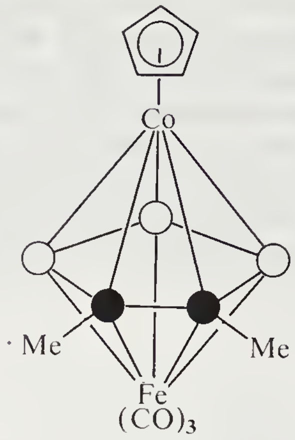


Scheme 6

Many derivatives of (**47**) and (**48**) have been made by modifying the starting materials (**49**), (**51**) and NaCp with substituents or by modifying the triple-decked products.[44] Alternative modes of formation have also been observed. Thus, direct insertion of CoCp fragments from [Co-$(CO)_2$Cp] into *closo*-1,6-$C_2B_4H_6$ gives (**48**) as a by-product.[45] Cocondensation of gaseous Co, C_5H_6, but-2-yne and *nido*-B_5H_9 affords some 2,3-dimethyl derivative of the 1,7,2,3-isomer (**47**).[46] In some other work the complexes (**55**)[47,48] and (**56**)[49] have been described as unexpected trace products.



(55)



(56)

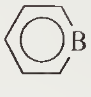
The close similarity of (**47**) and (**48**) with (other) cobaltacarboranes emphasizes the participation of the metal atoms in the delocalized cage bonding.[50] This view is supported by a detailed ^{1}H NMR study[44] and an electrochemical investigation.[31] Transmission of substituent effects across one metal centre is of the same magnitude as in metallocenes and, in some cases, may even be observed across two metal centres, in spite of the large distance of 645 pm[48] between the outer ring centres.[44] Compounds (**47**) and (**48**) undergo a series of redox reactions (equations 2 and 3) in acetonitrile which, with the exception of the second oxidation step of (**47**), are completely reversible in slow cyclic voltammetry. The species thus observed have numbers of valence electrons from 28 to 32. All redox potentials are separated by 0.8 V or more in accord with strong interaction of the two metal centres through electron delocalization.[31]

$$(\mathbf{47})^{2-} \rightleftharpoons (\mathbf{47})^{-} \rightleftharpoons (\mathbf{47}) \rightleftharpoons (\mathbf{47})^{+} \rightleftharpoons (\mathbf{47})^{2+} \qquad (2)$$

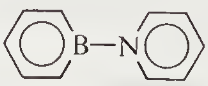
$$(\mathbf{48})^{2-} \rightleftharpoons (\mathbf{48})^{-} \rightleftharpoons (\mathbf{48}) \rightleftharpoons (\mathbf{48})^{+} \qquad (3)$$

5.3.2.2 Borabenzene Derivatives

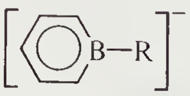
The hypothetical borabenzene or borin C_5H_5B (**57**), as well as neutral adducts thereof such as pyridine–borin (**58**), are unknown. Anionic combinations (**59**), called borinate ions (the formal relationship between (**57**) and (**59**) being the same as that between boranes BR_3 and borates BR_4^-) by this author[51] or as boratabenzene ions in *Chemical Abstracts*, are known in the form of alkali metal borinates, thallium borinates and as numerous transition metal complexes. A review is available.[52]



(57)



(58)

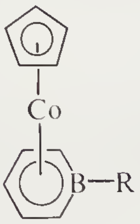


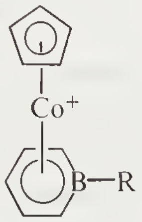
(59)

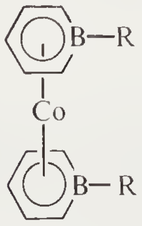
The bonding properties of the ligand C_5H_5BH (type (**6**)) have been analyzed in relation to C_6H_6 and C_5H_5 by INDO-SCF methods.[22] Accordingly, C_5H_5BH is more similar to C_5H_5 than any other ring system. In first row transition metal complexes, C_5H_5BR ligands mainly act as anionic π^6-donor systems bound to positive metal centres. However, the overall donor–acceptor property is less of the donor-type than in the Cp case and this is in agreement with diverse spectroscopic and chemical evidence[23,24,53–56] (*cf.* also Section 5.3.1.3).

5.3.2.2.1 Synthetic methods

The first route to borabenzene derivatives was found in 1970 in the reaction of cobaltocene, $[\mathrm{CoCp_2}]$, with boron halides ($\mathrm{MeBBr_2}$, $\mathrm{PhBCl_2}$, $\mathrm{BCl_3}$, $\mathrm{BBr_3}$).[51,53,57] This reaction takes place between −80 °C and room temperature. Cobaltocene in part is oxidized and in part undergoes insertion of borylene groups RB to afford three types of cobalt sandwich complexes (**60**)–(**62**) with borinato ligands. The neutral complexes (**60**) and (**62**) are paramagnetic and have the same rare 19-electron configuration as cobaltocene whereas (**61**) is a diamagnetic 18-electron cation.

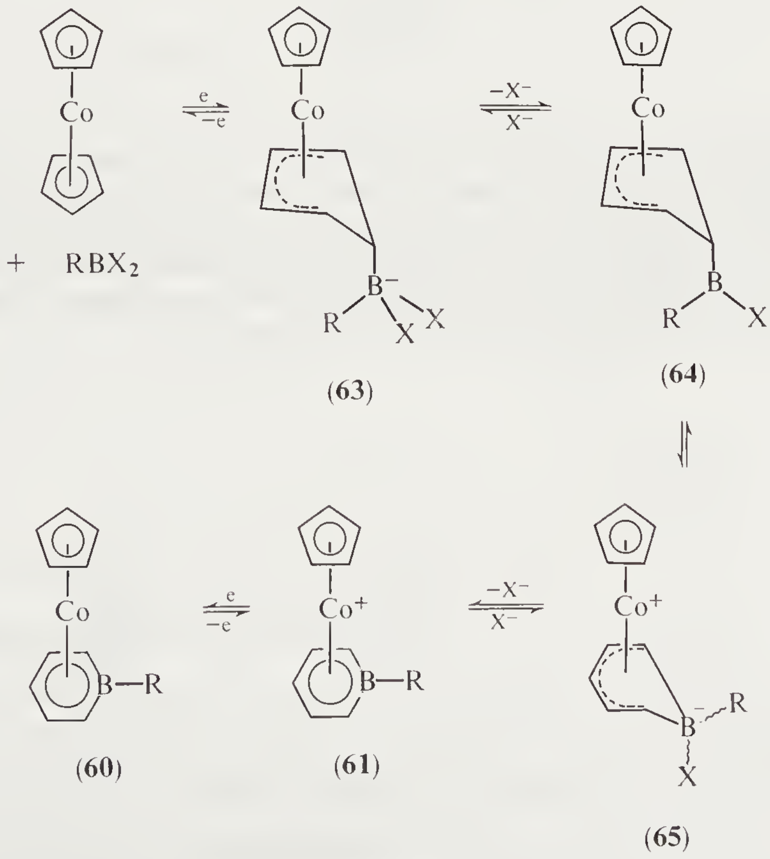

(**60**)


(**61**)


(**62**)

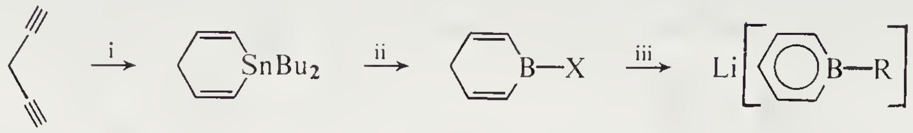
R = Me, Ph, in part also Br, OH, OMe

This unique borylene insertion may be rationalized (Scheme 7) with reference to well established cobaltocene chemistry.[57,58] The important steps are formation of radical anions $[\mathrm{RBX_2}]^{\cdot-}$, addition of these to cobaltocene to give the borate (**63**), ring expansion of (**64**) to the zwitterion (**65**) and reduction of the cation (**61**) to the observed product (**60**).[57] All steps are assumed to be reversible (see the discussion of ring contraction reactions in Section 5.3.2.2.2).[58] The product (**60**) is formed under Lewis acidic and reducing conditions with the two necessary reducing equivalents being furnished by two further moles of cobaltocene. Compounds (**60**) may again undergo borylene insertion to afford products (**61**) and (**62**). It should be noted that the reducing power and the ability to undergo radical addition reactions are both intimately connected with the 19-electron configuration of cobaltocene and of (**60**).



Scheme 7

The second route to borabenzene derivatives (Scheme 8) starts from penta-1,4-diyne which, following a general synthetic scheme,[59] is transformed into 1-boracyclohexa-2,5-dienes. These are analogues of cyclopentadiene and likewise readily deprotonate to form borinates provided the base used cannot add at boron.[5,55]



(66)

X = Me, Ph, Br and R = Me, Ph, Bu^t

i, Bu_2SnH_2, 100 °C; ii, $XBBr_2$, −78 °C; iii, $LiBu^t$

Scheme 8

Alkali metal borinates (**67**) can also be made by cyanide degradation of bis(borinato)cobalt complexes (**62**) (Scheme 9).[6] Thus a point of convergence for the cobaltocene route and the tin route is reached.

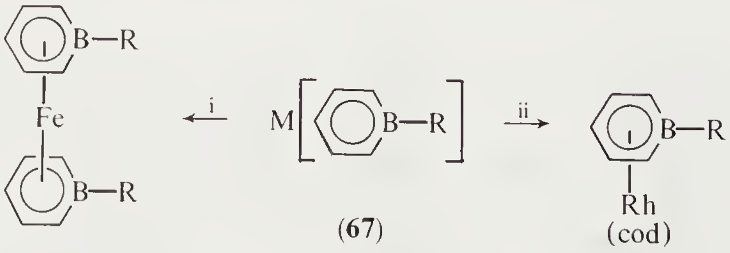
(67)

M = Na, K and R = Me, Ph

i, MCN in MeCN, 80 °C, 2–10 h

Scheme 9

Alkali metal borinates (**67**), although never isolated in pure form, are key intermediates in numerous syntheses (*e.g.* of (**68**), Scheme 10) which usually are closely analogous to reactions in cyclopentadienyl chemistry.[6,55] Simple metathesis with TlCl affords thallium borinates $Tl(C_5H_5BR)$ (R = Me, Ph)[60] which are the only main group metal borinates to be isolated in pure form. They are useful for the preparation of cationic complexes (Scheme 11) where the basicity of the alkali metal borinates cannot be tolerated.[58]



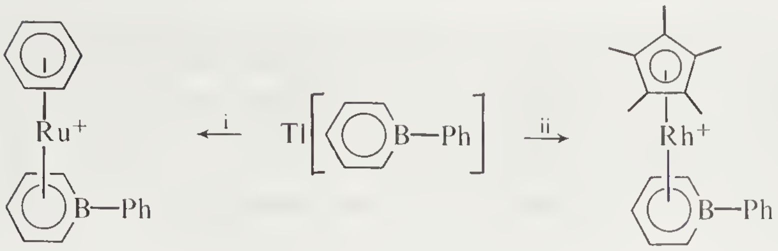
(67)

(68)

M = Li, Na, K and R = Me, Ph

i, $FeCl_2$; ii, [{RhCl(cod)}$_2$].

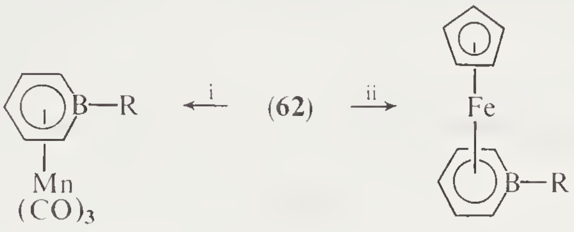
Scheme 10



i, [{RuCl$_2$(C$_6$H$_6$)}$_2$], MeCN, 4 h, 40–50 °C; ii, [{RhCl$_2$(C$_5$Me$_5$)}$_2$], MeCN, 4 h, 40–50 °C

Scheme 11

Both routes have useful ramifications. Direct ligand transfer from complexes (**62**) is advantageous in some cases, *e.g.* in the preparation of the mixed ligand complexes (**69**) and (**70**) (Scheme 12).[61,62] Direct interaction of 1-boracyclohexa-2,5-dienes with metal carbonyls and other metal atom sources should eventually prove to be a versatile synthetic method. In the 4,4-dimethyl derivative (**71**), product formation is accompanied by loss of a methyl group (Scheme 13) but some methyl migration to the neighbouring C(3) occurs as a side reaction.[63] This complication is avoided with the simpler ligand precursors (**66**).[64]

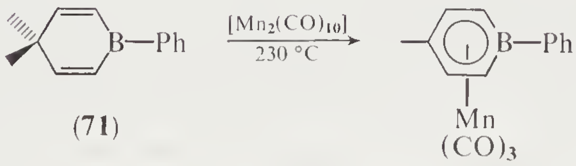


(**69**) (**70**)

R = Me, Ph

i, [Mn$_2$(CO)$_{10}$], 115–160 °C; ii, [{Fe(CO)$_2$Cp}$_2$], 165 °C

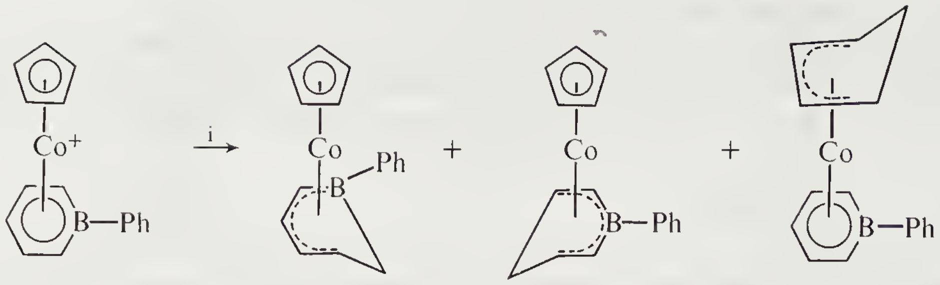
Scheme 12



Scheme 13

5.3.2.2.2 Nucleophilic addition at borinato ligands

Nucleophilic attack at coordinated borinate rings in general does not occur when the complex is uncharged or even anionic. In cationic compounds, however, nucleophilic addition is a general reaction. Whereas [CoCp$_2$]$^+$ is only attacked by the very strongest nucleophiles (*e.g.* LiPh or H$^-$ from LAH) the mixed cation (**72**)$^+$ with one borinato ligand is quite prone to nucleophilic attack. Hydride addition occurs at C(2) giving (**73**) with an (η^5-1-borapenta-2,4-diene)-type ligand, at C(4) giving (**74**) with an (η^5-divinylborane)-type ligand and at the counter-ligand giving a cyclopentadiene complex (**75**) (Scheme 14) with isolated yields of 12, 30 and 51%, respectively.[58]



(72)+ **(73)** **(74)** **(75)**

i, $NaBH_4$ in MeCN, 0 °C, 5 min

Scheme 14

Harder nucleophiles such as amines, CN^-, OH^- and F^- attack at boron. With tertiary amines like pyridine, reversible formation of an adduct of type (**65**) is observed. With the other nucleophiles mentioned, addition is followed by more or less rapid ring contraction. In the presence of an oxidant quantitative borylene extrusion with formation of $[CoCp_2]^+$ is observed whereas in the absence of an added oxidant two further moles of $(\mathbf{72})^+$ are reduced (Scheme 15).[58] Obviously these transformations are the exact reversal of the borylene insertion treated earlier (Scheme 7), with Lewis basic and oxidizing conditions favouring the removal of the borylene group.[58]

$$(\mathbf{72})^+ \xrightarrow{\text{i, ii}} [CoCp_2]^+ + PhB(OH)_2$$

$$3(\mathbf{72})^+ \xrightarrow{\text{iii, ii}} [CoCp_2]^+ + 2(\mathbf{72}) + PhB(OH)_2$$

i, Et_2NH/O_2 in CH_2Cl_2, 0.5 h, 0 °C; ii, H_2O; iii, Et_2NH in THF, 2 h, 0 °C

Scheme 15

5.3.2.2.3 Redox reactions

Bis(borinato)metal complexes can exist in several oxidation states just like the metallocenes. On going from cyclopentadienyl complexes to analogous borinato complexes all redox potentials are shifted anodically (see Section 5.3.1.3 and Table 1).[23,56] Consequently all cationic borinato complexes are less easily accessible and more reactive than their cyclopentadienyl counterparts.

The 19-electron cobalt complexes of type (**60**) and (**62**) are all easily oxidized and oxidation is often followed by borylene extrusion depending on the basicity of the medium and the electrophilicity of the cation. Thus, the mixed ligand complexes (**60**) give the cations (**61**) in acidic solution, *e.g.* with aqueous Fe^{3+} (equation 4) whereas in basic solution borylene extrusion takes place (Scheme 15). The symmetric complexes (**62**) normally give borylene extrusion even in acidic solution (equation 5). Cations of type $(\mathbf{62})^+$ can be made in the extremely non-basic solvent CH_2Cl_2 (equation 6). They are highly electrophilic against hard nucleophiles, with even traces of water or methanol inducing ring contraction (equation 7, *cf.* Scheme 15).[58]

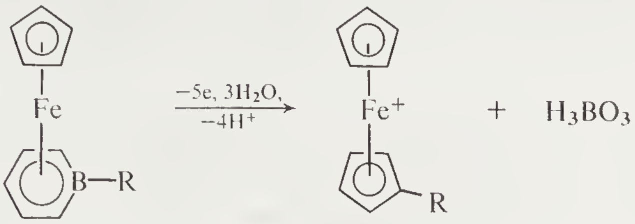
$$\underset{(\mathbf{60})}{[CoCp(C_5H_5BR)]} \xrightarrow{-e} \underset{(\mathbf{61})}{[CoCp(C_5H_5BR)]^+} \quad (4)$$

$$\underset{(\mathbf{62})}{[Co(C_5H_5BR)_2]} \xrightarrow[-2H^+]{-3e,\ 2H_2O,} \underset{(\mathbf{61})}{[CoCp(C_5H_5BR)]^+} + RB(OH)_2 \quad (5)$$

$$[Co(C_5H_5BPh)_2] + [FeCp_2]PF_6 \longrightarrow [Co(C_5H_5BPh)_2]PF_6 + [FeCp_2] \quad (6)$$

$$3[Co(C_5H_5BPh)_2]^+ \xrightarrow{MeOH} 2[Co(C_5H_5BPh)_2] + [CoCp(C_5H_5BPh)]^+ + PhB(OMe)_2 + 2H^+ \quad (7)$$

The ferrocene analogues (**70**) and (**68**) are relatively inert to oxidation which, when forced, affords substituted ferricenium ions (Scheme 16).[62] In marked contrast to the reactions described above, the group R at boron becomes a substituent of the newly formed cyclopentadienyl ring. Cationic species $(\mathbf{70})^+$ can be observed by cyclic voltammetry in CH_2Cl_2 and the same is true for $(\mathbf{68})^+$ at high sweep rates. In more basic solvents like THF, the electrochemical oxidation is irreversible which indicates extreme electrophilicity of these cations.[23]



(**70**)

Scheme 16

The electrochemical data also show that anionic (borinato)metal complexes are more easily accessible and more stable than their cyclopentadienyl analogues.[23,56] Bis(borinato)cobaltates are the best known example.[24,56] Bis(borinato)cobalt complexes (**62**) are easily reduced by sodium amalgam giving sodium salts (**76**) (Scheme 17).[24] Solutions of (**76**) and crystalline $[PPh_4][Co(C_5H_5BPh)_2]$ ($\mu_{eff} = 2.85 \pm 0.05$ BM) show magnetic moments corresponding to two unpaired electrons per cobalt, thus indicating the presence of 20-electron sandwich anions which structurally and chemically resemble nickelocene.

$$\underset{(\mathbf{62})}{[Co(C_5H_5BR)_2]} \xrightarrow{i} \underset{(\mathbf{76})}{Na[Co(C_5H_5BR)_2]}$$

R = Me, Ph

i, $NaHg_x$, THF, 20 °C, 0.3 h

Scheme 17

Solutions of (**76**) in THF slowly decompose at reflux temperature whereas in acetonitrile the same decomposition takes place below room temperature (equation 8). This remarkable solvent effect can probably be ascribed to participation of the biphilic acetonitrile in the decomposition pathway. Simultaneous reduction and decomposition result in complete reductive degradation of (**62**) with formation of alkali metal borinates and elemental cobalt. This procedure, however, does not offer any preparative advantages over the cyanide degradation (Scheme 9). In the presence of suitable ligands only one ligand is removed and complexes such as the cycloocta-1,5-diene complexes (**77**) are formed in excellent yields (Scheme 18).[24,66]

$$2(\mathbf{76}) \longrightarrow Co + (\mathbf{62}) + 2Na[C_5H_5BR] \qquad (8)$$

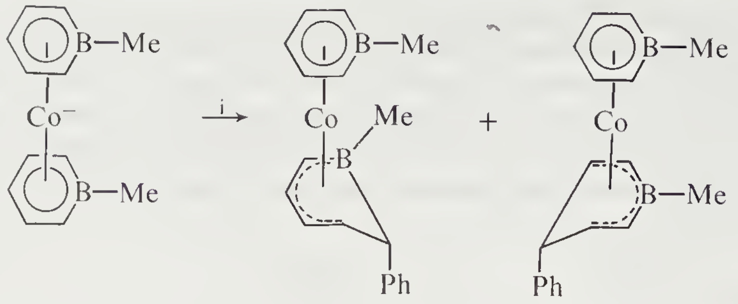
$$\underset{(\mathbf{62})}{[Co(C_5H_5BR)_2]} \xrightarrow{i} \underset{(\mathbf{77})}{[Co(C_5H_5BR)(cod)]}$$

R = Me, Ph

i, Li, cod in THF, 65 °C, 12 h

Scheme 18

Electrophilic addition at C(2) and C(4) seems to be another general reaction of the 20-electron anions of (**76**). Protonation with H_2O has been observed at C(2) (with R = Ph). Interaction of (**76**) (R = Me) with iodobenzene produces two isomeric compounds (**78**) and (**79**) with isolated yields of 30% and 36% respectively (Scheme 19).[24]



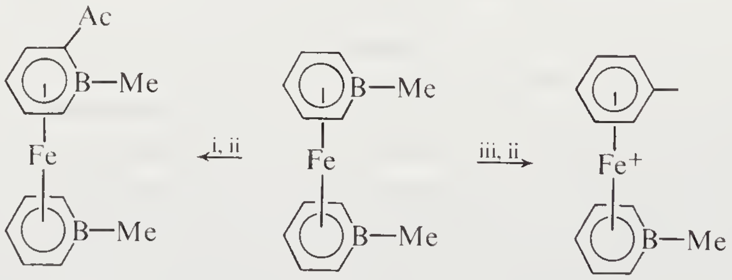
(78) (79)

i, PhI, THF, 20 °C, 0.5 h

Scheme 19

5.3.2.2.4 *Electrophilic substitution and ring-member substitution*

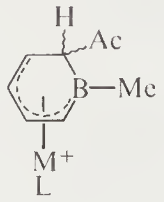
The iron complexes (**70**)[62] and (**68**)[55,64,65] are expected to be susceptible to electrophilic substitution reactions in much the same way as ferrocene. When the model complex (**80**) is treated with CF_3CO_2D at 25 °C the four protons in the α-position to the boron exchange but no further exchange is observed even after 24 h at reflux temperature.[55] Attempted Friedel–Crafts acetylation of (**80**) with a large excess of MeCOCl–$AlCl_3$ results in smooth formation of the cation (**81**) (Scheme 20).[62] In this remarkable ring-member substitution one MeB group of (**80**) is replaced with a MeC fragment of CH_3COCl with concurrent formation of what is probably $(MeBO)_3$. Under normal reaction conditions, *i.e.* with a ratio of the reactants probably close to 1 : 1 : 1, monoacetylation of (**80**) at C(2) to give a 20% yield of (**82**) is observed (Scheme 20).[55] It is reasonable to assume that both reactions have a common intermediate of type (**83**) which under less acidic conditions deprotonates to give the acetyl derivative (**82**), while it may rearrange under more acidic conditions to give (**81**). Some other (borinato)metal complexes are known to react similarly. From the literature data the qualitative reactivity order (**84**) < (**80**) < $[FeCp_2]$ < (**85**) may be inferred.



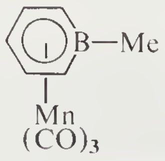
(82) (80) (81)

i, $AcCl/AlCl_3$ (equimolar) in CH_2Cl_2, 0 °C; ii, H_2O; iii, $AcCl/AlCl_3$ (fourfold excess) in CH_2Cl_2, 0 °C

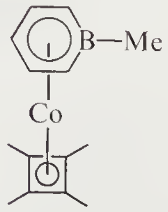
Scheme 20



(83)

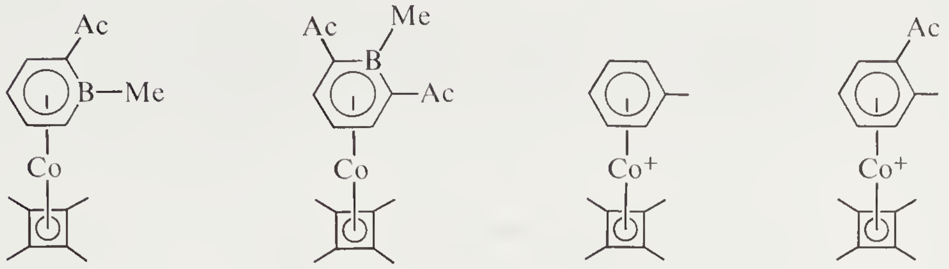


(84)



(85)

The cobalt complex (**85**)[66] is much more reactive even than ferrocene. CF_3CO_2D effects exchange of all protons of the borabenzene moiety of (**85**) within one week at ambient temperature with the qualitative reactivity order being H(2), H(6) $\gg$ H(4) $\gg$ H(3), H(5). Acetylation affords four products (**86**)–(**89**) (Scheme 21). The course of the reaction depends largely on the acidity of the Friedel–Crafts milieu. With the weak catalyst $AsCl_3$ monoacetylation (63% yield) dominates but quite remarkably, homoannular disubstitution (3% yield) is also observed. With more active catalysts like $SnCl_4$ the primary acetylation products are slowly transformed into ring-member substitution products while with $AlCl_3$ only the very rapid formation of a mixture of the cations (**88**) and (**89**) is observed. The acetylation products may also be protonated by superacids and then slowly rearrange to give the corresponding cations (Scheme 22).[66] Obviously very high acidity is necessary in the reaction medium to switch from kinetic to thermodynamic control.



(86) (87) (88) (89)

$$(86) + (87) \xleftarrow{i} (85) \xrightarrow{ii} (88) + (89)$$

i, $AcCl/AsCl_3$ in CH_2Cl_2, 40 °C, 80 h; ii, $AcCl/AlCl_3$ in CH_2Cl_2, 0 °C, 5 min

Scheme 21

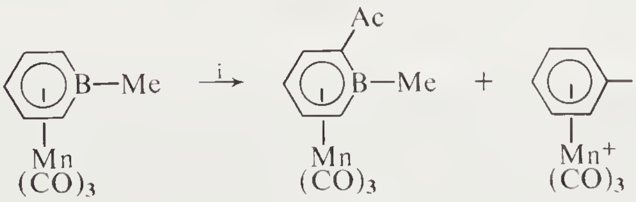
$$(86) \xrightarrow{i} (88) + \{MeB(OH)_2\}$$

$$(87) \xrightarrow{ii} (89) + \{MeB(OH)_2\}$$

i, CF_3SO_3H, 20 °C, 1 d; ii, CF_3CO_2H/BF_3, 20 °C, 3 d

Scheme 22

The manganese complex (**84**) is rather unreactive. Acetylation with $MeCOCl–AlCl_3$ affords both the 2-acetyl derivative (**90**) (in $MeNO_2$ 98% selectivity and 80% yield) and cation (**91**) (Scheme 23).[61] The product ratio is kinetically controlled since the 2-acetyl derivative (**90**), once formed, cannot be reprotonated at C(2) due to the low basicity of this particular complex.



(84) (90) (91)

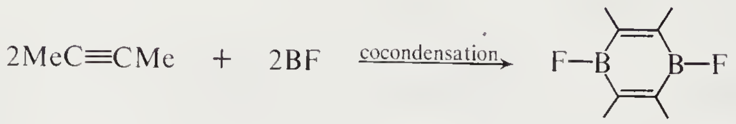
i, $AcCl/AlCl_3$ in CH_2Cl_2 or $MeNO_2$, 0 °C, 0.5 h

Scheme 23

5.3.2.3 Derivatives of 1,4-Diboracyclohexa-2,5-diene

Very few uncomplexed 1,4-diboracyclohexa-2,5-dienes $XB(CR{=}CR)_2BX$ (with X = F, R = H, Me[67] and with X = Fc, OMe, R = H[68]) are known. Theoretical investigation indicates that with fluorine as the substituent at boron (R = H, X = F) the classical planar structure of the 1,4-diboracyclohexa-2,5-diene is stabilized through π-interaction between boron and fluorine whereas with substituents not allowing for such π-interaction (for the calculation R = X = H) the isomeric non-classical *nido*-carborane structure is lower in energy.[69] In agreement with this result all the known 1,4-diboracyclohexa-2,5-dienes show strong π-interactions of the kind described.

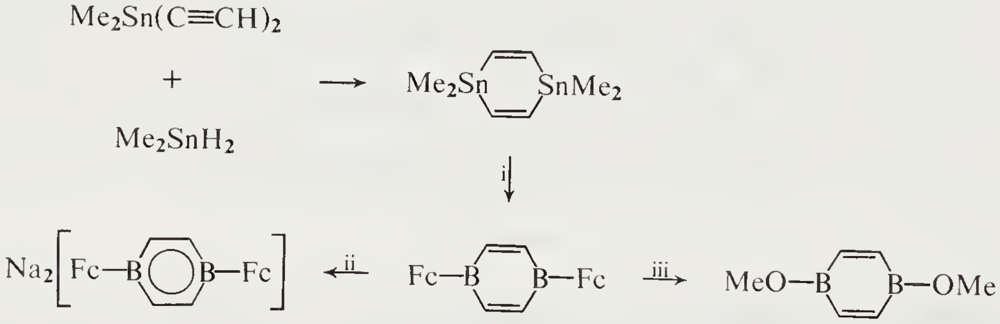
Two routes to the 1,4-diboracyclohexa-2,5-diene derivatives are known. Cocondensation of simple alkynes (C_2R_2 with R = H, Me) with BF affords the free ring systems of which the tetramethyl derivative (**92**) is the most important example (Scheme 24).[67]



(92)

Scheme 24

The second approach is a further variation of the tin route[59] which is successful with ferrocenyldibromoborane $FcBBr_2$ (Scheme 25) but not with simpler boron halides such as BCl_3, BBr_3, $MeBBr_2$ and $PhBCl_2$.[68] The 1,4-diferrocenyl derivative (**93**) can be reduced to the corresponding six-π-electron anion in (**94**)[7] and on controlled methanolysis affords the 1,4-dimethoxy derivative (**95**).[68]

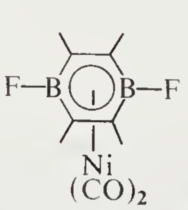


(94) (93) (95)

i, $FcBBr_2$; ii, $NaHg_x$ in THF; iii, MeOH

Scheme 25

Each one of the compounds (**92**)–(**95**) may be used as the starting point for syntheses of transition metal complexes. The compounds (**96**) (from (**92**)/$[Ni(CO)_4]$),[70] $[(\mathbf{93})\cdot Pt(cod)]$ (from (**93**)/$[Pt(cod)_2]$),[7] (**97**) (from (**94**)/$[\{NiCl_2(C_4Me_4)\}_2]$)[7] and (**98**) (from (**95**)/$[\{RhCl_2(C_5Me_5)\}_2]$/$[CoCp_2]$ (as reductant) in CH_2Cl_2)[7] may serve as examples. The complexes of (**95**), by way of nucleophilic substitution reactions at boron, give access to complexes of further 1,4-diboracyclohexa-2,5-diene ligands which are unknown in the free state, *e.g.* with H, Me, Ph and Cl as substituents at boron.



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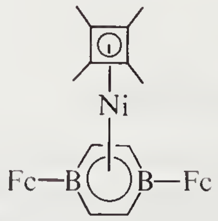

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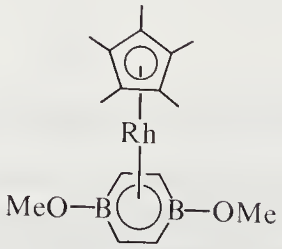
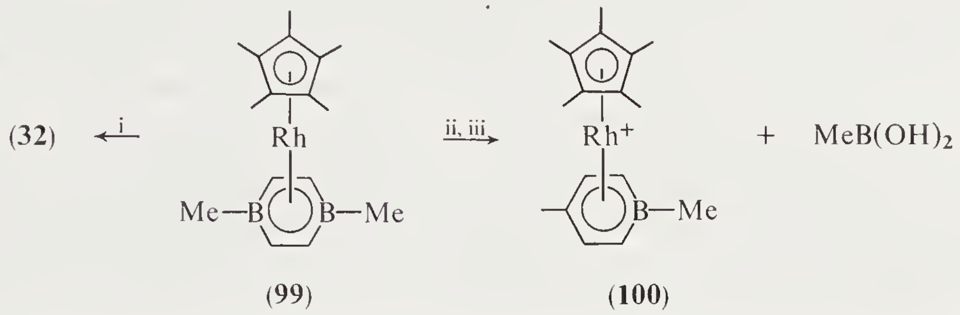


(98)

All available chemical and spectroscopic evidence shows that 1,4-diboracyclohexa-2,5-diene ligands are very strongly back-bonding ligands. Structural investigations on nickel complexes of **(92)**[15,70] and on [CpCo(MeBC$_4$H$_4$BMe)] **(27)** (X = Me),[25] however, show that the changes of intra-ring bond distances which are induced by back-bonding are more pronounced in the cobalt complex **(27)** (X = Me) (C—C (av.) = 142.3, B—C (av.) = 151.4 pm) than for example in the 1 : 1 adduct [**(96)**·**(92)**] containing complexed **(92)** (C—C (av.) = 139.5, B—C (av.) = 152.7 pm) and an additional molecule of free **(92)** (C—C (av.) = 133.9, B—C (av.) = 156.7 pm). Obviously, π-interactions with exocyclic substituents at boron diminish the back-bonding ability of the ligand and MeBC$_4$H$_4$BMe is a much stronger acceptor than **(92)**.

Two more special reactions deserve mention (Scheme 26). The rhodium complex **(99)** is quite susceptible to protonation resulting in clean formation of the unusual triple-decked cation **(32)**. This may also be obtained from **(99)** by addition of a [Rh(C$_5$Me$_5$)]$^{2+}$ fragment under Lewis acidic conditions.[29] Attempted Friedel–Crafts acetylation effects ring-member substitution to produce the borabenzene derivative **(100)**.[7]

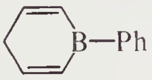


i, CF$_3$CO$_2$H or [{RhCl$_2$(C$_5$Me$_5$)}$_2$]/AlCl$_3$ in CH$_2$Cl$_2$; ii, AcCl/AlCl$_3$ in CS$_2$; iii, H$_2$O

Scheme 26

5.3.2.4 Complexes of Non-conjugated Ring Ligands

A large variety of non-conjugated boron–carbon ligands may be conceived. The published work, however, deals with very few ring systems such as **(101)**–**(104)** and 1-phenyl-4,5-dihydro-1H-borepin **(35)**.



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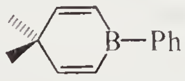
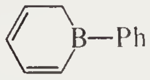


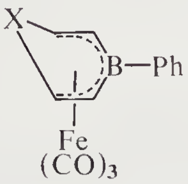
(102)

(103)

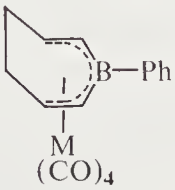


(104)

The tin route[59] provides access to the divinylborane-type ligands **(101)**–**(103)** and **(35)**.[5,71] These may then be incorporated into transition metal complexes of type **(105)** (with the ligands **(35)**, **(102)** and **(103)**), **(106)** (with M = Cr, Mo, W) and **(107)** (with M = Ni, Pd, Pt and the ligands **(35)**, **(102)** and **(103)**).[71–73] The range of applicable synthetic methods is limited by the



(105)



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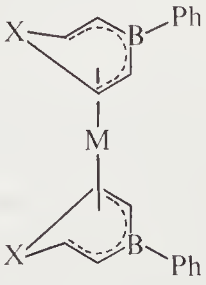


(107)

X = Me$_2$C, Me$_2$Si, (CH$_2$)$_2$

M = Cr, Mo, W

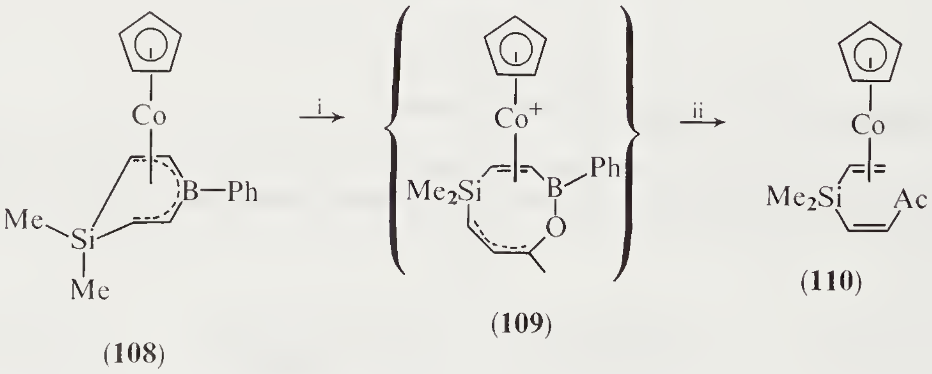
M = Ni, Pd, Pt

high reactivity of unsaturated organoboranes. Thus, complexation methods which involve the use of protic or strongly Lewis basic solvents or agents are not feasible. Complexes of (**101**), (**104**) and closely related systems may also be obtained from complex borabenzene derivatives by nucleophilic addition reactions to cationic complexes and by electrophilic addition reactions to anionic complexes (Schemes 14 and 19).[24,58]

In all cases the ligands are η^5-bound according to the ^{11}B NMR criterion and a detailed interpretation of ^{1}H NMR spectra. Thus, the ligands are non-planar with a small bend of the RB group away from the metal as usual and a strong bend of the non-bonded ring members, *e.g.* the CH_2 group in complexes of (**101**) and (**104**) or of the Me_2Si group in complexes of (**103**). These conclusions are supported by X-ray diffraction studies on (**105**) (X = Me_2Si)[71] and on (**107**) (M = Ni, X = Me_2Si) where the ligands are rotated by a right angle with respect to each other.[73] The ligand geometry is reminiscent of the structures of cyclohexadienyl complexes, thus indicating strong back-bonding into the unsaturated organoborane moiety of the ligands.

As a consequence of stronger back-bonding the complexes are generally less air sensitive, less reactive and thermally more stable than comparable (diene)metal complexes even when the diene chosen for comparison is cycloocta-1,5-diene. This may be exemplified by the exceptional thermal stability of (**107**) (M = Ni, X = Me_2Si) (dec. 350–360 °C) and the homologous Pd complex (dec. 190–200 °C) as compared to other Ni(0) and Pd(0) compounds respectively.[73]

Little is as yet known about the reactivity of the coordinated ligands. An example worthy of mention is the Friedel–Crafts acetylation of the cobalt complex (**108**) (Scheme 27).[74] This reaction proceeds *via* electrophilic attack at the carbon atom α to the boron followed by rearrangement to the hypothetical intermediate (**109**). Hydrolysis then yields the deborylated *cis* acetyl derivative (**110**) which slowly isomerizes to the corresponding *trans* isomer. This reaction is clearly related to the ring-member substitution reaction of complex borabenzene (Schemes 20–23) and diborabenzene derivatives (Scheme 26).



i, $AcCl/AlCl_3$ in CH_2Cl_2, 0 °C, 6 h; ii, H_2O, 20 °C

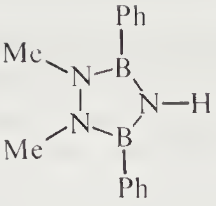
Scheme 27

5.3.3 SYSTEMS WITH BORON–NITROGEN RING LIGANDS

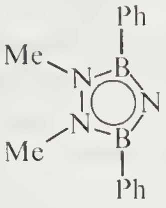
The ready availability of some heterocyclic boron–nitrogen compounds prompted the earliest attempts, in 1967, to synthesize transition metal complexes of boron-containing ring systems.

The first starting point was the 1,2,4,3,5-triazadiborolidine (**111**) and the lithio derivative Li·(**112**).[75] These compounds have an obvious formal resemblance to pyrrole and alkali metal pyrrolides and to cyclopentadiene and lithium cyclopentadienide. Treatment of $FeCl_2$ with Li·(**112**) readily yields a dark brown diamagnetic solid [Fe·(**112**)$_2$] (Scheme 28) which according to NMR spectral data is likely to have the structure of an 'inorganic ferrocene' (**113**).[75] This, however, has not been ascertained by X-ray structural work.

Borazines (**114**) are the second class of potential ligands to be considered here. They are isoelectronic analogues of benzene. Considerable efforts to develop a chemistry of η^6-bonded borazine–metal complexes have led to two types of half-sandwich complexes (**115**) and (**116**) where a borazine, mostly peralkylated, is attached to $Cr(CO)_3$ and $Mo(CO)_3$ fragments respectively. This work has been reviewed in detail.[76]



(111)



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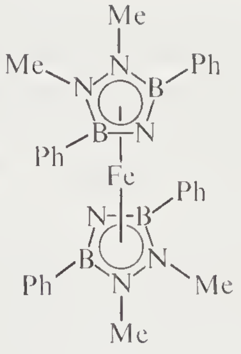
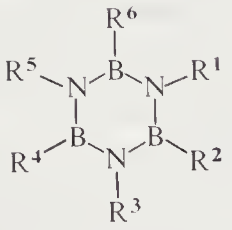


(113)

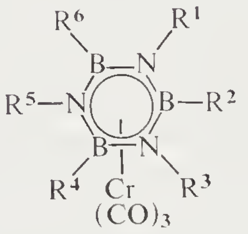
$$(\mathbf{111}) \xrightarrow{\text{i}} \text{Li}(\mathbf{112}) \xrightarrow{\text{ii}} [\text{Fe}(\mathbf{112})_2]$$

i, LiMe in Et_2O, 0 °C; ii, $FeCl_2$ in THF

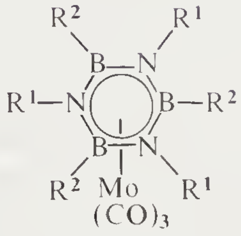
Scheme 28



(114)



(115)



(116)

The range of synthetic methods applicable to the preparation of (borazine)tricarbonylchromium complexes (**115**) is severely limited by the low stability and the high reactivity of these compounds. While direct interaction of $[Cr(CO)_6]$ with arenes in a suitable refluxing solvent commonly leads to (arene)tricarbonylchromium complexes this same method results in decomposition with borazines. With the more reactive $[Cr(CO)_3(MeCN)_3]$ an entrainment method (Scheme 29) is applicable.[9] Although the underlying ligand displacement equilibria (equations 9–11) are unfavourable to product formation the acetonitrile may be removed from the equilibrium mixture by using the more weakly bound dioxane as solvent and repeatedly pumping off the volatiles. Photochemical substitution of $[Cr(CO)_6]$ is also possible (equation 12) provided the carbon monoxide evolved is removed *in vacuo* (10^{-6} bar) to prevent the reverse reaction.[77] Borazine complexes (**115**) and free borazines (**114**) undergo ring exchange reactions at somewhat elevated temperatures.[78] This reaction is synthetically useful in special cases, for instance for the preparation of $[Cr(CO)_3(Et_3B_3N_3Et_3)]$[78] (**24**) and of $[Cr(CO)_3(Me_3B_3N_3H_3)]$.[79] The entrainment method

$$[\text{Cr(CO)}_3(\text{MeCN})_3] \xrightarrow{\text{i}} [(\text{OC})_3\text{Cr}\{\mu\text{-O}(\text{C}_2\text{H}_4)_2\text{O}\}_3\text{Cr(CO)}_3] \xrightarrow{\text{ii}} (\mathbf{115})$$

i, (**114**) in dioxane, 30 °C, 2×10^{-5} bar; ii, removal of solvent

Scheme 29

$$[\text{Cr(CO)}_3(\text{MeCN})_3] + (\mathbf{114}) \rightleftharpoons (\mathbf{115}) + 3\text{MeCN} \tag{9}$$

$$2[\text{Cr(CO)}_3(\text{MeCN})_3] + 3\text{O}(\text{C}_2\text{H}_4)_2\text{O} \rightleftharpoons [(\text{OC})_3\text{Cr}\{\mu\text{-O}(\text{C}_2\text{H}_4)_2\text{O}\}_3\text{Cr(CO)}_3] + 6\text{MeCN} \tag{10}$$

$$[(\text{OC})_3\text{Cr}\{\mu\text{-O}(\text{C}_2\text{H}_4)_2\text{O}\}_3\text{Cr(CO)}_3] + 2(\mathbf{114}) \rightleftharpoons 2(\mathbf{115}) + 3\text{O}(\text{C}_2\text{H}_4)_2\text{O} \tag{11}$$

$$[\text{Cr(CO)}_6] + (\mathbf{114}) \xrightarrow{h\nu} (\mathbf{115}) + 3\text{CO} \tag{12}$$

and the photochemical method also permit the syntheses of molybdenum complexes (**116**) ($R^1 = Me, R^2 = Et$ and $R^1 = Et, R^2 = Me$).[80]

The structure of the borazine complexes (**115**) as established for the hexaethyl derivative (**24**)[16] follows the general pattern described earlier (*cf.* Section 5.3.1.2). The intra-ring bond distances of the borazine do not change significantly upon complexation, thus indicating rather weak metal–ligand interactions. The out-of-plane distortions of the ring skeleton conform to idealized C_{3v}-symmetry. The N_2BC and B_2NC fragments of the hexaethylborazine ligand are approximately planar indicating essential sp^2-hybridization at boron and nitrogen. The difference of the bonding distances to the metal (Cr—B (av.) = 231, Cr—N (av.) = 222 pm) is similar to the difference of the covalent radii of boron and nitrogen implying η^6-bonded borazine. (It should be noted that the review mentioned above[76] gives a different interpretation of the bonding situation which is at variance with the original literature. The assumption of sp^3-hybridized nitrogen and localized σ-bonds between nitrogen and chromium is not compatible with the structural data and would also result in a large low-field shift of the ^{11}B resonance whereas a moderate high-field shift (7.7 p.p.m.)[9] is observed).

The overall donor–acceptor properties of the isoelectronic rings in $[Cr(CO)_3(C_6Me_6)]$ and $[Cr(CO)_3(Me_3B_3N_3Me_3)]$ are very similar according to the carbonyl stretching frequencies and dipole moments of the two compounds.[9] However, as a consequence of the uneven electron density distribution in the borazines (**114**) the σ-donor contribution to the bonding in the borazine complexes (**115**) is probably more localized between chromium and nitrogen and the π-acceptor contribution between chromium and boron.[78] This also implies a rather high barrier to internal rotation.[81] Furthermore, the bond enthalpy contribution is much less for the borazine complex ($D(Cr—C_6Me_6) = 206$ kJ mol^{-1} and $D(Cr—Me_3B_3N_3Me_3) \approx 105$ kJ mol^{-1}).[82]

The borazine ligands in (**115**) and (**116**) are readily displaced. These reactions occur with many σ-donor molecules[9] (*e.g.* equation 11) and apparently with almost all π-acceptors (*e.g.* equations 13[82] and 14[80]), usually at room temperature. A kinetic analysis in the system (**115**)/$P(OR)_3$ (R = Et, Ph) reveals a second order rate law and the reaction rate is dominated by steric effects. The rate decreases as the bulkiness of the alkyl group increases, particularly if the alkyl group is *N*-bonded and hence closer to the metal centre.[82]

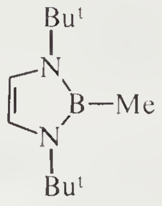
$$[Cr(CO)_3(Me_3B_3N_3Me_3)] + 3P(OEt)_3 \longrightarrow [\textit{fac}\text{-}Cr(CO)_3\{P(OEt)_3\}_3] + Me_3B_3N_3Me_3 \quad (13)$$

$$[Mo(CO)_3(Me_3B_3N_3Et_3)] + C_6H_6 \longrightarrow [Mo(CO)_3(C_6H_6)] + Me_3B_3N_3Et_3 \quad (14)$$

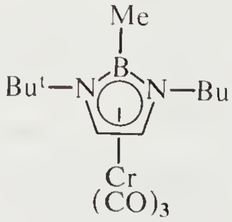
5.3.4 SYSTEMS WITH BORON–CARBON–NITROGEN RING LIGANDS

Transition metal derivatives with ligands of types (**15**)–(**18**) have been reported from 1976 onwards. In each case only very few complexes are known and much promise lies in future work.

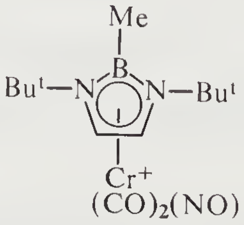
Δ^4-1,3,2-Diazaborolines, *e.g.* (**117**), are six-π-electron systems and are isoelectronic with pyrrole. They readily form tricarbonylchromium complexes such as (**118**) (equation 15) and the analogous bis(*N*-trimethylsilyl) derivative.[8] Attempts to prepare the corresponding compounds of molybdenum and tungsten have as yet been unsuccessful.[8] The spectral data are consistent with the presence of η^5-bonded ligands. From the carbonyl stretching frequencies it may be inferred that Δ^4-1,3,2-diazaborolines resemble pyrroles in their donor–acceptor properties showing strongly predominant donor character. Mesitylene readily displaces (**117**) from (**118**) giving tricarbon-



(**117**)



(**118**)



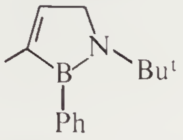
(**119**)

$$[Cr(CO)_3(MeCN)_3] + (\mathbf{117}) \longrightarrow (\mathbf{118}) + 3MeCN \quad (15)$$

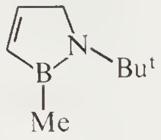
yl(mesitylene)chromium while hexamethylborazine is unable to effect reaction. The formation of the cation (**119**) (equation 16) adds a further facet to this chemistry. This cation of only moderate stability probably owes its existence to the strong donor ability of (**117**).[8]

$$(\mathbf{118}) \quad + \quad \mathrm{NO^+PF_6^-} \quad \longrightarrow \quad (\mathbf{119})\mathrm{PF_6^-} \quad + \quad \mathrm{CO} \qquad (16)$$

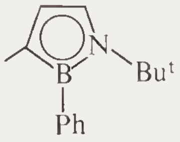
Two Δ^3-1,2-azaborolines (**120**) and (**121**) are known. These systems are isoelectronic with cyclopentadiene and thus salts like Na·(**122**) and complexes with the ligand (**122**) are expected to exist. Whereas deprotonation of (**120**) and (**121**) to give alkali metal 1,2-azaborolinides has not yet been achieved, treatment of (**120**) with [Fe(CO)$_5$] (Scheme 30) readily yields the dinuclear complex (**123**) with the 1,2-azaborolinyl ligand (**122**). The reported reactions of (**123**) (Scheme 31) closely parallel the chemistry of [{Fe(CO)$_2$Cp}$_2$].[83] The same sequence of reactions is also possible with (**121**) as the starting material.[84]



(**120**)



(**121**)



(**122**)

$$(\mathbf{120}) \quad + \quad [\mathrm{Fe(CO)_5}] \quad \xrightarrow{\text{i}} \quad [\{\mathrm{Fe(CO)_2}(\mathbf{122})\}_2]$$

(**123**)

i, reflux, 10 h

Scheme 30

$$[\mathrm{FeI(CO)_2}(\mathbf{122})] \quad \xleftarrow{\text{i}} \quad [\{\mathrm{Fe(CO)_2}(\mathbf{122})\}_2] \quad \xrightarrow{\text{ii, iii}} \quad [\mathrm{Fe(SiMe_3)(CO)_2}(\mathbf{122})]$$

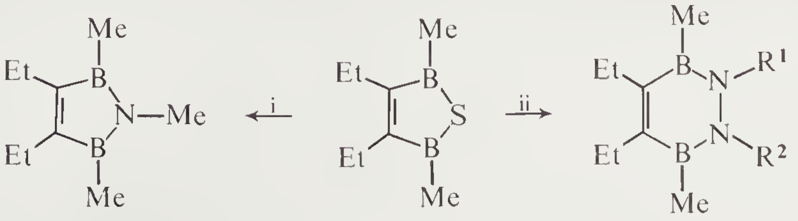
(**124**) (**123**)

i, I_2 in C_6H_6, r.t.; ii, K in dioxane, reflux, 0.5 h; iii, Me_3SiCl

Scheme 31

X-ray analyses of the racemic, doubly CO-bridged *cis* isomer of (**123**) and of (**124**) confirm the expected η^5-bonding mode of the ligand (**122**). The deviations from planarity of the ligand are somewhat unusual in that the nitrogen atom is tilted away from the metal (in *cis*-(**123**): Fe—B = 225.8, Fe—C(ring) (av.) = 204.3, Fe—N = 215.1 pm).[83] The origin of this effect is unclear but steric crowding cannot be excluded as a possible reason.

The well elaborated synthesis of the Δ^3-1,2,5-thiadiborolene (**125**)[11] also provides access to two further boron–carbon–nitrogen ring systems (**126**) and (**127**) (Scheme 32).[10,14] The Δ^3-1,2,5-azadiboroline (**126**) is a potential four-electron ligand which is closely related to boroles

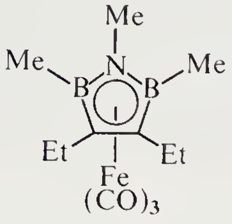


(**126**) (**125**) (**127**)

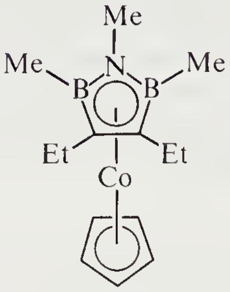
i, $(Me_3Sn)_2NMe$ in C_6H_6, r.t.; ii, R^1NHNHR^2 (R^1, R^2 = H, Me) in hexane, r.t., then reflux

Scheme 32

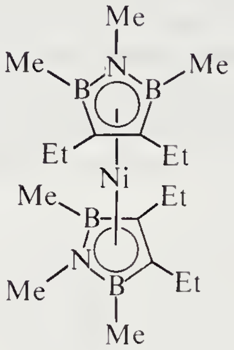
in its bonding properties. Straightforward complexation reactions with [Fe(CO)$_5$], [Co(CO)$_2$Cp] and [Ni(CO)$_4$] afford the complexes (**128**), (**129**) and (**130**) respectively. With [Co$_2$(CO)$_8$] a dinuclear complex [{Co(CO)$_2$·(**126**)}$_2$] is formed for which a double bridged *trans* structure is deduced from the carbonyl stretching frequency pattern.[10] Many attempts have been made to synthesize triple-decked complexes with (**126**) as the central ligand which, however, were essentially unsuccessful.[10]



(**128**)



(**129**)



(**130**)

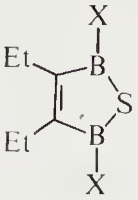
X-ray diffraction data are not yet available for these complexes. However, the spectral data leave no doubt that the structures conform to the general pattern. It is worth noting that the bis(ligand)nickel complex (**130**), according to its room temperature ^{1}H NMR spectrum, shows the same frozen conformation as compound (**25**) and the nickel complexes of type (**107**).[10]

The 1,2-diaza-3,6-diboracyclohex-4-enes (**127**) are six-electron ligands which have an intermediate position between arenes and borazines. With [Cr(CO)$_3$(MeCN)$_3$] they are readily transformed into tricarbonylchromium complexes [Cr(CO)$_3$·(**127**)].[14]

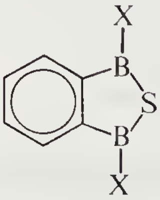
In one instance (R^1, R^2 = H; *i.e.* (**22**)), the structure has been determined by X-ray methods (see Section 5.3.1.2). According to carbonyl stretching frequencies the donor–acceptor properties of the ligand (**127**) (R^1, R^2 = Me)[14] are indeed very similar to those of hexamethylbenzene and hexamethylborazine[9] whereas the five-membered six-π-electron rings pyrrole and the Δ^4-1,3,2-diazaboroline (**117**) show more pronounced donor character.[8]

5.3.5 SYSTEMS WITH BORON–CARBON–SULPHUR RING LIGANDS

Boron–carbon–sulphur ring ligands of type (**19**) and (**20**) are known. All reported work is based on two key compounds (**131**) (X = I)[11] and (**132**) (X = I).[12] Whereas the carbon skeleton is largely dictated by the synthetic approach to these ring systems, a wide range of groups X at boron may be introduced by suitable substitution reactions.[11,12] For preparative and spectroscopic convenience the methyl group is the preferred substituent at boron and so this subsection deals mainly with complexes of the ligand (**125**).



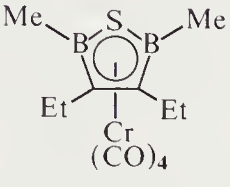
(131)



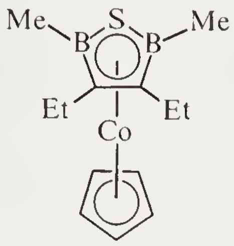
(132)

5.3.5.1 Sandwich-type Complexes

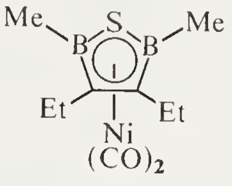
Δ^3-1,2,5-Thiadiborolenes are four-electron ligands. Thus, **(125)** combines preferentially with 14-electron fragments to give stable compounds such as $[Cr(CO)_4 \cdot (\mathbf{125})]$ **(133)**,[85] the homologous molybdenum complex $[Mo(CO)_4 \cdot (\mathbf{125})]$,[85] $[Fe(CO)_3 \cdot (\mathbf{125})]$ **(26)** (X = Me),[18] $[CoCp \cdot (\mathbf{125})]$ **(134)** (*cf.* refs. 19 and 86) and $[Ni(CO)_2 \cdot (\mathbf{125})]$ **(135)**.[19] Due to the strong acceptor character of **(125)** the remaining CO ligands in **(133)** and **(135)** permit further substitution to give bis(ligand)metal complexes (*e.g.* Scheme 33).[19,85] In addition, a series of tricarbonyliron complexes **(26)** (with X = Cl, Br, I, OEt, SMe, NMe_2, H, Me)[17] and a single benzo derivative **(23)**[18] are known.



(133)



(134)



(135)

$$[Ni(CO)_4] \xrightarrow{i} \underset{(\mathbf{135})}{[Ni(CO)_2(\mathbf{125})]} \xrightarrow{ii} \underset{(\mathbf{25})}{[Ni(\mathbf{125})_2]}$$

i, **(125)**, r.t.; ii, **(125)**, reflux, 0.5 h

Scheme 33

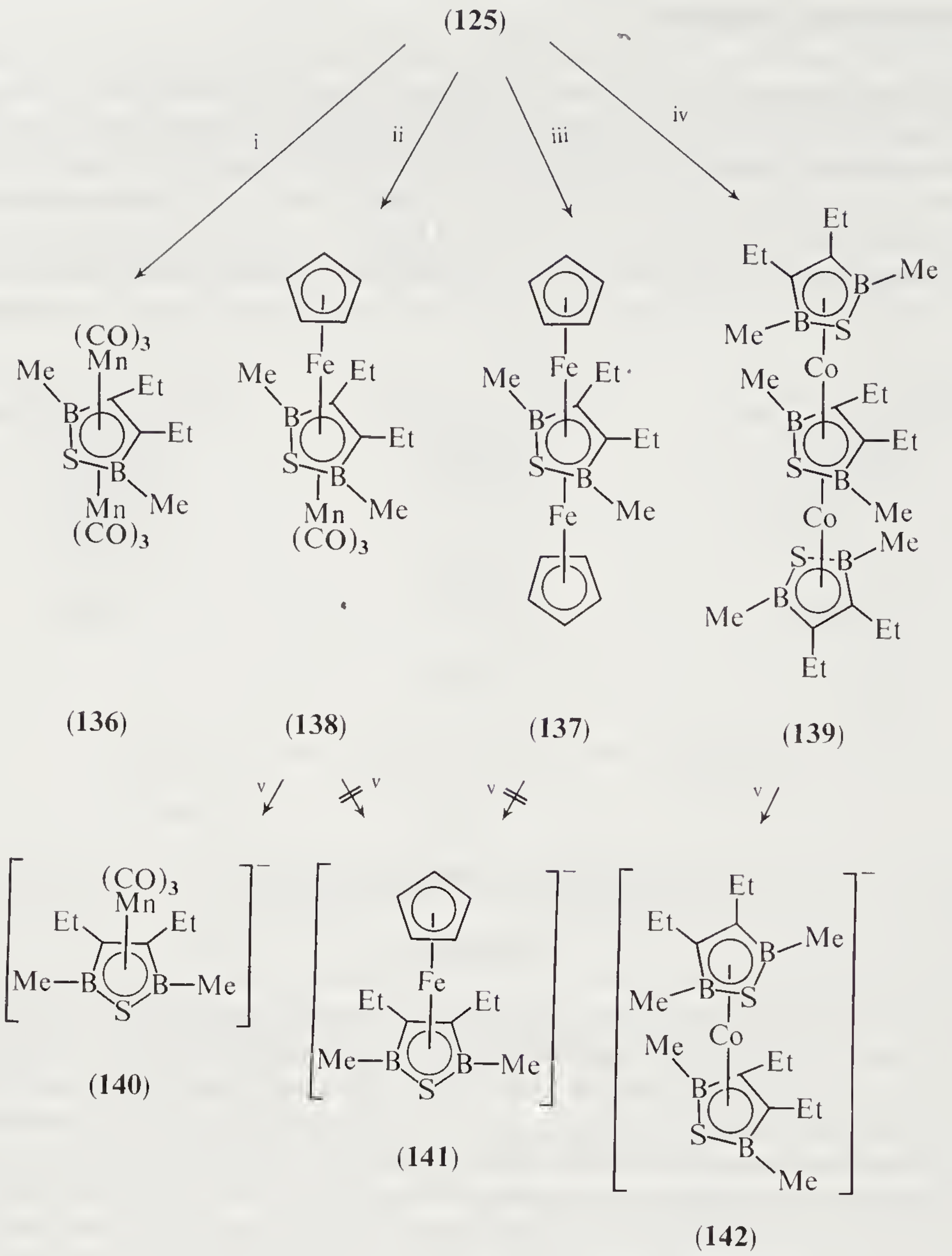
The donor–acceptor properties of the ring ligands in **(26)** greatly depend on the nature of the exocyclic substituent X. The CO stretching frequencies of approximate A_1 character decrease in the order $Br > Cl \gg H > I \gg Me > SMe \gg OEt \gg NMe_2$ (from 2075 cm^{-1} to 2034 cm^{-1} in C_2Cl_4).[17] Obviously, this order represents the combined influence of dominant mesomeric and less important inductive substituent effects. Even in the case of weakest acceptor character (*i.e.* for X = NMe_2), back-bonding considerably changes the intra-ring bond distances (with C(3)—C(4) = 144.7, B—C(ring) (av.) = 154.4, B—S (av.) = 187.6 pm for **(26)** (X = NMe_2) and C(3)—C(4) = 136.3, B—C(ring) = 159.0, B—S = 184.4 pm for the free ligand **(131)** (X = NMe_2)). The strong π-interaction with the exocyclic substituent results in an extremely long metal–boron distance (Fe—B (av.) = 241.4 pm)[17] indicating weak direct metal–boron bonding in this case. The same π-interaction also causes the barrier to internal rotation around the B—N bond of 43.1 kJ mol^{-1}.[17]

5.3.5.2 Multiple-decked Complexes

The ligand **(125)** also shows a remarkable tendency to combine with 13-electron fragments thereby affording triple-decked 30-electron complexes **(136)**,[87] **(137)**,[88] **(138)**[28] and **(139)**[89] in moderate yields (Scheme 34). The most important reaction of these complexes studied to date is a degradation with cyclopentadienide ion (Scheme 34) which affords pairs of uncharged and anionic sandwich species.[86] Thus, **(138)** gives ferrocene and the anion **(140)**. **(137)** fails to react similarly and anion **(141)** can only be obtained by an independent approach (Scheme 35).[90]

The species **(140)**–**(142)** constitute a further example of the ability of boron-containing acceptor ligands to stabilize anionic sandwich complexes. They furthermore provide a systematic and versatile approach to the synthesis of quadruple-decked complexes.[86,90] Thus with $FeCl_2$, 42-electron compounds are obtained (*e.g.* equation 17) which in all three cases have centrosymmetric quadruple-decked structures according to X-ray investigations.[28,86,90] Analogous 43- and 44-electron complexes may be obtained with $CoCl_2$ and $NiCl_2$ in some cases.[86,90] Although not many details have yet been disclosed the novelty and the synthetic potential of these reactions are apparent.

$$2Na^+(\mathbf{140}) + FeCl_2(THF)_2 \longrightarrow (\mathbf{31}) + 2NaCl + 2THF \qquad (17)$$



i, $[Mn_2(CO)_{10}]$, 165 °C; ii, $[Mn_2(CO)_{10}]/[\{Fe(CO)_2Cp\}_2]$; iii, $[\{Fe(CO)_2Cp\}_2]$, 165 °C; iv, $[Co_2(CO)_8]$, 110 °C; v, NaC_5H_5 in THF, r.t.

Scheme 34

$$[\{Fe(cod)Cp\}_2Zn] \xrightarrow{i} [\{FeCp(\mathbf{125})\}_2Zn] \xrightarrow{ii} K^+(\mathbf{141})$$

i, (**125**) in hexane, reflux; ii, K in THF, r.t.

Scheme 35

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5.4

Polyhedral Organoboranes

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5.4.1 GENERAL COMMENTS AND SCOPE OF COVERAGE

This chapter addresses itself to the chemistry of those organoboranes in which carbon is either an integral part of a polyhedral cage (carboranes) or directly attached, as a member of a substituent group, exopolyhedral to a polyboron hydride. No attempt is made here to give a comprehensive report on these compounds, and only representative details in the literature are cited to clarify structural and chemical principles. Earlier reviews[1,2] and recent articles[3] on theoretical bonding calculations concerning polyboranes, as well as Chapter 1 of this volume of *Comprehensive Organometallic Chemistry*, should be consulted when assimilating the section on structural interrelationships. Prior reviews covering the general chemistry of carboranes and organopolyboranes[4-9] are recommended for completeness.

Both chemical preparation and properties are organized along reaction types; the reader interested in the chemistry of a specific compound, or a class of compounds, is advised to consult the subject index in Volume 9 or other reviews which emphasize this aspect.[7]

5.4.2 CARBORANES

5.4.2.1 Introduction

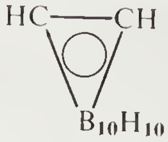
The term *carborane*, a contraction of IUPAC approved *carbaborane*, is designated for compounds having clusters of carbon and boron atoms. Most of the known polyhedral compounds of this type contain 5 to 12 cage atoms, but a few are known to exist outside this range. Much of the initial interest in these compounds can be attributed to the greater stability of these cluster species compared with the air- and moisture-sensitive polyboron hydride precursors. More recently, rules[10] devised to account for the structural patterns of the carboranes, as well as for other polyborane framework structures, have been usefully extended to include many other cluster species.[11] Although this is discussed in Chapter 1, some attention is given here to the structural systematics as applied to cage compounds of boron and carbon only. Additional material on carborane-containing compounds will also be found in Chapters 5.5 and 5.6.

5.4.2.2 Nomenclature

The IUPAC approved prefix designations indicating the degree of 'closed' and 'open' polyhedral character for the carboranes are *closo* (for closed polyhedra having triangular faces only), *nido* (for closed polyhedra *minus one* skeletal atom) and *arachno* (for closed polyhedra *minus two* vertices) (see Section 5.4.2.3). An adaptation of organic chemistry replacement nomenclature is employed as follows:

2,4-dicarba-*closo*-heptaborane(7) for *closo*-2,4-$C_2B_5H_7$
2-carba-*nido*-hexaborane(9) for *nido*-2-CB_5H_9
undecahydro-7,8-dicarba-*nido*-undecaborate(2−) for [*nido*-7,8-$C_2B_9H_{11}]^{2-}$
1,3-dicarba-*arachno*-nonaborane(13) for *arachno*-1,3-$C_2B_7H_{13}$

The numbering procedure begins with an apex atom of the polyhedron with successive rings or belts numbered in a clockwise direction. Should there be no apparent apex, the number '1' is assigned to the atom with the lowest coordination number; thus carbon atoms are usually given the lowest numbers with these rules. The symbol shown below is commonly used in the literature to represent *closo*-1,2-$C_2B_{10}H_{12}$ and is employed particularly for depicting substitution reactions at carbon. $HCB_{10}H_{10}CH$ and $H\overline{CB_{10}H_{10}C}H$ are used to designate 1,7-$C_2B_{10}H_{12}$ and 1,12-$C_2B_{10}H_{12}$, respectively.[12]



5.4.2.3 Structural Interrelationships

The principal architectural feature intrinsic to carborane structures is a polyhedral (or polyhedral fragment) framework of carbon and boron atoms. A polyhedral-series thesis,[10] consistent with characterized structures (Section 5.4.2.4 and Figures 1 to 4), and theory[1,13] accounts for the geometrical similarities of three classes of carboranes: (1) *closo*, (2) *nido* and (3) *arachno*. *closo* Compounds are defined as closed polyhedra with triangulated faces (Figures 1, 2). Formal removal of a highest-coordination vertex from any member of the *closo* polyhedral series generates the carbon–boron skeleton of a related *nido* system (Figures 3, 4). Removal of an additional skeletal atom from the open face of a *nido* structure produces an *arachno* structure (Figure 5). The series of compounds *closo*-2,4-$C_2B_5H_7$ (pentagonal bipyramid) (Figure 1f), *nido*-2,3-$C_2B_4H_8$ (pentagonal pyramid) (Figure 3c) and the polyborane *arachno*-B_5H_{11} (pentagonal pyramid minus one vertex along open face) is representative of this process (consider that formal isoelectronic interchange of boron for carbon is allowed, *i.e.* $C \equiv BH \equiv B^-$). Another series exemplifying this pattern is *closo*-1,7-$C_2B_{10}H_{12}$ (icosahedron) (Figure 2g), [*nido*-7,9-$C_2B_9H_{12}$]$^-$ (icosahedron minus one vertex (Figure 4h) and *arachno*-6,9-$C_2B_8H_{14}$ (icosahedron minus two vertices (Figure 5c). Table 1 (p. 417) cites nearly all known parent carboranes with 5 to 12 skeletal atoms and assigns each to one of the three structural (*closo*, *nido* or *arachno*) categories. All three of these

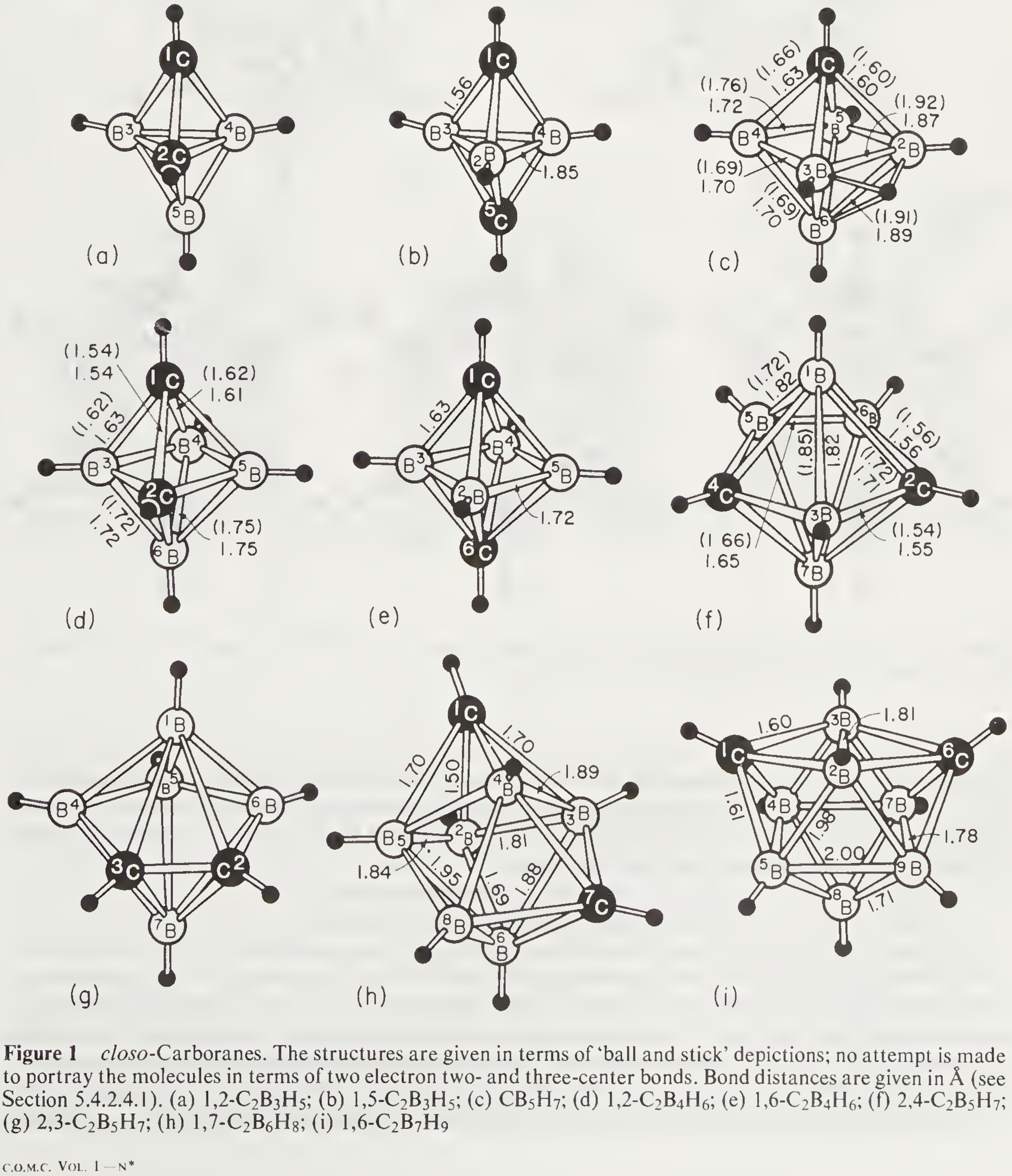


Figure 1 *closo*-Carboranes. The structures are given in terms of 'ball and stick' depictions; no attempt is made to portray the molecules in terms of two electron two- and three-center bonds. Bond distances are given in Å (see Section 5.4.2.4.1). (a) 1,2-$C_2B_3H_5$; (b) 1,5-$C_2B_3H_5$; (c) CB_5H_7; (d) 1,2-$C_2B_4H_6$; (e) 1,6-$C_2B_4H_6$; (f) 2,4-$C_2B_5H_7$; (g) 2,3-$C_2B_5H_7$; (h) 1,7-$C_2B_6H_8$; (i) 1,6-$C_2B_7H_9$

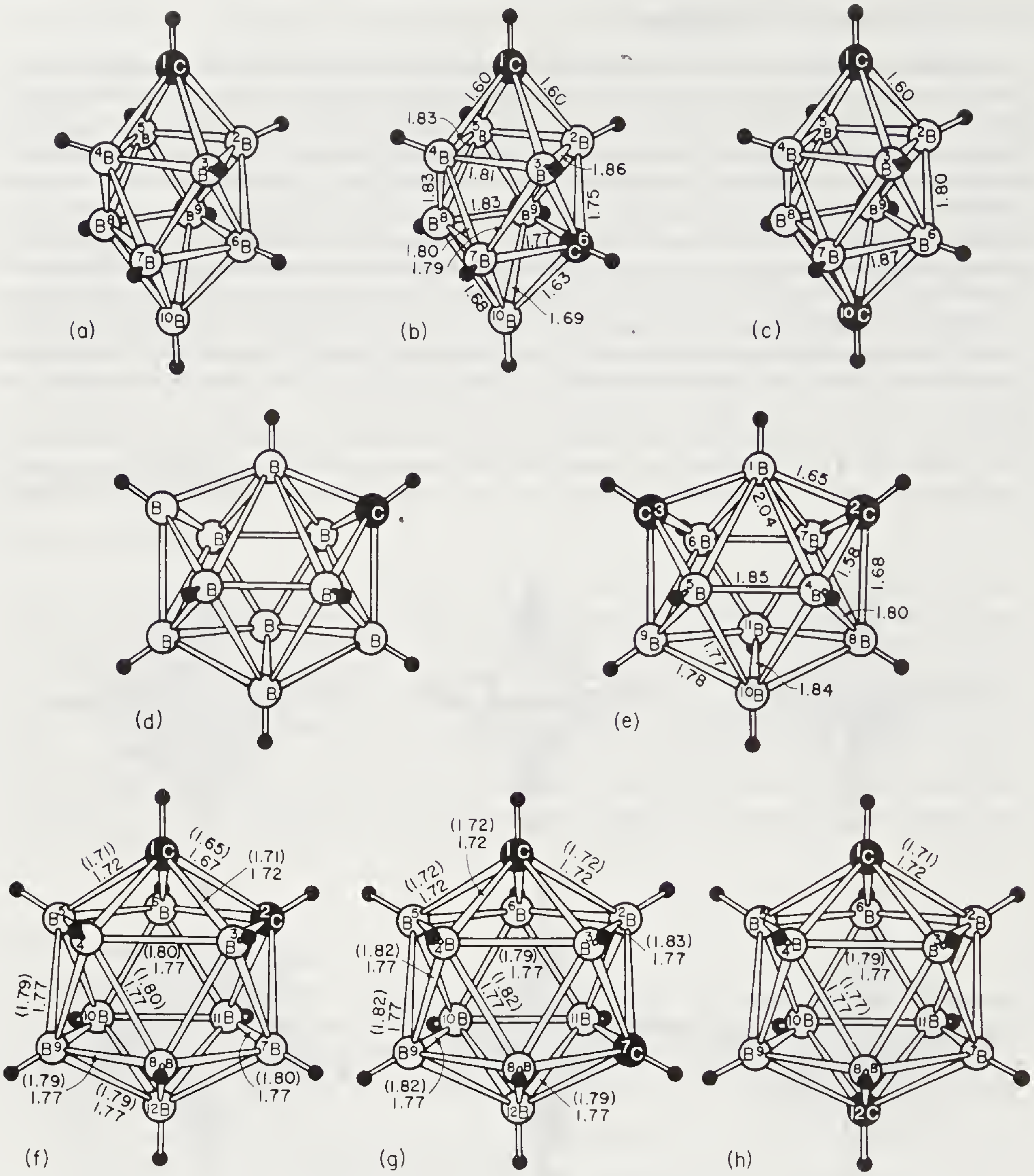


Figure 2 *closo*-Carboranes. (a) $CB_9H_{10}^-$; (b) 1,6-$C_2B_8H_{10}$; (c) 1,10-$C_2B_8H_{10}$; (d) $CB_{10}H_{11}^-$; (e) 2,3-$C_2B_9H_{11}$; (f) 1,2-$C_2B_{10}H_{12}$; (g) 1,7-$C_2B_{10}H_{12}$; (h) 1,12-$C_2B_{10}H_{12}$

structural classes can be regarded as having the general parent formula[11] $[(CH)_a(BH)_m H_b]^{c-}$. Each H of H_b can be a hydrogen bridging two or three boron atoms or an extra terminal hydrogen on a skeletal atom. In this regard it should be noted that no stable carborane is known to have a bridging hydrogen bonded to carbon.

When $a + b + c = 2$, a *closo* geometry is strongly suggested.
When $a + b + c = 4$, a *nido* geometry is strongly suggested.
When $a + b + c = 6$, an *arachno* geometry is strongly suggested.

As a consequence of the above structural relationships it is to be noted that progressive cage opening should accompany formal addition of electron pairs to a *closo* species. Adding two electrons to a *closo*-carborane containing n skeletal carbon and boron atoms moves these atoms to n corners of the $n + 1$ *closo* polyhedron, thus generating a *nido* framework. In turn, adding two additional electrons to the *nido*-carborane produces an *arachno* geometry. Examples of this cage opening principle are noted in Section 5.4.2.7.3 which discusses carborane reduction reactions,

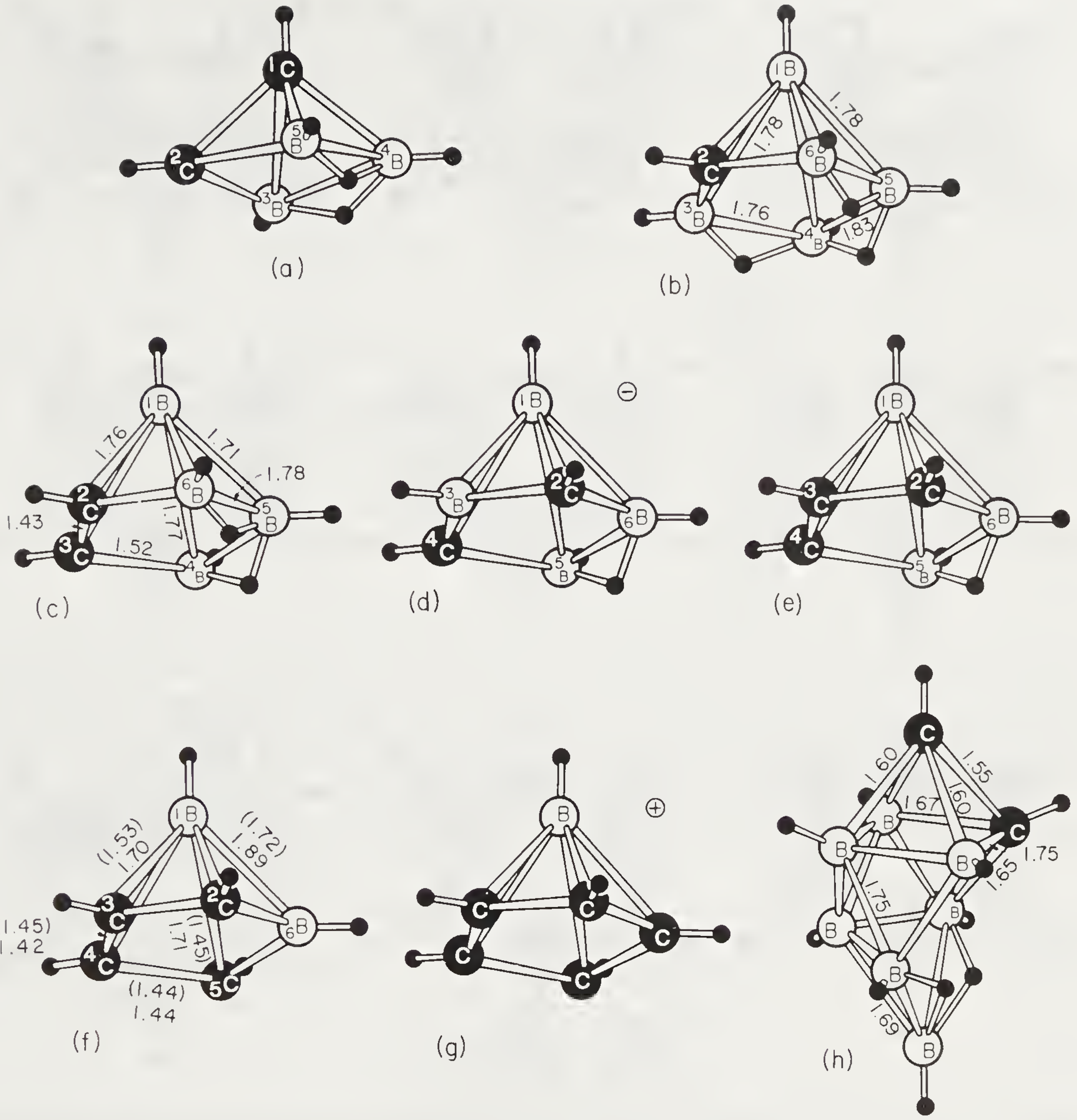


Figure 3 *nido*-Carboranes. (a) 1,2-$C_2B_3H_7$; (b) 2-CB_5H_9; (c) 2,3-$C_2B_4H_8$; (d) 2,4-$C_2B_4H_7^-$; (e) 2,3,4-$C_3B_3H_7$; (f) 2,3,4,5-$C_4B_2H_6$; (g) $C_5BH_6^+$; (h) $C_2B_7H_{11}$

and Section 5.4.2.7.4 which treats the Lewis-base chemistry of the carboranes. Another means by which cage framework bonding may have access to additional electrons is through π-electron back-donation of an appropriate substituent. Hence, replacement of the two boron-attached hydrogens of *nido*-2,3,4,5-$C_4B_2H_6$ (Figure 3f) with fluorine atoms opens up the parent pentagonal pyramidal cage[14] to a 'classical' 1,4-diboracyclohexa-2,5-diene arrangement of skeletal B and C atoms.[15] From theoretical calculations it appears that appropriate fluorine substitutions on to *closo*-$C_2B_3H_5$ (Figure 1b) should also convert this cage molecule to a classical form;[16] it is to be noted, however, that neither the structures of *B*-mono- nor of *B*,*B*′-di-fluoro derivatives of pentagonal-bipyramidal *closo*-2,4-$C_2B_5H_7$ (Figure 1f) appear significantly different than the parent cage.[17]

Although both the four-carbon carborane $Me_4C_4B_8H_8$ (Figure 6) and the $[C_2B_{10}H_{13}]^-$ ion (Figure 4i) contain the same number of framework electrons, the crystalline structure of the four-carbon carborane differs from the ion in that the former has two square faces[18] whereas the latter has a single large open face[19] (see also Sections 5.4.2.7.1 and 5.4.2.7.2). Another carborane deserving special mention is the only known three-carbon *closo*-carborane, $C_3B_5H_7$. Equilibrated

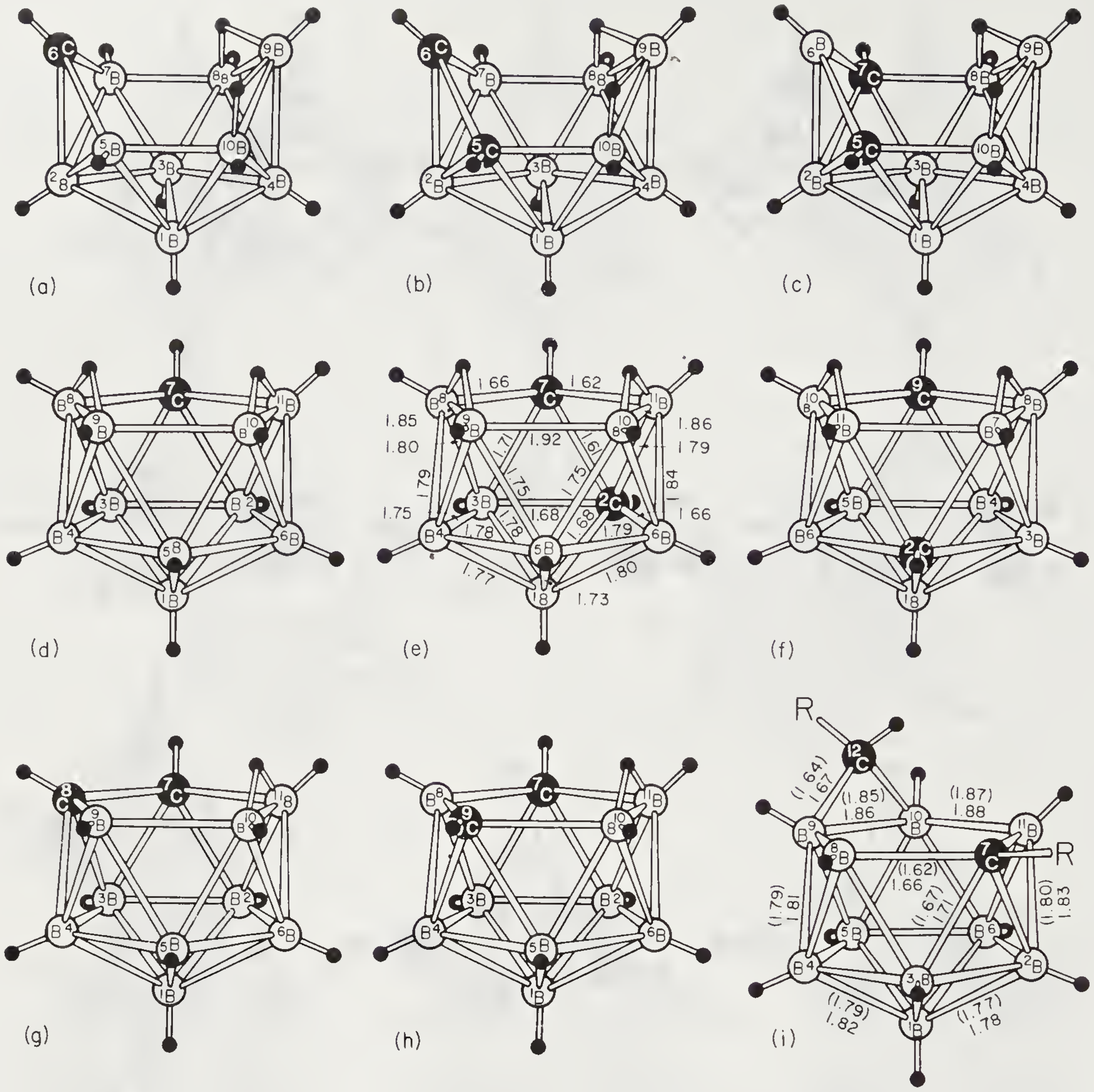


Figure 4 *nido*-Carboranes. (a) $CB_9H_{12}^-$; (b) 5,6-$C_2B_8H_{12}$; (c) 5,7-$C_2B_8H_{12}$; (d) $CB_{10}H_{13}^-$; (e) 2,7-$C_2B_9H_{13}$; (f) 2,9-$C_2B_9H_{13}$; (g) 7,8-$C_2B_9H_{12}^-$; (h) 7,9-$C_2B_9H_{12}^-$; (i) $R_2C_2B_{10}H_{11}^-$

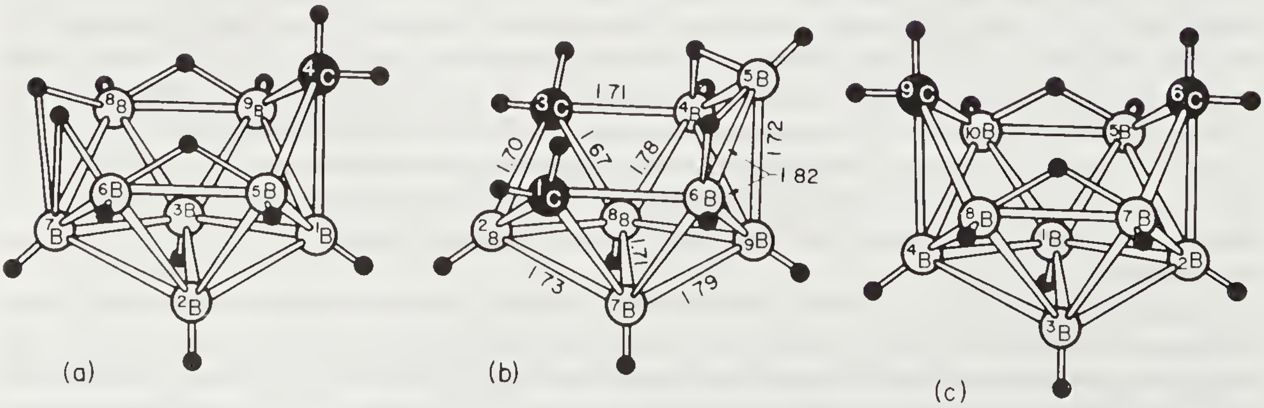


Figure 5 *arachno*-Carboranes. (a) 4-CB_8H_{14}; (b) 1,3-$C_2B_7H_{13}$; (c) 6,9-$C_2B_8H_{14}$

Table 1 Geometrical Systematics for the Parent Carboranes, $[(CH)_a(BH)_mH_b]^{c-}$

Skeletal e^- pairs	*Geometry of* closo *polyhedron*	$(a+b+c)$ 2 closo	 4 nido	 6 arachno
6	trigonal bipyramid	$C_2B_3H_5$		
7	octahedron	$C_2B_4H_6$ CB_5H_7	$C_2B_3H_7$	
8	pentagonal bipyramid	$C_2B_5H_7$	$[C_5BH_6]^+$ $C_4B_2H_6$ $C_3B_3H_7$ $C_2B_4H_8$ CB_5H_9	
9	dodecahedron	$C_2B_6H_8$		
10	tricapped trigonal prism	$C_2B_7H_9$	$C_4B_4H_8$ $C_2B_6H_{10}$	
11	bicapped square antiprism	$C_2B_8H_{10}$ $CB_9H_{10}^-$	$C_2B_7H_{11}$ CB_8H_{12}	
12	octadecahedron	$C_2B_9H_{11}$ $CB_{10}H_{11}^-$	$C_2B_8H_{12}$ $CB_9H_{12}^-$	$C_2B_7H_{13}$ CB_8H_{14}
13	icosahedron	$C_2B_{10}H_{12}$ $CB_{11}H_{12}^-$	$C_2B_9H_{13}$ $C_2B_9H_{12}^-$ $CB_{10}H_{13}^-$	$C_2B_8H_{14}$

dodecahedral structures (Figure 7) are proposed to account for the spectroscopic properties of this novel molecule.[20] It is suggested that one of the three carbon atoms in $C_3B_5H_7$ is 'bare' in that it does not contain an attached terminal hydrogen (or other single bonded atom) as do all other carbon atoms in all other known carboranes. Formally, only two of the four electrons of the 'bare' carbon atom are contributing to the cage total of 18 electrons, with the other two occupying an exopolyhedral orbital as an unshared electron pair. Other carborane compounds in which cage fluxionality appears certain are discussed in Section 5.4.2.7.2.

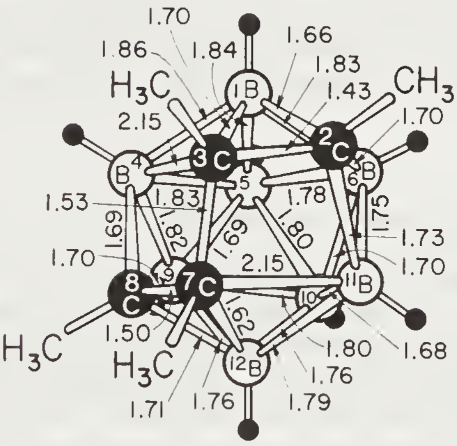
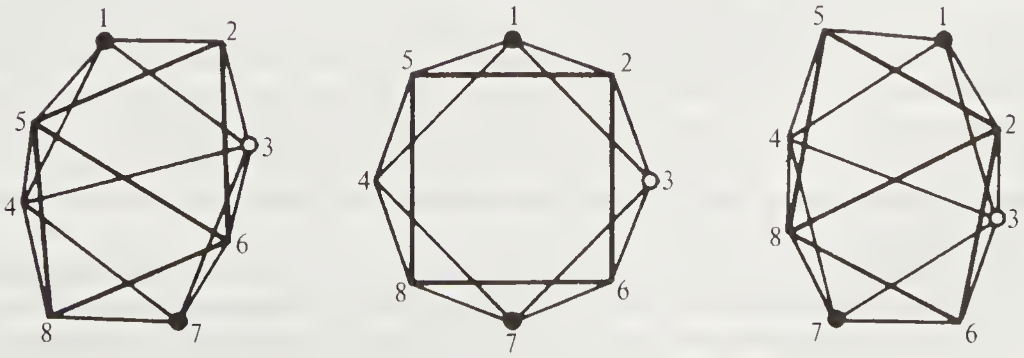


Figure 6 The tetramethyl derivative of $C_4B_8H_{12}$; see also Section 5.4.2.7.2



(a) (c) (b)

Figure 7 Dodecahedral structures (a) and (b) and square antiprism time-averaged geometry (c) for $C_3B_5H_7$ ●, CH groups, ○, unsubstituted carbon atom; the remaining vertices are occupied by BH groups.

Among formula isomers, the structural isomer with the largest number of B—C bonds is generally found to be the most stable. Also, the change in the carbon coordination number seems to have a very significant effect on the relative stabilities of isomers, in keeping with an empirical rule that carbon prefers the position of least coordination (among the coordination numbers 4 to 7). Table 2 shows the progressive build-up of higher coordination vertices in a *closo* series; the most stable isomer within a set of compounds featuring the same general polyhedral shape will contain carbon atoms at available low coordination sites (see Section 5.4.2.7.1 which discusses cage rearrangements). Thus, within the *closo* series $C_2B_nH_{n+2}$ (n = 3 to 10), the carbon atoms of the most stable isomers avoid a coordination number of 6 (and 7 in the case of the nine-atom skeleton) with the exception of the icosahedral $C_2B_{10}H_{12}$, where there is no choice.

Table 2 Coordination Number of Skeletal Atoms for *closo* Polyhedral Compounds

Coordination number	*Number of skeletal atoms* 5	6	7	8	9	10	11	12
4	2							
5	3	6	5	4	3	2	2	0
6		0	2	4	6	8	8	12
7							1	

5.4.2.4 Spectroscopic Properties

5.4.2.4.1 Diffraction and microwave structural studies

Detailed structural parameters obtained for numerous parent carboranes, as determined by X-ray and electron diffraction and microwave techniques, are given in Figures 1 to 6 with literature citations in Table 3. An inspection of available data indicates that cage bond distances vary considerably, with C—C ranging from 1.42–1.67 Å; C—B, 1.50–1.77 Å, and B—B, 1.65–2.04 Å. Bonds at atomic sites having a smaller coordination number tend to be shorter; the smaller covalent radius of carbon is probably a major factor which appears to shorten distances near carbon atoms.[1,21–23] The structure of 1,12-$C_2B_{10}H_{12}$ as determined by electron diffraction[24] shows a distortion from icosahedral geometry of the boron–carbon cage in that the diameter along the C· · ·C axis is ~10% shorter than a diameter along a B· · ·B axis, again reflecting the shorter covalent radius of carbon.

5.4.2.4.2 Nuclear magnetic resonance spectroscopy

Carborane boron-11 resonances can appear in the very wide region of δ +53 to −60 p.p.m. ($BF_3{\cdot}Et_2O$ = 0.0) and each is split into a doublet, $J \approx 125$ to 205 Hz, when attached to a terminal hydrogen. Should neighboring bridge-hydrogens be present, further splitting may be observed, $J \approx 20$ to 50 Hz. Boron-attached terminal proton resonances usually appear in the region δ = −1.2 to 4.0 p.p.m., C(cage)—H resonances vary from δ = −1 to 7 p.p.m., and bridging hydrogens are usually observed as broad resonances centered in the high-field region of δ = −4 to 0.[7,25]

Quantitative correlations of NMR data in the polyhedral carboranes are scarce, but the ^{11}B NMR chemical shift values,[26] as well as BH coupling constants,[26,27] for several carboranes have been correlated to calculated charge densities.[26,27] Also, an attempt to use a classical free-electron model for the pentagonal-pyramidal systems $C_{6-n}B_nH_{n+4}$ (n = 2, 3, 4, 5, 6) has met with limited success in predicting the unusually high-field position of apex located nuclei (^1H or ^{11}B) relative to basal located nuclei (^1H or ^{11}B). In this approach the six 'delocalized' electrons bonding the apex to the pentagonal base are treated in a manner similar to the ring current approach used for benzene. The apical atoms are centered above the general plane of current loops placed parallel to the base of the pyramid and are thus shifted to higher field; the basal atoms lie outside such loops and are shifted to lower field.[28]

Significant upfield shifts for an atom (B or C) antipodal to the point of substitution have been noted for a number of carborane derivatives.[7] This suggests an electronic structure for the carboranes which is delocalized to a degree; thus the chemical shift positions of framework atoms are imagined to be sensitive to electronic perturbations caused by substitution on distant atoms. This receives some support from photoelectron studies which show, in the case of *closo*-1,6-$C_2B_4H_6$ (Figure 1e), that high-lying π-*endo* (surface) orbitals of the cage provide a possible mechanism for substantial antipodal 2,4 atom interactions with certain substituents.[29]

Table 3 Structure Determinations on Parent Compound (or *C*-Methyl Derivatives) Using X-Ray Diffraction (XR), Electron Diffraction (ED), and Microwave (MW) Techniques

Compound	*Figure*	*Technique*
closo-1,5-$C_2B_3H_5$	1a	ED[1]
closo-1,2-$C_2B_4H_6$	1d	MW[2], ED[3]
closo-1,6-$C_2B_4H_6$	1e	ED[1,4]
closo-CB_5H_7	1c	MW[5], ED[3]
closo-2,4-$C_2B_5H_7$	1f	MW[6], ED[7]
closo-1,7-$C_2B_6H_8$	1h	MW[8], XR[9]
closo-1,6-$C_2B_7H_9$	1i	MW[10], XR[11]
closo-1,6-$C_2B_8H_{10}$	2b	XR[12]
closo-1,10-$C_2B_8H_{10}$	2c	ED[13]
closo-2,3-$C_2B_9H_{11}$	2e	XR[14]
closo-1,2-, 1,7- and 1,12-$C_2B_{10}H_{12}$	2f, 2g and 2h	ED[15]
nido-2,3,4,5-$C_4B_2H_6$	3f	MW[16], ED[17]
nido-2,3-$C_2B_4H_8$	3c	XR[18]
nido-2-CB_5H_9	3b	MW[19]
nido-1,2-$C_2B_7H_{11}$	3h	XR[20]
(*nido*)-2,3,7,8-$C_4B_8H_{12}$	6	XR[21]
[(*nido*)-$C_2B_{10}H_{13}]^-$	4i	XR[22]
arachno-1,3-$C_2B_7H_{13}$	5b	XR[23]

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A quantitative relationship between MO-derived hydrogen charges and aromatic solvent induced ^1H NMR chemical shifts (ASIS effect) has been derived for various carborane hydrogens, including those of *closo*-1,6-$C_2B_4H_6$, *nido*-2,3-$C_2B_4H_8$ and *closo*-2,4-$C_2B_5H_7$. With benzene as the solvent, the magnitude of observed *upfield* ^1H NMR shifts follow the general order HC $> H_\mu B > H_t B$. With C_6F_6 the same order is followed for observed *downfield* shifts of these same hydrogens.[30]

Cage ^{13}C—H coupling constants for several small and large *closo*-carboranes are found in the range of 180 to 210 Hz, corresponding to approximately 40% *s*-character for the carbon atom orbital directed toward the attached hydrogen; in general, there are larger coupling constants,

J(CH), associated with penta- or hexa-coordinated than with tetracoordinated cage carbon atoms. An increase in J(CH) is also related to an increase in the number of boron atoms directly attached to the carbon.[31] For *nido*-2,3-$C_2B_4H_8$ (Figure 3c), a measured value of $J(^{13}C—H)$ = 160 Hz is in the region assigned to carbon with sp^2 hybridization.[32] This is in agreement with a proposed bonding description for this *nido*-carborane in which a carbon–carbon double bond is involved in π-donation to the apical boron atom.[33]

Antipodal proton–proton coupling constants determined for the small *closo*-carborane compounds 1,5-$C_2B_3H_5$, 1,2-$C_2B_4H_6$, 1,6-$C_2B_4H_6$, CB_5H_7 and $C_2B_5H_7$ range typically from 6 to 14 Hz, which contrasts with significantly smaller near-neighbor H/H couplings.[34] Three-bond proton–proton spin coupling constants of the type H—X—Y—H are generally found to be largest when X,Y = cage carbon atoms, smallest when X,Y = boron, and intermediate in value when X = carbon, Y = boron.[35]

The broadness of many of the carborane ^{11}B NMR resonances is attributed to a complex overlap of long- and short-range B/B as well as B/H coupling. In some instances, values of J(BB) have been directly determined: J(BB) = 26 Hz for B(1)—B(5) of *nido*-2,3-$C_2B_4H_8$ (Figure 3c), and 18 Hz for B(1)—B(4) of 2-CB_5H_9 (Figure 3b).[27,36] These values are considerably smaller than J(BB) = 109 Hz found between the cage attached boron atoms of the coupled compound 1,5′-(*closo*-2,4-$C_2B_5H_6)_2$,[37] but the B(1)—B(5′) linkage in the latter compound is undoubtedly closer to approximating a 'standard' two-electron two-center single bond with substantial '*s*'-orbital character contributed by each boron atom. Few boron–carbon coupling constants have been determined: $J(^{13}C—^{11}B)$ = 50 Hz for *nido*-2,3-$C_2B_4H_8$[31] and 18 Hz for *closo*-1,5-$C_2B_3H_5$.[34] The values for the latter compound, when combined with other coupling data, suggest that most of the cage *s*-orbital density in *closo*-1,5-$C_2B_3H_5$ is found in the C—B bonds and very little in the B—B bonds.[34]

5.4.2.4.3 Vibrational spectroscopy

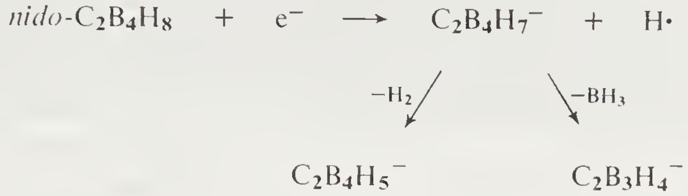
The C—H stretching vibrations of the three small *closo* cage molecules 1,5-$C_2B_3H_5$ (Figure 1b), 1,6-$C_2B_4H_6$ (Figure 1e) and 2,4-$C_2B_5H_7$ (Figure 1f) occur at a very high frequency, 3100–3160 cm^{-1}, and their low intensities suggest that these bonds are almost homopolar. The C—H bond strengths follow the sequence $C_2B_3H_5 > C_2B_4H_6 > C_2B_5H_7$; and a correlation between the B—H stretching frequencies and the ^{11}B—H NMR coupling constants of a number of carboranes indicates the expected trend of larger vibrational frequencies being associated with larger $J(^{11}B—H)$ values. The most significant feature of the observed cage deformation frequencies is the high energy of these modes. This reflects strong bonding within the framework of rigid polyhedral molecules having all triangular faces and is consistent with the relatively high barriers observed experimentally for polyhedral rearrangements. The least rigid of the three smallest bipyramids is the pentagonal one because of the relatively easy in-plane deformations of the pentagon; accordingly, the average frequency of the cage modes for 2,4-$C_2B_5H_7$ is lower than the values obtained for 1,5-$C_2B_3H_5$ and 1,6-$C_2B_4H_6$. Average cage-stretching frequencies for 1,5-$C_2B_3H_5$ and 1,6-$C_2B_4H_6$ are 1077 and 1109 cm^{-1}, respectively, whereas the average for 2,4-$C_2B_5H_7$ is lower, 1011 cm^{-1}.[38] An extensive vibrational analysis has been made on *nido*-2,3-$C_2B_4H_8$ and two *C*-methyl derivatives, and it is noted that although the C_{cage}—H stretching frequencies of this *nido*-carborane and benzene are similar, the C—C stretching frequencies are very different.[39]

A broad survey of IR spectra for both *closo*- and *nido*-carboranes yield the following common assignments: bridging hydrogens are usually found in one or both of the regions 1800–2050 and 1460–1500 cm^{-1}, B—H_t stretch 2500–2660 cm^{-1}, and C—H stretch 2900–3160 cm^{-1}.[7]

5.4.2.4.4 Mass spectrometry

Positive-ion mass spectrometric profiles of the parent mass regions for a number of *closo*- and *nido*-carboranes indicate that the intensity ratio of the parent ion to the sum of its fragments becomes greater as the polyhedron is completed.[22,40] *closo*-Carboranes normally give rather intense parent ions, but conventional electron-impact mass spectra of the three-carbon *closo*-carborane $C_3B_5H_7$ (Figure 7) shows essentially the spectrum of $C_2B_5H_7$. The parent region for this compound can be elicited by carrying out a chemical ionization in the presence of methane. This gives a cut-off peak corresponding to the $C_3B_5H_8^+$ ion, which arises from protonation of the parent $C_3B_5H_7$ species by CH_5^+.[20]

The negative-ion mass spectra of *nido*-2,3-$C_2B_4H_8$ exhibits a much more intense $P - 1$ ion than the parent ion, indicating the ease with which conjugate base anions of this *nido*-carborane are formed (Section 5.4.2.7.6). Spectra reported at both high (70 eV) and low (8 eV) voltages demonstrate that the conjugate base anions of both the *closo*-carboranes $C_2B_3H_5$ and $C_2B_4H_6$ are important ion fragments (equation 1). Studies with methyl and deuterio derivatives of $C_2B_4H_8$ suggest that formation of negative ions occurs predominantly *via* resonance capture and dissociative resonance capture mechanisms, and that the $P - 1$ anion is a result of bridge hydrogen loss.[41] The negative-ion mass spectra of the *closo*-carboranes 1,5-$C_2B_3H_5$, 1,2-$C_2B_4H_6$, 1,6-$C_2B_4H_6$ and 2,4-$C_2B_5H_7$ also exhibit much more intense $P - 1$ ions than parent ions, but ionization efficiency measurements suggest that negative ions of *closo*-carboranes are formed with somewhat more difficulty than those of *nido*-carboranes, reflecting a lack of bridging hydrogens in the former.[42]



(1)

5.4.2.5 Miscellaneous Physical Properties

From photoelectron spectra of several *closo*-carboranes, 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, 2,4-$C_2B_5H_7$ and 1,7-$C_2B_{10}H_{12}$, as well as the *nido* systems 2-CB_5H_9 and 2,3-$C_2B_4H_8$, the electronic structures of these cluster compounds can be considered to consist of π-*endo*-, σ-*exo*- and σ-*endo*-polyhedral orbitals. In all cases the ordering of cluster orbitals is $E(\pi\text{-}endo) > E(\sigma\text{-}exo) > E(\sigma\text{-}endo)$. In going from closed (*closo*) clusters to more open (*nido*) systems there is a reduction in the number of high-lying π-*endo*-polyhedral orbitals due to protonation. The π-*endo*-polyhedral or surface orbitals are of particular interest as they lie at high energy and have π-symmetry with respect to *exo* substituents. Therefore they should be strongly perturbed by substituent orbitals of π-symmetry in the same manner as the π-system in benzene.[43] Recent work substantiates this conclusion for the $C_2B_3H_5$[44] and $C_2B_4H_6$[29] systems.

Dipole moment measurements of *closo*-1,2-$C_2B_{10}H_{12}$ (4.31 D), 1,2-Br_2-1,2-$C_2B_{10}H_{10}$ (2.82 D) and 9,12-Br_2-1,2-$C_2B_{10}H_{10}$ (7.21 D) indicate that the carbon atoms are at the positive end of the cage dipole. The dipole moment of 1,7-$C_2B_{10}H_{12}$ is 2.78 D, which is consistent with the greater separation of carbon atoms. The magnitude of dipole moment values reported for *nido*-$C_4B_2H_6$ (2.26 D), *closo*-CB_5H_7 (1.4 D), *nido*-CB_5H_9 (1.53 D), *closo*-2,4-$C_2B_5H_7$ (1.32 D), *closo*-1,6-$C_2B_7H_9$ (2.1 to 2.4 D), *closo*-1,6-$C_2B_8H_{10}$ (2.22 D) and *closo*-2,3-$C_2B_9H_{11}$ (2.60 D) are not unexpected considering the pertinent structure and symmetry of these molecules (Figures 1 to 3).[7]

The electrochemical behavior of the monocarbon carboranes $CB_9H_{10}^-$, $CB_{10}H_{11}^-$, $CB_{10}H_{13}^-$ and $CB_{11}H_{12}^-$ parallels the behavior of isoelectronic and isostructural polyhedral borane ions, but the monocarbon carboranes exhibit higher oxidation potentials. Also, although the cyclic voltammetry of Cs[$CB_{11}H_{12}$] in acetonitrile shows no oxidation waves to the anodic limit of the solvent system, $CB_9H_{10}^-$ undergoes a one-electron oxidation to yield the coupled $[C_2B_{18}H_{18}]^{2-}$.[45]

The rotational barriers around the carbon–nitrogen bonds in the amides 1-Me_2NCO-1,2-$B_{10}C_2H_{11}$ and 1-Me_2NCO-1,7-$B_{10}C_2H_{11}$ are substantially lower than in ordinary amides and are attributable to the formation of a π-bond between the carbonyl carbon atom and the carborane cage.[46]

5.4.2.6 Syntheses

Almost all of the known synthetic routes to the parent, and partially substituted, *closo*-, *nido*- and *arachno*-carboranes involve the use of polyboranes (*e.g.* B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, B_8H_{12} and $B_{10}H_{14}$) at some step in the preparation. The polyboranes are relatively expensive, and many behave poorly toward air and water. Furthermore, the yields of carboranes (in particular the nonicosahedral compounds) from the polyboron hydrides, whether obtained directly or by a circuitous many-step route, is often low. Clearly, better synthetic routes to most of the carboranes would be most welcome.

5.4.2.6.1 Carboranes from polyboranes and alkynes

The production of carboranes from boron hydride/alkyne mixtures has been useful for obtaining parent cage compounds and some of the cage-carbon substituted derivatives. High-temperature and electric discharge induced reactions of this type usually give rise to the *closo* systems, whereas milder conditions often lead to *nido*-carboranes. The synthetically preferred route to the *closo* compounds 1,6-$C_2B_4H_6$ and 2,4-$C_2B_5H_7$ is the direct thermal reaction (500–600 °C) of pentaborane(9) and acetylene in a continuous-flow system. Also produced in this reaction is the smallest known *closo*-carborane, 1,5-$C_2B_3H_5$, in which the combined yields of products approach 70% and the product distribution of $C_2B_5H_7/C_2B_4H_6/C_2B_3H_5$ is around 5:5:1 (equation 2).[47] The only known preparation of the 2,3-isomer of $C_2B_5H_7$ employs the rather mild reaction of octaborane(12) with alkynes.[48] A 1,7-dimethyl derivative of *closo*-1,7-$C_2B_6H_8$ (Figure 1h) is found to be a low-yield product of the thermal (*ca.* 200 °C) reaction between B_6H_{10} and dimethylacetylene. With UV irradiation (equation 3) the yield of carborane is somewhat improved, the mechanistic implications of which are yet unknown.[49]

$$B_5H_9 \xrightarrow[500\text{–}600\ ^\circ\mathrm{C}]{C_2H_2} closo\text{-}2,4\text{-}C_2H_5H_7 + closo\text{-}1,6\text{-}C_2B_4H_6 + closo\text{-}1,5\text{-}C_2B_3H_5 \quad (2)$$

$$B_6H_{10} \xrightarrow[h\nu]{MeC\equiv CMe} 1,7\text{-}Me_2\text{-}closo\text{-}1,7\text{-}C_2B_6H_6 + 2H_2 \quad (3)$$

A mixture of *nido*-carborane products is formed from the reaction of B_4H_{10} and acetylene under ambient conditions in the vapor phase.[50,51] These products include various alkyl derivatives of *nido*-2,3,4-$C_3B_3H_7$ (Figure 3e)[51] as well as *nido*-1,2-$C_2B_3H_7$ (Figure 3a), the yield of the latter increasing with excess acetylene present.[52] A rate study of the reaction discloses a first-order dependence on B_4H_{10} and zero order with respect to the acetylene. Formation of the $C_3B_3H_7$ derivatives displays first-order dependence on B_4H_{10} but shows a negative first-order dependence on acetylene.[53] Use of C_2D_2 in the reaction gives deuterated derivatives of $C_3B_3H_7$ in which all of the incorporated deuterium appears bound to carbon.[54] The mechanistic scheme consistent with these and other observations is suggested[53] in equations (4)–(11).

$$B_4H_{10} \xrightarrow{\text{slow}} B_4H_8 + H_2 \quad (4)$$

$$B_4H_8 + C_2H_2 \xrightarrow{\text{fast}} [C_2B_4H_{10}] \quad (5)$$

$$[C_2B_4H_{10}] \longrightarrow C_2B_3H_7 + [BH_3] \quad (6)$$

$$[C_2B_4H_{10}] + C_2H_2 \xrightarrow{\text{fast}} [C_4B_4H_{12}] \quad (7)$$

$$[C_4B_4H_{12}] \longrightarrow 2\text{-}CH_3C_3B_3H_6 + [BH_3] \quad (8)$$

$$[C_4B_4H_{12}] + C_2H_2 \xrightarrow{\text{fast}} [C_6B_4H_{14}] \quad (9)$$

$$[C_6B_4H_{14}] \longrightarrow 2,3\text{- and }2,4\text{-}(CH_3)_2C_3B_3H_5 + [CBH_3] \quad (10)$$

$$[C_6B_4H_{14}] + C_2H_2 \xrightarrow{\text{fast}} [C_2BH_4]_x\text{(solid)} \quad (11)$$

Alkyl derivatives of the *nido*-carboranes 2-CB_5H_9, 2,3-$C_2B_4H_8$ and 2,3,4-$C_3B_3H_7$ are produced from the reactions of tetraborane(10) and pentaborane(11) with acetylene, methylacetylene and dimethylacetylene, but the products and yields vary considerably with choice of reactants. With either B_4H_{10} or B_5H_{11} the parent acetylene tends to give the C_3B_3 rather than the C_2B_4 *nido*-carboranes, whereas the reverse is true in reactions with the higher alkynes.[55]

The reaction of the square-pyramidal *nido*-1,2-$C_2B_3H_7$ with HC≡CH yields the pentagonal-pyramidal 2,3,4,5-$C_4B_2H_6$ (Figure 3f), *via* a straightforward alkyne insertion process.[52,56] Using MeC≡CH in place of HC≡CH affords predominantly 3-Me-*nido*-2,3,4,5-$C_4B_2H_5$ and a smaller quantity of 2-Me-*nido*-2,3,4,5-$C_4B_2H_5$, while a similar reaction using MeC≡CMe produces 2,3-$Me_2C_4B_2H_4$ with a lesser amount of 3,4-$Me_2C_4B_2H_4$. Alkyne insertion into the C—C bond of the starting carborane obviously occurs to some extent, but the primary insertion process takes place at the C—B bonds without cage C—C cleavage.[56]

Common preparations of the *nido*-carborane 2,3-$C_2B_4H_8$ (Figure 3c) are effected by reactions between pentaborane(9) and acetylene either at *ca.* 200 °C[32] or in the presence of an appropriate base catalyst such as 2,6-dimethylpyridine at ambient temperature (equation 12).[57] The ease with which this *nido*-carborane and its *C*-alkyl derivatives are formed increases with the more highly substituted alkynes,[32] and suggests that nucleophilic attack by the alkyne may be indicated in the initial step. The catalytic effect of the relatively weak base 2,6-dimethylpyridine probably involves a delicate extraction of a 'formal' borane unit. There is some evidence that a much stronger base may not be as effective because of the tendency to tear apart the pentaborane into unusable small fragments before a reaction with the alkyne can take place. This problem can be avoided by the application of below-ambient reaction temperatures. In this way triethylamine has been successfully used as the base in the preparation of *C*-substituted *nido*-2,3-$C_2B_4H_8$ derivatives from appropriately substituted alkynes. Combining this method with the known synthesis of B_5H_9 from $[B_3H_8]^-$ salts provides a convenient route to $C_2B_4H_8$ derivatives without the isolation or handling of the very air-sensitive B_5H_9.[58]

$$B_5H_9 + C_2H_2 \begin{cases} \xrightarrow{200\ ^\circ C} nido\text{-}2,3\text{-}C_2B_4H_8 \\ \xrightarrow[\text{pyridine}]{\text{2,6-dimethyl-}} nido\text{-}2,3\text{-}C_2B_4H_8 + [\text{2,6-dimethylpyridine}\cdot BH_3] \end{cases} \qquad (12)$$

Several methyl derivatives of the *nido*-carborane 2-CB_5H_9 are found as side products from the thermal (200 °C) reaction between pentaborane(9) and acetylene. The molecular formulae, $C_2B_5H_{11}$, of these products are the same as a proposed vinylpentaborane(9) intermediate which can be simply visualized as an addition of a B—H bond across the triple bond of acetylene. Such an intermediate, under the thermal conditions of the experiment, is probably prone to further hydroboration and should this step occur intramolecularly (with a net 1,1-diaddition of B—H bonds), and this be followed by minor skeletal rearrangement, the methyl derivatives of 2-CB_5H_9 can be derived.[59] Supporting this hypothesis are recent studies showing that alkyl derivatives of *nido*-CB_5H_9 are formed in good yield from the pyrolysis of 2-(*cis*-2-butenyl)pentaborane(9).[60] From deuterium tracer studies the 2-CB_5H_9 derivatives can be ruled out as possible intermediates to the major product, 2,3-$C_2B_4H_8$, from the B_5H_9/HC≡CH reaction.[61]

Another example of the production of *nido*-carboranes from polyboron hydrides and alkynes is the formation of the *C,C′*-dimethyl derivatives of both $C_2B_7H_{11}$ (Figure 3h) and 5,6-$C_2B_8H_{12}$ (Figure 4b) from the reaction of octaborane(12) with 2-butyne in ethyl ether (equation 13). By analogy with the B_4H_{10} and B_5H_9 reactions with alkynes, the $C_2B_7H_{11}$ derivative is probably formed with ejection of a borane unit from the octaborane at some stage (equation 14).[48]

$$B_8H_{12} \xrightarrow{MeC\equiv CMe} Me_2\text{-}nido\text{-}C_2B_7H_9 + 5,6\text{-}Me_2\text{-}nido\text{-}5,6\text{-}C_2B_8H_{10} \qquad (13)$$

$$B_8H_{12} + MeC\equiv CMe \longrightarrow Me_2\text{-}nido\text{-}C_2B_7H_9 + [BH_3] \qquad (14)$$

A useful preparation of the icosahedral carborane *closo*-1,2-$C_2B_{10}H_{12}$ (Figure 2f) employs the reaction of an alkyne with $(Et_2S)_2B_{10}H_{12}$; the latter complex is the reaction product of Et_2S with $B_{10}H_{14}$ (equations 15, 16). Other Lewis bases, particularly aliphatic nitriles and other dialkyl sulfides, can be substituted for Et_2S in this preparation. It is not necessary to isolate the $L_2B_{10}H_{12}$ intermediate and the alkyne is normally reacted directly with a solution containing the Lewis base and $B_{10}H_{14}$.[5] From kinetic studies it is suggested that the rate-determining step for the formation of 1,2-$C_2B_{10}H_{12}$ from $(Me_2S)_2B_{10}H_{12}$ and various monosubstituted acetylenes involves the attack of the acetylene on the monosulfide, $(Me_2S)B_{10}H_{12}$.[62]

$$B_{10}H_{14} + 2Et_2S \longrightarrow (Et_2S)_2B_{10}H_{12} + H_2 \qquad (15)$$

$$(Et_2S)_2B_{10}H_{12} + HC{\equiv}CH \longrightarrow closo\text{-}1,2\text{-}C_2B_{10}H_{12} + 2Et_2S + H_2 \qquad (16)$$

The use of substituted acetylenes, $RC{\equiv}CH$ and $RC{\equiv}CR'$, in the above reaction offers a method of preparing a number of carbon-substituted 1,2-$C_2B_{10}H_{12}$ derivatives. Representative R groups are alkyl, aryl, alkenyl and alkynyl,[5] although a dialkyne reaction will lead to some biscarborane (equation 17).[63] In other reactions of substituted alkynes, R and R′ have represented ester, amine, amide, acyl halide, halogen and ether groups. The preparation of *B*-substituted carboranes by this method using substituted $L_2B_{10}H_{12}$ is less common, although *B*-substituted halogen and alkyl derivatives have been prepared in this manner.[5]

$$(MeCN)_2B_{10}H_{12} + HC{\equiv}C{-}C{\equiv}CH \longrightarrow$$

(17)

Circulation of diborane/acetylene mixtures through an electric discharge produces low yields of a number of the *closo*-carboranes, including the parent and several alkyl derivatives of 1,2- and 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_5$ and 2,4-$C_2B_5H_7$. Many of these same carboranes, as well as trace quantities of some of the medium-size *closo*-carboranes (*e.g.* $C_2B_8H_{10}$), are formed from thermally induced flash reactions of tetraborane(10) and pentaborane(11) with acetylenes and from the electric discharge of acetylene/pentaborane(9) mixtures. Among the products in the latter reaction is the less stable isomer (1,2-) of *closo*-$C_2B_4H_6$. Reactions of alkynes with alkyldiboranes produce polyalkylated derivatives of 1,5-$C_2B_3H_5$, 2,4-$C_2B_5H_7$ and 2-CB_5H_9.[4]

5.4.2.6.2 Carboranes from boron hydrides and acetylides or cyanides

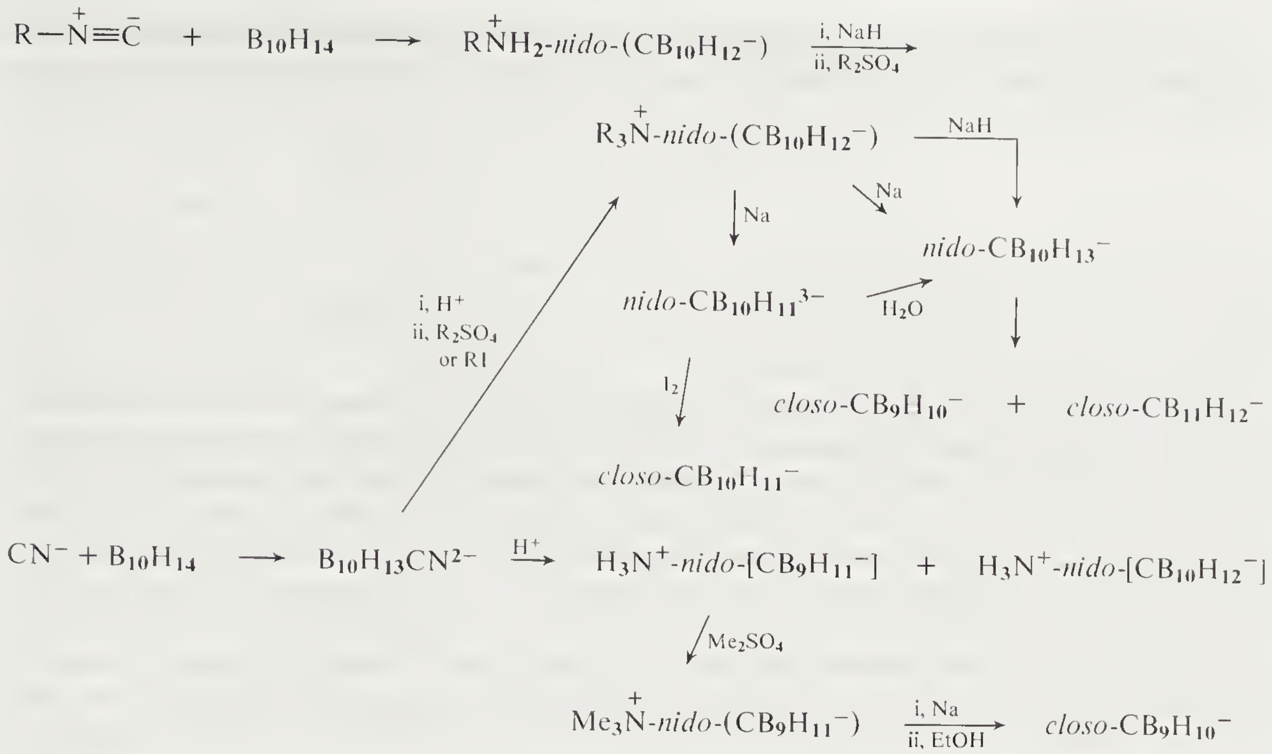
Nucleophilic attack by acetylides, cyanides or isocyanides at a boron site of a polyboron hydride can provide routes to monocarbon carboranes. By using the propynylide ion with pentaborane(9), the 2-ethyl derivative of 2-CB_5H_9 (Figure 3b) is obtained in low yield. A $MeC{\equiv}CB_5H_9^-$ ion is a plausible intermediate which upon subsequent rearrangement, including internal hydrobration, provides a temporary working mechanism (equation 18).[6]

$$Li[C{\equiv}CCH_3] + B_5H_9 \longrightarrow [CH_3C{\equiv}CB_5H_9]^- \longrightarrow$$

$$[CH_3CH_2CB_5H_7]^- \xrightarrow{H^+} 2\text{-}C_2H_5\text{-}2\text{-}nido\text{-}CB_5H_8 \qquad (18)$$

A zwitterionic $RNH_2^+{-}(CB_{10}H_{12}^-)$ realized from the direct action of alkyl isocyanides with decaborane(14) formally represents an insertion of one carbon atom into a boron hydride framework to give a compound in the *nido*-carborane series CB_nH_{n+4}. The amino derivative can be formed upon acidification of $B_{10}H_{13}CN^{2-}$, the latter prepared from the reaction of decaborane(14) with aqueous sodium cyanide. Deamination of a trialkylamino derivative with either sodium hydride or sodium gives the parent $CB_{10}H_{13}^-$ ion (Figure 4d). In the latter reaction an intermediate $CB_{10}H_{11}^{3-}$ ion can be isolated which upon hydrolysis gives the *nido*-$CB_{10}H_{13}^-$ ion, or upon iodine oxidation affords the *closo*-$CB_{10}H_{11}^-$ ion (Figure 2d). An amino derivative of the *nido*-monocarborane $CB_9H_{12}^-$ (Figure 4a) is formed from the action of acid on the $B_{10}H_{13}CN^{2-}$ ion.[4,64,65] The formation of the *nido*- and *closo*-carboranes originating from the reactions of decaborane(14) both with isocyanides and cyanide ion is summarized in Scheme 1.

The zwitterion carborane $(C_6H_{11}NH_2^+){-}nido\text{-}(CB_{18}H_{20}^-)$ is obtained from the reaction between *i*-$B_{18}H_{22}$ and cyclohexyl isocyanide.[66]



Scheme 1

5.4.2.6.3 **closo** *Compounds from* **nido-** *and* **arachno-***carboranes; dehydrogenation and disproportionation*

Two major pathways (equations 19 and 20) prevail in the known conversions of *nido-* to *closo*-carboranes. These are loss of hydrogen only, or a combination of both boron disproportionation and hydrogen loss. One of the smallest *nido*-carboranes known to afford *closo*-carboranes by both pathways is 2,3-$C_2B_4H_8$ (equation 21). A high conversion is effected by a flow pyrolysis (*ca.* 450 °C) technique in which equation (20) appears to predominate by a factor of approximately 4:1 over equation (19). Although the carbon atoms are directly bonded in the starting *nido* compound, the *closo* products are found to be the energetically favored isomers in which carbons are separated by one boron atom. Less stable *closo* intermediates may have formed and subsequently rearranged to the more stable entities, as evidenced by the low-yield production of 1,2-$C_2B_4H_6$ when very short residence times and somewhat lower temperatures are used.[67] Static pyrolysis of *nido*-$C_2B_4H_8$ can be effected at lower temperatures (*ca.* 300 °C) than the flow method and also result in the production of 2,4-$C_2B_5H_7$ and 1,6-$C_2B_4H_6$. The absence of 1,5-$C_2B_3H_5$ under the latter conditions reflects the instability of this carborane during an extended residence at this temperature. The yield of 1,6-$C_2B_4H_6$ can be improved at the expense of 2,4-$C_2B_5H_7$ by adding trimethylamine which appears to be a catalyst in this reaction, for the conversion can then be effected at slightly lower temperatures.[57] In a related study, flash thermolysis of $(ClMe_2SiCH_2)C_2B_4H_7$ gives silylorgano derivatives of 1,5-$C_2B_3H_5$ and 1,6-$C_2B_4H_6$.[68]

$$\text{Hydrogen loss: } C_2B_nH_{n+4} \longrightarrow C_2B_nH_{n+2} + H_2 \tag{19}$$

$$\text{Boron disproportionation: } 2C_2B_nH_{n+4} \longrightarrow C_2B_{n-1}H_{n+1} + C_2B_{n+1}H_{n+3} + 2H_2 \tag{20}$$

$$nido\text{-}2,3\text{-}C_2B_4H_8 \xrightarrow{450\ ^\circ C} closo\text{-}1,5\text{-}C_2B_3H_5 + closo\text{-}1,6\text{-}C_2B_4H_6 + closo\text{-}2,4\text{-}C_2B_5H_7 \tag{21}$$

The decomposition of 2,3-$C_2B_4H_8$ in a silent electric discharge also results in the formation of the small *closo*-carboranes 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$ and 2,4-$C_2B_5H_7$ and, in addition, provides another route to the less stable 1,2-isomer of $C_2B_4H_6$.[6,32] However, photolytic decomposition of *nido*-$C_2B_4H_8$ is probably the best synthetic route to 1,2-$C_2B_4H_6$.[69] Other *closo* products, 1,5-$C_2B_3H_5$ and 1,6-$C_2B_4H_6$, are also formed in this reaction, but apparently this method is sufficiently gentle not to induce all of the $C_2B_4H_x$ molecules to undergo C—C cleavage. Overall processes that occur in the photolytically catalyzed reaction can be represented in equation (22).

$$\begin{tikzcd} & nido\text{-}2,3\text{-}C_2B_4H_8 \arrow[r, "h\nu"] \arrow[dl] \arrow[dr] & closo\text{-}1,2\text{-}C_2B_4H_6 + H_2 \\ closo\text{-}1,5\text{-}C_2B_3H_5 + [BH_3] & & closo\text{-}1,6\text{-}C_2B_4H_6 + H_2 \end{tikzcd} \tag{22}$$

Disproportionation of a *nido*-carborane to the next higher and the next lower *closo*-carboranes may also account for some of the products in the pyrolysis of $Me_2C_2B_7H_9$ (equation 23).[48] Also, the nearly equivalent yields of *closo*-1,7-$C_2B_6H_8$ and *closo*-1,6-$C_2B_8H_{10}$, and the low yield of 1,6-$C_2B_7H_9$, from the pyrolysis of the *arachno*-carborane 1,3-$C_2B_7H_{13}$ suggest that the predominant reaction is, again, boron disproportionation (equation 24). In order to increase the yield of 1,6-$C_2B_8H_{10}$, the pyrolysis is carried out in the presence of a continuous supply of diborane(6).[70] Consistent with this observation is the increased yield of the lower carborane 1,7-$C_2B_6H_8$ when a *flow* technique is used in which a borane unit is undoubtedly irreversibly removed from the *arachno*-carborane, or related intermediate, and subsequently prevented from extensive reaction with the product *closo*-carborane (see following section) by rapid low-temperature quenching.[71]

$$nido\text{-}Me_2C_2B_7H_9 \xrightarrow{100\ °C} 1,2\text{-}Me_2\text{-}closo\text{-}1,2\text{-}C_2B_8H_8 + 1,7\text{-}Me_2\text{-}closo\text{-}1,7\text{-}C_2B_6H_6 \tag{23}$$

$$2arachno\text{-}1,3\text{-}C_2B_7H_{13} \longrightarrow closo\text{-}1,7\text{-}C_2B_6H_8 + closo\text{-}1,6\text{-}C_2B_8H_{10} + 4H_2 \tag{24}$$

Conversion of 1,3-$C_2B_7H_{13}$ to its mono- or di-sodium salt followed by pyrolysis at 200 °C is an alternate route to the 1,6-$C_2B_7H_9$ (equation 25).[70,72]

$$\begin{tikzcd} arachno\text{-}1,3\text{-}C_2B_7H_{13} \arrow[r, "NaH"] \arrow[dr, "2NaH"'] & C_2B_7H_{12}^- \arrow[r, "\Delta"] & closo\text{-}1,6\text{-}C_2B_7H_9 \\ & C_2B_7H_{11}^{2-} \arrow[ur, "\Delta"'] & \end{tikzcd} \tag{25}$$

Thermal decomposition of *nido*-5,7-$C_2B_8H_{12}$ (Figure 4c) follows a dehydrogenation pathway exclusively (equation 26), with the quantitative production of *closo*-1,6-$C_2B_8H_{10}$.[73] Similarly, *nido*-5,6-$C_2B_8H_{12}$ (Figure 4b) undergoes pyrolytic dehydrogenation to give the 1,2-, 1,6- and 1,10-isomers of *closo*-$C_2B_8H_{10}$, as well as the products from boron disproportionation, *closo*-1,6-$C_2B_7H_9$ and *closo*-2,3-$C_2B_9H_{11}$. Thermolysis of the sodium salt of $[5,6\text{-}C_2B_8H_{11}]^-$ results in the loss of hydrogen and the simultaneous formation of the disproportionated products 1,2-$C_2B_8H_{10}$ and its dinegative ion.[48,74]

$$nido\text{-}5,7\text{-}C_2B_8H_{12} \longrightarrow closo\text{-}1,6\text{-}C_2B_8H_{10} + H_2 \tag{26}$$

The monocarborane *arachno*-4-CB_8H_{14} (Figure 5a) also undergoes dehydrogenation (at 350 °C) to give CB_8H_{12}.[75] For the larger monocarborane $[nido\text{-}CB_{10}H_{13}]^-$, disproportionation appears to be the predominant pathway (equation 27).[76] This, in turn, is in contrast to its isoelectronic and isostructural analogue *nido*-$C_2B_9H_{13}$, which undergoes dehydrogenation at 75–100 °C to give *closo*-$C_2B_9H_{11}$.[70,77] Another route to the *closo*-$CB_9H_{10}^-$ ion is through the deamination of the *nido* derivative $Me_3\overset{+}{N}—CB_9H_{11}^-$ in which the expected product *nido*-$CB_9H_{12}^-$ is not found.[76]

$$2Cs[nido\text{-}CB_{10}H_{13}] \xrightarrow{\Delta} Cs[closo\text{-}CB_9H_{10}] + Cs[closo\text{-}CB_{11}H_{12}] + 2H_2 \tag{27}$$

Alkyl derivatives of the *closo*-carboranes $C_2B_3H_5$ and $C_2B_5H_7$ are presumed products of the pyrolysis of a peralkylated *nido*-CB_5H_9,[78] a reaction in which an extensive cage reorganization must be occurring.

Whereas the *C*-silyl derivative of 2,3-$C_2B_4H_8$ can be thermally (300 °C) converted to the prospective *C*-silyl-2,4-$C_2B_5H_6$,[79] bridge or 4-silyl-2,3-dicarba-*nido*-hexaborane(8) both give, unexpectedly, the only known *closo*-three-carbon carborane $C_3B_5H_7$ (Figure 7).[20]

5.4.2.6.4 Cage growth and insertion reactions

The *nido*-carborane $C_2B_6H_{10}$, as well as the *closo* compounds $C_2B_7H_9$ and $C_2B_8H_{10}$, are products from the thermally induced growth reaction of *closo*-1,5-$C_2B_3H_5$ in the presence of B_2H_6.[80] Several other intermediate size carboranes are also known to react with diborane to form larger closed polyhedra (equations 28–30).[70,71] If the *arachno*-carborane 1,3-$C_2B_7H_{13}$ is first treated with sodium hydride and this is followed by the addition of diborane, the *nido*-carborane 5,7-$C_2B_8H_{12}$ is one of the principal products.[73] The *C,C′*-dimethyl derivative of 1,7-$C_2B_{10}H_{12}$ has been prepared in the reaction of B_2H_6 with 1,6-Me_2-1,6-$C_2B_8H_8$ at 225 °C;[70] the parent ion 1,7-$C_2B_{10}H_{12}$ can be produced directly from *nido*-2-CB_5H_9.[81]

$$closo\text{-}1,7\text{-}C_2B_6H_8 \quad + \quad 0.5B_2H_6 \quad \longrightarrow \quad closo\text{-}1,6\text{-}C_2B_7H_9 \quad + \quad H_2 \qquad (28)$$

$$closo\text{-}1,6\text{-}C_2B_7H_9 \quad + \quad 0.5B_2H_6 \quad \longrightarrow \quad closo\text{-}1,6\text{-}C_2B_8H_{10} \quad + \quad H_2 \qquad (29)$$

$$arachno\text{-}1,3\text{-}C_2B_7H_{13} \quad + \quad 0.5B_2H_6 \quad \longrightarrow \quad closo\text{-}1,6\text{-}C_2B_8H_{10} \quad + \quad 3H_2 \qquad (30)$$

Cage expansion of $CsCB_{10}H_{13}$ by pyrolysis at 300–320 °C or reaction at 180 °C with Et_3NBH_3 affords the cesium salt of *closo*-$CB_{11}H_{12}^-$.[82]

Pyrolysis of Me_3B yields a range of carboranes, including the *B*-permethylated *closo* species $H_2C_2B_3Me_3$ and $H_2C_2B_5Me_5$, whereas copyrolysis of Me_3B/H_2 mixtures gives high yields of carboranes of formulae *closo*-$H_2C_2B_5Me_xH_{5-x}$ ($x = 2$ to 5).[83] The reaction of *nido*-2,3-$C_2B_4H_8$ with Me_3B at 230 °C leads to a two-boron cage expansion yielding *B*-Me_x-*closo*-1,7-$C_2B_6H_{8-x}$ as well as a one-boron expansion to give *B*-Me_x-*closo*-$C_2B_5H_{7-x}$. Both *closo*-2,4-$C_2B_5H_7$ and its *B*-methyl derivatives do not undergo *B*-methyl exchange with Me_3B at this temperature; this observation together with $^{10}B/^{11}B$ isotope studies on the $C_2B_4H_8/Me_3B$ cage-expansion reaction suggest that the *B*-methylated five-boron *closo*-product(s) could well be produced *via* six-boron intermediate(s). In a related cage-expansion reaction, *closo*-1,6-$C_2B_4H_6$ reacts with excess Me_3B at 550–600 °C to give *B*-Me_2-*closo*-2,4-$C_2B_5H_5$ together with minor quantities of its mono- and tri-methyl derivatives.[84,85]

The $[C_2B_9H_{11}]^{2-}$ ion can react with a number of different compounds to give products in which the icosahedral cage has been reformed with the insertion of a new boron atom. For example, 3-Ph-*closo*-1,2-$C_2B_{10}H_{11}$ is prepared from the reaction of $PhBCl_2$ and $[7,8\text{-}C_2B_9H_{11}]^{2-}$ (equation 31). The product of this reaction can be degraded to the $[3\text{-}Ph\text{-}7,8\text{-}C_2B_9H_{11}]^-$ ion, and subsequent treatment of this ion with phenylboron dichloride leads to the formation of 3,6-Ph_2-*closo*-1,2-$C_2B_{10}H_{10}$.[86] In other insertion reactions, 3-R-1,2-$C_2B_{10}H_{11}$ and 2-R-1,7-$C_2B_{10}H_{11}$ (R = R_2N, RO, vinyl, halogen, *etc.*) are prepared by reaction of the appropriate RBX_2 species with a $[C_2B_9H_{11}]^{2-}$ ion.[87] Additional growth reactions are mentioned in Section 5.4.2.6.3; for metal insertion reactions involving $[C_2B_9H_{11}]^{2-}$, as well as many other carboranes, see Chapter 5.5.

$$nido\text{-}7,8\text{-}C_2B_9H_{11}{}^{2-} \quad + \quad C_6H_5BCl_2 \quad \longrightarrow \quad 3\text{-}C_6H_5\text{-}closo\text{-}1,2\text{-}C_2B_{10}H_{11} \quad + \quad 2Cl^- \qquad (31)$$

5.4.2.6.5 Carboranes from alkylpolyboron hydrides

A fully saturated carbon atom attached as an alkyl ligand to a polyboron hydride may be encouraged to lose hydrogen at elevated temperatures (500–600 °C) with consequent incorporation of the carbon into the polyhedral framework of a carborane system. Examples of this are seen in equations (32–35).[14,88–90]

$$1,2\text{-}(CH_3)_2\text{-}B_5H_7 \quad \longrightarrow$$

$$closo\text{-}1,5\text{-}C_2B_3H_5 \quad + \quad closo\text{-}1\text{-}CB_5H_7 \quad + \quad nido\text{-}2\text{-}CB_5H_9 \quad + \quad 3\text{-}CH_3\text{-}nido\text{-}2\text{-}CB_5H_8 \qquad (32)$$

$$1\text{-}CH_3\text{-}B_5H_8 \text{ or } 2\text{-}[Cl(CH_3)_2SiCH_2]\text{-}B_5H_8 \longrightarrow \textit{closo}\text{-}1\text{-}CB_5H_7 + \textit{nido}\text{-}2\text{-}CB_5H_9 \qquad (33)$$

$$1\text{-}C_2H_5\text{-}B_5H_8 \longrightarrow 1\text{-}CH_3\text{-}\textit{closo}\text{-}1\text{-}CB_5H_6 + 2\text{-}CH_2\text{-}\textit{nido}\text{-}2\text{-}CB_5H_8 + \textit{closo}\text{-}1,5\text{-}C_2B_3H_5 \qquad (34)$$

$$1,2\text{-}(CH_2)_4B_2H_4 \longrightarrow \textit{nido}\text{-}2,3,4,5\text{-}C_4B_2H_6 + \textit{closo}\text{-}1,5\text{-}C_2B_3H_5 + \textit{closo}\text{-}1,6\text{-}C_2B_4H_6 \qquad (35)$$

The carborane yields from these reactions are modest; however, for most of the one-carbon carboranes, equations (32–34) represent the best and/or most facile synthetic routes. The fair-yield conversion of 1,2-$Me_2B_5H_7$ to the *closo*-carborane 1,5-$C_2B_3H_5$ is accompanied by the production of a rather substantial quantity of diborane(6), suggesting that a significant fraction of the pyrolysis can be summarized as in equation (36). A possible intermediate in this reaction may be 3-Me-*nido*-2-CB_5H_8, found only as a minor product.[88] There is also indication that the CB_5H_9 framework (Figure 3b) is an intermediate in the other alkylpentaborane reactions and that the pyrolysis can take place stepwise (equation 37). Pyrolysis of ethyldiborane at 170 °C yields a complex mixture of products from which a polyalkylated derivative of *closo*-2,4-$C_2B_5H_7$ has been suggested for the structure of one of the isolated products.[91]

$$1,2\text{-}(CH_3)_2B_5H_7 \longrightarrow \textit{closo}\text{-}1,5\text{-}C_2B_3H_5 + B_2H_6 + H_2 \qquad (36)$$

$$CH_3B_5H_8 \xrightarrow{-H_2} \textit{nido}\text{-}2\text{-}CB_5H_9 \xrightarrow{-H_2} \textit{closo}\text{-}1\text{-}CB_5H_7 \qquad (37)$$

Another method to encourage alkyl carbon atoms to become an integral part of a carborane cage is use of an electric discharge, of which the conversion of 1-MeB_5H_8 to the monocarborane *closo*-1-CB_5H_7 (Figure 1c) is one example.[92]

5.4.2.6.6 Selective cage degradation

Reaction of the icosahedral 1,2- and 1,7-$C_2B_{10}H_{12}$ with strong bases, such as alkoxide ion, produces *nido*-7,8- and -7,9-$C_2B_9H_{12}^-$ ions (Figures 4g and 4h), respectively (equation 38). The boron atom removed in each of the two *closo* isomers is the one (because of close proximity to the carbon atoms) expected to be the most positive, B(3 or 6) in 1,2-$C_2B_{10}H_{12}$ and B(2 or 3) in 1,7-$C_2B_{10}H_{12}$.[77,86,93] Treatment of *closo*-1,7-Me_2-1,7-$C_2B_{10}H_{10}$ with alcoholic base can result in degradative substitution to give 3-alkoxy derivatives of the [*nido*-7,9-Me_2-7,9-$C_2B_9H_{10}$]$^-$ ion.[94] By comparison, intramolecular nucleophilic cleavage of 3-HO-1,2- and 2-HO-1,7-$C_2B_{10}H_{11}$ with aqueous NaOH or KOH eliminates $B(OH)_3$ and yields the 7,8- and 7,9-$C_2B_9H_{12}^-$ ions, respectively.[95]

$$\textit{closo}\text{-}C_2H_{10}H_{12} + RO^- + 2ROH \longrightarrow [\textit{nido}\text{-}C_2B_9H_{12}]^- + B(OR)_3 + H_2 \qquad (38)$$

The oxidation of [7,8-$C_2B_9H_{12}$]$^-$ by aqueous acidic ferric chloride affords 5,6-$C_2B_8H_{12}$ (Figure 4b) as the major volatile product, and 5,6-$C_2B_8H_{11}$(OH), 10-Cl-5,6-$C_2B_8H_{11}$ and 4,5-$C_2B_7H_{11}$ (Figure 3h) as lower yield by-products. By decreasing the concentrations of reactants the 4,5-$C_2B_7H_{11}$ becomes a major constituent of the carborane products.[74,96]

The selective degradation of *nido*-7,9-$C_2B_9H_{12}^-$ with chromic acid is the preferred synthetic route to *arachno*-1,3-$C_2B_7H_{13}$ (equation 39);[97] also, oxidation of *closo*-2,3-$C_2B_9H_{11}$[98] and hydrolysis of $[C_2B_8H_{10}]^{2-}$, prepared from 1,2-$C_2B_8H_{10}$/Na, in acid medium,[74] will accomplish the same objective.

$$7,9\text{-}C_2B_9H_{12}^- + 6H_2O \longrightarrow 1,3\text{-}C_2B_7H_{13} + 2B(OH)_3 + 5H^+ + 6e^- \qquad (39)$$

Basic hydrolysis degrades 1,6-$C_2B_8H_{10}$ to the $C_2B_7H_{12}^-$ ion in high yield (equation 40), but under the same conditions the 1,10-isomer is relatively unaffected. A rationalization of this difference between the two isomers is based on the presence, in the 1,6-isomer, of boron atoms (2,

$$closo\text{-}1,6\text{-}C_2B_8H_{10} \xrightarrow[H_2O]{OH^-} arachno\text{-}C_2B_7H_{12}^- \quad + \quad B(OH)_3 \qquad (40)$$

3) both of which have two relatively electropositive carbon atoms as nearest neighbors, and hence are the most electropositive boron atoms in the polyhedron and the most susceptible to attack by base. In the case of the 1,10-isomer, all eight borons neighbor only one carbon atom and thus the charge distribution is presumably not as favorable toward facile nucleophilic attack.[99] The smaller two-carbon carboranes 2,4-$C_2B_5H_7$, 1,6-$C_2B_4H_6$ and 1,5-$C_2B_3H_5$ cannot be selectively degraded to other carboranes using reagents similar to those used in the above reactions. In the case of the smallest *closo*-carborane 1,5-$C_2B_3H_5$ the results of hydrolysis or methanolysis are the products $(RO)_2BCH_2B(OR)CH_2B(OR)_2$, $(RO)_2BCH_2B(OR)_2$, $MeB(OR)_2$ and $B(OR)_3$.[100]

In the monocarba carborane series, degradation of Me_3N^+—$(CB_{10}H_{11}OH^-)$ with hydroxide ion gives the next lower *nido* derivative Me_3N^+—$(CB_9H_{11}^-)$.[76,82] Treatment of the *nido*-$CB_9H_{12}^-$ ion (Figure 4a) with a $FeCl_3$/10% HCl solution gives a high yield of 4-*arachno*-CB_8H_{14} (Figure 5a), with a CH_2 group and four bridge hydrogens associated with a chair-configuration hexagonal CB_5 open face.[101] Stepwise degradation of the ten-vertex 6-Me_3N—6-CB_9H_{11} by treatment with concentrated MeOH/KOH followed by neutralization with CO_2 produces a *hypho*-carborane Me_3N—CB_5H_{11}, which is an analogue of B_5H_{11} where the 3,4-H bridge is replaced by a $>$CHNMe$_3$ bridge. A topological structure has been put forward (Figure 8) which is consistent with a unique *hypho*-type structure.[102] One method of preparing the parent CB_5H_9 (Figure 3b) is the reaction of HCl with the ion formed from 1,7-$C_2B_6H_8$ and borohydride ion. This is a unique example of the removal of a single carbon atom from a closed carborane polyhedron.[103]

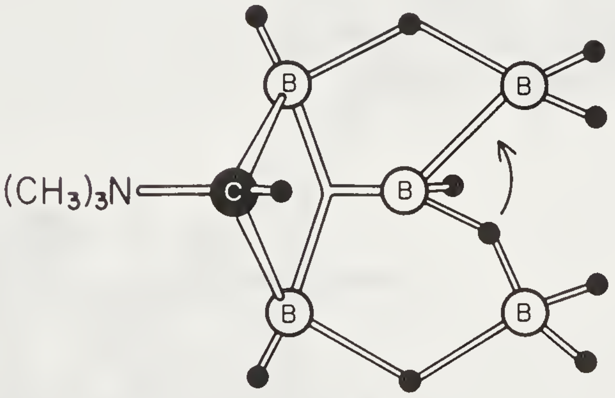


Figure 8 Topological structure of $(CH_3)_3N$-CB_5H_{11}

5.4.2.6.7 Coupled carboranes

Thermolysis and/or photolysis of several carboranes has resulted in a net 'oxidation' to give coupled products having *exo*-cage B—B bonds (equations 41,[44,104] 42[105,106] and 43[107]). The D_{2d} symmetry assigned to the 2,2′-$(1,5\text{-}C_2B_3H_4)_2$ dimer is attributed to π-type interaction of orbitals associated with each individual cage; the barrier to rotation of the *exo*-cage B—B bond is traced to an under-utilization of the B $2p_x$ orbitals compared to the B $2p_z$ orbitals in the individual monomer cages.[44]

$$closo\text{-}1,5\text{-}C_2B_3H_5 \xrightarrow[3\text{ atm}]{165\,°C} (1,5\text{-}(C_2B_3H_4)_2 \quad + \quad (C_2B_3H_4)\text{-}(C_2B_3H_3)\text{-}(C_2B_3H_4) \qquad (41)$$

$$closo\text{-}2,4\text{-}C_2B_5H_7 \xrightarrow[\text{or heat}]{h\nu/Hg} (2,4\text{-}C_2B_5H_6)_2,\ \text{six B—B bonded isomers} \qquad (42)$$

$$closo\text{-}1,2\text{-}C_2B_{10}H_{12} \xrightarrow{600\,°C}$$

$$(C_2B_{10}H_{11})_2,\ \text{eight isomers containing 1,7- and 1,12-}C_2B_{10}\text{ cages attached by B—B bonds} \qquad (43)$$

The *nido*-carborane anion $[2,3\text{-}Me_2C_2B_4H_5]^-$ reacts readily with $HgCl_2$ to form the bis(carboranyl)mercury(II) complex μ,μ'-$(Me_2C_2B_4H_5)_2Hg$, which upon heating eliminates mercury to yield the B—B linked *nido*-carborane 5,5′-$(Me_2C_2B_4H_5)_2$ as a single pure isomer.[108] Air oxidation of 5,5′-$(Me_2C_2B_4H_5)_2$ cleaves the linking B—B bond and allows oxidative addition of benzene to yield the air-stable 4-Ph-*nido*-2,3-$Me_2C_2B_4H_5$.[108]

Using the two reagents $Li[C_4H_9]$ and $CuCl_2$, in sequence, on *closo*-1,10-$C_2B_8H_{10}$, the dimer 1,1′-(1,10-$C_2B_8H_9$)$_2$ is formed in 80% yield.[109] In a similar manner the synthesis of tetra-1,7-dicarba-*closo*-dodecaborane(12) is fashioned from bis-1,7-dicarba-*closo*-dodecaborane(12).[110] For a method to prepare 1,1′-(1,2-$C_2B_{10}H_{11}$)$_2$ from bis-acetylene and decaborane, see Section 5.4.2.6.1; for a route to coupled carboranes in which the two cages are attached by a B—C bond, see Section 5.4.2.7.4. Additional cage coupling reactions include the production of $[10,10'\text{-}closo\text{-}(1\text{-}CB_9H_9)_2]^{2-}$ from the electrolysis of $Cs[1\text{-}CB_9H_{10}]$ in acetonitrile at 1.95 V (*vs.* sce),[45] and the formation of the fused bis-*nido* compound $C_4B_{18}H_{12}$ (Figure 9) and a related anion, $[C_4B_{18}H_{23}]^-$, upon oxidation of $[nido\text{-}7,8\text{-}C_2B_9H_{12}]^-$ with chromic acid.[111]

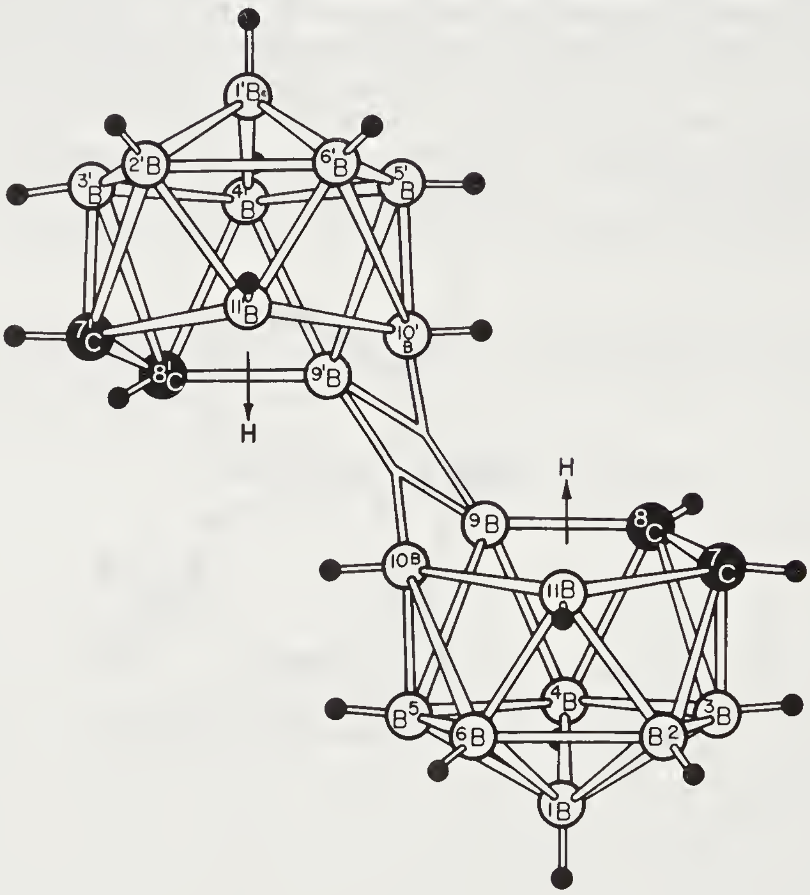
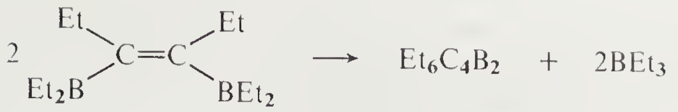


Figure 9 $C_4B_{18}H_{22}$

5.4.2.6.8 *Miscellaneous methods of carborane preparation*

Halogenide abstraction from $(Me_5C_5)BX_2$ with BX_3 (X = Cl, Br, I) or $AlCl_3$ produces salts of the pentamethyl derivative of the novel pentagonal-pyramidal *nido*-carborane cation $C_5BH_6^+$ (Figure 3g). An analogue of the $C_5BH_6^+$ ion, in which the apex substituent is the pentamethylcyclopentadienyl group, is obtained upon treating $(Me_5C_5)_2BCl$ with BCl_3.[112]

Derivatives of *nido*-2,3,4,5-$C_4B_2H_6$ (Figure 3f) are reported from the reactions of a stannaboracyclohexadiene or 3-(diethylboryl)-1-stannacyclopentadiene with $MeBBr_2$.[113] A peralkyl derivative of $C_4B_2H_6$ is proposed for one of the products from a reaction of *cis*-1,2-bis(diethylboryl)-1,2-dialkylethylene catalyzed by diethylchloroborane (equation 44);[114] and a perphenyl derivative of the same cage system is obtained from an addition dehalogenation reaction (equation 45).[115] Photochemical irradiation of 2-butyne with $B_4H_8Fe(CO)_3$ results in the formation of a *C*-tetramethyl carborane species $Me_4C_4B_4H_4$ (see Section 5.4.2.7.2) isoelectronic with $C_2B_6H_{10}$. Additional products from the reaction are tentatively formulated as the first six- and eight-carbon carborane species, $Me_6C_6B_4H_4$ and $Me_8C_8B_4H_4$.[116] Synthesis of a peralkylated $C_4B_4H_8$ carborane



(44)

$$2Ph_2C_2 + 2PhBBr_2 + 4K \longrightarrow Ph_6C_4B_2 + 4KBr \qquad (45)$$

is achieved by the elimination of sulfur from the correspondingly substituted Δ^3-1,2,5-thiadiborolene using potassium in THF.[117] The tetra-*C*-methylated derivative of the *nido*-2,3,7,8-$C_4B_8H_{12}$ (Figure 6) (see Section 5.4.2.7.2) is produced by the air oxidation of the metallocarboranes $(Me_2C_2B_4H_4)_2CoH$ or $(Me_2C_2B_4H_4)_2FeH_2$.[118]

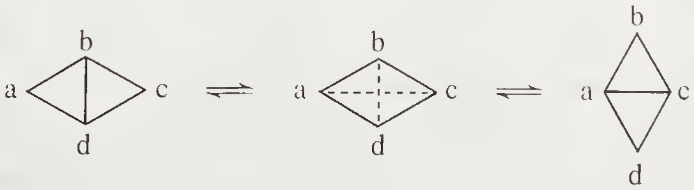
By way of an apparent carbon-insertion process, 1,2-bis(trimethylsilyl)pentaborane(9) gives, on flash thermolysis, a number of *C*-silyl derivatives of the smallest *closo*-carborane, *i.e.* 1-H_3Si-1,5-$C_2B_3H_4$, 1-MeH_2Si-1,5-$C_2B_3H_4$ and 2-Me-1-(H_3Si)-1,5-$C_2B_3H_3$, as well as an equilibrium mixture of 2- and 4-methyl derivatives of *closo*-CB_5H_7 (Figure 1c). The 6-methyl derivative, produced in very small quantities from this same reaction,[119] is the primary carborane product from the pyrolysis of 2-Me_3Si-μ-Me_2B-B_5H_7.[120] Pyrolysis of trimethylborane at 475–520 °C yields a per-*B*-methyl derivative of 1,5-$C_2B_3H_5$ as well as $C_4B_6H_{10}$, which is proposed to have an adamantane-like cage arrangement of carbon and boron atoms;[121] the air-stable 2,3,4-triethyl-1,5-dicarba-*closo*-pentaborane(5) is found as a product of the interaction of tris-(diethylboryl)methane with $AlEt_3$ at 150 °C.[122] Dehalogenation of alkylhaloboranes with alkali metals produces a variety of peralkylated carboranes, including derivatives of 2-CB_5H_9, 1,5-$C_2B_3H_5$ and 2,4-$C_2B_5H_7$.[78,123]

Hydroboration of alkynylboranes gives a number of products, among which a peralkylated derivative of 1,5-$C_2B_3H_5$ is proposed for one of the major products.[122,124] Reduction of $HC(BCl_2)_3$ with $LiBH_4/AlCl_3$ gives low yields of CB_3H_7 and CB_4H_{10}, both of which possibly have cage structures;[125] the octahedral *closo*-1-CB_5H_7 can be obtained from an apparent insertion of a vapor phase carbon atom into pentaborane(9).[126]

5.4.2.7 Chemical Properties

5.4.2.7.1 Thermal stability and skeletal rearrangement

The *nido*- and *arachno*-carboranes are generally less thermally stable and more air sensitive than their *closo* relatives. In part, this can be attributed to the lack of a completed polyhedron in the former systems compared with the latter. When the *nido* and *arachno* compounds are subjected to decomposition temperatures, copious quantities of related *closo*-carboranes are usually generated (Section 5.4.2.6.3). Except for $C_2B_3H_5$, the *closo*-carboranes are reasonably stable toward decomposition to 400 °C under static conditions, and in some cases well above this temperature. Before the decomposition temperatures are reached, less stable position isomers are known to rearrange to more stable cage configurations of carbon and boron. Thus, the thermal rearrangements of 1,2- to 1,6-$C_2B_4H_6$ (Figures 1d and 1e) (*ca.* 250–300 °C),[32] of 1,6- to 1,10-$C_2B_8H_{10}$ (Figures 2b and 2c)[70] and of 1,2- to 1,7- to 1,12-$C_2B_{10}H_{12}$ (Figures 2f, 2g, 2h) (*ca.* 600–700 °C)[127] reflect the preference of carbon for a position of least coordination and/or greater distance from other carbon atom(s) in the same molecule (Section 5.4.2.3). In order to account for these rearrangements, mechanistic schemes have been advanced based on diamond-square-diamond (*dsd*) and triangular-face-rotation processes.[128–130] The *dsd* rearrangement mechanism involves the cooperative stretching and squeezing of opposite corners of bent diamond-shaped groups of atoms into a bent square and back into a diamond (equation 46).



(46)

For the 1,2- to *closo*-1,6-$C_2B_4H_6$ rearrangement, a classical intermediate (which can be structurally described as a [2.1.1] bicyclic compound with the two carbon atoms at the bridgehead positions) is shown by MO calculations to be more energetically accessible[131] than one previously proposed to have distorted trigonal prism geometry.[132]

At 300 °C an equilibrium can be established between B-Me$_x$-2,4-$C_2B_5H_{7-x}$ ($x = 1, 2, 3$ or 4) isomers where methyl positional preference follows the order $3 > 1{,}7 > 5{,}6$. The mechanism of isomer interconversions most probably involves cage atom skeletal rearrangement rather than substituent migration. Within presumed energy-preferred diamond-square-diamond (*dsd*) conversions of one 2,4-cage isomer to another 2,4-cage isomer, the allowed equilibria for interconversion of B,B'-Me$_2$-2,4-$C_2B_5H_5$ isomers are 5,6-Me$_2$-2,4-$C_2B_5H_5 \rightleftharpoons$ 1,5- $\rightleftharpoons$ 3,5- $\rightleftharpoons$ 1,7-, and 1,5- $\rightleftharpoons$ 1,3-. Consistent with the *dsd* mechanism, a carefully controlled thermal rearrangement of 5,6-Me$_2$-2,4-$C_2B_5H_5$ produces the 1,5-dimethyl isomer prior to the 1,3-, 3,5- and 1,7-isomers.[133] As with the methyl derivatives, rearrangements of both 5-Cl-2,4-$C_2B_5H_6$ and 5,6-Cl$_2$-2,4-$C_2B_5H_5$ to isomeric B-chloro or B,B'-dichloro products also proceed at reasonable rates in the vicinity of 300 °C.[134]

Among several mechanisms proposed to account for the parent $C_2B_{10}H_{12}$ rearrangements, the most satisfactory pathway involves rotation of triangular faces on an unstable cuboctahedral intermediate, the latter formed from six cooperative *dsd* processes (Figure 10).[130,135,136] It is interesting to note that the major product, 5,12-Cl$_2$-1,7-Me$_2$-*closo*-1,7-$C_2B_{10}H_8$, from the thermal rearrangement of 9,12-Cl$_2$-1,2-Me$_2$-1,2-$C_2B_{10}H_8$ is the only one expected from a mechanism involving a cuboctahedral intermediate.[137] The relative stabilities of *closo*-1,2-, 1,7- and 1,12-$C_2B_{10}H_{12}$ appear to be reversed when converted to the dinegative ion, $[C_2B_{10}H_{12}]^{2-}$,[138] supporting an earlier prediction from MO calculations.[139] Thus, the reduction of 1,12-$C_2B_{10}H_{12}$ to $[C_2B_{10}H_{12}]^{2-}$ followed by an oxidation step produces the isomeric 1,7-$C_2B_{10}H_{12}$.[138,140] Similarly, the oxidation of the $[C_2B_{10}H_{12}]^{2-}$ ion produced from 1,7-$C_2B_{10}H_{12}$ affords 1,2-$C_2B_{10}H_{12}$.[141] The protonation of the $[C_2B_{10}H_{12}]^{2-}$ ion produced from either 1,2- or 1,7-$C_2B_{10}H_{12}$ produces two distinct isomers (A and B) of $C_2B_{10}H_{13}^-$ depending upon the reaction conditions. Only one of these $C_2B_{10}H_{13}^-$ ions, B, is generated upon protonation of the $C_2B_{10}H_{12}^{2-}$ ion obtained from 1,12-$C_2B_{10}H_{12}$; this same $C_2B_{10}H_{12}^-$ isomer, B, is nearly quantitatively formed upon thermal rearrangement of isomer A at 100 °C;[142] see also Section 5.4.2.7.3.

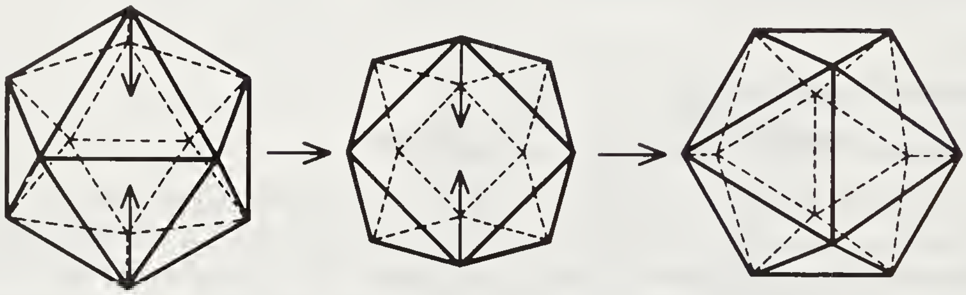


Figure 10 Rearrangement of icosahedral carboranes *via* a cuboctahedral intermediate

The only known three-carbon *closo*-carborane, $C_3B_5H_7$, is thermally unstable at 400 °C, at which temperature it ejects a carbon atom and quantitatively converts to 2,4-$C_2B_5H_7$. The driving force for this conversion may arise from the considerable thermal stability of the $C_2B_5H_7$ polyhedron, although the presumed presence of an unshared electron pair on $C_3B_5H_7$ is most likely a determining factor contributing to the course of this reaction.[20]

Among known *nido* systems it has been observed that 5-Me$_3$N$^+$-*nido*-$C_2B_4H_6^-$ rearranges in CHCl$_3$, or thermally, to the corresponding 3-Me$_3$N isomer; although a mechanism for this reaction has not been fully elucidated, it is believed that cage atom rearrangement rather than surface substituent migration is responsible.[143]

5.4.2.7.2 Cage fluxional behavior; hydrogen tautomerism

Most of the carboranes are considered to have rather rigid framework structures at ambient conditions; only at sufficiently high temperatures will some of these polyhedral systems rearrange to a structurally similar isomer (see prior Section 5.4.2.7.1). There are some carboranes, however, which show evidence of cage plasticity near room temperature. In the case of $[CB_{10}H_{11}]^-$ ion the ^{11}B NMR spectrum shows three BH doublets in an area ratio of 1:5:4. This is interpreted in terms of an 11-particle polyhedron having C_{2v} symmetry (the carbon atom at position 2) in which the two halves of the molecule rotate relative to each other (Figure 11).[45]

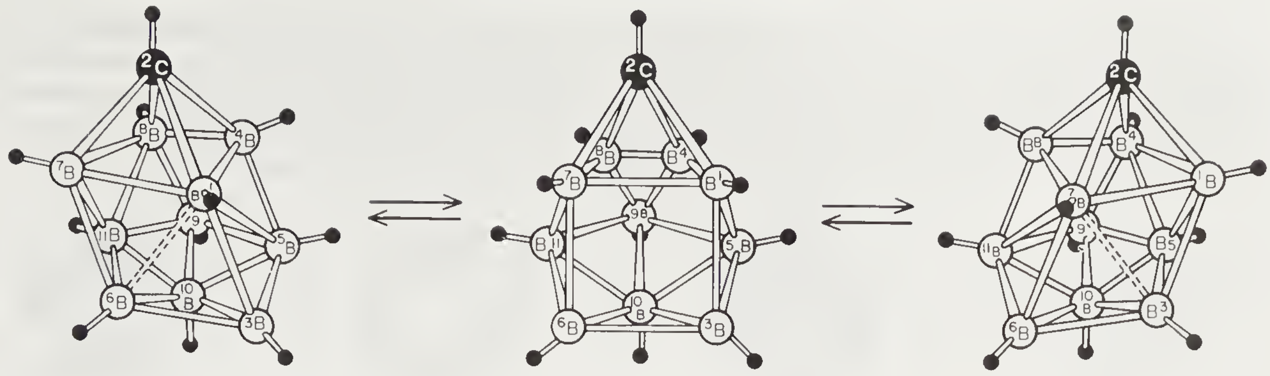


Figure 11 Sequence of *dsd* type rearrangements resulting in rotation of belts in $CB_{10}H_{11}^-$

Whether or not the observation of only two of the required three types of ^{11}B resonances for *closo*-$C_2B_6H_8$ and its *C,C'*-dimethyl derivative implies accidental peak overlap or cage fluxionality in the liquid phase has not been completely resolved.[49,144] Relevant to this same problem it is noted that equilibrated dodecahedral structures are proposed to account for the spectroscopic properties of the isoelectronic *closo*-$C_3B_5H_7$ (Figure 7).[20]

Although the molecular formula of $C_2B_6H_{10}$ is that expected for a *nido*-carborane, an *arachno* framework (Figure 12) is proposed from the observation of only two BH doublets in the boron NMR spectrum. Alternatively, the *nido* valence bond tautomers may be in equilibrium with each other and with the *arachno* structure.[80] Isoelectronic with $C_2B_6H_{10}$ is the four-carbon carborane $Me_4C_4B_4H_4$ (Figure 13) and again a question of an *arachno versus* equilibrating *nido* frameworks has been raised.[116]

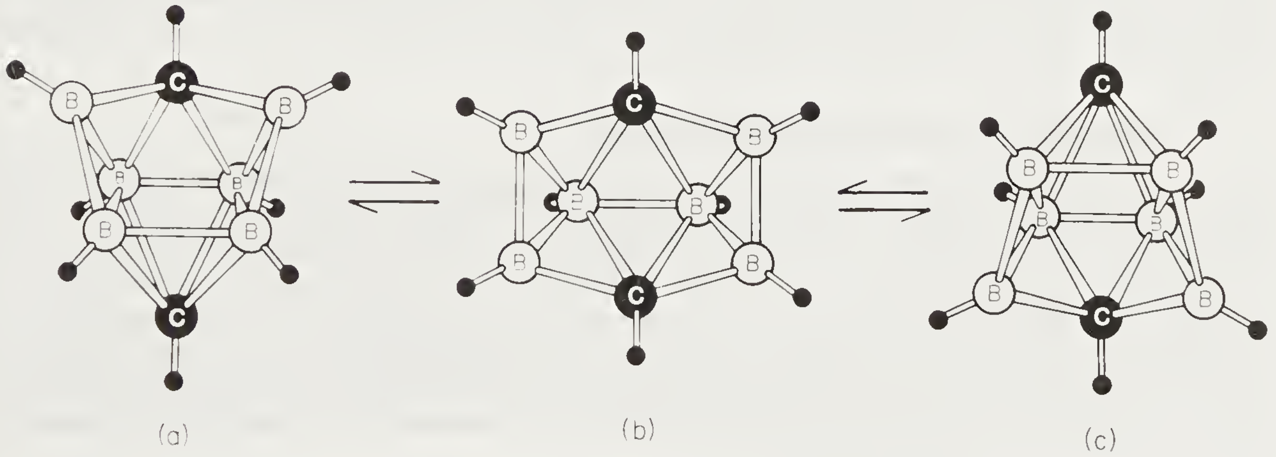


Figure 12 $C_2B_6H_{10}$. (a) and (c) *nido* structures; (b) *arachno* structure; bridging hydrogen atoms not shown

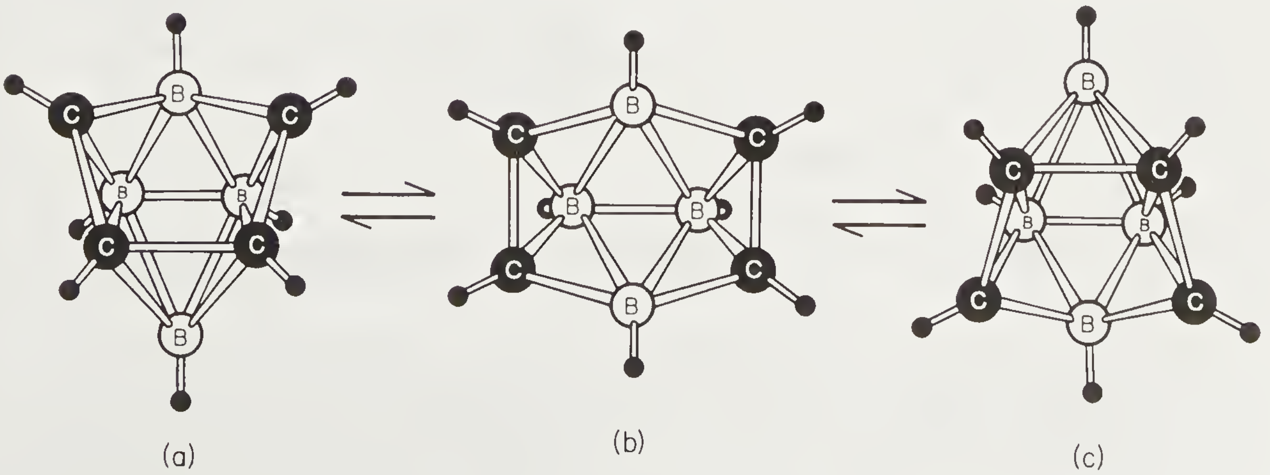


Figure 13 Possible structures for $(CH_3)_4C_4B_4H_4$. (a) and (c) *nido* structures; (b) *arachno* structure

The larger four-carbon carborane $Me_4C_4B_8H_8$[118] (Figures 6, 14), having two square faces in the crystalline form (isomer A),[145] equilibrates with another polyhedral form (isomer B) in solution. Isomer B is believed to exhibit fluxional behavior (see figure) which involves a time-averaged cube-octahedral intermediate (structure C).[146] Fluxional behavior is also proposed to account for the rapid interconversion of two $[Me_4C_4B_8H_8]^{2-}$ dianion isomers.[146]

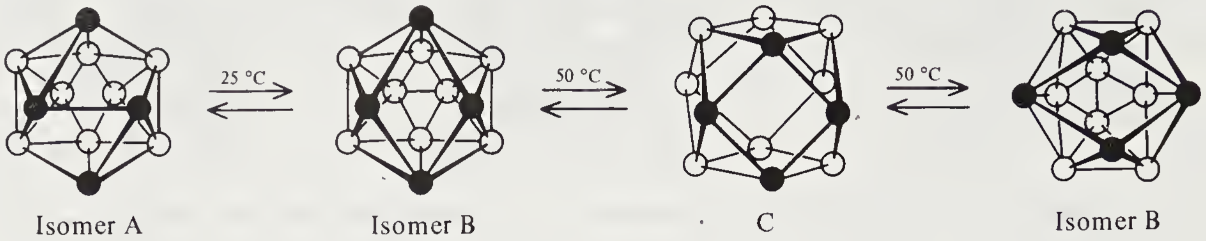


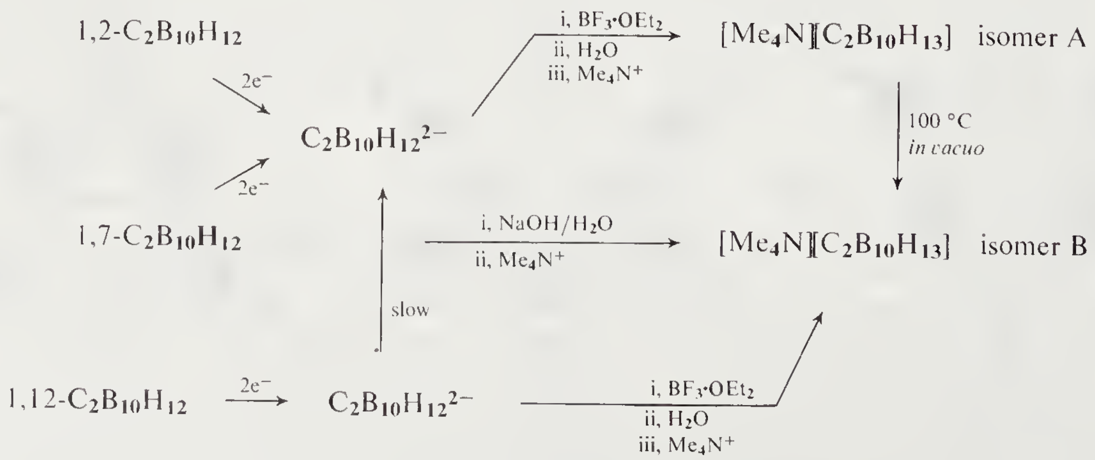
Figure 14 Isomers A and B, $(CH_3)_4C_4B_8H_8$. Closed circles represent C—CH_3 groups, open circles represent B—H groups; see also Figure 6

Hydrogen tautomerism in neutral carboranes is known to occur only for *closo*-1-CB_5H_7 (Figure 1c). At 100 °C the bridging hydrogen tautomerizes on the NMR time scale from one trigonal B_3 face to three other such faces of this octahedral cage molecule. From studies on the parent compound and its *C*-methyl derivative activation energies, $\Delta G^{\ddagger} = 58$ and 50 kJ mol^{-1}, respectively, are estimated for this process.[88,147] It is presumed that bridging hydrogen tautomerism can occur in some or all of the carborane anions when such a hydrogen neighbors a nucleophilic B—B bond. Such a situation is found in $[nido\text{-}2,3\text{-}C_2B_4H_7]^-$ (Section 5.4.2.7.6), where the bridging hydrogen is capable of oscillating between the B(4)B(5) and the B(5)B(6) basal positions. In the $[nido\text{-}2,4\text{-}C_2B_4H_7]^-$ anion (Figure 3d), only one basal boron–boron bond (containing the lone bridging hydrogen) exists along the open basal face of the pentagonal pyramid of skeletal atoms and consequently bridging hydrogen tautomerism is considered very unlikely in this isomer.[143] Similarly, hydrogen tautomerism may well occur between B(9)B(10) and B(10)B(11) bridging positions of the $[nido\text{-}7,8\text{-}C_2B_9H_{12}]^-$ isomer but not in the 7,9- isomer, which only has one open-face boron–boron connection.[148]

5.4.2.7.3 Reduction reactions and related chemistry

closo-Carboranes, in particular the larger cage compounds, undergo facile reduction with an alkali metal to give dinegative cage ions (equation 47). Typically, *closo*-1,2-, -1,7- and -1,12-$C_2B_{10}H_{12}$ (Figures 2f, 2g and 2h), and some of their derivatives, react with sodium to form $[C_2B_{10}H_{12}]^{2-}$ ions[138,140–142,149,150] which in turn can be protonated to afford $[nido\text{-}C_2B_{10}H_{13}]^-$.[141,142,151] The formal net result of this two-step process is an overall reduction of $C_2B_{10}H_{12}$ with H^-. Scheme 2 summarizes the two-electron reduction of the icosahedral carboranes, and subsequent protonation.[142] The structure of one of the two $C_2B_{10}H_{13}^-$ ions, as the *C,C′*-R_2 derivative, has been determined to be 7-R-*exo*-12-R-*nido*-7,12-$C_2B_{10}H_{11}^-$ (R = Me or Ph); Figure 4i);[19] see also Section 5.4.2.7.1.

$$closo\text{-}C_2B_xH_{x+2} \quad + \quad 2e^- \quad \longrightarrow \quad [nido\text{-}C_2B_xH_{x+2}]^{2-} \qquad (47)$$



Scheme 2

Acidification of $C_2B_8H_{10}^{2-}$, prepared from the addition of sodium to *closo*-1,2-$C_2B_8H_{10}$, gives rise to *nido*-5,6-$C_2B_8H_{12}$ as the main product.[74] Reduction of 5,6-$C_2B_8H_{12}$ with sodium amalgam in ethanol gives *arachno*-6,9-$C_2B_8H_{14}$, which is isostructural with $B_{10}H_{14}^{2-}$ but having CH_2 groups at opposite corners along the open face,[152] and reduction of 6-Me_3N-6-CB_9H_{11} with sodium in liquid ammonia produces the 6-$CB_9H_{12}^-$ anion with a $B_{10}H_{14}$-like skeleton.[101]

Among other carboranes known to undergo reduction to dinegative ions are $C_2B_6H_8$,[153] 1,6-$C_2B_8H_{10}$[154] and $C_4B_8H_{12}$ (as the *C*-tetramethyl derivative).[155] Many of the dinegative ions have been widely used in reactions with metal compounds to form metallocarboranes (Chapter 5.5).

For still other reactions involving net reduction reactions of carboranes, see Section 5.4.2.7.4 below.

5.4.2.7.4 Reaction of Lewis bases with closed cage carboranes

The results of known Lewis-base reactions with *closo*-carboranes (equations 48–55) are consistent with the thesis that the introduction of one electron pair opens the cage to a *nido* framework; see Section 5.4.2.3 (literature references to the chemistry given in equations 48–55 are: equation 48,[143,156] 49,[143] 50,[70] 51–53,[157] 54,[158] 55[159]).

$$\mathrm{Me_3N} + closo\text{-}1,6\text{-}\mathrm{C_2B_4H_6} \longrightarrow 5\text{-}\mathrm{Me_3N}\text{-}nido\text{-}2,4\text{-}\mathrm{C_2B_4H_6} \tag{48}$$

$$\mathrm{NaH} + closo\text{-}1,6\text{-}\mathrm{C_2B_4H_6} \longrightarrow \mathrm{Na}[nido\text{-}2,4\text{-}\mathrm{C_2B_4H_7}] \tag{49}$$

$$\mathrm{L} + closo\text{-}2,3\text{-}\mathrm{C_2B_9H_{11}} \longrightarrow \mathrm{L}\text{-}nido\text{-}\mathrm{C_2B_9H_{11}}\ (\mathrm{L = Et_3N, Ph_3P, OH^-}) \tag{50}$$

$$\mathrm{MeLi} + closo\text{-}2,3\text{-}\mathrm{C_2B_9H_{11}} \longrightarrow \mathrm{Li}[10\text{-}\mathrm{Me}\text{-}7,9\text{-}\mathrm{C_2B_9H_{11}}] \tag{51}$$

$$closo\text{-}2,3\text{-}\mathrm{C_2B_9H_{11}} \xrightarrow{\mathrm{NaBH_4}} 7,9\text{-}\mathrm{C_2B_9H_{12}}^- \tag{52}$$

$$\mathrm{Li}[1,10\text{-}\mathrm{C_2B_8H_9}] + 2,3\text{-}\mathrm{C_2B_9H_{11}} \longrightarrow \mathrm{Li}[10\text{-}[1'\text{-}(1',10'\text{-}\mathrm{C_2B_8H_9})]\text{-}7,9\text{-}\mathrm{C_2B_9H_{11}}] \tag{53}$$

$$closo\text{-}2,3\text{-}\mathrm{C_2B_9H_{11}} + \mathrm{Me_2S} \longrightarrow 10\text{-}\mathrm{Me_2S}\text{-}nido\text{-}7,9\text{-}\mathrm{C_2B_9H_{11}} \tag{54}$$

$$2,3\text{-}\mathrm{R_2}\text{-}closo\text{-}2,3\text{-}\mathrm{C_2B_9H_9} + [\mathrm{RO}]^- \longrightarrow [10\text{-}\mathrm{RO}\text{-}7,9\text{-}\mathrm{R_2}\text{-}nido\text{-}7,9\text{-}\mathrm{C_2B_9H_9}]^- \tag{55}$$

With both *closo*-1,6-$C_2B_4H_6$ and *closo*-2,3-$C_2B_9H_{11}$ a Lewis base effectively displaces a terminal hydrogen to an immediately adjacent bridging B—B position upon cage opening, *e.g.* Figure 15. Hydride ion can also effect this type of cage opening giving, in the case of *closo*-1,6-$C_2B_4H_6$, the previously unknown 2,4-isomer of the [*nido*-$C_2B_4H_7$]$^-$ ion.[143]

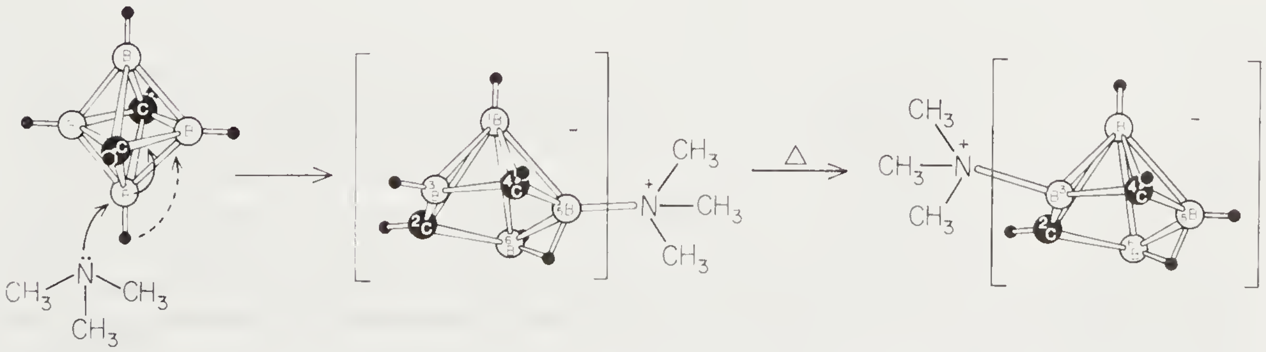


Figure 15 Reaction of $(CH_3)_3N$ with *closo*-1,6-$C_2B_4H_6$ to give 5-$(CH_3)_3N$-*nido*-2,4-$C_2B_4H_6$, and subsequent rearrangement to 3-$(CH_3)_3N$-*nido*-2,4-$C_2B_4H_6$

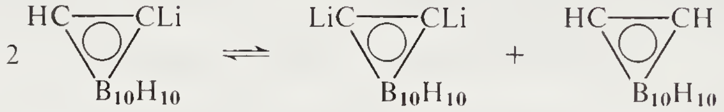
Although the parent *closo*-2,4-$C_2B_5H_7$ and *closo*-1,2-$C_2B_{10}H_{12}$ do not react with tertiary amines or phosphines, the presence of an appropriately *B*-attached halogen atom on to these two carboranes greatly improves the cage reactivity toward adduct formation. Treatment of 5-Cl-*closo*-2,4-$C_2B_5H_6$ with Me_3L (L = N, P) gives an adduct of undetermined structure but probably having some, or all, *nido* character. The cage reverts back to a *closo* pentagonal pyramid upon extracting the halide ion from the adduct using BCl_3, forming [5-Me_3N-*closo*-2,4-$C_2B_5H_6$]$^+$.[160]

The reactivity of some brominated derivatives of 1,2-$C_2B_{10}H_{12}$ toward Lewis bases such as hexamethylenetetramine, pyridine, triphenylphosphine and triethylamine increases in the order 8,9,12-Br_3- > 1-Br- > 9,12-Br_2-. A 9-bromo derivative of *closo*-1,2-$C_2B_{10}H_{12}$ forms an adduct only with hexamethylenetetramine among the above bases.[161] The structure of the adducts remains in doubt but some degree of 'open-cage' character may be competing with a stable icosahedral *closo* geometry. For related chemistry, see sections 5.4.2.7.3 and 5.4.2.7.8.

5.4.2.7.5 H—C_{cage} ***proton abstraction and consequent derivative chemistry***

The weakly acidic character of cage carbon-attached hydrogens is demonstrated by the reaction of *closo*-carboranes with butyllithium (equation 56). Such behavior has been observed for, among others, 1,6-$C_2B_4H_6$,[162] 2,4-$C_2B_5H_7$,[163] 1,6- and 1,10-$C_2B_8H_{10}$,[99] 1,2-, 1,7- and 1,12-$C_2B_{10}H_{12}$;[4,5] even in the monocarboranes $[CB_9H_{10}]^-$ [76,82] and $[CB_{11}H_{12}]^-$,[82] a single C—H proton is removed. The rate of reaction to form $Li_2[C_2B_{10}H_{10}]$ salts diminishes in proceeding from *closo*-1,2- to -1,7- to -1,12-$C_2B_{10}H_{12}$, consistent with the expected decrease in C—H hydrogen atom acidity. Preparation of monolithium derivatives of $C_2B_{10}H_{12}$ is complicated by an equilibrium that exists between the monolithium compound and the dilithium and unsubstituted compound in certain solvents (equation 57). Fortunately, this equilibrium appears to be shifted to the left in benzene, and monosubstituted derivatives (see below) are best prepared using this solvent.[4,5]

$$C_2B_nH_{2+n} \quad + \quad 2LiC_4H_9 \quad \longrightarrow \quad Li_2[C_2B_nH_n] \quad + \quad 2C_4H_{10} \qquad (56)$$



(57)

The anions seem to retain structural integrity in that they have been used to form *C*-substituted derivatives in which the position of the cage carbon atoms in the polyhedron has not changed. Formation of these derivatives (*e.g.* Me, CH_2CH_2OH, CH(OH)R, COR, CO_2H, PR_2, SiR_3, halogen, NO, CN, OH, SO_2H, SR) is accomplished by taking advantage of the nucleophilic character of the carborane anion, as indicated in equations (58)–(61).[7]

$$1,6\text{-}Li_2C_2B_4H_4 \xrightarrow[\text{ii, }Br_2]{\text{i, MeI}} 1\text{-Me-6-Br-}closo\text{-}1,6\text{-}C_2B_4H_4 \qquad (58)$$

$$2,4\text{-}Li_2C_2B_5H_5 \xrightarrow[\text{ii, }H^+]{\text{i, }(CF_3)_2PI} 2\text{-}(CF_3)_2P\text{-}closo\text{-}2,4\text{-}C_2B_5H_6 \qquad (59)$$

$$1,10\text{-}Li_2C_2B_8H_8 \xrightarrow[\text{ii, }H^+]{\text{i, }CO_2} 1,10\text{-}(HO_2C)_2\text{-}closo\text{-}1,10\text{-}C_2B_8H_8 \qquad (60)$$

$$1\text{-Li-2-Me-}1,2\text{-}C_2B_{10}H_{10} \xrightarrow[\text{ii, }H^+]{\text{i, }(PhCO)_2O_2} 1\text{-HO-2-Me-}closo\text{-}1,2\text{-}C_2B_{10}H_{10} \qquad (61)$$

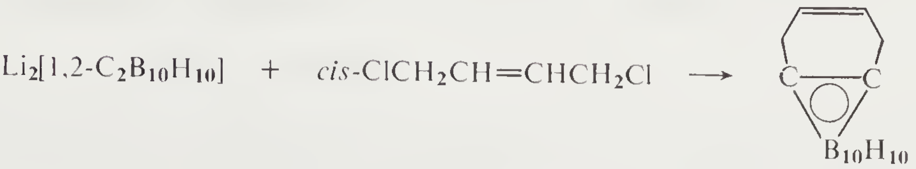
Na, K and Ca salts of the conjugate base ion of $C_2B_{10}H_{12}$ have also been prepared using metal amide in liquid ammonia as the reagent. Grignard reagents react with 1,2- and 1,7-$C_2B_{10}H_{12}$ to give the corresponding $XMgC_2B_{10}H_{11}$ compounds. One of the more useful methods of preparation of cage carbon attached metal derivatives involves the carborane salts (equations 62–64).

$$2[2\text{-R-}1,2\text{-}C_2B_{10}H_{10}]^- \quad + \quad HgX_2 \quad \longrightarrow \quad Hg[2\text{-R-}1,2\text{-}C_2B_{10}H_{10}]_2 \qquad (62)$$

$$[2\text{-R-}1,2\text{-}C_2B_{10}H_{10}]^- \quad + \quad (\eta\text{-}C_5H_5)Fe(CO)_2I \quad \longrightarrow \quad 1\text{-}(OC)_2(\eta\text{-}C_5H_5)Fe\text{-2-R-}1,2\text{-}C_2B_{10}H_{10} \qquad (63)$$

$$[2\text{-R-}1,2\text{-}C_2B_{10}H_{10}]^- \quad + \quad Ph_3PAuCl \quad \longrightarrow \quad 1\text{-}Ph_3PAu\text{-2-R-}1,2\text{-}C_2B_{10}H_{10} \qquad (64)$$

The nearness of the cage carbon atoms in 1,2-$C_2B_{10}H_{12}$ promotes the probability of forming exocyclic ring derivatives from the dimetallated carborane and dihalides (equation 65). The latter compound in turn can be dehydrogenated with NBS to form benzocarborane (Figure 16). Two other of the many known preparations of exocyclic derivatives are given in equations (66) and (67).



(65)

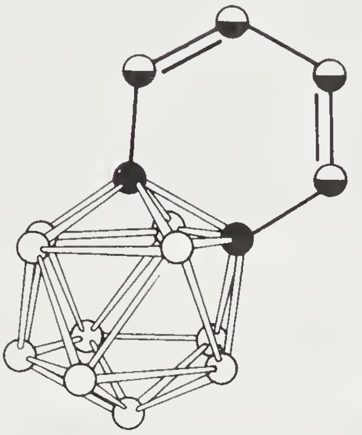
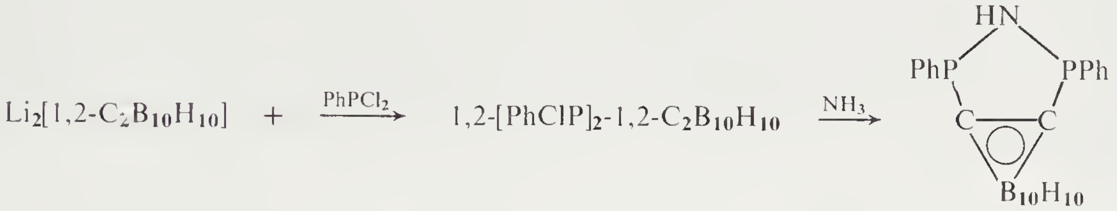


Figure 16 Structure of benzocarborane. Open circles BH, filled circles C, half-filled CH



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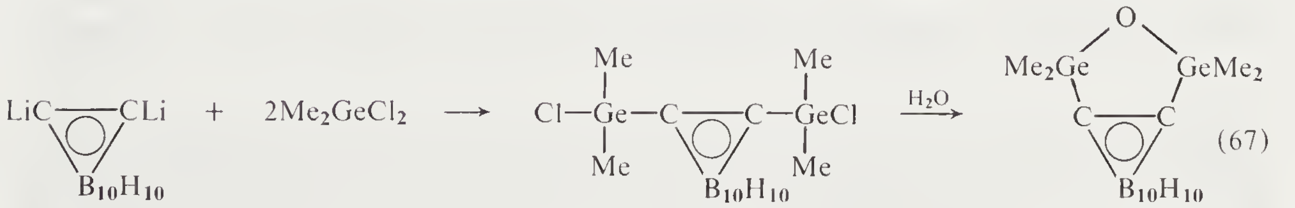


(67)

Much more *C*-derivative chemistry is known than can be covered in this short space and the reader is advised to consult recent and past reviews for completeness.[4-9]

The enhanced acidity of the axial methylene hydrogens of the *arachno*-carborane 1,2-$C_2B_7H_{13}$ (Figure 5b) has been demonstrated by the formation of mono-[70,98] and di-anions[77] using aqueous hydroxide and sodium hydride, respectively. In agreement with experimental observations the calculated positive charge densities are the following: axial CH > bridge BHB > equatorial CH.[164] This compound, in this respect, is rather unusual in carborane chemistry for it is usually observed that bridge hydrogens are more acidic than cage CH hydrogens (see Section 5.4.2.7.6 below).

5.4.2.7.6 Bridging-proton abstraction, B—B bond protonation and relevant chemistry

Boron bridging hydrogen atoms are normally the most acidic in the *nido*-carboranes. A single bridging hydrogen is removed from each of the *nido* compounds CB_5H_9,[78] $C_2B_4H_8$,[165] $C_3B_3H_7$[54] and $[C_2B_9H_{12}]^-$ [166] by reacting the carborane with an appropriate metal hydride, *e.g.* equation (68). As evidenced by the quantitative regeneration of the original neutral carborane with the addition of HCl (equation 69), the anion so produced in equation (68) retains cage structural integrity. Upon treating the anion with DCl a bridge-deuterated derivative is obtained. The

$[2,3\text{-}C_2B_4H_7]^-$ anion is also known to react with either trialkylchlorosilicon (equation 70), or the germanium analogue, to give a bridge-substituted product and these bridging derivatives may be thermally rearranged to terminally substituted isomers.[68,167]

$$2,3\text{-}C_2B_4H_8 + NaH \longrightarrow Na^+[2,3\text{-}C_2B_4H_7^-] + H_2 \quad (68)$$

$$Na^+[2,3\text{-}C_2B_4H_7^-] + HCl \longrightarrow 2,3\text{-}C_2B_4H_8 + NaCl \quad (69)$$

$$[2,3\text{-}C_2B_4H_7]^- + Me_3SiCl \longrightarrow \mu\text{-}[Me_3Si]\text{-}2,3\text{-}C_2B_4H_7 + Cl^- \quad (70)$$

The only known *closo*-carborane with a bridging hydrogen, CB_5H_7, also reacts with NaH to give the corresponding $[CB_5H_6]^-$ ion; as observed for the above *nido* system, the $[CB_5H_6]^-$ ion can be protonated with HCl to give back the neutral *closo*-CB_5H_7.[126]

The bridging hydrogen atom of each of the [*nido*-$C_2B_9H_{12}]^-$ ions is considered to be located at the open face. Several different strong bases can be used to remove this twelfth hydrogen from the 11-atom boron–carbon cages of the $[C_2B_9H_{12}]^-$ ions to produce $[C_2B_9H_{11}]^{2-}$ (equation 71).[166,168] The $[C_2B_9H_{11}]^{2-}$ ion has been utilized to form 12-atom icosahedral cage compounds *via* boron (Section 5.4.2.6.4) or metal atom (Chapter 5.5) insertion reactions. Both the [7,8- and $[7,9\text{-}C_2B_9H_{12}]^-$ ions can be reversibly protonated to afford a pair of neutral *nido*-$C_2B_9H_{13}$ isomers.[93]

$$C_2B_9H_{12}^- + NaH \longrightarrow Na^+ + C_2B_9H_{11}^{2-} + H_2 \quad (71)$$

The ability of certain carborane anions to accept protons to form neutral species is, of course, not surprising for the anions are most often formed, as mentioned above, by treating the corresponding neutral cage compounds with a sufficiently strong base. Only recently, however, have certain neutral carboranes, *i.e.* *closo*-1,6-$C_2B_4H_6$ and *closo*-2,4-$C_2B_5H_7$, been found to accept a proton. As studied by ion cyclotron resonance, the smaller of the two *closo*-carboranes, 1,6-$C_2B_4H_6$, is determined to have a proton affinity of 869 ± 17 kJ mol^{-1}, whereas that of 2,4-$C_2B_5H_7$ is 723 ± 4 kJ mol^{-1}.[169] The protonated form of 1,6-$C_2B_4H_6$ is isoelectronic and probably isostructural with the known *closo*-1-CB_5H_7, which has a lone bridging hydrogen on a BBB triangular face (Figure 1c).

5.4.2.7.7 *Derivatives containing* exo-*cage B—C, B—Si, B—Ge, B—Sn and B—Pb bonds*

Methyl–hydrogen exchange between 1,5-$C_2B_3H_5$ and BMe_3 is effected at elevated temperatures; in addition to mono-, di- and tri-methyl derivatives of the *closo*-dicarbapentaborane, *B*-mono-, di-, tri- and tetra-methyl derivatives of 2,2′-$(C_2B_3H_4)_2$ are also produced from this reaction.[170] A *B*-1-propenyl derivative of 1,5-$C_2B_3H_5$ is the product of a reaction of propyne with the parent trigonal bipyramidal *closo*-carborane.[104]

B-Mono- and poly-methylation of pentagonal-bipyramidal *closo*-2,4-$C_2B_5H_7$ with methyl chloride in the presence of aluminum chloride follows a positional preference 5,6 > 1,7 > 3 which is in agreement with that predicted by an electrophilic substitution mechanism.[171] Alkylation of 1,2- and 1,7-$C_2B_{10}H_{12}$ under similar conditions is also known to occur.[172]

Alkylation of the $[7,8\text{-}C_2B_9H_{11}]^{2-}$ ion with alkyl halides gives mono-, di- and tri-alkyl derivatives. Eventually, additional alkylation followed by hydrolysis degrades the cage to $C_2B_7H_{12}R$.[173] Alkylation of $[7,8\text{-}C_2B_9H_{11}]^{2-}$ with RX (X = halogen) below 0 °C in water, alcohol or THF yields the $[11\text{-}R\text{-}2,7\text{-}C_2B_9H_{11}]^-$ (R = Me, Et, Bu, $CH_2CH{=}CH_2$), but at room temperature rearrangement occurs to yield $[8\text{-}R\text{-}7,9\text{-}C_2B_9H_{11}]^-$.[174] Protonation of the $[11\text{-}Me\text{-}2,7\text{-}C_2B_9H_{11}]^-$ gives 11-Me-2,7-$C_2B_9H_{12}$, an isomer of dicarba-*nido*-undecaborane(13) having the structure of an icosahedron with one vertex missing and the C atoms adjacent but only one in the open pentagonal face (Figure 4e). The methyl group is attached to the boron atom of the open face bonded to both C atoms, and the open face has two BHB bridges symmetric to the open-face C atom.[175] Alkylation of $[7,9\text{-}C_2B_9H_{11}]^{2-}$ by alkyl halides is proposed to proceed through the formation of a bridging alkyl carborane, $[\mu\text{-}Me\text{-}7,9\text{-}C_2B_9H_{11}]^-$ (where the carbon atom of the alkyl group is linked by a three-center two-electron bond to B(10) and B(11)), which rearranges at room temperature to yield $[10\text{-}Me\text{-}7,9\text{-}C_2B_9H_{11}]^-$. If B(10) and B(11) are already substituted, as in $[\mu,8,10,11\text{-}Me_4\text{-}7,9\text{-}C_2B_9H_8]^-$, rearrangement is not observed. Reaction of this latter anion with nucleophilic reagents such as NH_2^-, OH^- and H_2O opens the three-center bond, yielding products such as [8,10,11-Me_3-7,9-$C_2B_9H_8]^{2-}$ and [11-NH_2(or OH)-8,10,10,11-Me_4-7,9-$C_2B_9H_8]^{2-}$, a derivative of the unknown *arachno*-$C_2B_9H_{15}$, which on hydrolysis gives 7-Me-6,8-$C_2B_7H_{12}$.[176] Acylation of both the 7,8- and 7,9-$C_2B_9B_{12}^-$ anions has resulted in *B*-acyl derivatives of this *nido*-carborane system.[177] Alkyl halides, in liquid ammonia, react with the aminated dianions formed from 1,2- and 1,7-$C_2B_{10}H_{12}$ and their *C*-methyl and *C*-halomethyl derivatives to give the neutral carborane derivatives $HCB_{10}H_8NH_2(R)CR'$ (R' = H or Me; R = Me, Pr or Bu).[178]

Reactions of 1,2-dicarbadodecaborate(14) dianions with arylmagnesium halides and aryllithiums afford the dianions of *B*-aryldicarbadodecaborates(14), which on oxidation with $CuCl_2$ yield a mixture of 3-, 4-, 8- and 9-aryl-1,2-$C_2B_{10}H_{11}$ (Ar = Ph, *m*- and *p*-FC_6H_4, *m*- and *p*-MeC_6H_4). Oxidation of dianions prepared from 3- and from 4-aryl-1,2-$C_2B_{10}H_{11}$ using $CuCl_2$ yields the same proportions of 3-, 4-, 8- and 9-aryl-1,2-$C_2B_{10}H_{11}$. Similar reactions starting with 1,12-$C_2B_{10}H_{12}$ yield a mixture of *B*-aryl derivatives of 1,7-$C_2B_{10}H_{12}$. The dianion prepared from 3-aryl-1,2-$C_2B_{10}H_{11}$ reacts with transition metals to yield metallocarboranes which on oxidation with $CuCl_2$ in THF lead to the isolation of *B*-aryl-1,2-, -1,7- and -1,12-$C_2B_{10}H_{11}$. Other *B*-substituted derivatives of the type *B*-R-1,2-$C_2B_{10}H_{11}$ (R = Me, Bu, $CH{=}CH_2$, $CH{=}CHPh$) have also been prepared by reaction of $[1,2\text{-}C_2B_{10}H_{12}]^{2-}$ with appropriate organolithium or Grignard reagents followed by treatment with $CuCl_2$.[179]

3-Ph-*closo*-1,2-$C_2B_{10}H_{11}$ can be obtained by insertion of $PhBCl_2$ into the $[C_2B_9H_{11}]^{2-}$ ion[86] (see section on growth reactions). The only example of a *B*-aryl derivative of a small carborane is the preparation of 4-Ph-2,3-Me_2-*nido*-2,3-$C_2B_4H_5$ by an oxidative addition of benzene to the coupled carborane 5,5′-$(Me_2C_2B_4H_5)_2$. When this reaction is carried out in the presence of C_6D_6 there is evidence to indicate that one of the six deuterium atoms enters a bridging position of the carborane product, replacing a bridging hydrogen which in turn moves to a terminal location on B(5).[108]

It has been recently found that the 1,2-$C_2B_{10}H_x$ polyhedron can act as a transport system for a carbene, as evidenced by the formation of 1-$CH_2{=}CH$-1,2-$C_2B_{10}H_{11}$ as well as 1,2-Me_2-1,2-$C_2B_{10}H_{10}$ and 1,2-[—CH_2CH_2—]-1,2-$C_2B_{10}H_{10}$ from the pyrolysis of 1-N_2CH-2-Me-1,2-$C_2B_{10}H_{10}$.[180] There are several examples of a boron-substituted organocarborane being derived from another,[7] an example being the preparation of boron-substituted carboxylic acid derivatives of 1,2- and 1,7-$C_2B_{10}H_{12}$ from the CrO_3 oxidation of the corresponding *B*-$(Me_3SiCH_2CH_2)C_2B_{10}H_{11}$.[181]

Bridging species μ-R_3M-*nido*-2,3-$C_2B_4H_7$ (R = Me, M = Si, Ge, Sn, Pb; R = H, M = Si, Ge) are obtained from the reaction of R_3MX (X = halogen) with the $[2,3\text{-}C_2B_4H_7]^-$ ion[167,182] (see Section 5.4.2.7.6). The silicon and germanium compounds are known to rearrange to *B*-terminal substituted isomers. In contrast, the tin and lead compounds μ-Me_3Sn-*nido*-$C_2B_4H_7$ and μ-Me_3Pb-*nido*-$C_2B_4H_7$ fail to undergo thermal rearrangement to the respective terminal derivatives, but are known to react with DCl to generate μ-$DC_2B_4H_7$. The reaction of μ-Me_3Si-*nido*-$C_2B_4H_7$ with NaH involves both bridge deprotonation and bridge-to-terminal silicon migration, giving the [4-Me_3Si-*nido*-$C_2B_4H_6]^-$ anion; treatment of this ion with DCl gives μ-D-4-Me_3Si-*nido*-$C_2B_4H_6$ and with Me_3SiCl yields μ,4-$(Me_3Si)_2$-*nido*-$C_2B_4H_6$.[182] The [*nido*-2,3-$C_2B_4H_7]^-$ ion reacts with $ClCH_2SiMe_2Cl$ to give the bridged silyl derivative μ-$ClCH_2SiMe_2$-$C_2B_4H_7$ and, as expected, mild heating rearranges this compound to a basal terminally substituted Si—B isomer. A 1,2-shift of the carboranyl unit from the silicon to the methylene carbon atom is catalyzed by $AlCl_3$ to yield 4-$(ClMe_2SiCH_2)$-*nido*-$C_2B_4H_7$. A similar shift giving a mixture of 4- and 5-$(ClMe_2SiCH_2)$-*nido*-$C_2B_4H_7$ is observed without a catalyst at 150 °C.[68] 9-Substituted-7,8-dicarba-*nido*-undecaborate containing a B—Si bond has been synthesized as a salt by the reactions of $[7,8\text{-}C_2B_9H_{11}]^{2-}$ with either Me_3SiCl or $PhMe_2SiCl$.[183]

5.4.2.7.8 Carborane derivatives containing exo-cage B—N and B—P bonds

Reactivities of the small *closo*-carboranes toward Me_3L (L = P or N) follow the order 1,5-$C_2B_3H_5 >$ 1,6-$C_2B_4H_6 >$ 2,4-$C_2B_5H_7$. The smallest cage forms unstable adducts whereas 1,6-$C_2B_4H_6$ gives the dipolar 5-Me_3L^+-*nido*-2,4-$C_2B_4H_6^-$;[156,143] the largest of these three cage compounds, 2,4-$C_2B_5H_7$, does not react with Me_3L, but is readily cleaved by Me_2NH to give products such as $Me_2NH{\cdot}BH_3$ and $[Me_2NBHCH_3]_x$ (x = 1, 2). The 5-Me_3L^+-*nido*-2,4-$C_2B_4H_6^-$ is found to rearrange in chloroform, or thermally, to the corresponding 3-Me_3L isomer; and reaction of 3- or 5-Me_3N^+-2,4-$C_2B_4H_6^-$ with NaH produces the parent 2,4-$C_2B_4H_7^-$ ion.[143]

Treatment of *nido*-5,7-$C_2B_8H_{12}$ (Figure 4c) with trimethylamine leads to the formation of a ligand adduct in which the nitrogen is attached to the unique B(6).[73]

[9-Ph_2P-7,8-$C_2B_9H_{11}$]$^-$ is prepared by reacting Ph_2PCl with [7,8-$C_2B_9H_{11}$]$^{2-}$;[183] substituted *nido*-7,9-$C_2B_9H_{12}^-$ ion derivatives, obtained by reaction of Lewis bases (*e.g.* NEt_3) with *closo*-2,3-$R_2C_2B_9H_9$, have the base attached to the B(10) position.[159]

Additional carborane chemistry of compounds containing B—N and B—P bonds is given in Section 5.4.2.7.4.

5.4.2.7.9 Carborane derivatives containing exo-cage B—O and B—S bonds

Oxidation of *C,C′*-Me_2-*nido*-$C_2B_9H_9$ with chromic acid,[184] or with sodium periodate,[185] affords *B*-hydroxy derivatives which on pyrolysis are converted to carboranyl ethers.[184,185] The use of ^{18}O enriched ethylene glycol in a reaction with 4,7-$(HO)_2$-2,3-Me_2-*nido*-2,3-$C_2B_9H_7$ to form an exocyclic B—O—C—C—O—B ring[186] indicates, surprisingly, that the hydroxy groups on the carborane polyhedron are displaced during this condensation. The 10-alkoxy derivative of *nido*-7,9-Me_2-7,9-$C_2B_9H_{10}^-$ is obtained upon interaction of *closo*-2,3-Me_2-2,3-$C_2B_9H_9$ and RO^-.[159] Replacement of the NH_2 group of 1,2-Me_2-3-NH_2-*closo*-1,2-$C_2B_{10}H_9$ with an OH group is effected by *p*-toluenesulfonic acid.[187] A *B*-diethoxy derivative of $Me_4C_4B_8H_8$ is obtained from the EtOH/KOH treatment of $(Me_2C_2B_4H_4)_2FeH_2$.[188]

Reaction of atomic sulfur (^1D) with the small *closo*-carboranes 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$ and 2,4-$C_2B_5H_7$ affords a convenient method of synthesis for the corresponding *B*-mercaptocarboranes, including 2-SH-1,5-$C_2B_3H_4$, 2-SH-1,6-$C_2B_4H_5$, 5-SH-2,4-$C_2B_5H_6$, 1-SH-2,4-$C_2B_5H_6$ and 3-SH-2,4-$C_2B_5H_6$. Photolytic decomposition of the *B*-mercapto derivatives of 2,4-$C_2B_5H_7$ results in the formation of several isomers containing boron-bonded bridging —S_2— groups, 5,5′-$S_2(2,4\text{-}C_2B_5H_6)_2$, 1,1′-$S_2(2,4\text{-}C_2B_5H_6)_2$ and 3,3′-$S_2(2,4\text{-}C_2B_5H_6)_2$.[189] Sulfur insertion into the B—H bonds of icosahedral *closo*-carboranes occurs on heating 1,2-, 1,7- or 1,12-$C_2B_{10}H_{12}$ with S and $AlCl_3$. Products isolated in high yield are 9-HS-1,2-$C_2B_{10}H_{11}$, 9-HS-1,7-$C_2B_{10}H_{11}$ and 2-HS-1,12-$C_2B_{10}H_{11}$; other products include 8-HS-1,2-$C_2B_{10}H_{11}$ and 9,9′-$S_2(1,2\text{-}C_2B_{10}H_{11})_2$. The acidity of 9-HS-1,2-$C_2B_{10}H_{11}$ is very much less than that of 1-HS-1,2-$C_2B_{10}H_{11}$ and is a good measure of both the electron acceptor and donor character of the substituted skeletal atom.[190] Transformations of the HS group in 9-HS-1,7-$C_2B_{10}H_{11}$ to SMe, $\overset{+}{S}Me_2$, SOMe, SO_2Me, —S—S—, SO_3^-, SO_2Cl and SO_2NR_2 have also been effected.[191]

Sulfur also reacts with some *nido*- and *arachno*-carboranes in the presence of aluminum trichloride to form thiol derivatives. In this way, *nido*-5,6-$C_2B_8H_{12}$ yields 3-HS-, 4-HS- and 10-HS-5,6-$C_2B_8H_{11}$ and *arachno*-6,9-$C_2B_8H_{14}$ produces 1-HS-6,9-$C_2B_8H_{13}$.[192]

Various isomers of Me_2S-*nido*-$C_2B_9H_{11}$ have been prepared by the diverse methods given in equations (72–76).[111,158]

$$\text{9-MeS-1,2-}C_2B_{10}H_{11} \xrightarrow[\text{ii, MeI}]{\text{i, KOH, MeOH}} \text{5-}Me_2S\text{-}\textit{nido}\text{-7,8-}C_2B_9H_{11} \qquad (72)$$

$$\text{7,8-}C_2B_9H_{12}^- \xrightarrow[H_3O^+]{Me_2SO} \text{9-}Me_2S\text{-}\textit{nido}\text{-7,8-}C_2B_9H_{11} \qquad (73)$$

$$\mu\text{-9,10-}\mu\text{-9}',10'\text{-}(7,8\text{-}C_2B_9H_{11})_2 \xrightarrow{Me_2S} \text{10-}Me_2S\text{-}\textit{nido}\text{-7,8-}C_2B_9H_{11} + \text{9-}Me_2S\text{-}\textit{nido}\text{-7,8-}C_2B_9H_{11} \qquad (74)$$

$$\text{7,9-}C_2B_9H_{12}^- \xrightarrow[H_3O^+]{Me_2SO} \text{8-}Me_2S\text{-}\textit{nido}\text{-7,9-}C_2B_9H_{11} \qquad (75)$$

$$\text{2,3-}C_2B_9H_{11} \xrightarrow{Me_2S} \text{10-}Me_2S\text{-}\textit{nido}\text{-7,9-}C_2B_9H_{11} \qquad (76)$$

5.4.2.7.10 Halogenation

Many carboranes are known to undergo facile substitution reactions with molecular halogens at boron sites. Under conditions which suggest that an electrophilic mechanism is operating, the position of halogenation can be predicted from charge density rules derived from MO calculations, *i.e.* negative charge is usually greatest on borons farthest away from skeletal carbon atoms. Hence, mono- and di-chlorination of *closo*-2,4-$C_2B_5H_7$ in the presence of $AlCl_3$ yields primarily 5-Cl-2,4-$C_2B_5H_6$[193] and monobromination of *closo*-1,6-$C_2B_7H_9$ under similar conditions gives substitution at the 8-position (equation 77).[194] Substitution at the 8-position of 1,6-$C_2B_7H_9$ is also observed upon subjecting this carborane to a modified Friedel–Crafts reaction with methyl chloride (Section 5.4.2.7.7). These studies strongly imply that there is good correspondence between calculated ground-state negative charge densities and reactivity, although no knowledge of the transition state configuration is available. Another example of this correspondence is the monohalogenation of the *nido*-carborane 2,3-$C_2B_4H_8$ with chlorine, bromine or iodine monochloride in the presence of aluminum chloride to give mostly the 4-substituted derivatives.[195] This is in agreement with ground-state charge distribution in that the 4-position is considered less positive than the others.[196]

$$closo\text{-}1,6\text{-}C_2B_7H_9 + Br_2 \xrightarrow{AlCl_3} 8\text{-}Br\text{-}closo\text{-}1,6\text{-}C_2B_7H_8 + HBr \qquad (77)$$

Monochlorination of 2,4-$C_2B_5H_7$ under photolytic conditions is less selective than when electrophilic conditions are encouraged (*vide supra*) and gives rise to a mixture of 1-, 3- and 5-Cl-2,4-$C_2B_5H_6$.[193] Low-temperature fluorination of *closo*-2,4-$C_2B_5H_7$ with molecular fluorine results in considerable carborane decomposition but does afford low yields of 1-, 3- and 5-monofluoro and 1,3-, 1,5- and 5,6- difluoro derivatives of this pentagonal-bipyramidal cage compound.[197] Substantial decomposition also occurs upon the direct action of Cl_2 on smallest *closo*-carborane, 1,5-$C_2B_3H_5$, to give an unstable 2-Cl-1,5-$C_2B_3H_4$.[170] Even with next larger *closo* compound, 1,6-$C_2B_4H_6$, chlorination causes cage breakdown into $MeBCl_2$, BCl_3 and $Cl_2BCH_2BCl_2$ along with the formation of both 2-Cl-1,6-$C_2B_4H_5$[198] and the *trans*-bis-chloro isomer, 2,4-Cl_2-1,6-$C_2B_4H_4$.[29,134] Alternatively, 2-Cl-1,6-$C_2B_4H_5$ can be obtained from the photolysis of 4-Cl-*nido*-2,3-$C_2B_4H_7$.[198] Iodination of *closo*-1,6-$C_2B_4H_6$ affords the *B*-iodo derivative.[195c]

Direct chlorination of *closo*-1,10-$C_2B_8H_{10}$ in CCl_4 generates the *B*-octachloro derivative, and complete chlorination of the 1,10-dimethyl derivative of this carborane is effected by subjecting the reactants to UV light (equations 78 and 79).[99]

$$closo\text{-}1,10\text{-}C_2B_8H_{10} + 8Cl_2 \xrightarrow{CCl_4} B\text{-}Cl_8\text{-}closo\text{-}1,10\text{-}C_2B_8H_2 + 8HCl \qquad (78)$$

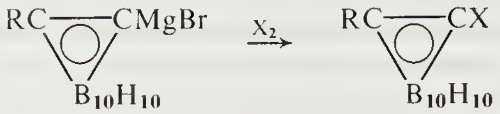
$$1,10\text{-}(CH_3)_2\text{-}1,10\text{-}C_2B_8H_8 + 14Cl_2 \xrightarrow[h\nu]{CCl_4} 1,10\text{-}(CCl_3)_2\text{-}1,10\text{-}C_2B_8Cl_8 + 14HCl \qquad (79)$$

In the Lewis acid catalyzed chlorination, bromination and iodination of *closo*-1,2-$C_2B_{10}H_{12}$ and its *C*-methyl derivatives, substitution occurs first at the 9,12-positions and then on borons-8,10. Except for fluorination, initial and principal halogen substitution in *closo*-1,7-$C_2B_{10}H_{12}$ occurs at positions-9,10. These borons have the highest calculated negative charge and are the only borons not adjacent to carbon. Electrophilic bromination of 1-Me-1,7-$C_2B_{10}H_{11}$ has been shown to yield 25% of the 4,9,10-tribromo and 73% of the 9,10,12-tribromo derivatives. In *closo*-1,12-$C_2B_{10}H_{12}$, all boron atoms are equivalent and so only one isomer of a monohalo derivative is possible. Electrophilic bromination and iodination of 1,12-$C_2B_{10}H_{12}$ yields both mono- and di-halo compounds, but electrophilic chlorination proceeds to the tetrachloro derivative. Numerous isomers of the polychloro derivatives are formed but gas chromatographic evidence shows that the halogenation is not entirely random and the initially attached chlorine atoms exert a substituent effect. Fluorine has been found to attack 1,2-, 1,7- and 1,12-$C_2B_{10}H_{12}$ in an essentially nonselective manner, yielding *B*-decafluorocarboranes as the ultimate product with no *C*-substitution.[4,5]

In contrast to the electrophilic halogenation reactions of the icosahedral carboranes, photochemical chlorination proceeds easily to the *B*-decachloro derivatives. The sequence of substitution of 1,2-$C_2B_{10}H_{12}$ parallels that of electrophilic halogenation, proceeding from the most negative boron atoms to the most positive. Final substitution occurs at borons-3,6, those closest to the cage carbon atoms. The photochemical chlorination of 1,7-$C_2B_{10}H_{12}$ leads to two monochloro isomers and is thus less specific than the electrophilic reaction. The photochemical chlorination of 1,12-$C_2B_{10}H_{12}$ appears to proceed in an almost random fashion. Both 1,2- and 1,7-$C_2B_{10}H_{12}$ resist photochemical bromination, yielding only monobromo derivatives in the absence of a catalyst.[4,5]

Halogen substitution at the carbons of the icosahedral carboranes is extremely difficult to effect by direct reaction with molecular halogen but can be achieved by reaction of the halogen with the lithio or Grignard derivatives of the carborane (equations 80 and 81) (see Section 5.4.2.7.5).

$$RCB_{10}H_{10}CLi \xrightarrow{X_2} RCB_{10}H_{10}CX \quad (80)$$



(81)

The electron-withdrawing character of the halogen substituents in the *B*-substituted halocarboranes renders the protons on carbon relatively acidic, especially in *B*-Cl_{10}-1,2-$C_2B_{10}H_2$ which is comparable to a carboxylic acid on the acidity scale. The metal salts of the *B*-decachloro derivative of 1,2-$C_2B_{10}H_{12}$, formed by treatment with aqueous alkali, react with chlorine to form the perchloro derivative. The same perchloro compound is also produced by reaction of *B*-Cl_{10}-1,2-$C_2B_{10}H_2$ with *N*-chlorosuccinimide.[4,5]

Included among other methods for the preparation of *B*-halogenated carboranes are: the action of molecular halogens on the *nido*-$Me_2C_2B_4H_5^-$ anion to give *B*-halo derivatives of *nido*-2,3-Me_2-2,3-$C_2B_4H_6$;[199] the interaction of 2-$BrB_{10}H_{13}$ with acetylene to yield several isomers of *B*-Br-1,2-$C_2B_{10}H_{11}$;[200] the action of HCl on the trimethylamine adduct of 5,7-$C_2B_8H_{12}$ to give 6-Cl-5,7-$C_2B_8H_{11}$;[73] and insertion reactions (Section 5.4.2.6.4).

5.4.2.7.11 Hydrogen–deuterium exchange

The facility with which boron-attached terminal hydrogens in the polyboron hydrides exchange with deuteriodiborane carries over into the smaller carboranes. For those *nido*- and *closo*-carboranes examined thus far, exchange occurs more rapidly with terminal hydrogens on the least coordinated boron atoms (equations 82 and 83).

$$nido\text{-}2,3\text{-}C_2B_4H_8 \xrightarrow[100\ °C]{B_2D_6} 4,5,6\text{-}D_3\text{-}2,3\text{-}C_2B_4H_5 \quad (82)$$

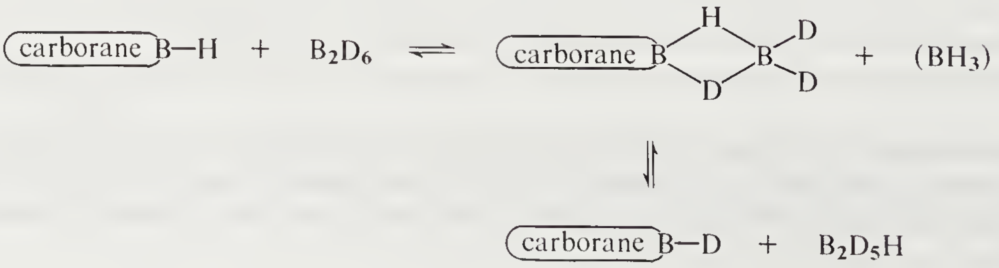
$$closo\text{-}2,4\text{-}C_2B_5H_7 \xrightarrow{B_2D_6} 3,5,6\text{-}D_3\text{-}2,4\text{-}C_2B_5H_4 \xrightarrow[100\ °C]{B_2D_6} 1,3,5,6,7\text{-}D_5\text{-}2,4\text{-}C_2B_5H_2 \quad (83)$$

The relative rates of exchange decrease in the column series *a* to *c*:

(*a*) 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, 2,4-$C_2B_5H_7$ (3,5,6-positions)
(*b*) 2,4-$C_2B_5H_7$ (1,7-positions), 2,3-$C_2B_4H_8$ (4,5,6-positions)
(*c*) 2,3-$C_2B_4H_8$ (1-position)

It seems likely that the mechanism of this exchange involves the formation of a $=BH_2B=$ bridging intermediate, increasing the coordination number of the cage boron by 'one', as schematically depicted in equation (84). The assumption that the transition state leading to this intermediate is more stable when a boron does not assume an extraordinarily high coordination environment, can account for the observed rate order. Diglyme catalyzes the exchange of the 4,6-positions of 2,3-$C_2B_4H_8$ with B_2D_6; deuterium/hydrogen exchange of all boron-bonded hydrogens of this same *nido*-carborane occurs with D_2 at *ca.* 250 °C, or at room temperature with a chromia–alumina catalyst. Both apical and basal B—H terminal exchange of the 2,3-dimethyl derivative of 2,3-$C_2B_4H_8$ can be effected with a $DCl/AlCl_3$ mixture, presumably *via* an electrophilic substitution mechanism.[6]

Acid-catalyzed D/H exchange of *arachno*-1,3-$C_2B_7H_{13}$ with D_2O takes place at the two axial



(84)

carbon-attached hydrogens only, whereas base-catalyzed exchange occurs at both C—H_{axial} and bridging B—H—B sites.[70,98] Both of these observations are consistent with the relative positive charge densities calculated using a nonempirical MO method.[164]

The *closo*-carboranes 1,6-$C_2B_8H_{10}$, 1,2-$C_2B_{10}H_{12}$, 1,7-$C_2B_{10}H_{12}$ and 1,12-$C_2B_{10}H_{12}$ are found to undergo catalytic isotope exchange of terminal hydrogen with deuterium gas in the presence of transition metal complexes. Stereoselective deuterium incorporation occurs with catalysts such as $(Ph_3P)_3RuHCl$ and $(Ph_3As)_2IrCl$, but with hydridometallocarborane catalysts $(Ph_3P)_2HMC_2B_9H_{11}$ (M = Rh, Ir), although more active, little or no stereoselectivity is found.[201]

Hydrogen/deuterium exchange of the [*nido*-7,8-$C_2B_9H_{12}]^-$ ion with D_2O under neutral or basic conditions occurs exclusively at the bridging hydrogen position; under acidic conditions exchange not only occurs at the bridging position but also at the 3, 5, 6, 9, 10 and 11 terminal positions.[148] Similarly, hydrogen/deuterium exchange between $[7,9\text{-}C_2B_9H_{12}]^-$ (Figure 4h) and D_2O under neutral or basic conditions occurs exclusively at the bridging hydrogen position; under acidic conditions additional exchange occurs at the terminal hydrogen sites located at the 1 and 8 positions.[148,159]

5.4.2.8 Polymer Applications

Siloxane polymers incorporating *closo* carborane units (equations 85 and 86 show the preparation of two examples) exhibit unusually high thermal and air stabilities. Carborane-containing elastomers of this type have been developed to withstand temperatures in the 400–800 °C region. A number of organic polymers (*e.g.* polyesters, polyurethanes, polymethacrylates, polyolefins) having *closo*-carborane groups in the polymer backbone have also been examined but, in general, do not appear to have any extraordinary properties.[202]

$$\begin{tikzcd}
Li_2[2,4\text{-}C_2B_5H_5] \arrow[r, "Me_2SiCl_2"] & 2,4\text{-}[Me_2SiCl]_2\text{-}2,4\text{-}C_2B_5H_5 \arrow[d, "H_2O"] \\
& \left[SiMe_2{-}CB_5H_5C{-}SiMe_2O \right]_n
\end{tikzcd} \qquad (85)$$

$$\begin{tikzcd}
Li_2[1,7\text{-}C_2B_{10}H_{10}] \arrow[r, "Me_2SiCl_2"] & 1,7\text{-}[Me_2SiCl]_2\text{-}1,7\text{-}C_2B_{10}H_{10} \arrow[d, "Me_2SiCl_2/ROH"] \\
& \left[SiMe_2{-}CB_{10}H_{10}C{-}SiMe_2OSiMe_2OSiMe_2O \right]_n
\end{tikzcd} \qquad (86)$$

5.4.3 ORGANOPOLYBORON HYDRIDES

5.4.3.1 Physical Properties

Only a few C—B bond distances (Table 4) are known for the organopolyboranes, and the average value (~1.58 Å) for these compounds is not significantly different from that found for the simple organoborane, Me_3B.[203] An X-ray structural study on 1-ethyldecaborane shows that no substantial change in the B_{10} framework has occurred upon substitution; also the C—C (1.55 Å) bond distance is nearly the value expected for relatively an unperturbed single bond.[204] A dipole moment of 1.93 ± 0.05 D is found for 1-MeB_5H_8 compared with 2.13 D for the parent pentaborane. The microwave data for 1-MeB_5H_8 are consistent with a model having free internal rotation and vibration–internal-rotation interactions; lack of barrier perturbations leads to an upper limit of 1 cm^{-1} for the twelvefold barrier.[205]

In both ^{11}B and proton magnetic resonance chemical shift studies, it is not surprising that the effect of alkyl substitution on polyborane cage systems is largely felt by the contiguously attached boron atoms and any neighboring bridge hydrogens. Thus, a substituted boron is shifted *ca.* 8–15 p.p.m. downfield and bridge hydrogens *ca.* 0.6 p.p.m. downfield compared with an unsubstituted

Table 4 C—B Bond Length as Determined by X-Ray Diffraction

Compound	*C—B bond length,* (Å)
$1\text{-}C_2H_5\text{-}B_{10}H_{13}$	1.59 ± 0.01[1]
$2,3\text{-}(CH_3)_2\text{-}B_5H_7$	1.55[2,3]
$1\text{-}CH_3\text{-}B_5H_8$	1.595 ± 0.005[4]
$2\text{-}CH_3\text{-}B_5H_8$	1.592 ± 0.005[4]
OCB_3H_7	1.54–1.57[5]
$9\text{-}C_6H_{11}\text{-}5\text{-}(CH_3)_2S\text{-}B_{10}H_{11}$	1.58[6]

1. A. Perloff, *Acta Crystallogr.*, 1964, **17,** 332.
2. L. B. Friedman and W. N. Lipscomb, *Inorg. Chem.*, 1966, **5,** 1752.
3. T. P. Onak, L. B. Friedman, J. A. Hartsuck and W. N. Lipscomb, *J. Am. Chem. Soc.*, 1966, **88,** 3439.
4. J. D. Wieser, D. C. Moody, J. C. Huffman, R. L. Hilderbrandt and R. Schaeffer, *J. Am. Chem. Soc.*, 1975, **97,** 1074.
5. J. D. Glore, J. W. Rathke and R. Schaeffer, *Inorg. Chem.*, 1973, **12,** 2175.
6. E. Mizusawa, S. E. Rudnick and K. Eriks, *Inorg. Chem.*, 1980, **19,** 1188.

system. The effects are generally additive for polysubstituted derivatives.[206–208] Although charge distribution and other effects may account for the chemical shift difference, $\Delta\delta(\text{apex} - \text{base}) = 0.35$ p.p.m., between apically situated methyl hydrogens of MeB_5H_8 and their basal counterparts,[207,209] it is also possible to account for this observation by adopting a classic free-electron model with current loops parallel to the base plane of the pyramidal boron framework.[28] The NMR coupling constants, $J(BC) \approx 73$ Hz and $J(CH) = 120$ Hz, measured for apex methyl-substituted pentaborane(9) compounds correspond to a nearly sp^3-hybridized carbon bonded to an approximately sp^2-hybridized boron atom. A boron–carbon coupling of 64 Hz found for 2-methylpentaborane probably indicates slightly more *p*-character contributed by the basal boron atom toward the *exo* terminal bond.[210–212]

A CO stretching frequency of 1570 cm^{-1}, observed for the $[2\text{-}PhCO\text{-}B_{10}H_9]^{2-}$ ion, is quite outside the normal range for benzoyl derivatives and establishes a highly polar nature for the carbonyl group in this ketone.[213]

Spectroscopic investigations of the very stable and highly colored tropenyliumyl-*closo*-nonahydrodecaborate(1−) and tropenylium-*closo*-undecahydrododecaborate(1−) ions (Figure 17) show that in both ions significant cage-to-ring electron donation occurs in both ground and excited states.[214] The UV spectra of 1- and $2\text{-}MeB_5H_8$ exhibit λ_{max} at 205 nm and 210 nm, respectively; in each, a $\pi \rightarrow \pi^*$ transition with some σ mixing is probably involved.[215]

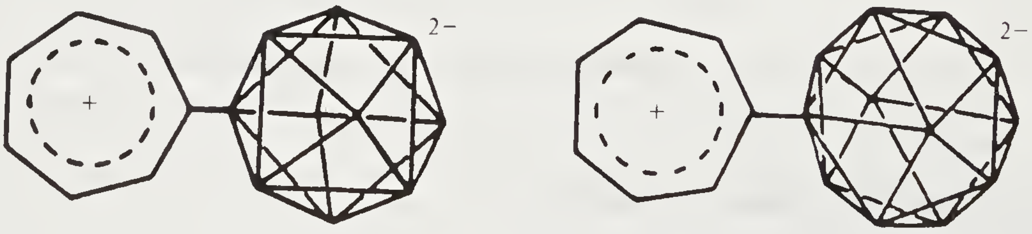


Figure 17 $C_7H_6\text{-}B_{10}H_9^-$ and $C_7H_6\text{-}B_{12}H_{11}^-$ ions

The bond energies of 1- and $2\text{-}MeB_5H_8$, calculated from electron impact methods, show the 2-isomer to have the larger B—C bond dissociation energy. This is consistent with rearrangement studies (Section 5.4.3.3.1), which indicate $2\text{-}MeB_5H_8$ is more stable than the corresponding 1-isomer.[216]

5.4.3.2 Preparation

5.4.3.2.1 Modified Friedel–Crafts reaction

Almost all substitutions at what are believed to be high electron-density sites of B_5H_9 (1-position) (Figure 18) and of $B_{10}H_{14}$ (2,4- and 1,3-) have been effected using 'Friedel–Crafts' type reagents and conditions. Although olefins or alkyl halides are normally used as the organic reactant, trialkylborates, alkyl ethers and alkyl silicates have also been successfully utilized. The position of boron group attachment to B_5H_9 is kinetically rather than thermodynamically controlled for thermal equilibration between 1-R-B_5H_8 and 2-R-B_5H_8 and shows that the latter isomer is the more stable of the two.[203]

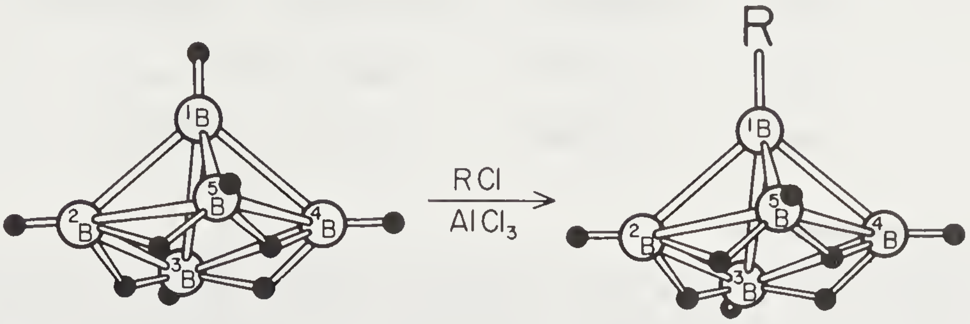


Figure 18 Reaction of B_5H_9 with $RCl/AlCl_3$ to give 1-RB_5H_8

Alkylation of B_5H_9 with $MeSiCH_2Cl$ in the presence of $AlCl_3$ gives 1-MeB_5H_8 and Me_3SiCl in quantitative yield, whereas use of Cl_3SiCH_2Cl as the alkylating agent gives 1-Cl_3SiCH_2-B_5H_8. From control experiments it is learned that the expected intermediate 1-Me_3SiCH_2-B_5H_8 in the former reaction undergoes a very fast Si—CH_2 cleavage with the HCl side-product in the presence of $AlCl_3$. The Si—CH_2 bond in the 1-Cl_3SiCH_2-B_5H_8 is apparently much more stable under similar conditions.[90]

An aluminum chloride catalyzed reaction of methylene chloride with pentaborane at 70 °C gives low yields of the di(1-pentaboranyl)methane and unexpectedly some 1-Cl_2BCH_2-B_5H_8.[217]

5.4.3.2.2 Reaction of alkenes and alkynes with polyboranes

Addition of ethylene (and other alkenes) to B_4H_{10} occurs with the elimination of H_2 from the polyborane moiety to form the unique bismethylene bridged $(CH_2)_2B_4H_8$ (Figure 19). In contrast, reaction of B_5H_9 with alkenes at elevated temperatures (in the absence of Friedel–Crafts type catalysts) generally gives good conversions but poor yields of 2-alkylpentaboranes (equation 87), a reaction which appears to be the result of a simple hydroboration. Similar results are found upon reacting ethylene and B_5H_{11}, forming both EtB_5H_{10} and $Et_2B_5H_9$. A mixture of alkylated pentaborane(9) and decaborane(14) compounds are products from the pyrolysis of a C_2H_4/B_2H_6 mixture.[203] Other reactions of alkenes with polyboranes include the additions of cyclohexene to $(Me_2S)_2B_{10}H_{12}$ to give 9-C_6H_{11}-5-Me_2S-*nido*-$B_{10}H_{11}$, which in turn reacts with NaH to afford $[2\text{-}C_6H_{11}\text{-}closo\text{-}B_{10}H_9]^{2-}$.[218] Also, propene reacts with $(H_3O)_2B_{12}H_{12}{\cdot}5H_2O$ to afford $[PrB_{12}H_{11}]^{2-}$; a similar reaction occurs with styrene.[213,219]

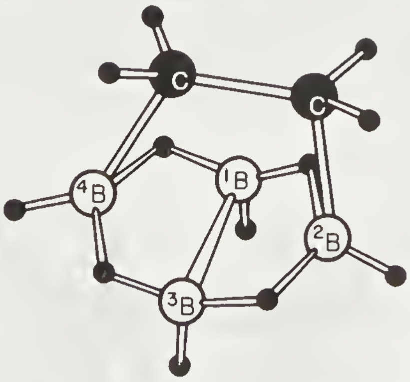


Figure 19 $(CH_2)_2B_4H_8$

$$EtCH{=}CH_2 \quad + \quad B_5H_9 \xrightarrow{150\ °C} 2\text{-}n\text{-}C_4H_9\text{-}B_5H_8 \tag{87}$$

In a recent study, dimethylacetylene has been found to react with B_5H_9 in the presence of dimethylacetylenehexacarbonyldicobalt to form 2-(*cis*-2-butenyl)pentaborane(9)[60] (see also Section 5.4.2.6.1).

5.4.3.2.3 Exchange reactions

Organic derivatives of polyboranes having two terminal B—H bonds can often be prepared by an exchange reaction that may involve boron–boron replacement (equations 88–90).[203]

$$B_4H_{10} + MeB_2H_5 \longrightarrow 2\text{-}MeB_4H_9 + B_2H_6 \tag{88}$$

$$B_5H_{11} + 1,2\text{-}R_2B_2H_4 \longrightarrow RB_5H_{10} + RB_2H_5 \tag{89}$$

$$RB_5H_{10} + 1,2\text{-}R_2B_2H_4 \longrightarrow R_2B_5H_9 + RB_2H_5 \tag{90}$$

5.4.3.2.4 Insertion reactions

The insertion of a methyl-containing boron fragment into a B_3 unit can be used to prepare 2-Me-B_4H_9 (equation 91). Both 1,2- and 2,4-$Me_2B_4H_8$ are obtained from the apparent insertion/displacement reaction of 1,2-$Me_2B_2H_4$ with $(F_3P)_2B_2H_4$; the 2,2-$Me_2B_4H_8$ isomer is produced by the action of Me_2BCl on Na[B_3H_8]. Similarly, the bridging boron compound μ-Me_2B-B_5H_8 (Figure 20), which easily rearranges to 4,5-$Me_2B_6H_8$ in the presence of ethers, is prepared from Li[B_5H_8] and Me_2BCl.[7,203] 2-MeB_6H_9 is formed in 55% yield by the addition of diborane to a dimethyl ether solution of K^+[1-Br-2-$MeB_5H_6^-$] at low temperature (−78 to −35 °C).[220] Alternatively, 2-methylhexaborane is produced in low yield from a reaction of trimethylborane with pentaborane(9) at 200 °C. The yield is improved when trimethylgallium is used as a catalyst.[221]

$$0.5(MeBH_2)_2 + Me_2O{\cdot}B_3H_7 \longrightarrow 2\text{-}Me\text{-}B_4H_9 \tag{91}$$

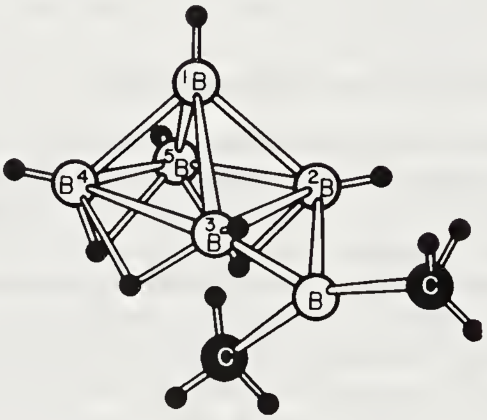


Figure 20 μ-$(CH_3)_2B$-B_5H_8

Reaction of MeB_6H_9 with B_3H_7, generated from a THF ligand species, produces two isomers of MeB_9H_{14}.[222] 6-Phenyldecaborane, 6-Ph$B_{10}H_{13}$ (Figure 21), is produced from the insertion of $PhBCl_2$ into $[B_9H_{13}]^{2-}$,[223] and 6-(3- and 4-fluorophenyl)decaboranes, 6-(3- and 4-FC_6H_4)-$B_{10}H_{13}$, are prepared in low yield from a similar insertion of 1,2-(3- and 4-fluorophenyl)diboranes, $(FC_6H_4BH_2)_2$, into K[B_9H_{14}].[224]

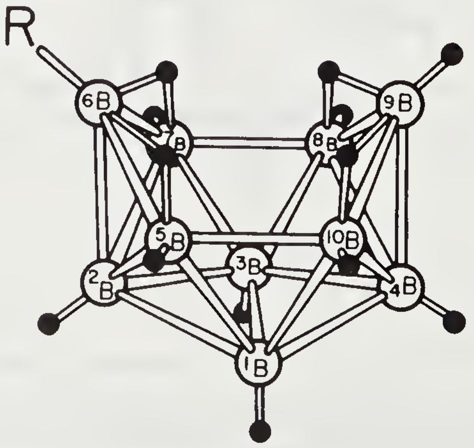


Figure 21 6-R$B_{10}H_{13}$

5.4.3.2.5 Preparation of polyborane carbonyls

Polyborane carbonyls with C—B attachment have been obtained from displacement reactions of the type shown in equations (92–95).

$$Me_2O{\cdot}B_3H_7 + CO + BF_3 \longrightarrow OCB_3H_7 + Me_2O{\cdot}BF_3 \tag{92}$$

$$B_4H_{10} + CO \longrightarrow OCB_4H_8 + H_2 \tag{93}$$

$$B_5H_{11} + 2CO \longrightarrow OCB_4H_8 + OCBH_3 \tag{94}$$

$$B_9H_{15} + CO \longrightarrow OCB_9H_{13} + H_2 \tag{95}$$

Kinetic data for the B_4H_{10}-based preparation of OCB_4H_8, with $-d(B_4H_{10})/dt = k(B_4H_{10})$, show that the reaction is independent of the CO pressure with $k = 0.50 \times 10^{-4}\ min^{-1}$ at 100 °C and $k = 0.57 \times 10^{-4}\ min^{-1}$ at 20 °C. The heat of activation for the reaction is 102.8 kJ mol^{-1}.[7,203]

Neutral carbonyl derivatives of the polyhedral $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ ions can be prepared from the zwitterion diazonium salts (equation 96). If the reaction is run in the presence of cyclohexane, $C_6H_{11}B_{10}H_7(CO)_2$ and $(C_6H_{11})_2B_{10}H_6(CO)_2$ are formed, suggesting a free radical mechanism. Although the carbonylation of 1,10-$(N_2)_2B_{10}H_8$ proceeds easily at 140 °C, the higher temperature required for the reaction of the chlorinated derivative, 1,10-$(N_2)_2B_{10}Cl_8$, with CO is consistent with electron withdrawal by chlorine atoms, thus strengthening the boron–nitrogen bond against thermal dissociation. Whereas the $(OC)_2B_{10}H_8$ from the bisdiazonium salt is apically substituted, the monocarbonylation of $[1\text{-}Me_2S\text{-}B_{10}H_9]^-$ or $[2\text{-}Me_3N\text{-}B_{10}H_9]^-$ with oxalyl chloride gives the equatorially substituted products 1,6-$Me_2SB_{10}H_8CO$ and 2,4- and 2,7(8)-$Me_3NB_{10}H_8CO$, respectively. Both 1,12- and 1,7-$(OC)_2B_{12}H_{10}$, as well as $B_{12}H_{11}CO^-$, are products from the carbonylation of hydrated $(H_3O)_2B_{12}H_{12}$.[203]

$$B_{10}H_{10}{}^{2-} \xrightarrow[\text{ii, NaBH}_4]{\text{i, HONO}} 1,10\text{-}(N_2)_2B_{10}H_8 \xrightarrow[120\text{–}140\ ^\circ C]{CO} 1,10\text{-}(OC)_2B_{10}H_8 \tag{96}$$

5.4.3.2.6 Other preparative reactions

The action of a nucleophile such as methyllithium or $B_{10}H_{14}$ gives primarily 6-(and 9-)-methyl substituted derivatives of this ten-boron polyborane. Grignard reagents also yield the 6-alkylated decaboranes but in low yield; the major product is $XMgB_{10}H_{13}$, which in turn reacts with a variety of organic reagents to form $RB_{10}H_{13}$ (equations 97a–97e). Similarly, the $B_{10}H_{13}^-$ ion, prepared from $B_{10}H_{14}$ and NaH, reacts with alkyl sulfates or benzyl chloride to give the same or similar decaborane derivatives to those obtained from $B_{10}H_{13}MgI$.[203,224]

$$B_{10}H_{13}MgI \begin{cases} \xrightarrow{Me_2SO_4} 5\text{-}Me\text{-}B_{10}H_{13} + 6\text{-}MeB_{10}H_{13} & (97a) \\ \xrightarrow{Et_3O^+BF_4^-} 5\text{-}Et\text{-}B_{10}H_{13} & (97b) \\ \xrightarrow{BuF} Bu\text{-}B_{10}H_{13} & (97c) \\ \xrightarrow{PhCH_2Cl} 6\text{-}PhCH_2B_{10}H_{13} & (97d) \\ \xrightarrow{CH=CHCH_2Br} CH_2{=}CHCH_2B_{10}H_{13} & (97e) \end{cases}$$

Both allyl iodide and benzyl bromide react with $K[B_5H_8]$ to give 2-allylpentaborane and 2-benzylpentaborane, respectively, in reactions that probably proceed *via* bridging intermediates.[225]

The cyano derivatives, $[(NC)B_{10}H_{13}]^{2-}$ and $Na[(NC)B_{10}H_{12}{\cdot}2Et_2O]$, are formed from an apparent nucleophilic interaction of NaCN with $B_{10}H_{14}$. Likewise, $[(Br)(NC)B_{10}H_{12}]^{2-}$ is obtained from 2-$BrB_{10}H_{13}$ and NaCN. The bis(ethyl isocyanide)decaborane, $(EtNC)_2B_{10}H_{12}$, is prepared by the reaction of $(Et_2S)_2B_{10}H_{12}$ with ethyl isocyanide; and the cyano derivatives of

$[B_{10}H_{10}]^{2-}$ and $[Cl_x\text{-}(NC)_{10-x}\text{-}B_{10}]^{2-}$ (x = 7, 8, 9) are produced upon UV irradiation of an aqueous solution of $Cs_2B_{10}Cl_{10}$ and KCN. Similar chemistry also takes place with halogen derivatives of $[B_{12}H_{12}]^{2-}$.[7,203]

A benzoyl derivative of the $B_{10}H_{10}^{2-}$ ion (Figure 22) is obtained from the acylation of this ion with PhCOCl. In a related reaction, the tropenylium ion reacts with either $B_{10}H_{10}^{2-}$ or $B_{12}H_{12}^{2-}$ ions to yield $[2\text{-}C_7H_6\text{-}B_{10}H_9]^-$ and $[C_7H_6\text{-}B_{12}H_{11}]^-$, respectively.[203]

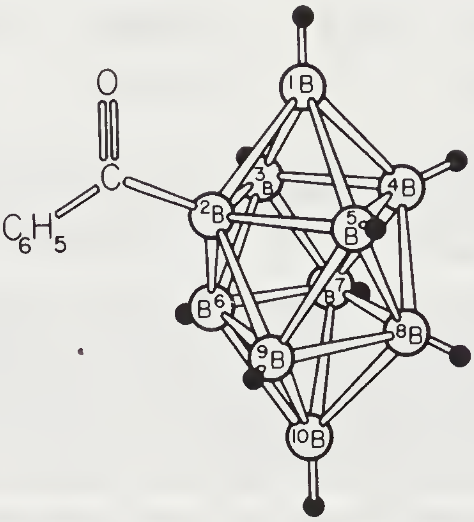


Figure 22 $2\text{-}C_6H_5CO\text{-}B_{10}H_9^{2-}$

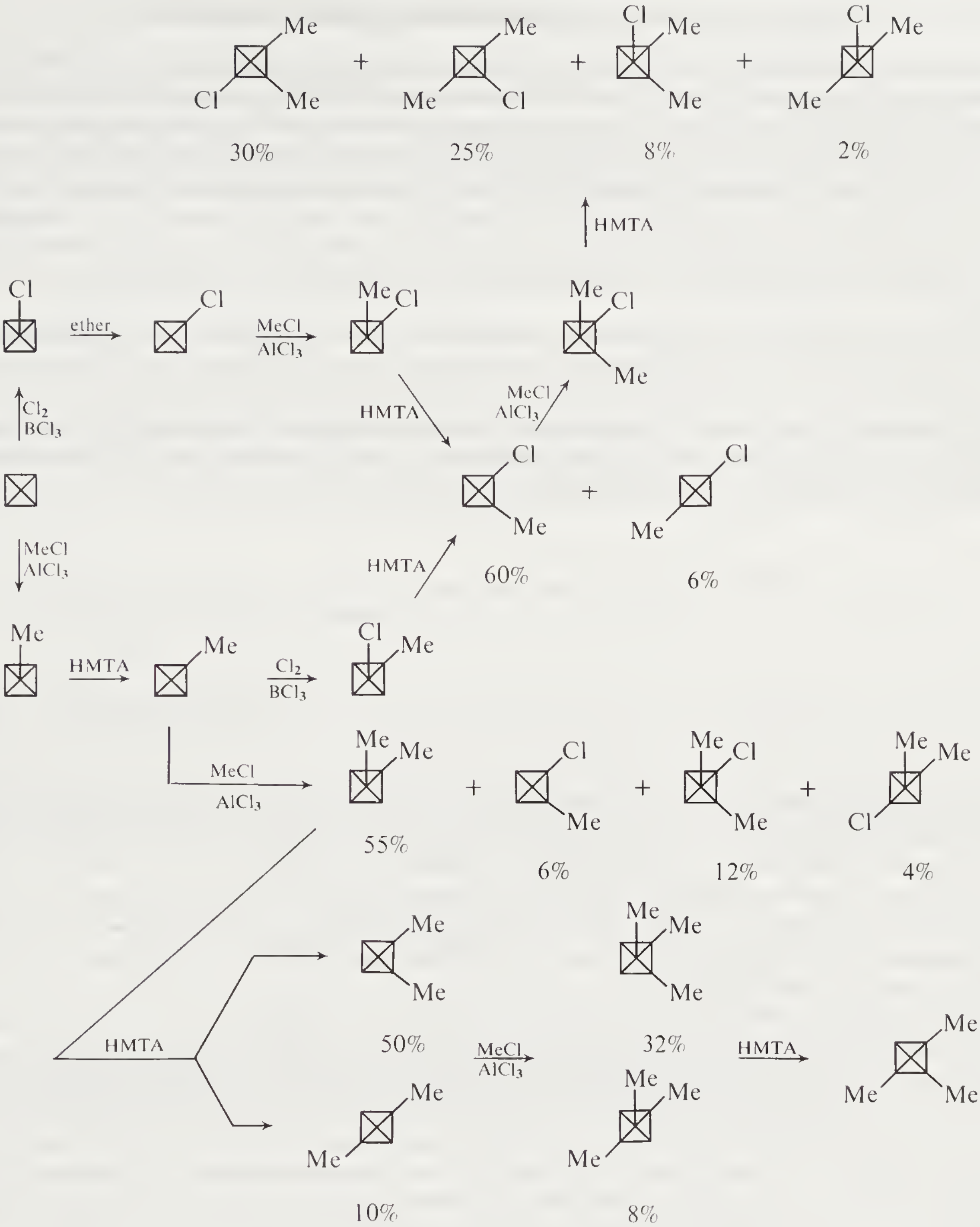
Introduction of a phenyl group on to a polyborane has been accomplished in one instance by the decomposition of $Ph_2SnB_{10}H_{13}$ at 95 °C to yield $6\text{-Ph-}B_{10}H_{13}$.[226] In another metal–metal exchange reaction, $2\text{-}MeB_4H_9$ is the primary product of Me_2Hg and B_4H_{10}.[7]

The apically substituted monomethyl derivative of B_5H_9 is a product of dimethyl ether cleavage by $1\text{-}BrB_5H_8$.[227] In the presence of $AlCl_3$ both 1- and $2\text{-}\{(ClCH_2)Me_2Si\}B_5H_8$ undergo a 1,2-shift of the polyboron cage from the silicon atom to the methylene carbon atom to give 1- and $2\text{-}(ClMe_2SiCH_2)B_5H_8$, respectively, in which the position of the boron attachment at the polyboron cage site has not changed. The $1\text{-}(ClMe_2SiCH_2)B_5H_8$ is also obtained directly from $2\text{-}(ClCH_2Me_2Si)B_5H_8$ upon heating to 100 °C.[90]

5.4.3.3 Reactions of Organopolyboranes

5.4.3.3.1 Rearrangements

An isomerization of $1\text{-}RB_5H_8$ to $2\text{-}RB_5H_8$ is effected at 200 °C with some decomposition.[228] With the use of a sterically hindered Lewis base such as 2,6-dimethylpyridine or hexamethylenetetramine (HMTA), the rearrangement of 1-alkylpentaboranes to the corresponding 2-alkylpentaboranes occurs at room temperature without noticeable build-up of an intermediate adduct.[206,208,227] Employment of a relatively strong base such as trimethylamine reportedly converts the 1-alkylpentaborane to an intermediate salt, $[Me_3NH]^+[RB_5H_7]^-$, which then yields the more stable 2-alkylpentaborane isomer upon treatment with an appropriate acid.[229] It is doubtful that this intermediate $[RB_5H_7]^-$ anionic species is solely responsible for the base-catalyzed rearrangement of alkylpentaboranes, for adduct formation provides a reasonable competing mechanism.[209,230] Product distribution analyses of the base-catalyzed rearrangements of polysubstituted pentaboranes[208] lend experimental support for a minimum atomic motion mechanism.[128,231] This involves only minor boron skeletal movement and the migration of adjacent bridge hydrogens at a particular basal boron atom (incipient apex) to positions about the apical (incipient basal) boron. A diagram that summarizes the rearrangement reactions (and preparations) of various methyl derivatives of pentaborane is shown in Scheme 3.[208]



Scheme 3

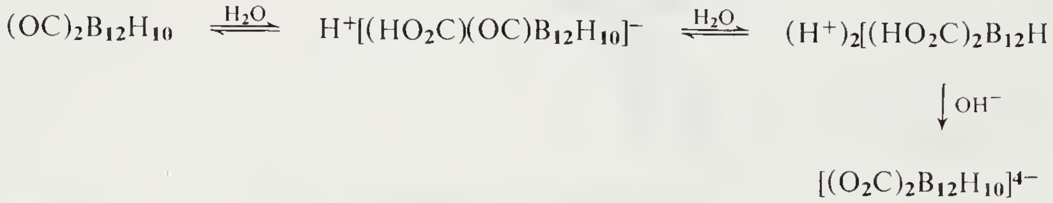
Of particular interest is the base-catalyzed rearrangement of $1,2\text{-}Me_2\text{-}3\text{-}ClB_5H_6$, which gives a mixture of dimethylchloro products. It is not surprising to find $2,3\text{-}Me_2\text{-}4\text{-}ClB_5H_6$ and $2,4\text{-}Me_2\text{-}3\text{-}ClB_5H_6$ produced in greater yield than $2,3\text{-}Me_2\text{-}1\text{-}ClB_5H_6$, for a basal preference of substituents has already been observed in the monosubstituted series. The isomer, $2,4\text{-}Me_2\text{-}1\text{-}ClB_5H_6$, is produced in very low yield, and $2\text{-}Cl\text{-}1,4\text{-}Me_2B_5H_6$ is absent altogether. Neither of these two isomers are allowed from a single rearrangement step proceeding through the minimum atomic motion mechanism. If this mechanistic scheme is hypothetically extended to include further rearrangement of the first three mentioned products, $2,3\text{-}Me_2\text{-}4\text{-}ClB_5H_6$ is a potential precursor to the low-yield isomer, $2,4\text{-}Me_2\text{-}1\text{-}ClB_5H_6$, and $2,4\text{-}Me_2\text{-}3\text{-}ClB_5H_6$ would be a precursor to the absent $2\text{-}Cl\text{-}1,4\text{-}Me_2B_5H_6$. The latter two rearrangements involve a net uphill energy change based on the substituent positional preference for the base of the pyramid and would account for the observed results.

Within the known larger organopolyboranes, the $1,10\text{-}(NC)_2B_{10}H_8^{2-}$ ion is known to rearrange at 350 °C to a predominantly equatorially substituted isomeric mixture.[232]

5.4.3.3.2 Protonation (deuteration), deprotonation and hydrogen tautomerism

The basicity of the basal B—B bond of 2-methylhexaborane(10) is demonstrated by the reaction of this compound with either liquid HBr or an HCl/BCl_3 mixture to give the salt, $[2\text{-}MeB_6H_{10}^+][BCl_4^-]$ in which the 'extra' hydrogen is found to exist in a bridging position. Also, the $B_{10}H_9^{2-}$ moiety is an electron-donating group, sufficiently so that $[2\text{-}PhCOB_{10}H_9]^{2-}$ readily forms the protonated species $[2\text{-}PhC(OH)B_{10}H_9]^-$. The ketocarbonyl group is even more basic when flanked by two B_{10} cages, and the $>BC(OH)B<$ unit might be described as containing a stabilized carbonium ion. Chlorination of the B_{10} cage reduces the basicity of the carbonyl group in $[B_{10}Cl_9COB_{10}Cl_8CO_2H]^{4-}$ to the point that tetrabasic salts of this ion can be isolated.[213,233]

In water, certain polyborane carbonyls are known to be in equilibrium with carboxylic acid derivatives, *e.g.* equation (98); acidity function studies indicate carboxyl proton ionization constants in the vicinity of 10^{-9}.[234] Thermodynamic and pK_a data for the proton ionization of $[1,12\text{-}(HO_2C)_2\text{-}closo\text{-}1,12\text{-}B_{12}H_{10}]^{2-}$ indicate that the ionic charges on the B_{12} cage are localized in the vicinity of the carboxyl group and that the second proton ionization is largely unaffected by the increased negative charge resulting from ionization of the first proton.[235]



$$\begin{array}{ccccc} (OC)_2B_{12}H_{10} & \overset{H_2O}{\rightleftharpoons} & H^+[(HO_2C)(OC)B_{12}H_{10}]^- & \overset{H_2O}{\rightleftharpoons} & (H^+)_2[(HO_2C)_2B_{12}H_{10}]^{2-} \\ & & & & \downarrow{\scriptstyle OH^-} \\ & & & & [(O_2C)_2B_{12}H_{10}]^{4-} \end{array} \qquad (98)$$

Proton competition studies reveal that both 1- and $2\text{-}MeB_5H_8$ are weaker acids than B_5H_9; and bridge deprotonation of 1- and $2\text{-}MeB_5H_8$ by sodium potassium hydride gives the mononegative ions $[1\text{-}MeB_5H_7]^-$ and $[2\text{-}MeB_5H_7]^-$, respectively. When the reaction using $1\text{-}MeB_5H_8$ is carried out at low temperature (−78 °C), structural integrity is preserved giving a bridge deprotonated $[1\text{-}MeB_5H_7]^-$ anion. Upon warming $[1\text{-}MeB_5H_7]^-$ in THF solution to 10 °C, a rearrangement to the $[2\text{-}MeB_5H_7]^-$ isomer occurs. Protonation of the $[2\text{-}MeB_5H_7]^-$ anion gives back the neutral $2\text{-}MeB_5H_8$.[230a]

Alkyldecaboranes, like decaborane, can be titrated as monoprotic acids in acetonitrile.[236] Consistent with the observation for the alkylpentaboranes, the Brønsted acidity of decaborane is lowered by increased alkyl substitution as seen in the series $6,9\text{-}(PhCH_2)_2B_{10}H_{12} < 6\text{-}PhCH_2B_{10}H_{13} < B_{10}H_{14}$.[237] In the case of 6-benzyldecaborane, reaction with triethylamine gives the salt $Et_3NH^+[6\text{-}(PhCH_2)B_{10}H_{12}]^-$, which in turn reacts with HCl to give back the $6\text{-}(PhCH_2)B_{10}H_{13}$.[238] In the presence of cineole, the four bridge hydrogens of 6-benzyldecaborane exchange rapidly with deuterium oxide. This is followed by an exchange of three other hydrogens (probably 8-, 9- and 10-positions) and eventually the remaining six terminal hydrogens.[239]

The nature of the temperature-dependent ^{11}B and ^1H NMR spectra for $2\text{-}Me\text{-}B_6H_9$ implies (a) rapid tautomerism of all four bridging hydrogens along the basal pentagonal plane at room temperature, (b) a static structure (Figure 23) with no mirror planes of symmetry at −115 °C, and (c) tautomerism of the two bridging hydrogens not adjacent to the methyl boron at intermediate temperatures.[240] Low-temperature ^1H NMR studies indicate a partial tautomeric quenching of the bridging protons in $[2\text{-}Me\text{-}B_5H_7]^-$, but not in the case of the apically substituted anion.[230]

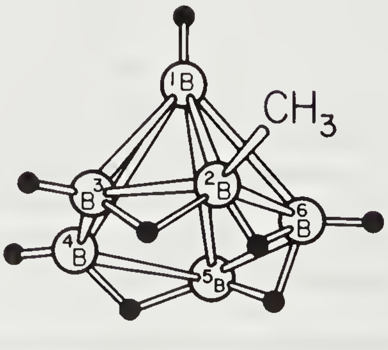


Figure 23 $2\text{-}CH_3B_6H_9$

5.4.3.3.3 *Hydrolytic, oxidative and thermal stability*

Consistent with the structural assignment of 2,4-$(CH_2)_2B_4H_8$ (Figure 19), hydrolysis and methanolysis of this compound produce ethylene glycol and 1,2-bis(dimethoxybora)ethane, respectively[241] (equations 99 and 100). The alkylpentaboranes are sensitive to air oxidation and to hydrolysis, the derivatives with smaller alkyl groups resembling pentaborane(9) more closely in this respect;[242] 6-$PhCH_2$-$B_{10}H_{13}$ is more stable toward hydrolysis than is the parent $B_{10}H_{14}$.[239]

$$(CH_2)_2B_4H_8 + 12H_2O \longrightarrow HOCH_2CH_2OH + 4B(OH)_3 + 9H_2 \quad (99)$$

$$(CH_2)_2B_4H_8 + 10MeOH \longrightarrow (MeO)_2BCH_2CH_2B(OMe)_2 + 2B(OMe)_3 + 9H_2 \quad (100)$$

The 1-methyl derivative of pentaborane(9) is thermally stable up to temperatures close to 200 °C, but at this temperature it rearranges to the 2-MeB_5H_8 isomer (Section 5.4.3.3.1). Flash thermolysis (500–600 °C) or electric discharge of alkylpentaboranes can give carboranes (Section 5.4.2.6.5).

5.4.3.3.4 *Polyborane carbonyl chemistry*

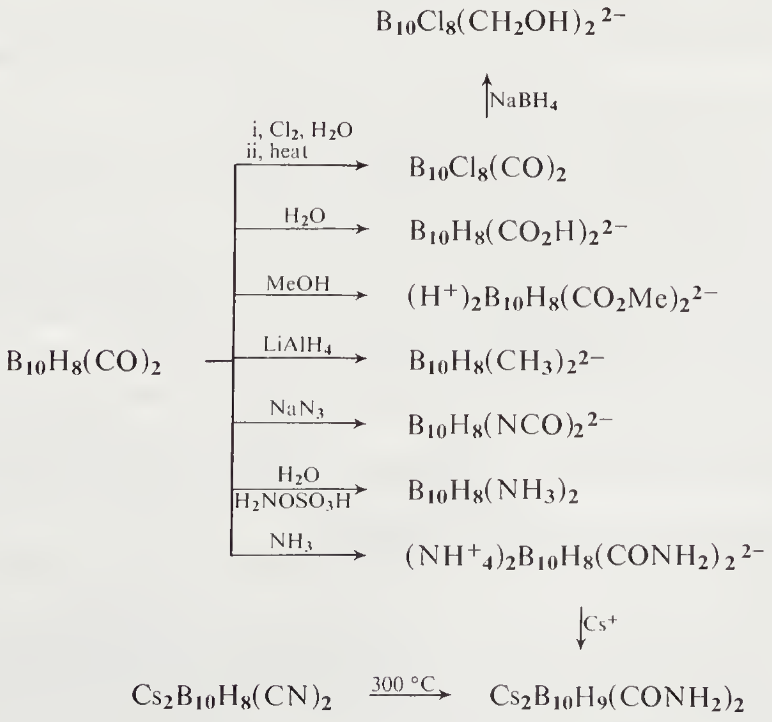
The polyborane carbonyl OCB_4H_8 is converted by CO displacement with Me_2NPF_2 to $Me_2NPF_2B_4H_8$, and in a similar reaction with PF_3 is converted to $F_3PB_4H_8$.[243] A reaction of OCB_4H_8 with ethylene or 2-butene displaces the OC to give $(RCH)_2B_4H_8$ (R = H, Me)[244] (see Sections 5.4.3.2.2 and 5.4.3.3.3). Some basic reagents attack OCB_4H_8 to form nonvolatile materials without liberation of carbon monoxide (equations 101–103).[243,245] On the basis of largely chemical evidence, the structure of $B_4H_8CO{\cdot}2NH_3$ appears to be ionic, $[NH_4][B_4H_8CONH_2]$.[245]

$$OCB_4H_8 + Me_3N \longrightarrow Me_3NB_4H_8CO \quad (101)$$

$$OCB_4H_8 + Me_2O \longrightarrow Me_2OB_4H_8CO \quad (102)$$

$$OCB_4H_8 + 2NH_3 \longrightarrow B_4H_8CO{\cdot}2NH_3 \quad (103)$$

The carbonyl derivatives of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ can be used to form carboxylic acids, esters and amides in a chemistry that parallels that of BH_3CO (Scheme 4).[233,234,246]



Scheme 4

5.4.3.3.5 Other chemistry of the organopolyboranes

A monoethyldecaborane mixture containing 40% 1-Et$B_{10}H_{13}$ and 60% 2-Et$B_{10}H_{13}$ reacts with triethylamine in benzene solution to give an 85% yield of $[Et_3NH^+]_2$[2-Et-*closo*-$B_{10}H_9^{2-}$].[247] Carborane formation from decaborane and acetylenes and from $B_{10}H_{13}CN^{2-}$ or $B_{10}H_{12}CN^-$ has been reviewed in Sections 5.4.2.6.1 and 5.4.2.6.2.

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5.5

Metallacarboranes and Metallaboranes

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5.5.1 INTRODUCTION AND HISTORICAL BACKGROUND

5.5.1.1 Metallacarboranes

The boron hydrides, or polyboranes, are the original cluster compounds as well as the first known family of electron-deficient, 'non-classical' covalent molecules.[1] The pioneering work of Stock[1e] on the boranes in the early years of the twentieth century actually preceded by several decades the discovery of an extensive series of metal clusters, although it was not until the 1950s that the cage-like stereochemistry of the boranes was revealed by X-ray diffraction methods.[1a] More recently has come the recognition that the boranes, metal clusters and many organometallic clusters have a close electronic and structural relationship, and that much of the experimental and theoretical work on boron cage systems can be used to advantage in understanding other classes of molecular polyhedra.[2]

Since the boranes and metallic clusters have much in common structurally, it is not surprising to find that intermediate species exist in which one or more metal atoms reside in a borane framework. What is truly remarkable, however, is the enormous variety of stable molecular structures that have emerged, and the complex, novel stereochemistry that has evolved, in the short interval of 17 years since the first such compounds were described.[3] The majority of the presently known metal–boron clusters contain skeletal carbon atoms and are known as metallacarboranes[4] (variously written 'metallocarboranes' and 'metallacarbaboranes'). These compounds form the central theme of this review, together with closely related metallaboranes[4c,4d,5] (metal–boron cages having no carbon in the framework). In general, this chapter will deal with boron clusters of four or more vertices containing at least one skeletal metal atom; metal–carborane or –borane σ-complexes in which the metal is outside the polyhedron are dealt with in other chapters of this work.

Although compounds with transition metal–boron bonds had been known for many years, the first true metallaboron clusters (in which a metal atom is covalently bound into a polyhedral borane framework) were 12-vertex metallacarboranes derived from the icosahedral carboranes[6] 1,2- and 1,7-$C_2B_{10}H_{12}$ by Hawthorne *et al.* in 1965.[3,7] These workers utilized abundant supplies of $B_{10}H_{14}$, a stable solid borane of which tons had been stockpiled by the U.S. Government for a rocket-fuel program (later abandoned), to generate 1,2-$C_2B_{10}H_{12}$ by a previously published method.[8] This compound and its 1,7-isomer, obtained by thermal rearrangement at 450 °C, are extremely stable to chemical and thermal degradation and had been subjected to intensive study by industrial groups who were developing novel carborane–siloxane polymers having extraordinary stability.[6] The carboranes are essentially impervious to attack by even the strongest acids, but strong bases effect removal of one boron atom, giving a $C_2B_9H_{12}^-$ ion which is an 11-vertex icosahedral fragment with a B—H—B hydrogen bridge on its open face. Treatment of 1,2- or 1,7-$C_2B_9H_{12}^-$ (or the conjugate base $C_2B_9H_{11}^{2-}$ ions) with metal reagents yields stable metallacarboranes in which the metal atom fills the 'hole' and completes a 12-vertex MC_2B_9 icosahedral cage (Figure 1).[4b,7]

Thus were born the icosahedral metallacarboranes, which at the time were viewed primarily as metal sandwich complexes analogous to the metallocenes with $C_2B_9H_{11}^{2-}$ ligands replacing $C_5H_5^-$. Metallacarboranes of the types $[(C_2B_9H_{11})_2M]^{n-}$ or $[(C_2B_9H_{11})M(C_5H_5)]^{m-}$, incorporating most of the transition metals, were eventually prepared, and a significant finding was that most of them are *more stable than their metallocene counterparts.* Indeed, in several cases such as $[(1,2\text{-}C_2B_9H_{11})_2Cu^{II}]^{2-}$, the analogous metallocene is not even known. The inherent stability of the metallacarborane frameworks allowed extensive investigation of their chemistry and led to the discovery of synthetic methods, discussed in Section 5.5.3, which permit additional metal atoms to be placed in the polyhedral framework and allow the cage to be expanded or contracted.

Development of the chemistry of the smaller (sub-icosahedral) metallacarboranes was hampered for a time by the limited availability of small carborane starting materials, but in recent years this situation has changed significantly, as will be described later. By stepwise degradation of 1,2- or 1,7-$C_2B_{10}H_{12}$ it is possible to obtain the intermediate-sized *closo*-carboranes $C_2B_9H_{11}$, $C_2B_8H_{10}$, $C_2B_7H_9$ and $C_2B_6H_8$, as well as open-cage carboranes such as $C_2B_7H_{13}$ and $C_2B_9H_{13}$.[6] Introduction of metal atoms into these systems generates mono- and di-metallacarboranes with as few as nine vertices, *e.g.* $CpCoC_2B_6H_8$.[4b,7] However, this chemistry was ultimately based on the $C_2B_{10}H_{12}$ carboranes and their precursor, $B_{10}H_{14}$; the production of six- and seven-boron species by degradation of 10-boron starting materials is inherently inefficient, and this line of investigation seems to have been abandoned in recent years.

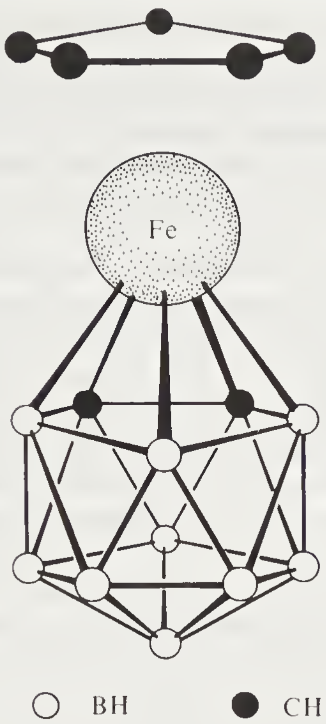


Figure 1 Structure of 1,2,3-$CpFeC_2B_9H_{11}$

An obvious route to small metallacarboranes, *a priori*, is the insertion of metals into small carboranes. The first such process, reported by Howard and Grimes in 1969, involved the treatment of the three-carbon *nido*-carborane 2-$MeC_3B_3H_6$[9] or its anion $MeC_3B_3H_5^-$ with manganese reagents to give 1,2,3,4-$(CO)_3MnMeC_3B_3H_5$, a yellow solid (Figure 2). However, as $C_3B_3H_7$ derivatives are not readily available, attention turned to the more accessible *nido*-carborane 2,3-$C_2B_4H_8$ and its derivatives as precursors to metallacarboranes. Following the synthesis in 1969 of a gallium species, 1-Me-1-$GaC_2B_4H_6$, by direct reaction of $GaMe_3$ and $C_2B_4H_8$,[10] the insertion of iron into $C_2B_4H_8$ to give *nido*-$(CO)_3FeC_2B_3H_7$ and *closo*-$(CO)_3FeC_2B_4H_6$ was reported.[11] Subsequently, the chemistry of $C_2B_4H_8$-based metallacarboranes has been explored in detail and has led to the discovery of oxidative ligand fusion (see Section 5.5.3.1.10) and the exploration of tetracarbon carborane and metallacarborane chemistry.[4c] In the course of this work the first neutral 'triple-decker sandwich' species, containing a planar C_2B_3 central ring coordinated to two metal atoms, were synthesized.[12]

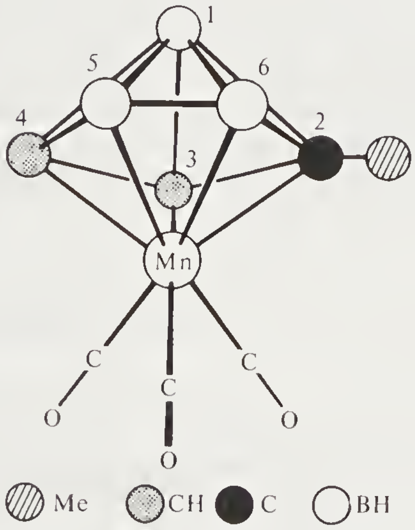


Figure 2 Proposed structure of 2-Me-1,2,3,4-$(CO)_3MnC_3B_3H_5$

The small *closo*-carboranes $C_2B_3H_5$, $C_2B_4H_6$ and $C_2B_5H_7$ were also utilized as starting materials for metallacarborane synthesis, although to a much lesser extent than $C_2B_4H_8$ owing to problems of availability. Thus, one can open the $C_2B_5H_7$ cage by reduction with sodium and insert metal units (*e.g.* $CpCo^{III}$ or $CpFe^{II}$) to generate mono- and di-metallacarboranes; in the cobalt reaction one obtains polyhedral systems of 7–10 vertices, thereby overlapping (in terms of cage size) the family of metallacarboranes derived from the icosahedral $C_2B_{10}H_{12}$ systems.[4a]

Metals can also be inserted into *closo*-carboranes directly, without prior opening of the cage, as has been demonstrated[13,14] for all members of the $C_2B_{n-2}H_n$ series from $n = 5$ to 12. Reactions of this type, utilizing neutral metal reagents such as $CpCo(CO)_2$ and $Pt(\textit{trans}\text{-stilbene})(PEt_3)_2$, led to a number of novel metallacarboranes including six-vertex *closo* systems (the smallest known) as well as species containing up to three metals per cage, in which, significantly, the metal atoms occupy adjacent locations in the framework. This observation will be elaborated on at a later point in the review.

At the present time, a decade and a half after the inception of the field, the range of structural types in the metallacarboranes is impressive and seems without visible limit. Hundreds of compounds have been prepared and fully characterized, and over 100 have been structurally established by X-ray crystallography (see Table 2, p. 533). Characterized systems range in size from 6 to 14 vertices, and in composition from one to three metal atoms and one to four carbon atoms, per cage; however, the vast majority have two carbons and no more than two metal atoms. For the most part, the structures and chemistry of the two-carbon systems are reasonably well understood and follow more or less rational patterns (an exception is the thermal rearrangement of *closo*-metallacarboranes, which involves migrations of metal atoms that are controlled by subtle factors not yet clearly defined). In the past four or five years, studies of the dicarbon 12-vertex metallacarboranes have centered on certain types of complexes that exhibit activity as homogeneous catalysts in hydrogenation, hydrosilylation and isomerization of alkenes. In virtually all cases, the active species are *closo* systems containing RhH, RuH_2 or IrH_2 groups.[15]

A major current problem in metallacarborane chemistry, and indeed in that of clusters generally, is the influence of skeletal electron population and distribution on molecular structure (see following Section). Metallacarboranes that are 'electron-rich' or 'electron-poor' (*i.e.* contain other than $2n + 2$ skeletal valence electrons) exhibit an intriguing and frequently unpredictable stereochemistry which often is markedly influenced by local electronic effects in particular regions of the cage structure. This is especially evident in metallacarboranes of the late transition metals such as Ni, Pt and Pd, and in the four-carbon metallacarboranes, most of which show pronounced structural distortions or highly irregular cage geometries; in general, these are traceable to electronic factors but in some cases kinetic effects are evident, as will be shown later.

5.5.1.2 Metallaboranes

The synthesis of polyhedral metallaboranes lacking framework carbon atoms, like that of the metallacarboranes, developed originally from $B_{10}H_{14}$ chemistry, with several of the first such species reported by Greenwood and co-workers,[5a,16] *e.g.* equation (1). Subsequently, a number of complexes of the formula $M(B_{10}H_{12})_2^{2-}$ (M = Mg, Zn, Cd, Ni) were also prepared,[5a] and metallaboranes containing other ligands derived from $B_{10}H_{14}$ were reported, *e.g.* $(Et_3P)_2Pt(H)$-$B_9H_{10}S$, $(Et_3P)_2PtB_8H_{12}$ and $[(B_{10}H_{10}S)_2Co]^-$. The structures of several of these large species are depicted in Section 5.5.7.2 (see also Table 3, p. 536). Although this early work was reported at about the same time as the first metallacarborane syntheses (*ca.* 1965–1971), there were only a few reported metallaborane species. Information on structure was scanty, and not for several years did clear patterns of structure and bonding in the polyhedral metallaboranes begin to emerge. Consequently, in comparison with the metallacarborane field, metallaborane chemistry was slow to develop and even now appears to lack the coherence and more or less rational organization of the metallacarborane family (this perception, however, is gradually changing as more of the pieces of the overall puzzle fall into place).

$$2B_{10}H_{14} \quad + \quad 2Et_2Cd \xrightarrow{Et_2O} [(Et_2O)_2CdB_{10}H_{12}]_2 \quad + \quad 4C_2H_6 \qquad (1)$$

In recent years, progress in the metallaborane area has accelerated, with the synthesis of the first closed polyhedral (*closo*) metallaboranes[17,18] (*e.g.* $Cp_2Co_2B_4H_6$, $Cp_3Co_3B_3H_5$, $Cp_3Co_3B_4H_4$ and $Cp_2Ni_2B_{10}H_{10}$). 'Sandwich' complexes such as $1\text{-}CpFeB_5H_{10}$[19] and $1\text{-}CpCoB_4H_8$[17] which contain planar borane ligands have been characterized, as have metal–boron 'hybrid' clusters with high M/B ratios, *e.g.* $Cp_4Co_4B_4H_4$[17b,20] and $Cp_4Ni_4B_4H_4$.[21] Intriguing and structurally unprecedented complexes incorporating beryllium, *e.g.* $B_5H_{10}BeBH_4$ and $(B_5H_{10})_2Be$, have been reported by Gaines,[22] several novel small ferraborane species by Fehlner[23] and by Shore,[24] and a number of thia- and selena-borane–metal complexes by the Rudolph[25] and Todd[26] groups. In much of this work (to be described in later sections) the borane reagents were small boron hydrides such as B_5H_9, B_2H_6 and B_6H_{10}, or their conjugate base anions, *e.g.* $B_5H_8^-$ or $B_6H_9^-$. Many of the characterized metallaboranes have proved surprisingly air-stable, in contrast to their boron hydride counterparts which are structurally analogous. Thus, 2-$CpCoB_4H_8$, a red air-stable crystalline solid,[17] is formally derived from B_5H_9 by replacement of a basal BH unit by CoCp; the contrast with B_5H_9, a volatile liquid that oxidizes explosively in air, is remarkable.

Current investigations of metallaborane chemistry range over a broad area and overlap a number of other fields, including the metal clusters, organometallic clusters, boron hydrides, metallocenes, homogeneous catalysts, organotransition metal reagents and transition metal hydrides. There is also, of course, a close relationship to the metallacarboranes and this will be accentuated in the Sections to follow.

The entire field of metallaboron cluster chemistry, including the metallaboranes and metallacarboranes, is advancing on so many fronts simultaneously that no one review can hope to do more than provide a snapshot of things as they are at the moment of writing, with perhaps some indication of the directions of future movement.

5.5.2 PRINCIPLES OF STRUCTURE AND BONDING

5.5.2.1 Introduction

Boranes and their heteroatom-substituted derivatives, including metallaboranes and metallacarboranes, are 'non-classical' molecules,[1] in that the bonding in the cage skeleton cannot be described entirely in terms of ordinary electron-pair bonds between each pair of bonded atoms. In general, there are fewer electrons than would be required for a classical Lewis structure, so that some type of multicenter bonding (distribution of a bonding electron pair over more than two atoms) is required. This so-called 'electron deficiency' has profound structural consequences and has forced truly revolutionary changes in the way chemists think about covalent bonding (it was in recognition of this broad impact that Lipscomb was awarded the 1976 Nobel Prize in chemistry for his contributions to borane structural chemistry).

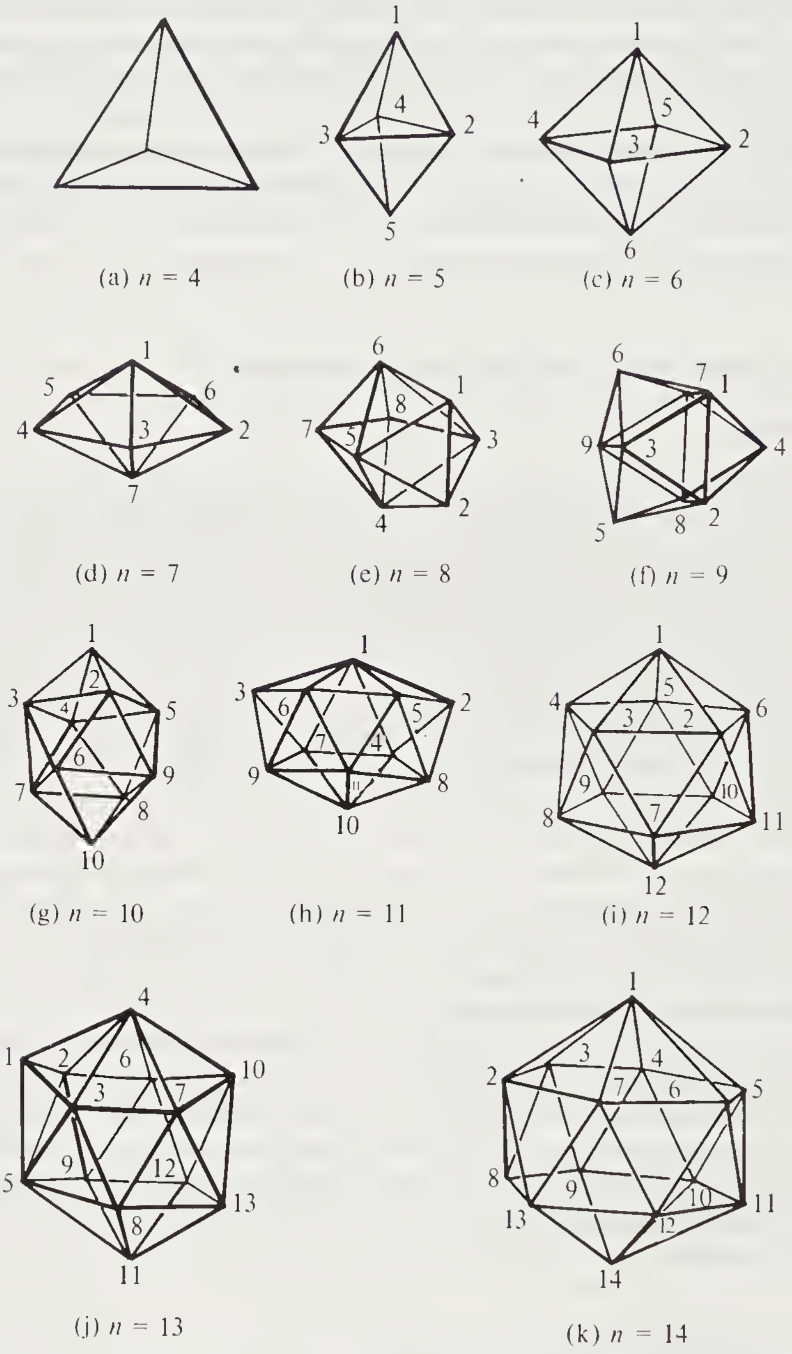
The term 'electron deficiency' when applied to boron cage compounds is an anachronism, a relic of an earlier era when the idea of multicenter bonding was novel and thought to be limited to a few unstable molecular oddities. It is, in fact, a highly misleading label, since most boranes actually have closed-shell electronic structures and are not at all, in any real sense, deficient in electrons. Indeed, few borane cage compounds exhibit any notable tendency to acquire electrons, and many of them (especially carboranes and metallacarboranes) compare favorably with hydrocarbons in thermal and chemical stability.

The bonding in boron cage compounds has been extensively discussed in books and review articles,[1,2,4,6,27] and a contemporary treatment of boranes as well as other clusters will be found in Chapter 1 of the present work. Consequently, the present discussion will be limited to an outline of basic principles having general applicability. The underlying philosophy throughout this Chapter is that boranes, carboranes and their metal-containing derivatives are but subclasses of the broader family of covalently bonded molecular clusters, and that there is no sharp division between boron and non-boron cage systems.

5.5.2.2 Structures of Polyhedral Boron Clusters

Boranes and heteroboranes are covalently bonded clusters with triangular faces. When *all* faces are triangular, the cluster is designated *closo*; polyhedra of this type (also known as deltahedra) are in general exceptionally stable and are characterized by extensive delocalization of electrons over the polyhedral surface. For this reason such systems have been described as aromatic, or more dramatically, superaromatic.[28] The properties of such *closo* species as 1,2-$C_2B_{10}H_{12}$ and the $B_{12}H_{12}^{2-}$ ion bear out the aromatic description very well, and hundreds of similar examples can be found among the metallacarboranes.

The common *closo* structures are depicted in Figure 3. Each of these geometries up to $n = 14$ is represented by known and characterized boron cage species, but some (such as the $n = 7$ and $n = 12$ cages) are much more common than others; thus, the lone example of a *closo* four-vertex boron cage is B_4Cl_4 (unless one counts the tricobalt species $(CO)_9Co_3BR$). The polyhedra in Figure 3 represent standard idealized geometries for n-vertex *closo* clusters, and are the established structures of the *closo* $B_nH_n^{2-}$ ions (n = 6–12) and the isoelectronic carborane series $C_2B_nH_{n-2}$ (n = 5–12). The 13- and 14-vertex polyhedra are presently known only in metallacarboranes, *e.g.* $CpCoC_2B_{10}H_{12}$ and $Cp_2Fe_2Me_4C_4B_8H_8$; polyhedra of still higher order have been predicted for the corresponding $B_nH_n^{2-}$ ions from MO calculations.[29] In large ($n \geqslant 12$) systems, instances have been found of kinetically stabilized geometries other than those depicted in Figure 3; examples will be given later in this discussion.



(a) n = 4 (b) n = 5 (c) n = 6

(d) n = 7 (e) n = 8 (f) n = 9

(g) n = 10 (h) n = 11 (i) n = 12

(j) n = 13 (k) n = 14

Figure 3 Geometries of *closo* polyhedra having 4 to 14 vertices, showing standard numbering system: (a) tetrahedron; (b) trigonal bipyramid; (c) octahedron; (d) pentagonal bipyramid; (e) dodecahedron; (f) tricapped trigonal prism; (g) bicapped square antiprism; (h) octadecahedron; (i) icosahedron; (j) docosahedron; (k) bicapped hexagonal antiprism

Many boron cluster compounds adopt *open-cage* geometries which can be regarded as *closo* systems with one or more vertices missing. Clusters with one, two or three vacant vertices are designated as *nido*, *arachno* and *hypho*, respectively, from the Greek words for nest, web and network (an interesting alternative nomenclature, not sanctioned by IUPAC, has been suggested by Lipscomb: *groucho*, *harpo*, *chico*, *zeppo* and *gummo*). Examples are shown in Figure 4. The majority of open-cage compounds contain 'extra' hydrogens, *i.e.* framework hydrogen atoms in excess of one per boron atom, and these usually adopt B—H—B bridging locations on the rim of the open face; in some cases they are found as BH_2 groups or (in carboranes) as CH_2 units. *In no known instance have hydrogen atoms been found in discrete, localized B—H—C bridges.*

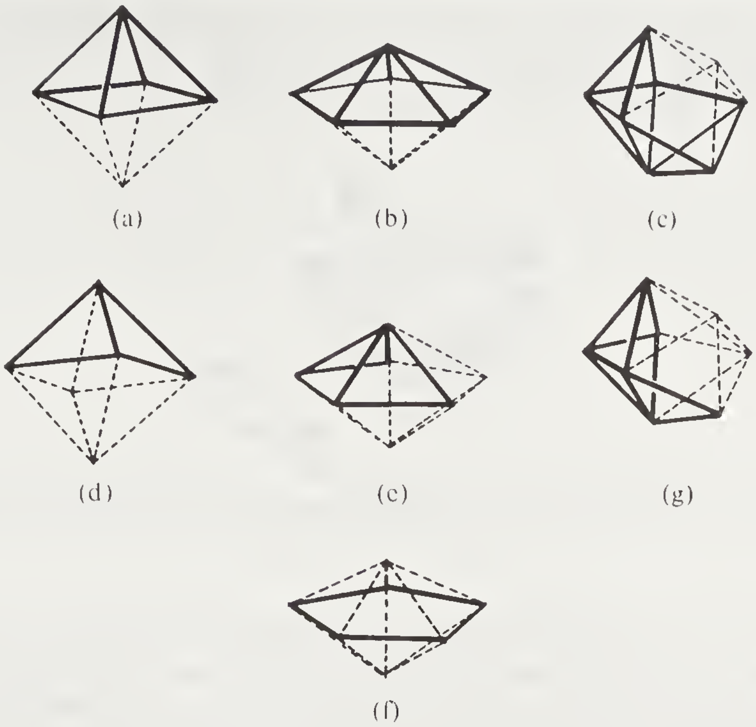
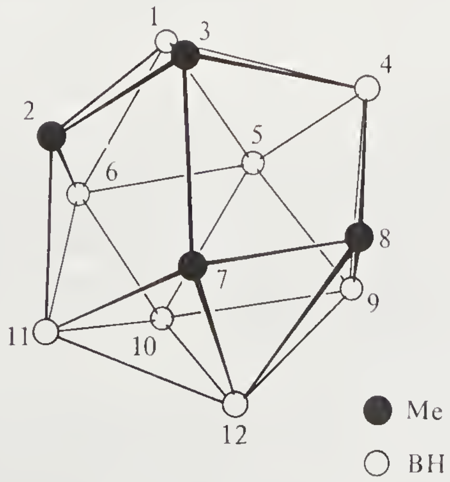


Figure 4 Examples of open polyhedra, with locations of 'missing vertices' shown by dashed lines: (a) square pyramid (*nido*); (b) pentagonal pyramid (*nido*); (c) 7-vertex *nido* cage (one possibility); (d) dihedral or 'butterfly' cluster (*arachno*); (e) and (f) 5-vertex *arachno* clusters; (g) 6-vertex *arachno* cluster (one possibility)

Open-cage clusters deviate more widely from the idealized geometries than do the *closo* systems, and thereby tend to produce a much more complex stereochemistry. There are several reasons for this. First, there is often more than one distinguishable way to generate formally a *nido* system by removal of a vertex from a given *closo* cage. Second, the placement of bridge hydrogens may strongly influence the locations of boron or other heavy atoms in the framework.[30] Third, in open cages the available pathways for rearrangement are apt to be more restricted and entail higher activation energies than in *closo* systems; hence one sees many examples of kinetically stabilized *nido* and *arachno* species whose geometries are quite far from the ideal, thermodynamically preferred arrangement. Fourth, open cages in general have less electron delocalization than *closo* systems (owing to the presence of a 'hole' in the polyhedral surface) and hence local electronic effects may profoundly affect the cluster shape; this phenomenon is particularly common in tetracarbon carboranes and metallacarboranes, as will be seen later. Consequently, while many *nido* and *arachno* species can be regarded as fragments of the idealized *closo* polyhedra in Figure 3, a significant number of others require more complex descriptions. For example, the solid-state structure of $Me_4C_4B_8H_8$ (Figure 5)[60] contains a 12-vertex C_4B_8 polyhedron which can be viewed



$Me_4C_4B_8H_8$-A

Figure 5 Cage geometry of $Me_4C_4B_8H_8$

as a distorted icosahedron with two nonbonding C—C interactions. Even more unusual structures are found, such as that of $CpCoMe_4C_4B_7H_7$, isomer II (Figure 6),[43a] and there are many other examples of what we shall refer to as 'irregular' cage geometry.

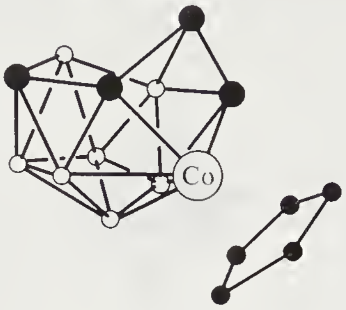


Figure 6 Cage geometry of $CpCoMe_4C_4B_7H_7$, isomer II; solid circles indicate carbon atoms, open circles boron; hydrogen atoms not shown

In addition to the *closo*, *nido*, *arachno* and *hypho* structural classes, there is another type of system which consists of a *closo* polyhedron with one or more triangular faces capped by a nonhydrogen (usually boron) atom. Few examples are known as yet, but Figure 7 illustrates the structure of $Cp_3Co_3B_4H_4$ in which a BH unit caps the Co_3 face of a *closo*-Co_3B_3 distorted octahedron.[36] As will be shown, this type of cage geometry is associated with a shortage or 'hyperdeficiency' of electrons relative to the normal *closo* system.

The structural types thus far discussed encompass not only the boranes but also, with few exceptions, the metallic and organometallic clusters, the majority of which are four-, five- and six-vertex *closo* systems. However, there are many cage structures among boranes and heteroboranes that are nearly unique to boron chemistry; this is true, for example, of all of the *closo* geometries in Figure 3 for $n \geqslant 10$. Thus, despite the hundreds of known icosahedral (12-vertex *closo*) boron species, only a single example of a non-boron icosahedral cluster has been found.

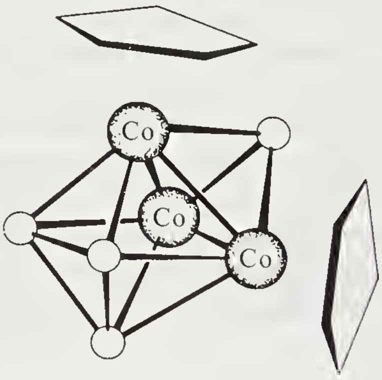


Figure 7 Structure of $Cp_3Co_3B_4H_4$; one cyclopentadienyl ligand is omitted for clarity

5.5.2.3 Bonding Descriptions

Borane cages have been approached in three basic ways. These are (1) localized valence-bond structures incorporating two- and three-center electron-pair bonds, (2) quantitative MO treatments of individual cluster systems, and (3) qualitative descriptions invoking skeletal electron-counting arguments. All three methods can be applied to metallaboranes and metallacarboranes, and each has special advantages for certain types of clusters. The last approach has, however, proved the more widely applicable and is particularly useful in emphasizing relationships between metallaboron clusters and other types of polyhedral cages.

Localized valence-bond arguments were developed by Lipscomb and co-workers for the boron hydrides,[1a] and are most useful in open-cage molecules where the number of resonance structures is minimal (Figure 8). In large cages, and particularly in closed polyhedral (*closo*) systems, there are usually many resonance forms, and localized bond descriptions may become unwieldy; moreover, it is often the case that individual resonance structures do not match the symmetry of the molecule particularly well, as, for example, in the *closo*-$B_nH_n^{2-}$ anions. In heteroboron cages there is the additional problem of dealing with the presence of non-boron atom(s) in the framework. However, in certain types of systems it is clear that localized bonding plays an important role in dictating structure; an example is the tetracarbon carboranes and metallacarboranes, where local carbon–carbon bonds in the framework often give rise to novel cage geometries. In such cases, localized valence-bond descriptions may be highly appropriate, and provide an approach to understanding reactivity and calculating charge distributions.[1a] Even in *closo* systems, localized-bond methods have been usefully applied with the aid of computers to calculate relative stabilities of isomers as well as charge distributions in carborane polyhedra.[1a,28a,29b] In general, however, localized treatments are of limited utility with respect to metal–boron cage systems.

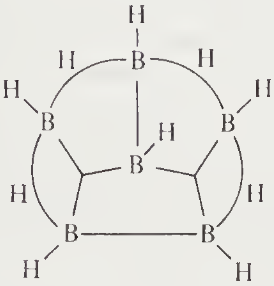


Figure 8 Localized-bond description of B_6H_{10}, showing two-center B—B and B—H bonds and three-center B—B—B and B—H—B bonds

Detailed MO calculations have been extensively carried out for boranes and carboranes, but very few metal-containing boron systems have been quantitatively treated. The inclusion of transition metals into MO calculations substantially increases the complexity and expense, and simplifying assumptions are necessary; in some cases these have led to published conclusions that are difficult to reconcile with observation. Nevertheless, quantitative treatments of such molecules can be of value in assessing the nature of the cage bonding, and many more such studies are needed. Reference to MO calculations on specific metallaborane and metallacarborane systems will be made at appropriate points in this review. For general purposes of discussion, organization, rationalization and prediction of metal–boron structures, the best approach is given by the skeletal electron-counting rules which we shall now describe.

5.5.2.4 Correlation of Polyhedral Structure and Skeletal Electron Population

A major contribution to cluster chemistry was the development by several groups[2,27] of a correlation between cage geometry and the number of valence electrons in the skeletal framework. In this approach, which was first explicitly described and applied to metal-containing systems by Wade[31] in 1971 (although it was implicit in the work of Lipscomb[32] on boranes and carboranes nearly two decades earlier), the crucial assumption is that the bonding in the polyhedral surface can be regarded as separate and distinct from the bonds to external ligands. Thus, a borane cluster is viewed as a collection of BH units in which the individual B—H bonds are localized; the remaining electrons are used to bind the BH groups together *via* molecular orbitals extending over the polyhedral surface. Since a boron atom utilizes one orbital and one electron in its bond to hydrogen, *each BH unit has available three orbitals and two electrons for bonding in the cage framework*. There are thus $3n$ atomic orbitals for cage bonding in a $(BH)_n$ cluster, and it has been shown that, in general, these will generate $n + 1$ *bonding* molecular orbitals provided the cluster is *closo*, *i.e.* a complete triangulated polyhedron.[2] Such a cluster will, therefore, accommodate $n + 1$ electron pairs or $2n + 2$ electrons in the skeletal framework.

A direct consequence of this generalization is that neutral B_nH_n polyhedra should not be stable, since they contain only $2n$ skeletal electrons, but that $B_nH_n^{2-}$ dianions should exist as stable *closo* systems. This is indeed the case for $B_nH_n^{2-}$ ions from $n = 6$ to 12 and for the isoelectronic $C_2B_{n-2}H_n$ carborane series from $n = 5$ to 12, as was noted earlier. The four-vertex cluster is a special case in which, for symmetry reasons, the predicted number of bonding molecular orbitals is six[2] and hence the optimal skeletal electron count is 12. Most four-vertex metallic and organometallic clusters are 12-electron systems; B_4Cl_4, the only known four-vertex B_4 cluster, is a *formal* eight-electron cage but there are indications that halogen substituents on boron clusters can directly affect the electron structure of the framework by extensive back-bonding into the cage skeleton.[27a,33]

It is not yet clear what is the upper limit of the '$2n + 2$ rule'. MO studies of large

$B_nH_n^{2-}$ polyhedra suggest that for certain values of n (*e.g.* 16, 19, 22), *closo* geometries may be favored for the *neutral* species rather than the anion; on the other hand, $B_{17}H_{17}^{2-}$ and $B_{14}H_{14}^{2-}$ are predicted to be particularly stable.[29b] However, no polyhedral borane clusters larger than 12 vertices and containing only boron in the framework have yet been prepared.

Open-cage clusters can be dealt with by this approach in a straightforward manner, since *removal of a vertex from a closed polyhedral system does not change the number of skeletal bonding molecular orbitals.*[2] Thus, both an octahedral cluster (*e.g.* $B_6H_6^{2-}$) and a square-pyramidal cluster (*e.g.* $B_5H_5^{4-}$) will have seven bonding MOs. This general conclusion is supported by arguments which are set forth in detail elsewhere,[1a,2] and by an extensive body of experimental evidence. As a consequence, a *nido* cluster (defined earlier as a *closo* cluster with one missing vertex) will have the same number of skeletal electron pairs as the parent *closo* polyhedron from which it is derived; since there is one less atom in the cage the requirement is $n + 2$ pairs, or $2n + 4$ electrons. By the same reasoning, an *arachno* cage (a *closo* polyhedron less two vertices) will have $n + 3$ electron pairs or $2n + 6$ electrons. To use the above illustration, the species $B_6H_6^{2-}$, $B_5H_5^{4-}$ and $B_4H_4^{6-}$ each have 14 skeletal electrons (derived by subtracting the localized B—H bonding pairs from the total number of valence electrons in the molecule), corresponding respectively to $(2n + 2)$, $(2n + 4)$ and $(2n + 6)$ electrons. Thus one expects $B_6H_6^{2-}$ to be *closo*, $B_5H_5^{4-}$ to be *nido* (a square pyramid) and $B_4H_4^{6-}$ to be *arachno* (either a square ring or a 'butterfly' cluster, depending on whether the two vacant vertices in the octahedron are adjacent or nonadjacent). As noted, $B_6H_6^{2-}$ is indeed an octahedron; the latter two species are known in protonated form as the neutral boranes B_5H_9 and B_4H_{10}, which have the predicted geometries (Figures 4a and 4d, respectively).

Clusters containing *fewer* than $2n + 2$ skeletal electrons, which have been labeled 'electron-poor' or 'electron-hyperdeficient',[34] constitute a small but growing class. It was shown long ago from MO arguments[35] that if one caps the triangular face of a *closo* polyhedron, the number of bonding MOs in the cage does not change; thus a monocapped octahedron and a normal (uncapped) octahedron each have seven framework bonding MOs. Hence the expected structure of a 7-vertex, 14-electron cluster is a capped octahedron, and this is indeed observed[36] in $Cp_3Co_3B_4H_4$ and $Os_7(CO)_{21}$ (the prototype borane, $B_7H_7^0$, has not been prepared, nor are there currently any known examples of capped polyhedral clusters containing only boron or carbon atoms in the framework). The general rule, then, is that a $2n$-electron cluster will adopt the shape of a *closo* polyhedron of $n - 1$ vertices, one face of which has been capped by an additional framework atom.

The principles outlined above, which have become popularly known as 'Wade's rules' (although Rudolph, Williams, Mingos and others have contributed to their development and extension) are readily applied to boron clusters containing heteroatoms. Carborane frameworks contain CH (or CR) units which contribute three electrons and three orbitals to cage bonding; similarly, an NH group is a four-electron donor, as is a sulfur atom if two electrons are assigned to an exo-polyhedral lone pair. For main group elements in general, the number of electrons (e) donated to skeletal bonding is $e = v + x - 2$, where v is the number of valence shell electrons on the neutral atom and x is the number of electrons supplied by the ligand.[2] Thus, for BH, with $v = 3$ and $x = 1$ we have $e = 2$, while a 'bare' nitrogen atom has $v = 5$ and $x = 0$ and is therefore a three-electron donor.

For transition metals, matters are different to the extent that there are nine valence orbitals rather than four as with first-row main group elements. However, the number of orbitals contributed to skeletal bonding is still three (symmetry considerations usually preclude the involvement of more than three orbitals, and full incorporation of the metal into the polyhedral framework requires no less than three). The six remaining metal orbitals are then available for bonding to external ligands such as CO, C_5H_5 or PR_3, and for storage of 'nonbonding' electron pairs. Since these six orbitals are usually filled (*i.e.* the 18-electron rule is satisfied), the electron donation from a transition metal group to the cage is given by $e = v + x - 12$. For example, an $Fe(CO)_3$ moiety has $v = 8$ and $x = 6$ and hence is a two-electron donor, as is CoCp with $v = 9$ and $x = 5$. It will be noted that both $Fe(CO)_3$ and CoCp are formal analogues of BH, and hence can substitute for BH in borane cage systems; hundreds of compounds supporting this analogy have been prepared.

Table 1 lists some typical cluster groups that are commonly encountered in metallaborane and metallacarborane systems, together with their formal skeletal electron contributions. The general procedure for predicting cluster geometry is as follows.

1. Determine the sum of skeletal electron donations for all groups occupying vertices in the n-vertex cage, including one electron for each 'extra' hydrogen atom (hydrogens are not, however, included in the n vertices since they do not affect the number of skeletal bonding MOs).
2. If face-bridging or edge-bridging carbonyl groups are present, include two electrons for each of these (CO groups, like hydrogen, are not included in the value of n).

Table 1 Common Polyhedral Cluster Units

Unit	*Electrons contributed to framework bonding*
BH	2
CH	3
NH	4
N:, P:[a]	3
S:[a]	4
CoCp	2
$Ni(CO)_2$	2
$Ni(Ph_3P)_2$	2
$Fe(CO)_3$	2
NiCp	3
$Co(CO)_3$	3
$Ni(CO)_3$	4

[a] Electron lone pair is directed outward from the cage framework and is not involved in skeletal bonding.

3. If the cluster is electrically charged, adjust the electron count accordingly.
4. Assign the cluster a capped-*closo*, *closo*, *nido*, *arachno*, or *hypho* geometry corresponding to a skeletal electron count of $2n$, $2n + 2$, $2n + 4$, $2n + 6$ or $2n + 8$ respectively.
5. 'Extra' hydrogen atoms in metallaboranes are placed in B—H—B or, preferably, M—H—B bridges on the open face; if the molecule is *closo*, the extra hydrogens will probably be associated with an edge or face involving a skeletal metal atom. In carboranes and metallacarboranes the above rules usually hold, but in large ($n \geqslant 12$) cages, extra hydrogens occasionally are found in $—CH_2—$ or —CHR— bridging units.

These considerations will in most cases yield at least a correct classification of the cage skeleton, if not the specific cage geometry. The placement of carbon, metal and other heteroatoms in the cage skeleton depends largely on the method and conditions of synthesis, and hence cannot be predicted from general rules. However, certain generalizations regarding *thermodynamically favored* isomers have been deduced from thermal isomerization studies, *e.g.* skeletal carbon atoms tend to prefer low-coordinate vertices with a minimum of carbon–carbon interaction.[4a–c] The thermodynamic preferences of metal atoms are more complex and, at present, largely unpredictable, as will be made clear in specific cases. Several examples will illustrate the application of these structural principles.

$CpCoB_9H_{13}$. The CoCp unit is a two-electron donor, as are the nine BH groups. The 20 electrons from these sources are added to the four contributed by the four extra (in this case, bridging) hydrogens, to give a total of 24 framework electrons. Since $n = 10$, the CoB_9 system has $2n + 4$ electrons and is of the *nido* type; this is in agreement with the structures of the three known isomers, each of which consists of a *closo* 11-vertex polyhedron (Figure 3h) from which the high-coordinate vertex has been removed. Figure 9 depicts the structure[37] of the isomer in which the metal occupies the 5-vertex. This cobaltaborane, as well as its 2- and 6-isomers, are isoelectronic and isostructural with $B_{10}H_{14}$, reflecting the BH/CoCp analogy referred to above.

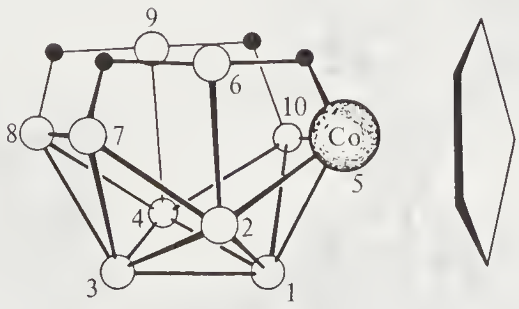


Figure 9 Structure of $5\text{-}CpCoB_9H_{13}$

$CpCoB_9H_9C{\cdot}NMe_3$. The $C{\cdot}NMe_3$ group formally contributes four electrons to the CoB_9C skeleton, so that the system is an 11-vertex, 24-electron ($2n + 2$) *closo* species. Its structure[38] (Figure 10) is in excellent agreement with this analysis.

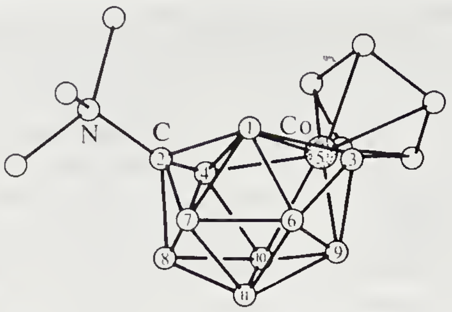
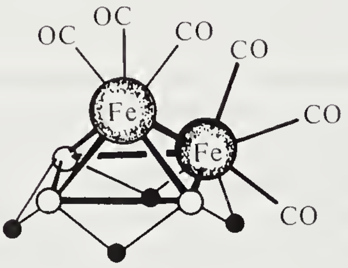


Figure 10 Structure of $CpCoB_9H_9C{\cdot}NMe_3$

$\{(CO)_3Fe\}_2B_3H_7$. Each $Fe(CO)_3$ and BH unit supplies two electrons, and there are four extra hydrogens. The molecule is therefore a 14-electron, five-vertex, $2n + 4$ system for which *nido* geometry is expected. The known structure (Figure 11),[39] allowing for distortions introduced by the size difference between boron and iron, is a square pyramid as predicted; the analogous borane is B_5H_9, demonstrating in this case the $BH/Fe(CO)_3$ isoelectronic relationship.



○ BH

Figure 11 Structure of $\{(CO_3)Fe\}_2B_3H_7$

$(CO)_3MnC_3B_3H_6$. The contributions of one electron from $Mn(CO)_3$, three from each CH, and two from each BH make this a seven-vertex, 16-electron ($2n + 2$) *closo* polyhedron, in conformity with the structure of its 2-methyl derivative (Figure 2), as deduced from NMR spectra.[9]

$(Me_2C_2B_3H_5)CoH(Me_2C_2B_4H_4)$. The cobalt atom occupies a vertex common to two cages (an arrangement designated by the prefix '*commo*' in current nomenclature). With six of its nine valence electrons assigned to 'nonbonding' orbitals, the cobalt atom and its attached hydrogen supply a total of four electrons to the two cages, or two per cage. Thus the molecule consists of a seven-vertex CoC_2B_4 *closo* polyhedron and a six-vertex CoC_2B_3 *nido* cage (containing two B—H—B bridges) joined at cobalt. This structure has been confirmed in an X-ray diffraction study of its 5-cobaltocenium derivative (Figure 12), in which the CoH proton is absent.[40]

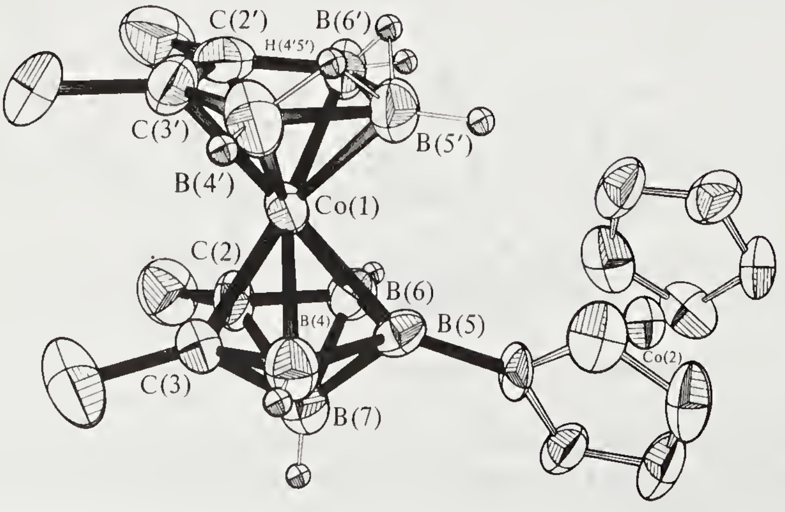


Figure 12 Structure of $(Me_2C_2B_3H_5)Co(Me_2C_2B_4H_3)$-$(C_5H_4)Co(C_5H_5)$

$Cp_2Co_2C_4B_6H_{10}$. The electron count is 28 (two from each BH and CoCp and three from each CH), so that *nido* geometry is expected for this 12-vertex, $(2n + 4)$-electron system. Actually, at least three *different* types of cage have been identified for various isomers of this compound (Figure 13).[41] Moreover, for 12-vertex, 28-electron systems in general, no fewer than seven classes of cage geometry have been found (Figure 14).[4c,42,43] Since all of them can be described as 'open'

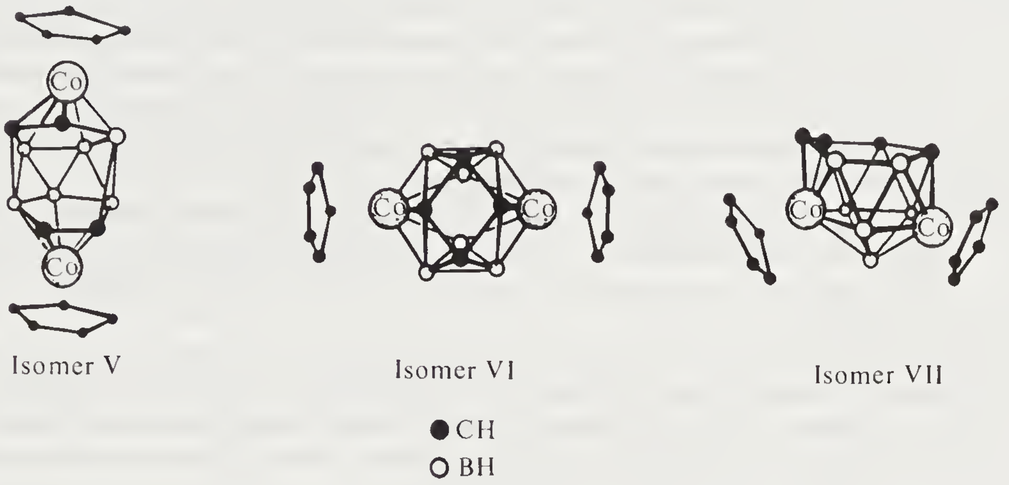


Figure 13 Isomers of $Cp_2Co_2C_4B_6H_{10}$; the structures of V and VII are established; that of VI is based on NMR evidence[41]

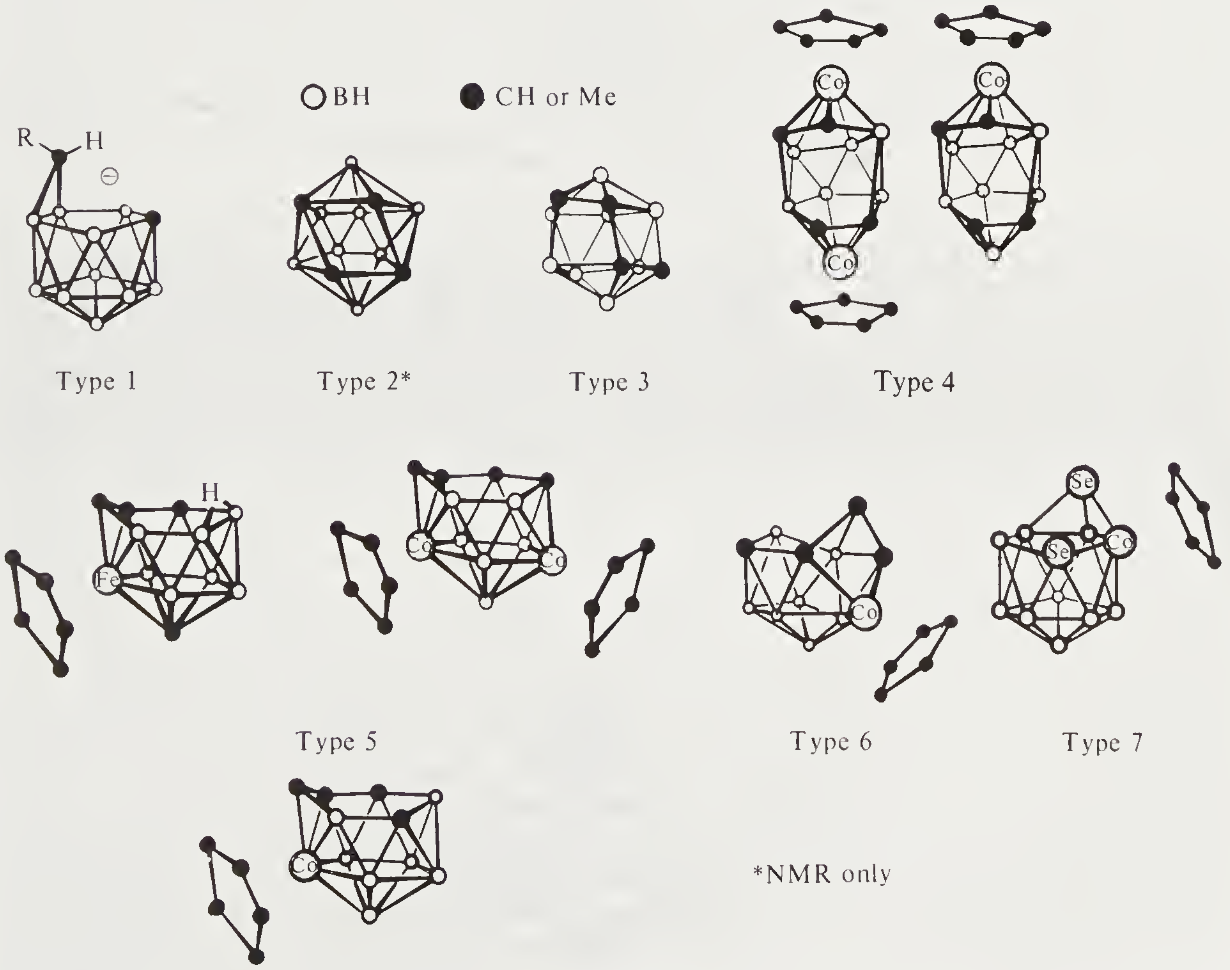


Figure 14 Structural types of 12-vertex, 28-electron (*nido*) cages;[43c] all cage structures depicted have been crystallographically characterized except that shown in Type 2. Type 1: $R_2C_2B_{10}H_{11}^-$ (R = Me, Ph). Type 2: proposed structure of $Me_4C_4B_8H_8$, isomer B, and of $Cp_2Co_2C_4B_6H_{10}$, isomer VI. Type 3: $Me_4C_4B_8H_8$, isomer A. Type 4: left, $Cp_2Co_2Me_4C_4B_6H_6$, isomer V; right, $CpCoMe_4C_4B_7H_7$, isomer I. Type 5: left, $CpFeMe_4C_4B_7H_8$; right, $CP_2Co_2C_4B_6H_{10}$, isomer VII; bottom, $CpCoMe_4C_4B_7H_7$, isomer III. Type 6: $CpCoMe_4C_4B_7H_7$, isomer II. Type 7: $CpCoSe_2B_9H_9$

(*i.e.* non-*closo*), the prediction based on skeletal electron count is basically valid, but clearly it is not of much value in this case as a guide to the actual structure. Here we encounter a major limitation of the electron-counting approach: it can classify clusters according to the *closo–nido–arachno* scheme, but may not necessarily predict the specific polyhedral structure. This is particularly true in large systems where local bonding interactions may strongly influence the molecular shape. Thus, in Figure 14 it will be noted that $Me_4C_4B_8H_8$ and $CpCoMe_4C_4B_7H_7$, which are cage-isoelectronic and are related by replacement of BH with CoCp in an apex position, have significantly different structures: the C_4B_8 cage has a central C—C bond and is a slightly distorted icosahedron, while in the cobalt species the corresponding C—C distance is nonbonding (2.85 Å) and the cage is much more open (note that if one replaces *both* apex BH units with CoCp, as in Figure 14, type 4, the structure is virtually the same as in the monocobalt complex). Clearly, while CoCp is formally analogous to BH for electron-counting purposes, the replacement of one by the other can have major structural consequences; in this case it would appear that the cobalt-skeletal carbon interaction is sufficiently localized that the central carbon–carbon link becomes depleted in electron density and is nonbonding.

The importance of local bonding effects in determining cage geometry appears to be greater in the larger clusters, especially those of $n \geqslant 12$. For small systems the structural possibilities are much more limited, so that, for example, a six-vertex, 16-electron (*nido*) cage is very likely to be a pentagonal pyramid.

$Me_5C_5Sn^+$. An important aspect of Wade's rules is that they are not limited to boron-containing species and thus serve to unify cluster chemistry.[2,27,44] In this molecule[45] the skeletal electron count is 16, derived from three per CMe group and two from tin (assigning a nonbonded lone pair to the tin atom) and subtracting one for the positive charge. Thus the prediction is a *nido* cage, as confirmed from a crystallographic study (Figure 15).

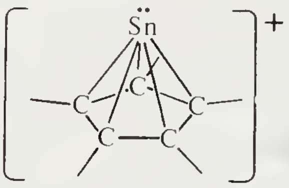


Figure 15 Structure of the $Me_5C_5Sn^+$ cation

$CpNiRu_3(CO)_8C_3EtMeH$. This cluster[46] consists of an $NiRu_3C_3$ seven-vertex polyhedron to which one formally assigns 16 framework bonding electrons, as follows. NiCp and the three carbon atoms are three-electron donors while each of the three $Ru(CO)_2$ units is formally a zero-electron contributor; however, the two 'extra' CO groups supply a total of four electrons (in terms of skeletal electron bookkeeping it makes no difference whether CO groups are terminal, edge-bridging or face-bridging). The anticipated geometry is therefore *closo*, as observed (Figure 16).

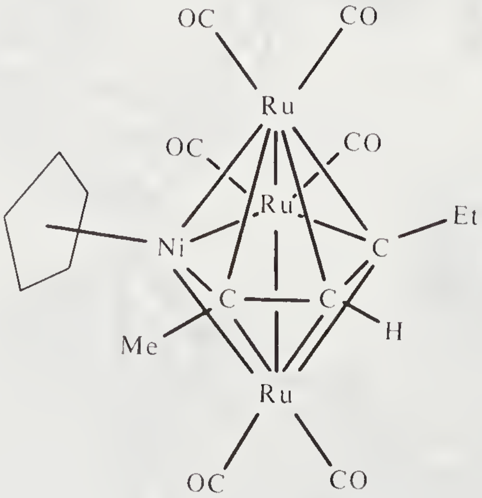


Figure 16 Structure of $CpNiRu_3(CO)_8C_3EtMeH$; two CO groups bridging the Ru—Ru edges have been omitted for clarity

5.5.2.5 Violations and Limitations of Wade's Rules

Reference was made earlier to the inability of the electron-counting formalism, at least in its simplest form, to take account of structural effects arising from local bonding interactions in the cage. Other situations have also been found to produce limitations, or even outright violations, of the theory. Since this subject is dealt with in detail by Wade in Chapter 1, we shall merely outline these at this point. The most conspicuous problems have involved the following situations.

1. The presence of heavy transition and post-transition elements frequently produces distortion from normal polyhedral geometry, as reflected, for example, in the irregular structures of many (but not all) platinum and palladium metallacarboranes.[47] The configuration of the metal in its formal oxidation state appears to be a major factor which must be taken into account for the heavier elements, as has been demonstrated by a comparison of metallacarborane structures involving d^6, d^8, d^{10} and $d^{10}s^2$ metals.[48]

2. Nonconforming cage geometry can be produced by kinetic stabilization of large clusters, which cannot rearrange to thermodynamically preferred structures under mild conditions; thus isomers of the $Cp_2Fe_2Me_4C_4B_8H_8$ system which form at room temperature are open-faced, despite the predicted *closo* geometry (14 vertices, 30 electrons). In this particular example, rearrangement to *closo* geometry does occur at high temperature,[4c,49] so that the room-temperature isomers do not, strictly speaking, 'violate' the rules, which implicitly apply only to thermodynamically favored structures. They do, however, illustrate a serious limitation of the electron-counting scheme in that its predictive accuracy is diminished when applied to large, kinetically stabilized cages.

3. A special situation arises in the case of eight-vertex polyhedra, which demonstrate a strong tendency to adopt *closo* (D_{2d} dodecahedral) geometry regardless of the skeletal electron count. This is clearly seen in $Cp_4Co_4B_4H_4$, a $2n$-electron system,[20] and $Cp_4Ni_4B_4H_4$, a $(2n + 4)$-electron cage,[21] both of which are *closo*, in violation of Wade's rules (the species $C_2B_6H_8$ and $B_8H_8^{2-}$ are also *closo* and are $(2n + 2)$-electron systems, in *accordance* with the rules). From theoretical and experimental studies[50] it is now reasonably clear that the source of the problem with eight-vertex polyhedra is the fact that the energies associated with several different geometries are very close, so that steric and/or other constraints may dominate in determining the structure. This can easily lead to fluxional behavior in solution, as is observed with $B_8H_8^{2-}$ and perhaps also with $Me_4C_4B_4H_4$. However, in more electron-rich eight-vertex clusters the anticipated cage-opening is seen, as in $Cp_4Fe_4S_4$ (20 electrons, *nido*), C_8H_8 (24 electrons, cube) and $(CO)_{12}Os_4O_4$ (24 electrons, cube).

4. In some cases, apparent violations of Wade's rules occur because of failure of metal atoms to obey the 18-electron rule. If the metal 'nonbonding' orbitals are incompletely filled, this should be taken into account in assigning the skeletal electron contribution.[48,51]

5. Certain clusters having an electron count corresponding to *nido* or *arachno* geometry adopt 'stretch-distorted' geometry, in which certain edges of a *closo* polyhedron are lengthened but the *closo* shape is preserved instead of opening the cage to produce a discrete open face.[44] This is observed in metal clusters such as $Cp_3Ni_3S_2$, which is an ostensibly *closo* trigonal bipyramid[52] despite its 17 $(2n + 7)$ skeletal electrons; the 'extra' five electrons actually occupy antibonding orbitals in the equatorial Ni—Ni edges, leading to a reduction in metal–metal bond order and lengthening of the Ni—Ni vectors. In the metallacarboranes a form of stretch-distortion occurs in MC_2B_9 12-vertex systems containing more than six metal d-electrons, which adopt 'slipped' geometry in which the metal is offset from the center of the pentagonal bonding face of the carborane ligand.[53] This phenomenon will be discussed further at later points in the Chapter.

6. Finally, *exo*-polyhedral substituents which donate electron density into (or extract from) the cage framework will obviously alter the electron-counting rules. This is conspicuously the case in neutral polyboron halides (B_nX_n) which are formal $2n$-electron systems, yet adopt *closo* structures; both theoretical[27a,33] and experimental[54] studies indicate that the B—X bonding is multiple and that the halogen atom back-donates electron density into the boron framework. Thus, the assignment of only $2n$ skeletal bonding electrons in such species is not correct. Further examples of nonconformity to the electron-counting rules by highly halogenated clusters are found in $C_4H_4B_2F_2$, which is a cyclic planar system[55] (in sharp contrast to its analogue $C_4B_2H_6$, a pentagonal pyramid) and the $M_6X_{12}^{2+}$ clusters (M = Nb, Ta) which have been discussed elsewhere.[2,44]

5.5.3 METHODS OF SYNTHESIS

Polyhedral metallaboranes and metallacarboranes, as the introduction makes clear, were discovered *via* the introduction of metals into borane and carborane cages. This is still, by far, the most common synthetic approach, but there is no intrinsic reason to exclude other avenues; for example, insertion of boron into metallic or organometallic clusters, or the construction of a metallacarborane directly from metal, borane and hydrocarbon reagents in a 'one-pot' reaction. Both procedures have, in fact, been successfully demonstrated.

In this section, synthetic routes to metallacarboranes and metallaboranes are classified into broad categories with illustrative examples given for each type. These preparative routes vary enormously, in that some are straightforward and 'rational' while others operate by obscure mechanisms and give products that could not reasonably have been predicted. As a general observation, metallacarborane and large metallaborane syntheses tend to be of the first kind, while many preparations of small metallaboranes fall in the second category. The difference is attributed in part to the higher stability of carboranes compared with boranes and to the presence of skeletal carbon atoms in carborane frameworks, which cause reactions (*e.g.* metal insertions) to be localized at specific sites on the polyhedral surface. Hence, syntheses of metallacarboranes from carboranes tend to give only one or two products, and in high yield; similar results are observed with large (nine- to eleven-atom) boranes and borane anions, which exhibit a tendency to retain the icosahedral-fragment geometry and resist degradation or rearrangement. In contrast, interactions of metal reagents with small neutral or ionic boranes are less stereospecific and often lead to complex mixtures of products, involving loss (or gain) of boron, oligomerization or polymerization of borane units, and other processes; it is characteristic of many metal–small borane interactions, even when conducted under mild conditions, that the products frequently seem to bear little structural relationship to the borane starting reagent. These generalizations are subject to many exceptions, but the overall contrast is very apparent.

5.5.3.1 Metallacarboranes

The construction of polyhedral cages containing metal, boron and carbon atoms has been achieved by a variety of methods, the most common of which involve the reaction of an existing carborane framework with a metal reagent. Other routes have been far less frequently utilized but have considerable potential for the synthesis of novel species. In addition, metallacarboranes can be prepared by modification of existing metallacarboranes, including polyhedral rearrangement, addition or removal of metal (or other) atoms, and the coupling and fusion of metallacarborane cages. A brief outline of these methods follows.

5.5.3.1.1 Insertion of metal-ligand groups into neutral carboranes

Carboranes of both the *closo* and open-cage (*nido*, *arachno*) types react with electrically neutral metal reagents, either in the gas phase or in solution, to effect incorporation of the metal into the cage framework. When the carborane substrate is *nido*, the metal invariably enters the open face of the cage, usually with loss of one or more bridging hydrogens on the carborane and displacement of ligands (CO, phosphine, *etc.*) from the metal reagent (Figure 17a, b).[56,57] Insertion into a *closo* system, however, involves an expansion of the polyhedral framework to accommodate the new member but does not usually entail loss of hydrogen (Figure 18).[13,14,58,59] The expansion is formally a reductive process and is accompanied by an addition of two electrons, supplied by the metal, to the skeletal bonding molecular orbitals (alternatively, as will be described below, the carborane can be reduced to a dianion which is then allowed to react with a *cationic* metal reagent). In some cases there is loss of boron, so that the metal merely replaces a BH unit and the polyhedron does not expand (equation 2).[14]

$$1,2\text{-}C_2B_{10}H_{12} + CpCo(CO)_2 \xrightarrow{-[BH]} CpCoC_2B_9H_{11} + 2CO \tag{2}$$

The insertion of metals into neutral carboranes is a quite general synthetic route[4a] and has been conducted with *closo*-carboranes ranging from $C_2B_3H_5$ to $C_2B_{10}H_{12}$ and with *nido* and *arachno* species as small as $C_2B_3H_7$ and as large as $C_2B_9H_{13}$. Moreover, it has proved successful with tricarbon and tetracarbon systems (*e.g.* 2-$MeC_3B_3H_6$ and $Me_4C_4B_8H_8$) (equation 3).[9,60]

$$Me_4C_4B_8H_8 + Mo(CO)_6 \longrightarrow (CO)_3MoMe_4C_4B_8H_8 + 3CO \tag{3}$$

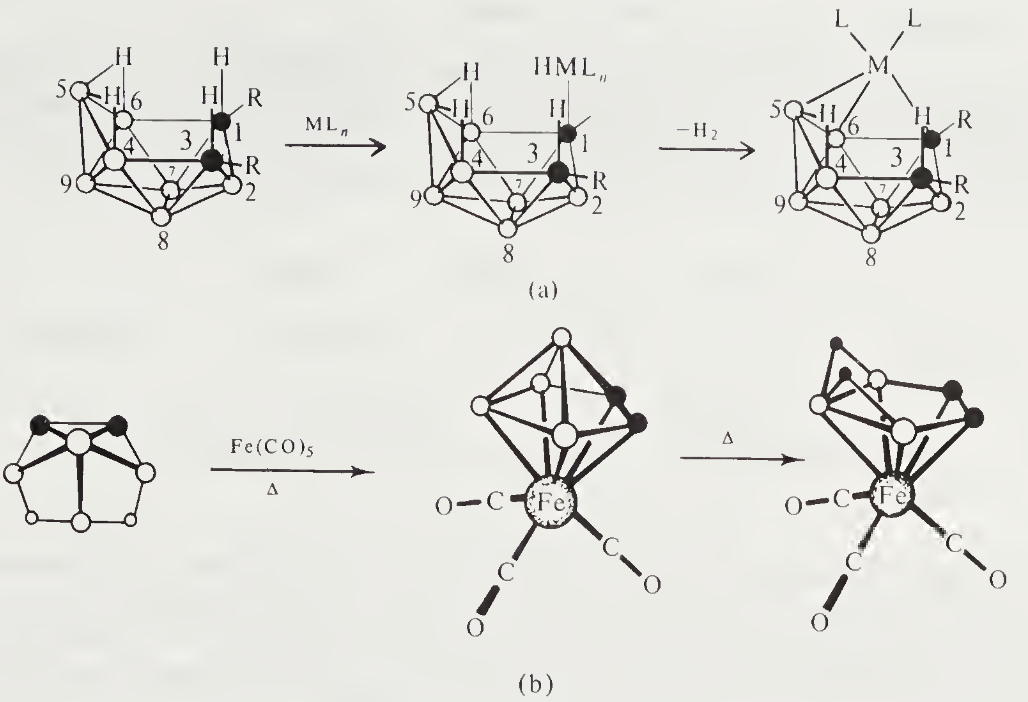


Figure 17 Examples of metal insertion into neutral open-cage carboranes: (a) insertion into $R_2C_2B_7H_{11}$ (R = H or Me; M = Pt or Ni; L = PEt_3 or PMe_3);[56] (b) insertion into 2,3-$C_2B_4H_8$[57]

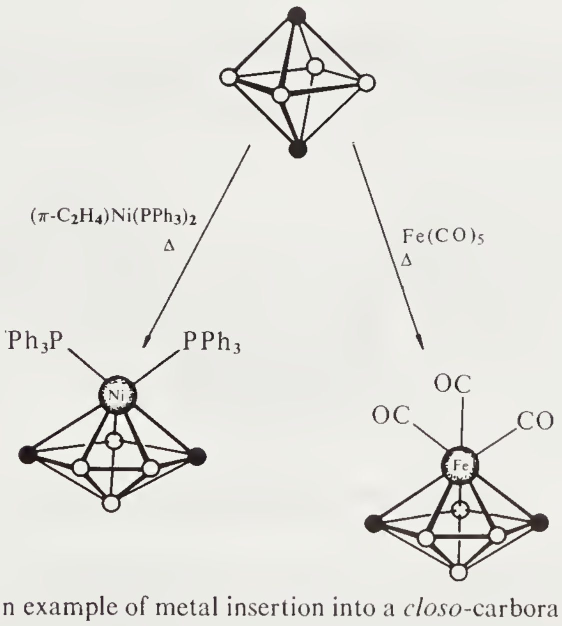


Figure 18 An example of metal insertion into a *closo*-carborane, $C_2B_4H_6$[14]

The most commonly employed metal reagents have readily displaceable ligands, and include metal carbonyls, phosphines and mixed-ligand complexes such as Ni(cod)(PEt_3)$_2$, Co(CO)$_2$Cp and Pt(PMe_3)$_2$(*trans*-stilbene). Many of the reported metal insertions occur at or below room temperature, but those involving the more stable *closo*-carboranes, such as 2,4-$C_2B_5H_7$ and 1,2-$C_2B_{10}H_{12}$, may require elevated temperature or UV light.

A closely related synthetic route involves the addition of metal reagents to derivatives of heterocylic boron-containing ligands such as 1,3-diborolene ($C_3B_2H_6$) and borole (C_4BH_5) to give mono- or di-metallic sandwich complexes.[4d] Although the products are by definition metallacarboranes, this chemistry is treated separately in Chapter 5.3 under the heading of metal complexes of boron ring systems.

5.5.3.1.2 Insertion of metals into carborane anions[4]

Both *nido*- and *arachno*-carborane anions can be generated either by bridge-deprotonation of open-cage neutral carboranes (equation 4) or by base-degradation of *closo*-carboranes (equation 5). Still another method for opening polyhedral cages utilizes alkali metals, such as sodium amalgam or sodium naphthalenide, as electron-transfer agents, *e.g.* equation (6).

$$nido\text{-}2,3\text{-}C_2B_4H_8 + NaH \xrightarrow[20\,°C]{THF} Na^+C_2B_4H_7^- + H_2 \quad (4)$$

$$closo\text{-}1,2\text{-}C_2B_{10}H_{12} + EtO^- + 2EtOH \xrightarrow{85\,°C} 1,2\text{-}C_2B_9H_{12}^- + B(OEt)_3 + H_2 \quad (5)$$

$$closo\text{-}2,4\text{-}C_2B_5H_7 + 2Na^0 \longrightarrow 2Na^+ + C_2B_5H_7^{2-}(nido) \quad (6)$$

The open-cage carborane anions complex easily with ionic transition metal reagents, as for example in the treatment of 1,2-$C_2B_9H_{12}^-$ ion with cobalt chloride (equation 7). In the course of this reaction the bridging hydrogen atom on the open face of $C_2B_9H_{12}^-$, an icosahedral fragment, is removed by base attack; alternatively, it can be removed prior to introduction of the metal reagent, forming the $C_2B_9H_{11}^{2-}$ (dicarbollide) anion (equation 8).

$$2C_2B_9H_{12}^- + CoCl_2 \xrightarrow[NaOH]{hot\ aq.} (C_2B_9H_{11})_2Co^{2-} \xrightarrow{air} (C_2B_9H_{11})_2Co^- + Co^0 \quad (7)$$

$$C_2B_9H_{12}^- + H^- \xrightarrow{THF} Na^+C_2B_9H_{11}^{2-} + H_2 \quad (8)$$

The $C_2B_9H_{11}^{2-}$ ion (Figure 19) has a five-membered C_2B_3 open face unencumbered with bridge hydrogens, and readily coordinates to metal ions to complete an MC_2B_9 12-vertex *closo* cage, as in Figure 1. This was historically the first route employed for the synthesis of metallacarboranes.[3,7]

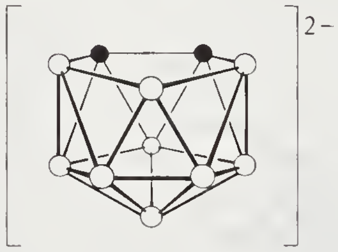


Figure 19 Structure of the 1,2-$C_2B_9H_{11}^{2-}$ ion

As explained in Section 5.5.2, in order for a metal to be fully incorporated into the polyhedral skeleton it must normally direct three bonding orbitals to the framework. If the inserting metal group can provide only one or two orbitals for that purpose, the metal adopts a strictly bridging role, *e.g.* equation (9). The structure of the product,[61] in which the metal is bound to each cage by a B—Hg—B three-center two-electron bond, is depicted in Figure 20. Examples of B—M—B bridging appear throughout this review.

$$2Me_2C_2B_4H_5^- + HgCl_2 \longrightarrow \mu,\mu'\text{-}(Me_2C_2B_4H_5)_2Hg + 2Cl^- \quad (9)$$

The metal ion/carborane anion method is exceedingly versatile[4] and has been applied to a wide variety of carborane systems having one to four carbon atoms, to heterocarboranes (species containing skeletal atoms in addition to boron and carbon), to the synthesis of supra-icosahedral and of optically active[62] metallacarboranes, and to the construction of metallacarborane polymers.[63] Since the reactions occur under mild conditions and are usually stereospecific (the metal entering a well-defined open face on the carborane substrate), the products in many cases are

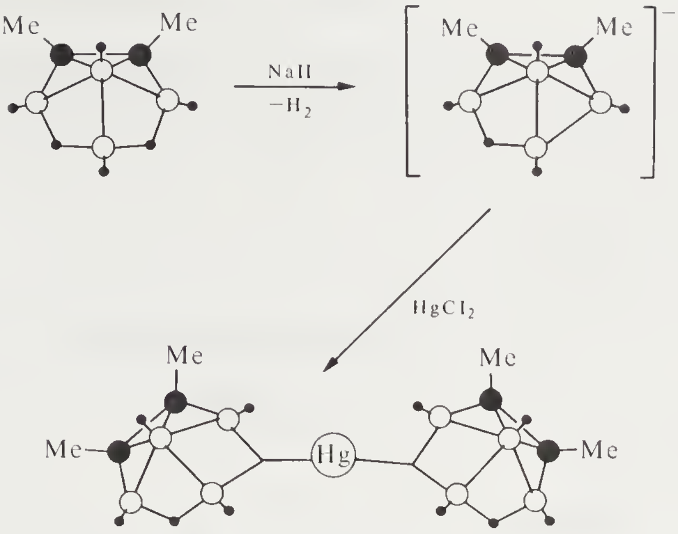


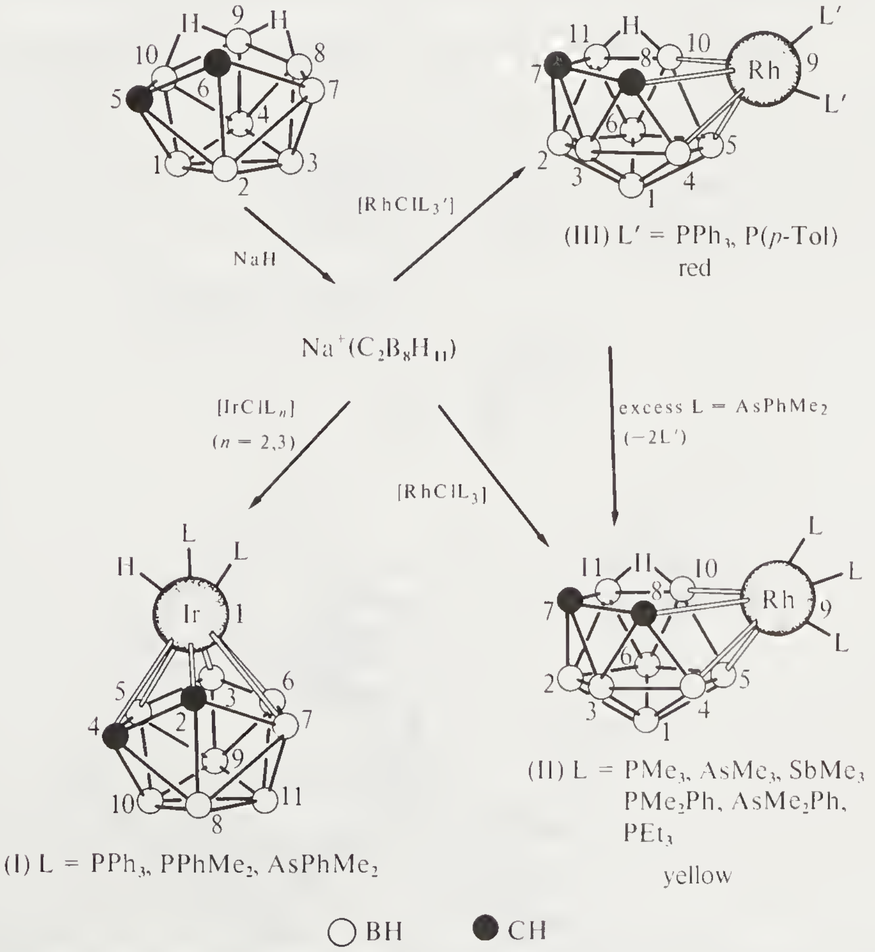
Figure 20 Formation of μ,μ'-$(Me_2C_2B_4H_5)_2Hg$

predictable and are obtained in reasonable yields. Reactions (10)–(17) illustrate the range of syntheses employing carborane anions, either as explicit starting reagents or as species formed *in situ*.

metallacarborane metal hydrides (see also Figure 21):[64]

$$\textit{nido}\text{-}C_2B_8H_{11}^- \quad + \quad IrClL_n \quad \longrightarrow \quad \textit{closo}\text{-}1,2,4\text{-}L_2HIrC_2B_8H_{10} \tag{10}$$

$(n = 2, 3;\ L = PMe_2Ph, AsMe_2Ph, PPh_3)$



(III) L' = PPh$_3$, P(p-Tol) red

(I) L = PPh$_3$, PPhMe$_2$, AsPhMe$_2$

(II) L = PMe$_3$, AsMe$_3$, SbMe$_3$, PMe$_2$Ph, AsMe$_2$Ph, PEt$_3$ yellow

Figure 21 Synthesis of rhodium and iridium metallacarborane hydrides from the $C_2B_8H_{11}^-$ ion

13-vertex polyhedra:[65]

$$\textit{nido}\text{-}C_2B_{10}H_{12}^{2-} + MCl_4 \longrightarrow M(C_2B_{10}H_{12})_2^{\ 2-} \qquad (11)$$

$$M = Ti, Zr, V$$

14-vertex, 4-carbon polyhedra:[49,60]

$$\textit{nido}\text{-}Me_4C_4B_8H_8^{\ 2-} + FeCl_2 + C_5H_5^- \longrightarrow \textit{closo}\text{-}Cp_2Fe_2Me_4C_4B_8H_8 + CpFeMe_4C_4B_7H_8 \qquad (12)$$

$$\text{(several isomers)}$$

trimetal, monocarbon system:[66]

$$\textit{nido}\text{-}2\text{-}CB_5H_9 + NiCp_2 + Na/Hg \longrightarrow Cp_3Ni_3CB_5H_6 \qquad (13)$$

$$\text{(several isomers)}$$

monometal, monocarbon system:[67,38]

$$\textit{nido}\text{-}CB_9H_{12}^- + MCl_2{\cdot}6H_2O \longrightarrow \textit{closo}\text{-}CpCoCB_9H_{10}^- \qquad (14)$$

$$M = Co, Fe$$

$$\textit{nido}\text{-}B_9H_{11}C \cdot NMe_3 + NaH \xrightarrow[C_5H_5^-]{CoCl_2} CpCoB_9H_9C \cdot NMe_3 \qquad (15)$$

main group metallacarboranes:[68]

$$\textit{nido}\text{-}1,2\text{-}C_2B_9H_{11}^{\ 2-} + MX_2 \longrightarrow MC_2B_9H_{11} + 2X^- \qquad (16)$$

$$M = Ge, Sn, Pb$$

incorporation of a metal via an isolable B—M—B bridged intermediate (see also Figure 22):[57]

$$\textit{nido}\text{-}C_2B_4H_7^- + CpFe(CO)_2I \longrightarrow \textit{nido}\text{-}\mu\text{-}\{CpFe(CO)_2\}\text{-}C_2B_4H_7 \xrightarrow{h\nu} \textit{closo}\text{-}CpFe(H)C_2B_4H_6 + 2CO \qquad (17)$$

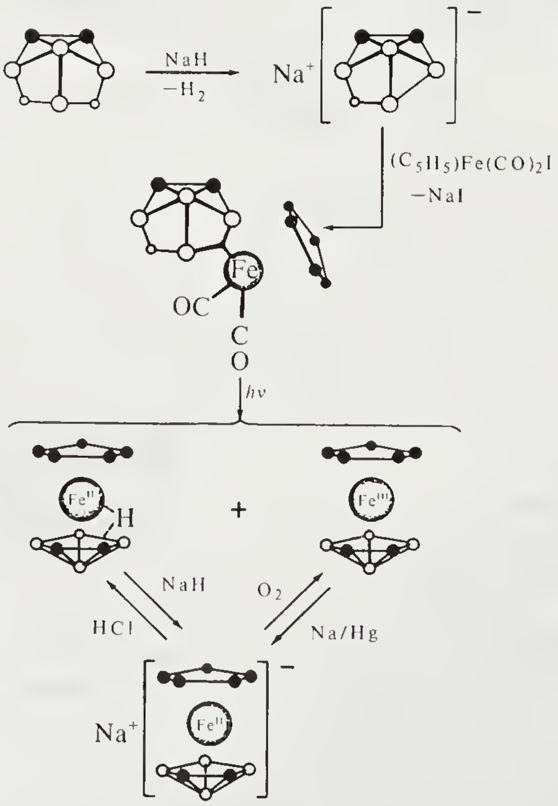
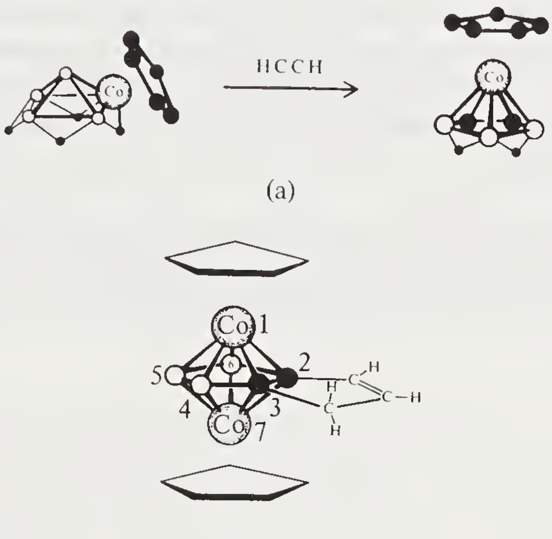


Figure 22 Synthesis of bridged and *closo*-ferracarboranes from the $C_2B_4H_7^-$ ion

5.5.3.1.3 Insertion of hydrocarbons into metallaboranes

Only a few examples of carbon insertion into metal–boron clusters have been reported, but it can be safely predicted that many more will be forthcoming; the method has enormous potential. The reaction of the small *nido*-cobaltaborane 2-$CpCoB_4H_8$ with alkynes generates *nido*-1,2,3-$CpCoC_2B_3H_7$ or its *C*-substituted derivatives[69] (Figure 23a), and in a serendipitous finding, a minor product of the interaction of $C_5H_5^-$, $CoCl_2$ and $B_5H_8^-$ was the *closo* species[70] μ-(2,3)-1,3-C_3H_4-1,7,2,3-$Cp_2Co_2C_2B_3H_3$ (Figure 23b), which evidently forms by insertion of a cyclopentadienide ring into a Co_2B_3 framework. An important recent observation[71] is the interaction of the square-pyramidal ferraborane $(CO)_3FeB_4H_8$ with two mole equivalents of MeC≡CMe to generate the novel species $(CO)_3FeMe_4C_4B_4H_4$, which in turn decomposes to give a four-carbon carborane, $Me_4C_4B_4H_4$. Such reactions demonstrate the utilization of metallacarborane intermediates in the condensation of alkyne and borane molecules to form carboranes.



(a)

(b)

Figure 23 (a) Insertion of acetylene into 2-$CpCoB_4H_8$; (b) structure of μ-C_3H_4-1,7,2,3-$Cp_2Co_2B_3H_3$

5.5.3.1.4 Conversion of σ-(metal carbonyl)boranes to metallacarboranes

The photolysis of 6-$\{CpFe(CO)_2\}B_{10}H_{13}$ in ether solvents results in the incorporation of the iron atom and one of the carbonyl carbons into the cage to generate a monocarbon 12-vertex *closo* polyhedron with a molecule of solvent (THF or diethyl ether) coordinated to the cage carbon atom (Figure 24). The reaction may occur *via* an intermediate in which the inserting CO group is first

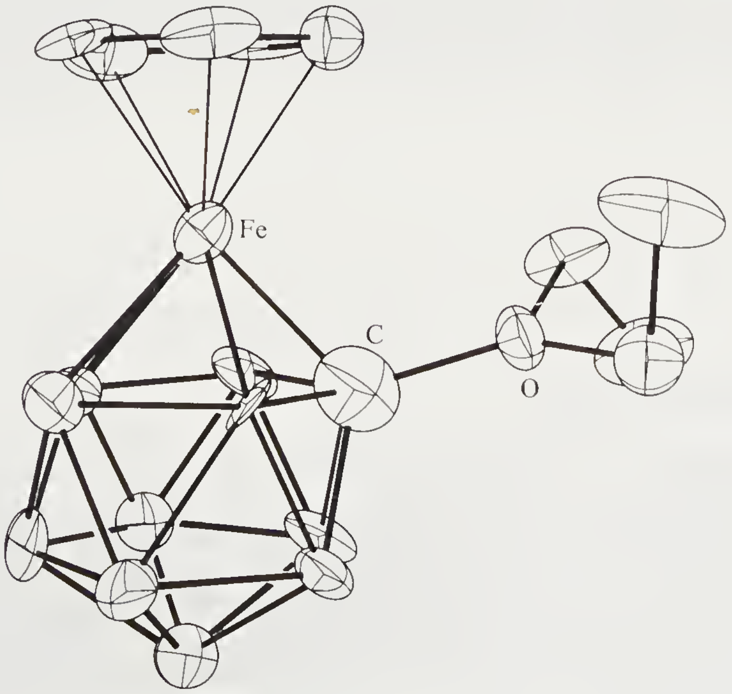


Figure 24 Structure of $CpFeCB_{10}H_{10}$-OEt_2

reduced to C—OH_2, with the water ligand subsequently displaced by the stronger Lewis base ether.[72] This process is related to the formation of another 12-vertex monocarbon system, $[(CO)_4MB_{10}H_{10}C—OH]^-$, in the photochemical reaction of $M(CO)_6$ (M = Cr, Mo or W) with $B_{10}H_{13}^-$ ion.[73] On deprotonation of this molecule, a novel ester linkage is formed between one of the carbonyl carbon atoms and the oxygen attached to the framework carbon.

5.5.3.1.5 Reaction of boranes with metal–hydrocarbon complexes

As we noted earlier, the insertion of boron into metal–carbon frameworks offers a potentially attractive route to metallacarboranes, and is in fact the counterpart of carbon insertion into metallaboranes. Again, however, few examples are known. Treatment of Cp complexes of transition metals with organoboron dihalides effects insertion of boron into one or both C_5H_5 ligands to give borabenzene sandwich complexes in which C_5B rings are hexacoordinated to metal atoms (see Chapter 5.3).

The photolysis of $(\eta\text{-}C_4H_4)Fe(CO)_3$ with B_5H_9 in ether generates a small quantity of a presumed six-vertex *nido* species, $(CO)_3FeC_4BH_5$, in which the iron and boron atoms are proposed to occupy basal positions in an FeC_4B pentagonal pyramid.[74]

5.5.3.1.6 Reaction of metal atoms or metal carbonyls with alkynes and boranes

The construction of metallacarboranes directly from metal, carbon and boron reagents in a single operation is an attractively simple approach, although it affords little or no control over the composition and structures of the products. Cocondensation of cobalt vapor, B_5H_9, cyclopentadiene and alkynes at −196 °C gave several mono- and di-cobaltacarboranes in low yields; however, the reaction of $CpCo(CO)_2$ with B_5H_9 and butyne at 200 °C gave only dicobaltacarboranes.[75] Similar co-condensations of cobalt vapor with B_6H_{10}, C_5H_6 and alkynes produce cobaltacarboranes having one or two metal atoms and 4–6 borons; a particularly interesting product of the diphenylacetylene reaction is *arachno*-1,4,5,7,8-$CpCoPh_4C_4B_3H_3$, which has an open C_4B_2 face.[75b] With $B_{10}H_{14}$, analogous reactions yield only CoB_9 complexes and no metallacarboranes.

5.5.3.1.7 Polyhedral rearrangement

The synthetic methods thus far discussed in Sections 5.5.3.1.1–5.5.3.1.6 are concerned with the formation of metallacarborane polyhedra from convenient laboratory reagents. Once obtained, metallacarboranes can undergo several kinds of alteration of the cage structure to produce not only isomers of existing species, but structurally different cage systems as well. One such process is the migration of metal or carbon atoms to new locations on the polyhedral surface, which normally occurs at elevated temperature although low-temperature rearrangements are known. In virtually no case has the detailed mechanism of a polyhedral carborane or metallacarborane isomerization been established, although it is generally accepted that the process(es) are nondissociative and involve cooperative motion of the framework atoms such that the migrating atom at all times is bound into the cage. A number of mechanisms have been postulated, several of which (diamond-square-diamond, rotating pyramids, rotating triangles) have been extensively discussed elsewhere;[1a,1d,6,76] none has proved entirely successful in accounting for the experimental facts, and indeed it is possible that in any given case more than one rearrangement pathway may operate concurrently.

The ultimate product of a thermal isomerization is presumed to represent the thermodynamically preferred polyhedral arrangement. Several general observations, based on detailed studies of a number of metallacarboranes,[49,58,77] are as follows. (1) Carbon atoms favor low-coordinate vertices. (2) Carbon atoms prefer to be separated from each other in the skeletal framework (however, high temperatures are usually required to effect such separations). (3) The preference for low-coordinate vertices usually takes precedence over the tendency to separate. (4) Metal atoms seem, in general, to prefer high-coordinate vertices although other factors often override this rule in specific instances. (5) In polyhedra with two or more metal atoms, the metals may or may not adopt adjacent vertices, depending on the specific system; indeed, in at least three instances involving *closo* $Co_2C_2B_5$ and $Co_2C_2B_3$ polyhedral systems, adjacent-metal and nonadjacent-metal dicobaltacarborane isomers have been found to exist *in equilibrium* at elevated temperatures.[77a,58] (6) As is true for most covalent cluster systems, the thermodynamically favored isomer will usually exhibit some symmetry (at least an axis or a mirror plane). Figure 25 illustrates some typical isomerizations.

The activation energy for polyhedral rearrangement in metallacarboranes is apt to be high, so that temperatures above 300 °C, or UV radiation, are often necessary in order to produce the thermodynamically favored isomer; thus the geometries of metallacarboranes formed at room temperature are likely to reflect primarily kinetic effects arising from the conditions of synthesis. A particularly striking example of this is given by the 14-vertex $Cp_2Fe_2Me_4C_4B_8H_8$ system (Figure 26).[49]

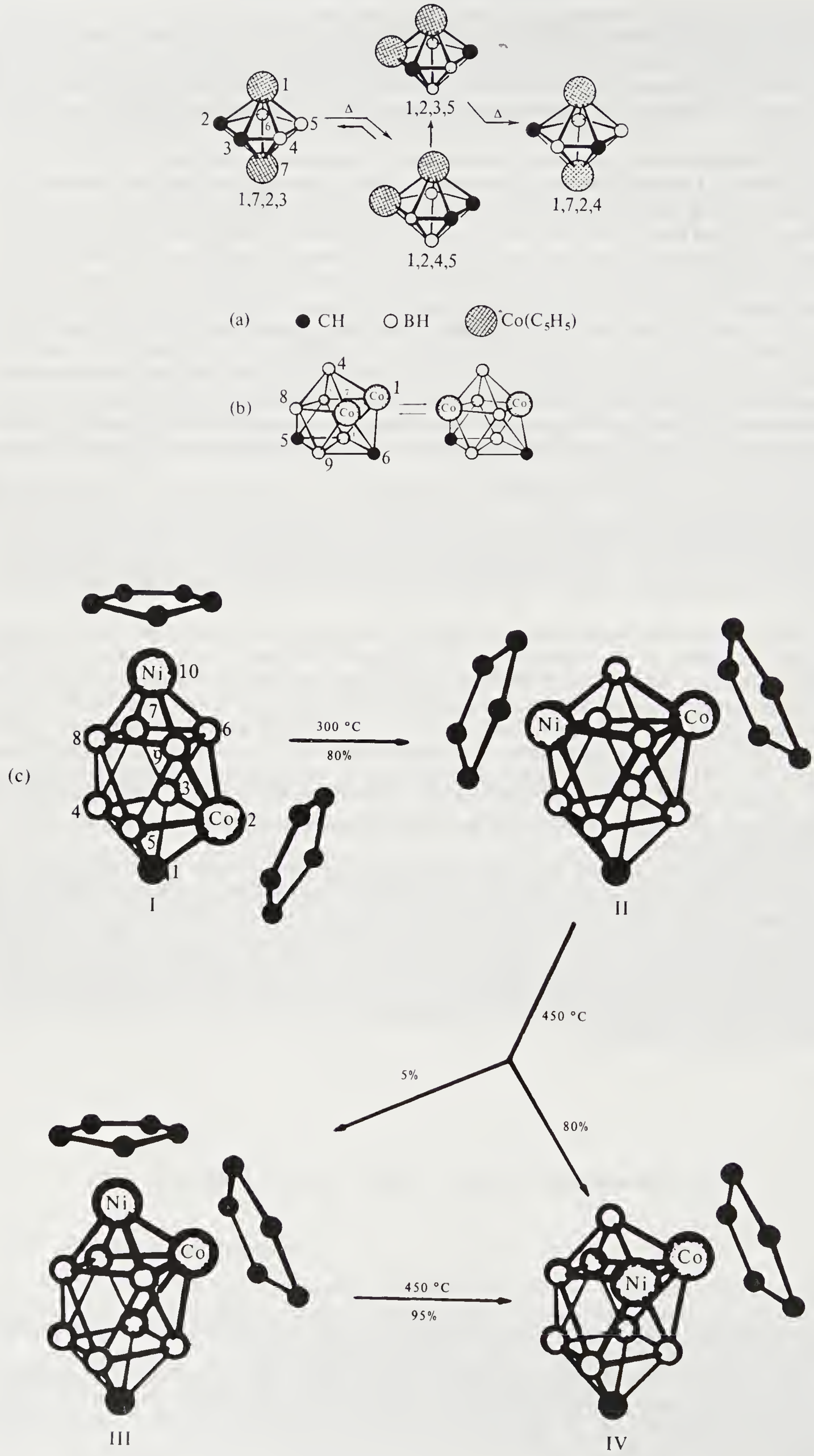
Thermal rearrangements of metallacarboranes can also involve migration of *exo*-polyhedral ligands, as shown in the conversion of 3,1,2-$(Ph_3P)_2NiC_2B_9H_{11}$ to 8-(Ph_3P)-3,1,2-(Ph_3P)-$Ni(H)C_2B_9H_{11}$, in which a nickel-bound phosphino ligand and a terminal hydrogen atom on boron exchange places.[78] Another interesting example[58] is given by the isomerization of the B—B linked cage system $Cp_2Co_2C_2B_5H_6$-2,4-$C_2B_5H_6$ (Figure 27), in which *three different* effects are observed: (1) at 220 °C the $C_2B_5H_6$ ligand alternates between the 2- and 3-positions on the cobaltacarborane cage; (2) at 340 °C the cobalt atoms alternate between adjacent and nonadjacent vertices (*i.e.* 1,7,5,6 and 1,8,5,6), as was previously observed[77a] for the parent $Cp_2Co_2C_2B_5H_7$ cobaltacarboranes; (c) at 400 °C the cobaltacarborane cage migrates to other positions on the *carborane* $(C_2B_5H_6)$ framework.

Still another type of metallacarborane cage rearrangement involves the conversion of a *nido* to a *closo* system, often (but not always) accompanied by the ejection of bridging hydrogen atoms. Equation (17) (see above) exemplifies one such reaction in which the original B—H—B hydrogen is retained in the *closo* product, evidently bound to an FeB_2 face.[57] A similar platinum-bridged compound converts to the 1,2,4-*closo*-platinacarborane with *loss* of hydrogen (equation 18).[79] Curiously, in this case the skeletal carbon atoms of the product adopt nonadjacent locations, whereas the corresponding *C,C′*-dimethyl derivative gives the 1,2,3 (adjacent carbon) isomer under identical conditions.

$$\textit{nido}\text{-}\mu\text{-}(PEt_3)_2Pt(H)\text{-}2,3\text{-}C_2B_4H_7 \xrightarrow[-H_2]{100\ ^\circ C} \textit{closo}\text{-}1,2,4\text{-}(PEt_3)_2PtC_2B_4H_6 \qquad (18)$$

Closo-to-*nido* thermal conversions are rare, but *closo*1,2,3-$(CO)_3FeC_2B_4H_6$ loses boron to form *nido*-1,2,3-$(CO)_3FeC_2B_3H_7$ on heating or electron impact.[57]

Most studies of metallacarborane thermal isomerizations have involved *closo* systems, but skeletal rearrangement has also been observed in open-cage species, as shown in Figure 26. Another example is the conversion of $CpCoMe_4C_4B_7H_7$, isomer I, to isomer III at 140 °C (Figure 28).[77f,43c,80]


1
2
6
5
3
4
7
1,7,2,3
Δ
1,2,3,5
Δ
1,2,4,5
1,7,2,4
(a)
● CH
○ BH
▨ Co(C$_5$H$_5$)
(b)
4
7
1
8
Co
Co
5
9
6
Co
Co
(c)
Ni
10
7
8
6
9
3
4
Co
2
5
1
I
300 °C
80%
Ni
Co
II
450 °C
5%
80%
Ni
Co
III
450 °C
95%
Co
Ni
IV

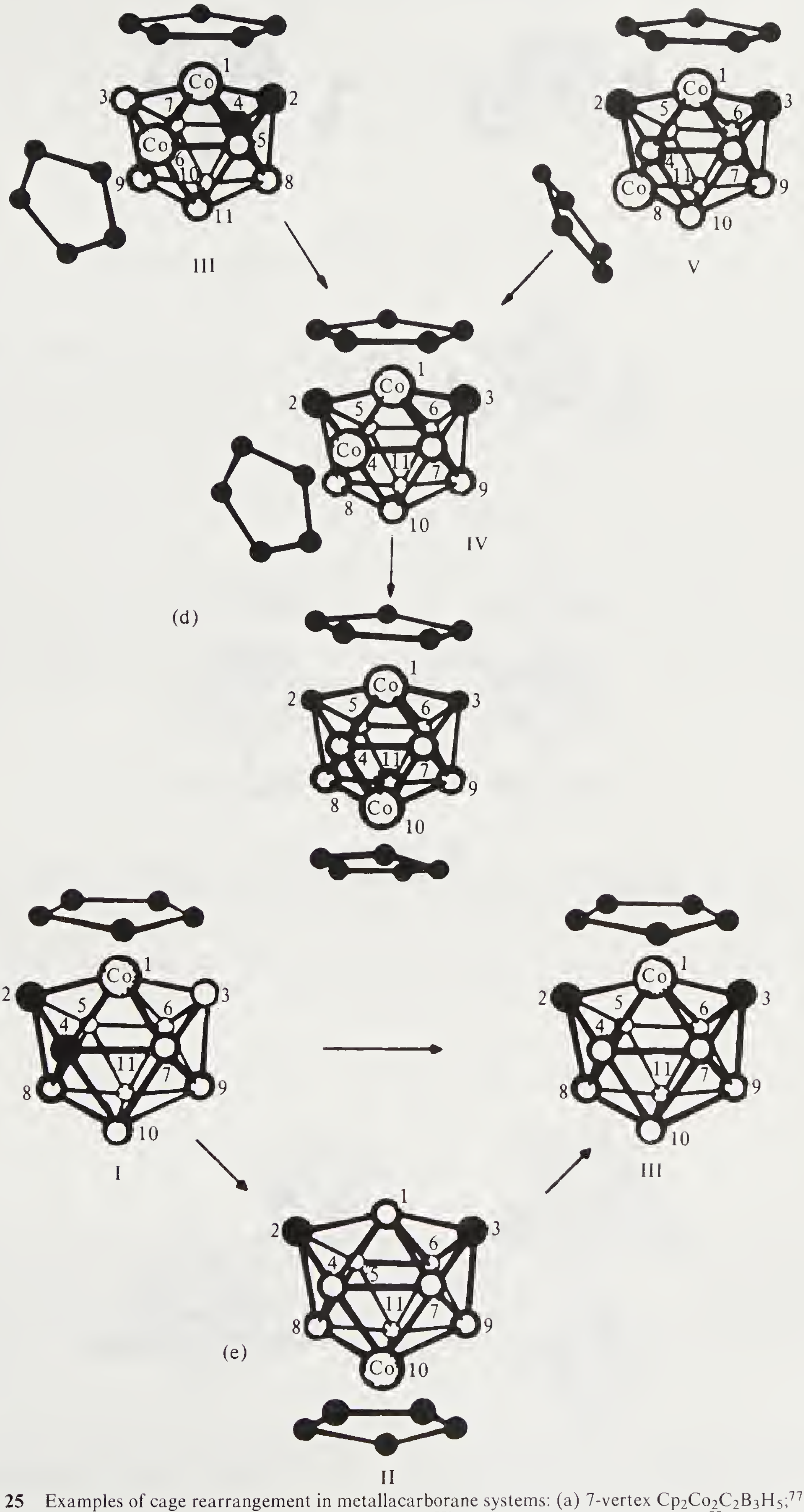


Figure 25 Examples of cage rearrangement in metallacarborane systems: (a) 7-vertex $Cp_2Co_2C_2B_3H_5$;[77a] (b) 9-vertex $Cp_2Co_2C_2B_5H_7$;[77a] (c) 10-vertex $Cp_2CoNiCB_7H_8$;[77b] (d) 11-vertex $Cp_2Co_2C_2B_7H_9$;[77c] (e) 11-vertex $CpCoC_2B_8H_{10}$[77e]

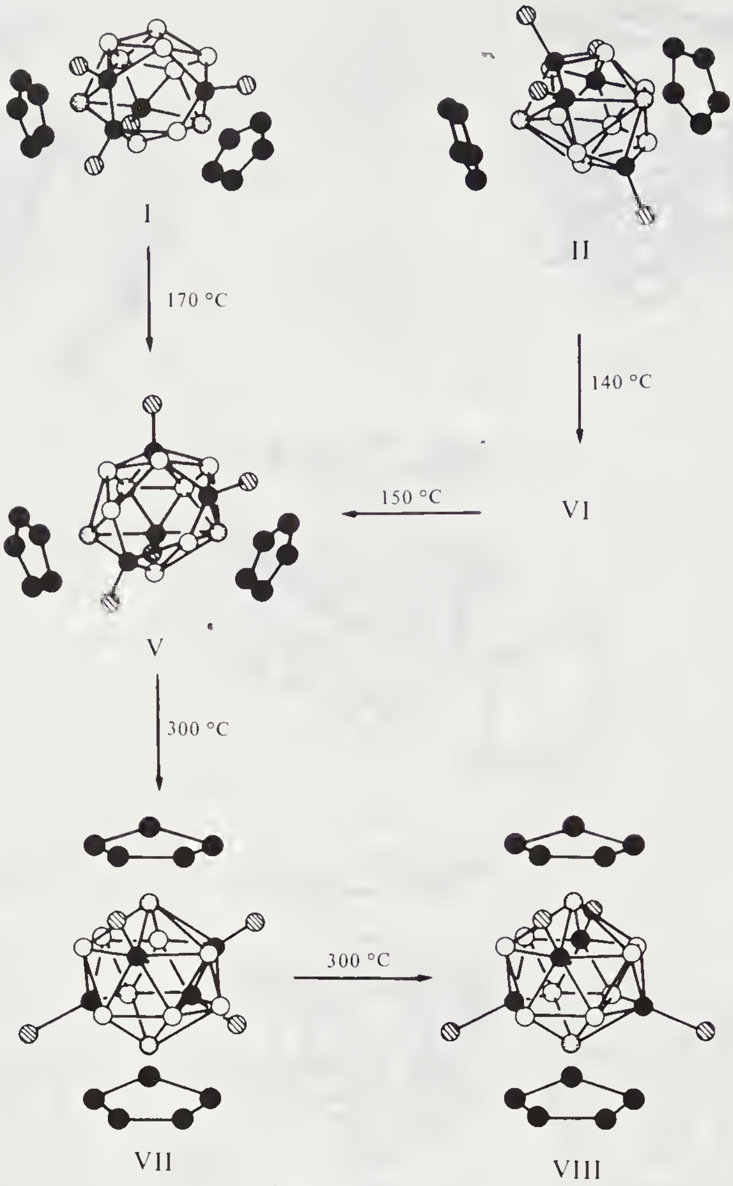


Figure 26 Rearrangement of 14-vertex $Cp_2Fe_2Me_4C_4B_8H_8$ isomers

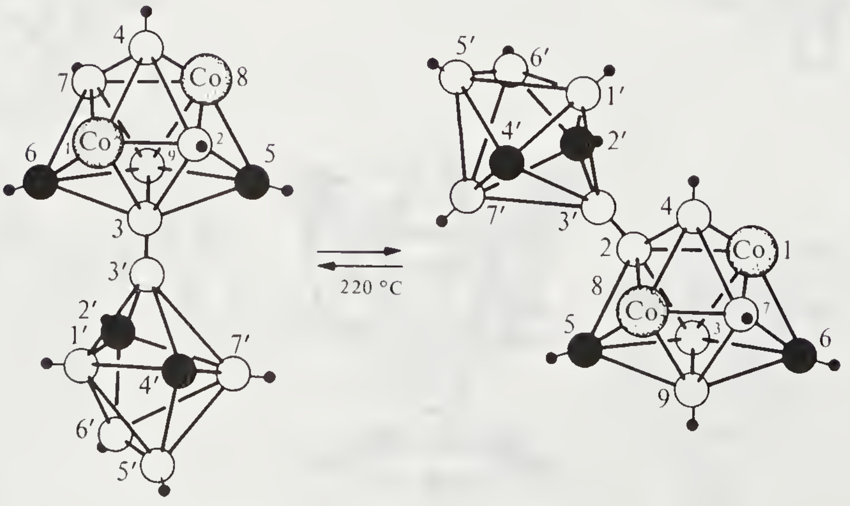


Figure 27 Rearrangement of the linked-cage system $Cp_2Co_2C_2B_5H_6$-$C_2B_5H_6$ at 220 °C, showing migration of the $C_2B_5H_6$ ligand on the metallacarborane polyhedron

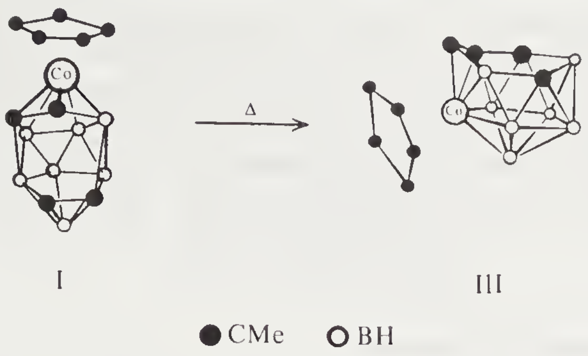


Figure 28 Rearrangement of $CpCoMe_4C_4B_7H_7$, isomer I, to isomer III

5.5.3.1.8 Polyhedral expansion and contraction

Characteristic of boron cluster chemistry are the phenomena of reductive cage opening and oxidative cage closure, which are a direct manifestation of the skeletal electron-counting rules described earlier. Thus, addition of two electrons to a $(2n + 2)$-electron system converts it to a *nido* $(2n + 4)$ cage; a two-electron oxidation of the latter would induce the re-closure of the polyhedron. Reductive cage-opening in metallacarboranes was observed experimentally[81] by Dunks and Hawthorne in 1970 prior to the development of the electron-counting rules, and was shown to be a useful synthetic tool by which a $C_2B_{n-2}H_n$ n-vertex *closo*-carborane can be expanded to an $(n + 1)$-vertex metallacarborane: (equation 19). This type of polyhedral expansion reaction has been applied to *closo*-carboranes of 7 to 12 vertices (although with $C_2B_3H_5$, $C_2B_4H_6$ and $C_2B_5H_7$ it does not proceed cleanly[82]) and also to mono- and di-metallacarboranes; with the latter species the end products are di- and tri-metallacarboranes.[4] As was noted in Section 5.5.3.1.1 above, polyhedral expansion can also be achieved by direct reaction of a neutral metal reagent with the neutral carborane, in which case the metal itself performs the function of a reducing agent.

$$1,7\text{-}C_2B_6H_8 \xrightarrow[\text{THF}]{\text{Na, }C_{10}H_8} [C_2B_6H_8{}^{2-}] \xrightarrow[C_5H_5^-]{CoCl_2} CpCoC_2B_6H_8 \qquad (19)$$

Cage expansion reactions provide an obvious potential route to large polyhedral systems, and at this writing 13- and 14-vertex metallacarboranes have been obtained by metal insertion into 12-vertex C_2B_{10} or C_4B_8 carboranes, as in equations (3), (11), (12) and (20). With $C_2B_{10}H_{12}$,[83] reduction to the dianion is necessary for expansion, as direct reaction of the neutral carborane with $CpCo(CO)_2$ affords only 12-vertex products (equation 2); however, expansion of $Me_4C_4B_8H_8$ has been conducted both directly and *via* the dianion (equations 3 and 12).[60,77f]

$$\begin{array}{l}1,2\text{-}C_2B_{10}H_{12} \xrightarrow[\text{THF}]{\text{Na, }C_{10}H_8} C_2B_{10}H_{12}{}^{2-} \xrightarrow[C_5H_5^-]{MCl_2} Cp\text{M}^{II}C_2B_{10}H_{12}{}^- \qquad (20)\\ \qquad\qquad\qquad\qquad\qquad\qquad Cp\text{M}^{III}C_2B_{10}H_{12} \xleftarrow{[O]} \\ \qquad\qquad\qquad\qquad\qquad \text{M} = \text{Fe, Co}\end{array}$$

The process known as polyhedral contraction involves removal of one or more skeletal atoms (usually boron) from an n-vertex polyhedron by the base-extraction technique described in Section 5.5.3.1.2 above, followed by oxidative closure of the anion to yield an $(n - 1)$-vertex product (equation 21).[84] In such reactions, as in polyhedral expansions, it is not necessary to isolate the anionic species; indeed, few carborane dianions other than $C_2B_9H_{11}^{2-}$ have ever been characterized as salts.

$$\begin{array}{lllll}CpCoC_2B_9H_{11} \xrightarrow{OH^-} \text{red intermediate} \xrightarrow{H_2O_2} & CpCoC_2B_8H_{10} & + & CpCoC_2B_7H_9 & (21)\\ & 63\% & & \text{2 isomers, } 10\% & \end{array}$$

The development of polyhedral expansion and contraction as synthetic methods represents important steps in the systematization of boron cluster chemistry, since they demonstrate that one can exert at least some degree of control over cluster structures by manipulation of skeletal electrons. In practical terms, the expansion process is more significant; polyhedral contraction seems limited to the more robust metallacarboranes, because base degradation of many species results in extensive break-up of the polyhedral framework rather than the desired removal of just one atom.

5.5.3.1.9 Metal replacement and transfer

The substitution of one metal for another in a metallacarborane cage has been clearly established only in the case of the 12-vertex thallium species $\mathrm{TlR_2C_2B_9H_9^-}$ (where R is hydrogen or alkyl), obtained as a $\mathrm{Tl^+}$ salt by treatment of 1,2-$\mathrm{C_2B_9H_{12}^-}$ or its alkyl derivatives with thallium(I) acetate in aqueous solution.[13a] The bonding between the skeletal Tl atom and the $\mathrm{C_2B_9}$ cage may be partially ionic;[85] in any event, that atom is easily displaced by transition metals,[13a,86] *e.g.* equation (22). Metal displacement in carboranes other than $\mathrm{TlC_2B_9}$ systems has not yet been demonstrated, although zinc complexes of $\mathrm{B_{10}H_{12}^{2-}}$ undergo such reactions (Section 5.5.3.2.3).

$$\mathrm{2TlC_2B_9H_{11}^-} + \mathrm{CoCl_2} \longrightarrow \mathrm{(C_2B_9H_{11})_2Co^{2-}} + \mathrm{2TlCl} \qquad (22)$$

$$\mathrm{(C_2B_9H_{11})_2Co^-} \xleftarrow{[\mathrm{O}]}$$

Transfer of metal-ligand groups such as CpCo from one polyhedron to another at elevated temperature is well known;[87] thus $\mathrm{CpCoC_2B_5H_7}$ undergoes disproportionation in the vapor phase at 340 °C to give 2,4-$\mathrm{C_2B_5H_7}$ and two isomers of $\mathrm{Cp_2Co_2C_2B_5H_7}$.[77a] In many cases, transfer of BH units between cages has also been observed. Since the temperature required for metal transfer is often comparable with that employed in direct thermal insertion of metals into *closo*-carboranes (see Section 5.5.3.1.1, above), such insertions are frequently accompanied by an interchange of metal or boron atoms as reflected in the product distributions; in addition, isomerization may also take place. Consequently, metal atom transfer at high temperature is not in general a controllable synthetic technique, although it may well produce novel metallacarborane products.

5.5.3.1.10 Oxidative cage fusion and cage coupling

A fundamentally different approach to the construction of large polyhedral cages is to join two open-cage species face-to-face to create a single polyhedron. Such a process requires the removal of electrons and is therefore described as oxidative fusion. A schematic representation might be, for example, as shown in equation (23). Reactions of this type were first demonstrated in the bis(carboranyl) complexes $\mathrm{(Me_2C_2B_4H_4)_2MH}_x$ (M = Fe, x = 2; M = Co, x = 1), which are oxidized in air to produce the carborane $\mathrm{Me_4C_4B_8H_8}$ (Section 5.5.5.1).[4c] Subsequently, it was found that six-vertex pyramidal metallacarboranes can also be fused to generate 12-vertex metallacarborane products,[88] as shown in Figure 29. Further discussion of cage fusion, which is now known to have considerable scope and synthetic utility, appears later in this review.

$$\mathrm{2C_2B_4H_6^{2-}} \xrightarrow{-4e^-} \mathrm{C_4B_8H_{12}} \qquad (23)$$

The coupling of two cages *via one* boron–boron bond is also an oxidative process but requires the removal of only two electrons (one per cage). Several methods have been successfully employed to link boranes and carboranes,[89] including electric discharge, pyrolysis, oxidative coupling of carborane anions and, more recently, mercury photosensitization of small boranes and carboranes[89] and thermal ejection of the metal from bis(μ-carboranyl)mercury complexes.[61] However, the formation of linked metallacarboranes directly from monomeric species has not been reported, although such compounds can be prepared by insertion of metal atoms into linked carboranes (Figure 30).[58] Complexes consisting of two metallacarboranes linked to a common mercury atom have also been prepared (Section 5.5.5.1).

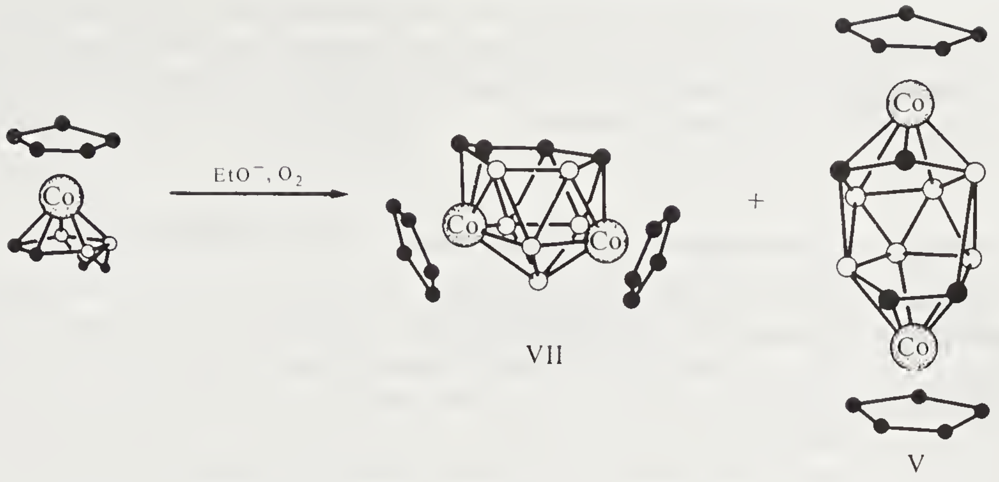


Figure 29 Fusion of $CpCoC_2B_3H_7$ (*via* the bridge-deprotonated anion) to form $Cp_2Co_2C_4B_6H_{10}$, isomers V and VII; a third isomer (VI, not structurally characterized) is also formed. Fusion of $CpCoMe_2C_2B_3H_5$ gives only a single isomer of $Cp_2Co_2Me_4C_4B_6H_6$, having the cage structure of V

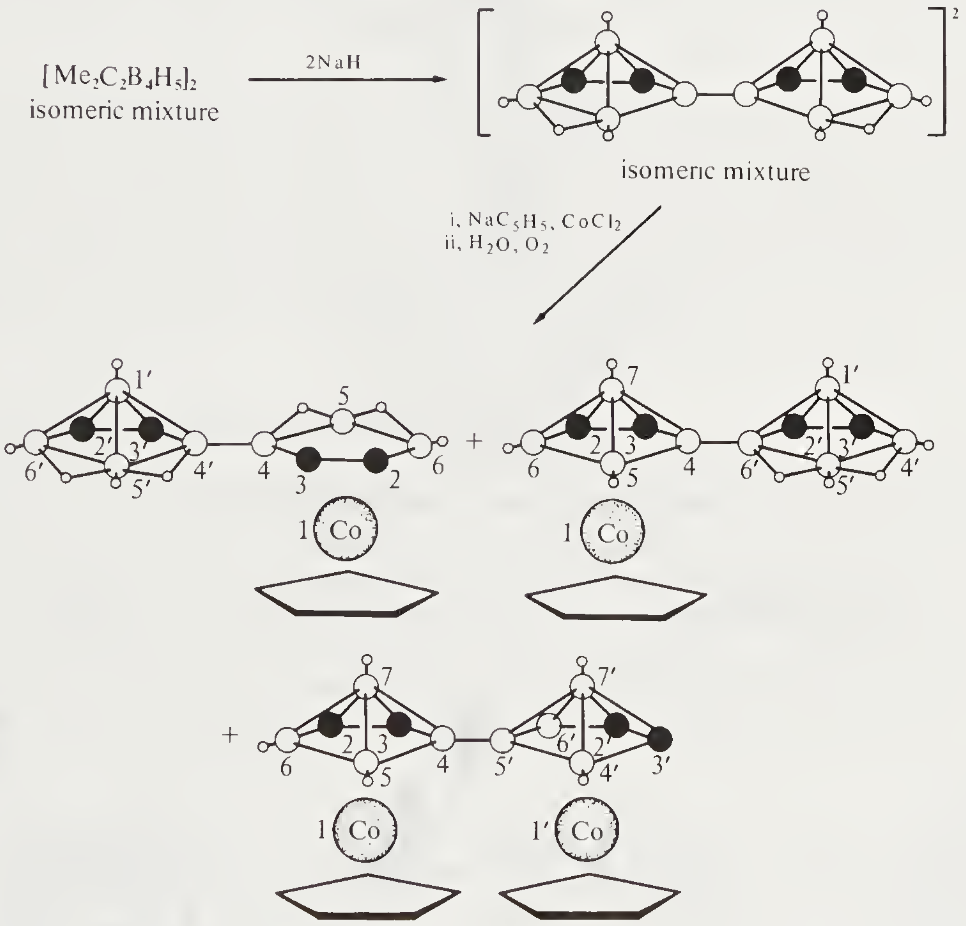


Figure 30 Synthesis of metallacarboranes from the linked *nido*-carborane $[Me_2C_2B_4H_5]_2$

5.5.3.2 Polyhedral Metallaboranes and Metallaheteroboranes

Virtually all reported primary syntheses of metallaboron clusters, which we define as open or closed polyhedra containing both metal and boron atoms in the skeletal framework, involve the reaction of a metal reagent with a polyhedral borane or heteroborane. The only exception, as of this writing, is the preparation of the tetrahedral cluster $(CO)_9Co_3B{\cdot}NEt_3$ (a direct analogue of the well-known $(CO)_9Co_3CR$ series) from the reaction of $Co(CO)_4^-$ ion, BBr_3 and triethylamine in benzene;[90] this species is also a rare example of a metallaboron cage compound containing more metal than boron atoms.

Otherwise, preparative routes to metallaboranes can be conveniently classified into two groups, namely those involving neutral boranes and those utilizing borane anions. For purposes of this review, syntheses in which borane anions are generated from neutral boron hydrides and utilized *in situ* will be included in the latter category.

5.5.3.2.1 Insertion of metal-ligand groups into neutral boranes and heteroboranes

Metal alkyls of main group and transition metals react directly with decaborane(14) in ether, as was mentioned in Section 5.5.1.2 (see equation 1). The products vary considerably in structure,[5] some having the metal coordinated to both borane and nonborane ligands (*e.g.* the $Me_2TlB_{10}H_{12}^-$ anion) and others exhibiting only metal-borane coordination, as in the $Zn(B_{10}H_{12})_2^{2-}$ ion (Figure 31).[5a] The nature of the product depends in part on the solvent; thus, the $M(B_{10}H_{12})_2^{2-}$ dianions are obtained by dissociation of initially formed dimers in polar solvents (equation 24). The thallium species mentioned above forms competitively with the Me_2Tl^+ salt of $B_{10}H_{13}^-$ on treatment of $B_{10}H_{14}$ with Me_3Tl in ether.[91] CpNi can also be inserted into the $B_{10}H_{14}$ framework to give *nido*-$CpNiB_{10}H_{13}$, by treatment of $B_{10}H_{14}$ with nickelocene (Figure 32).[18,92]

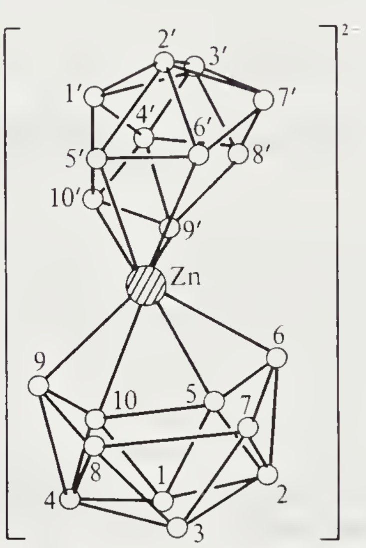


Figure 31 Structure of the $Zn(B_{10}H_{12})_2^{2-}$ ion

$$[(Et_2O)_2MB_{10}H_{12}]_2 \longrightarrow M^{2+} + M(B_{10}H_{12})_2{}^{2-} + 4Et_2O \qquad (24)$$

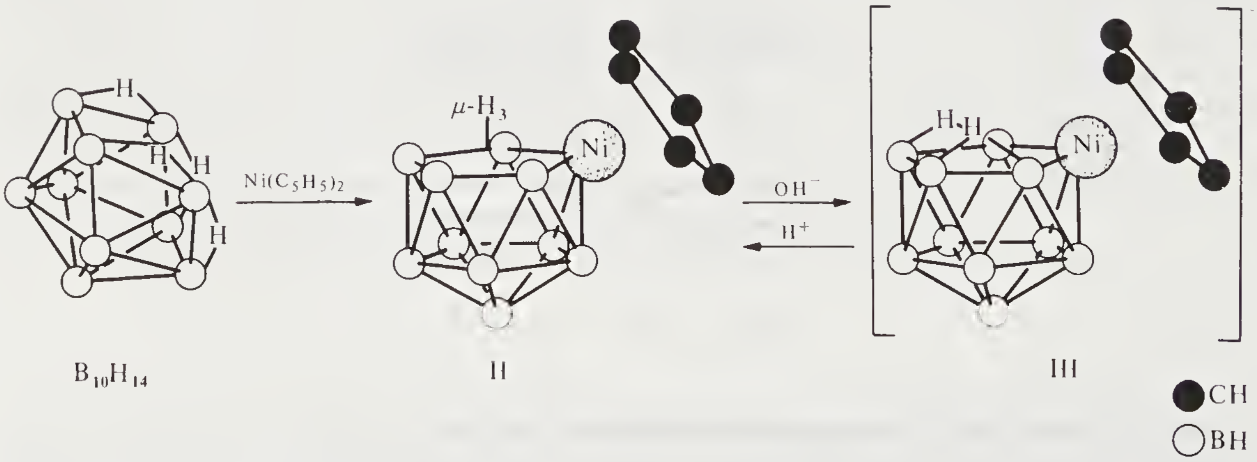


Figure 32 Synthesis of $CpNiB_{10}H_{13}$ (II) from $B_{10}H_{14}$[92]

Smaller boranes similarly react with metal alkyls, although few products have been characterized.[5a] However, a number of novel metallaboranes have been prepared from the direct reactions of small neutral boron hydrides with transition metal reagents in the gas phase or in solution. Thus the interaction of B_5H_9 with $Fe(CO)_5$ under various conditions gives *nido*-1-$(CO)_3FeB_4H_8$, *nido*-$(CO)_3FeB_5H_9$ and *closo*-$(CO)_3FeB_5H_3(CO)_2$ (Figure 33).[93] Similarly, B_5H_9 and $HMn(CO)_5$ [or B_5H_9, H_2 and $Mn_2(CO)_{10}$] produce *nido*-$(CO)_3MnB_5H_{10}$,[94] and the same borane

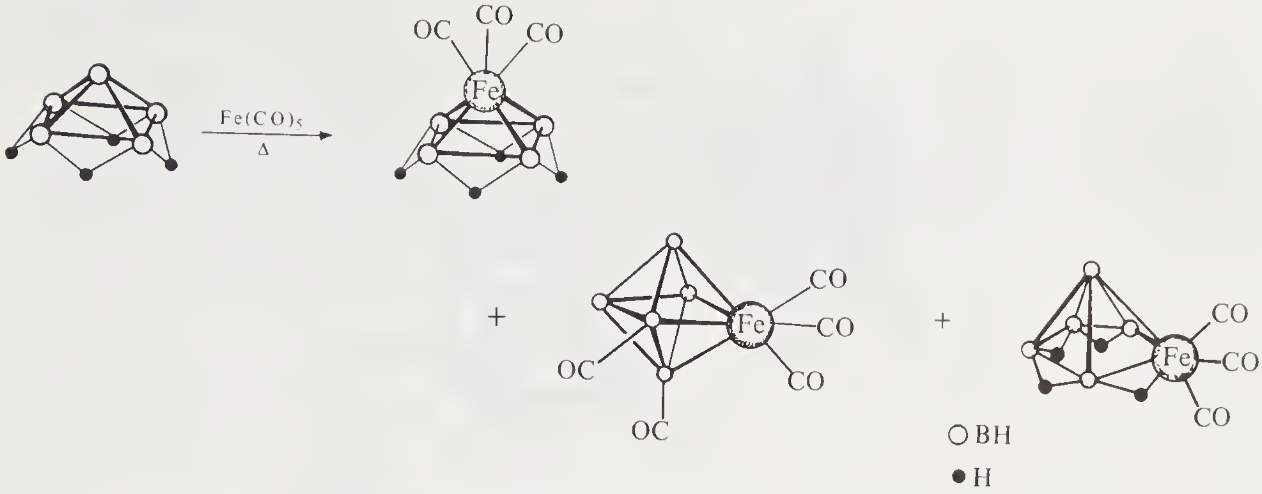


Figure 33 Synthesis of ferraboranes from B_5H_9

reagent on heating with $CpCo(CO)_2$ generates the *nido* species 1-$CpCoB_5H_9$ and 2-CpCo-B_9H_{13}.[95a] Cobaltaboranes have also been prepared directly from the metal vapor, cyclopentadiene and boron hydrides.[75b,95b]

Similar reactions can be used to incorporate additional metal atoms into a monometallaborane, as in the formation of $Cp_2Co_2(CO)_4FeB_3H_3$ from 2-$CpCoB_4H_8$ and $Fe(CO)_5$ under UV light.[69]

Neutral heteroboranes have also been employed in direct metal-insertion reactions. The *closo*-thiaboranes 1-SB_9H_9 and 1-$SB_{11}H_{11}$ on treatment with L_4Pt reagents ($L = PhMe_2P$, Et_3P or Ph_3P) form platinathiaboranes of the type $L_2PtSB_8H_{10}$ in which the platinum and sulfur atoms occupy the 6- and 9-positions in a 10-vertex *nido* ($B_{10}H_{14}$-like) framework.[96] Somewhat similarly, the azaborane NB_8H_{13} (an analogue of B_9H_{15}) reacts with $Pt(Ph_3P)_4$ in benzene at 60 °C to give the *nido*-platinaazaborane $(PPh_3)_2PtNB_8H_{11}$, another analogue of $B_{10}H_{14}$ in which the platinum and nitrogen atoms occupy the 6- and 9-vertices on the open face.[97]

5.5.3.2.2 Insertion of metal ions into borane anions

A wide variety of boron hydride anions is available, derived in most cases by deprotonation or partial degradation of a neutral borane with a suitable Lewis base. Reactions of the anions with metal halides or other metal reagents often result in the incorporation of metal into the cage framework, although in some cases only terminally substituted (σ-bonded) metal–borane complexes are obtained. Thus the $B_{10}H_{13}^-$ ion reacts with several kinds of transition metal halides to give complexes in which the metal is coordinated to a formal $B_{10}H_{12}^{2-}$ ligand (equations 25–27).[98] The structure of $Ni(B_{10}H_{12})_2^{2-}$, shown in Figure 34, is similar to that of $Zn(B_{10}H_{12})_2^{2-}$ (Figure 31) except that the open faces on the two ligands are roughly parallel in the nickel complex but are perpendicular in the zinc species.

$$4B_{10}H_{13}^- + (Ph_3P)_2MCl_2 \longrightarrow M(B_{10}H_{12})_2^{2-} + 2B_{10}H_{14} + 2Ph_3P + 2Cl^- \quad (25)$$

$$M = Ni, Pd, Pt$$

$$2B_{10}H_{13}^- + (Ph_3P)_2M(CO)Cl \longrightarrow (Ph_3P)_2(CO)MB_{10}H_{12}^- + B_{10}H_{14} + Cl^- \quad (26)$$

$$2B_{10}H_{13}^- + (Et_3P)_2PtCl_2 \longrightarrow (Et_3P)_2PtB_{10}H_{12} + B_{10}H_{14} + 2Cl^- \quad (27)$$

Similar reactions have been conducted with other anions derived from $B_{10}H_{14}$,[5a,99] *e.g.* $B_{10}H_{14}^{2-}$, $B_9H_{12}^-$, $B_9H_{14}^-$ and related thiaboranes such as $SB_9H_{12}^-$ and $SB_{10}H_{11}^-$. With $SB_9H_{12}^-$, for example, treatment with *trans*-$(Et_3P)_2Pt(H)Cl$ generates a neutral platinathiaborane, $(Et_3P)_2Pt(H)$-SB_9H_{10}, an 11-vertex *nido* complex with adjacent sulfur and platinum atoms on the five-membered open face.[100] In most cases the metal simply adds to the borane cage, but in some instances a BH group is replaced by the metal.

Some metallaborane syntheses have employed borane or heteroborane anions that are of uncertain structure or composition, but which react with metal reagents to form characterizable

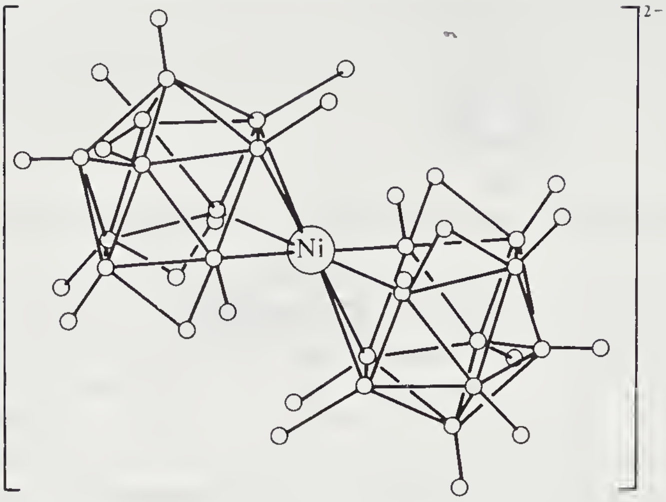


Figure 34 Structure of the $Ni(B_{10}H_{12})_2^{2-}$ ion[170]

metallaboranes. Thus the diselenium species $Se_2B_9H_9$ on treatment with ethanolic KOH forms an oxygen-containing anion which reacts with $CoCl_2$, cyclopentadiene and Et_3N to form a structurally novel complex, $CpCoSe_2B_9H_9$ (Figure 14);[43b] a similar reaction sequence starting with $SeSB_9H_9$ afforded $CpCoSeSB_9H_9$.

Numerous other metallaborane preparations involving large borane anions have been reported (*cf.* Sections 5.5.7 and 5.5.8). Both isomeric forms of $B_{18}H_{20}^{2-}$, obtained by deprotonation of *n*- and *i*-$B_{18}H_{22}$, form complexes with several transition metals.[101] The reaction of $B_9H_{12}^-$, $B_{10}H_{13}^-$ or $B_{11}H_{13}^{2-}$ with nickelocene (Cp_2Ni) in the presence of sodium amalgam affords both *nido*- and *closo*-nickelaboranes,[92] *e.g.* *closo*-$CpNiB_{11}H_{11}^-$, 1- and 2-$CpNiB_9H_9^-$, which are analogues of the *closo*-carboranes $CB_{11}H_{12}^-$ and $CB_9H_{10}^-$ (recall that NiCp is the skeletal electronic equivalent of CH). Particularly significant is the insertion of NiCp into *closo*-borane anions ($B_9H_9^{2-}$, $B_{10}H_{10}^{2-}$, $B_{11}H_{11}^{2-}$) by direct reaction with nickelocene or $CpNi(CO)_2$ in glyme; the products include 1,2-$Cp_2Ni_2B_{10}H_{10}$, a counterpart of 1,2-$C_2B_{10}H_{12}$ (*o*-carborane).[92] Incorporation of platinum into $B_{10}H_{10}^{2-}$ has also been reported, utilizing bis(arylphosphino)dichloroplatinum(II) reagents.[102]

Reactions of small borane anions with metal reagents have yielded a harvest of new compounds, including several structurally novel classes. The $(Ph_3P)_3Cu^+$ ion forms copper-bridged (B—Cu—B) complexes with the pyramidal $B_5H_8^-$ and $B_6H_9^-$ ions,[103] and the same metal species inserts into $B_4H_9^-$ or $B_5H_{12}^-$ to give $(Ph_3P)_2CuB_4H_9$, an analogue of B_5H_9 in which copper occupies a basal vertex in the square pyramidal framework.[104]

Interactions of the $B_5H_8^-$ ion with transition metal reagents and $C_5H_5^-$ or $C_5Me_5^-$ in cold THF give a variety of crystalline, air-stable metallaborane products whose structures differ strikingly from one metal to the next. Thus with $CoCl_2$ one obtains *closo* and *nido* species having one to four metal atoms and four to nine borons;[17,105] with $NiBr_2$, only dimetallic products, $Cp_2Ni_2B_nH_n$ ($n = 8$ or 10), have been isolated;[21] and with $FeCl_2$, the characterized products[19] are $CpFeB_5H_{10}$ and $CpFeB_{10}H_{15}$. The $B_5H_8^-$ ion is probably also involved in the reaction of B_5H_9 with $LiAlH_4$ and $Fe(CO)_5$ at 60 °C in dimethoxyethane, which produces the diiron species 1,2-$(CO)_6$-$Fe_2B_3H_7$.[39] In this compound, another B_5H_9 analogue, the iron atoms occupy an apex and a basal position, respectively. When the reaction is conducted in diethyl ether at room temperature, a different product, $(CO)_6Fe_2B_2H_6$, is obtained;[23] the proposed structure is an Fe_2B_2 distorted tetrahedron with Fe—H—B bridges along the four Fe—B edges.

Smaller borane anions such as $B_3H_8^-$ and BH_4^- also complex readily with metal reagents,[5a,99a] but the products are invariably chelates in which the metal is linked to the borane *via* M—H—B bridges and are not, therefore, clusters in the context of this chapter. In recent work in the author's laboratory,[106] 'mixed-ligand' reactions of $CoCl_2$ or $FeCl_2$ with the *nido*-carborane anion $Me_2C_2B_4H_5^-$ and the borane anions $B_5H_8^-$ or $B_3H_8^-$ have been found to give metallacarboranes containing $Me_2C_2B_7H_7^{2-}$ and other ligands. The formation of such complexes from $B_3H_8^-$ indicates that the utilization of this ion as a source of boron in polyhedral metallaborane synthesis is feasible.

5.5.3.2.3 *Metal exchange*

As is the case with metallacarboranes (Section 5.5.3.1.9), replacement of one metal by another in a metallaboron cage is rare. However, it has been reported that the treatment of $(THF)_2Zn(B_{10}H_{12})_2^{2-}$ with $CoCl_2$ in acetone produces the $Co(B_{10}H_{12})_2^{2-}$ ion which can be precipitated as the red tetramethylammonium salt. The thallaborane species $Me_2TlB_{10}H_{12}^-$ also undergoes metathesis (equation 28).[5a] The mercuraborane anion can be obtained in unsolvated form as the Ph_3MeP^+ salt.

$$MeHgCl \quad + \quad Me_2Tl^+[Me_2TlB_{10}H_{12}]^- \quad \xrightarrow{THF} \quad Me_2Tl^+[MeHgB_{10}H_{12}{\cdot}THF]^- \quad + \quad Me_2TlCl \tag{28}$$

5.5.3.2.4 *Polyhedral rearrangement*

Fewer examples of cage isomerization are known for metallaboranes than for metallacarboranes. In part, this can be attributed to the generally lower thermal stability of the former group, which tend to degrade on heating rather than rearrange. Nevertheless, a number of skeletal isomerizations involving both open and closed polyhedral metallaboranes are known. The pyramidal species $2\text{-}CpCoB_4H_8$ and $2\text{-}CpFeB_5H_{10}$ both convert to their respective 1-isomers (with the metal in the apex) at elevated temperature,[17b,19] and the *closo*-$2\text{-}CpNiB_9H_9^-$ ion rearranges to the 1-isomer both thermally and photochemically.[92] The corresponding perchloro species, $2\text{-}CpNiB_9Cl_9^-$, undergoes a similar thermal rearrangement but the photochemical process is reversible, producing a 1:2 equilibrium mixture of the 2- and 1-isomers.[92]

5.5.4 CAGE SYSTEMS WITH FOUR OR FIVE VERTICES

Metallacarboranes having fewer than six framework atoms are unknown, but a number of metallaboranes in this size range have been prepared. A variety of MB_4 species has been generated from reactions of $B_3H_8^-$ salts with transition metal halides.[5a,5b,107] In general the products are formulated as complexes of either the $B_3H_8^-$ or $B_3H_7^{2-}$ ligand. In the former case the structures invariably correspond to analogues of B_4H_{10} in which an 'end' BH_2 unit has been replaced by a metal-ligand group, as in $(Ph_3P)_2CuB_3H_8$ (Figure 35);[108] such species are chelates rather than true metalloboron clusters, inasmuch as the metal-ligand bonding involves B—H—M bridging and not direct metal-boron linkage. The $B_3H_7^{2-}$ complexes, on the other hand, are exemplified by $(Me_2PhP)_2PtB_3H_7$ (Figure 36),[107d] in which the metal occupies a 'middle' vertex in a B_4H_{10}-like framework. The latter type of species has also been described[107d] as a π-allyl complex since $B_3H_7^{2-}$ is isoelectronic with the π-allyl ion, $C_3H_5^-$.

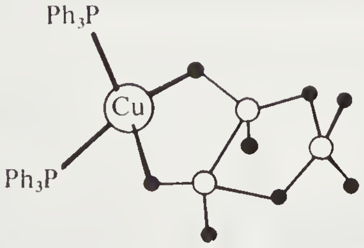


Figure 35 Structure of $(Ph_3P)_2CuB_3H_8$

Only two four-vertex *closo*-metallaboranes have been described. The first of these is $(CO)_9Co_3B{\cdot}NEt_3$,[90] containing a 12-electron Co_3B cage which is isoelectronic with the $(CO)_9Co_3CR$ cluster family.[109] The other example is the dimetallic complex $(CO)_6Fe_2B_2H_6$, a 12-electron Fe_2B_2 system, which is proposed to consist of a tetrahedral Fe_2B_2 core with hydrogen atoms bridging the four Fe—B edges.[23] This species, a highly air-sensitive yellow-brown liquid, was obtained from the room-temperature reaction of B_5H_9, $LiAlH_4$ and $Fe(CO)_5$ in diethyl ether. When the same reagents were heated in dimethoxyethane at 60–70 °C, a small yield of the five-vertex *nido* species $(CO)_6Fe_2B_3H_7$, an analogue of B_5H_9, was produced (Figure 11).[39] A mono-iron counterpart of this latter complex, orange liquid $1\text{-}(CO)_3FeB_4H_8$, has been obtained by the

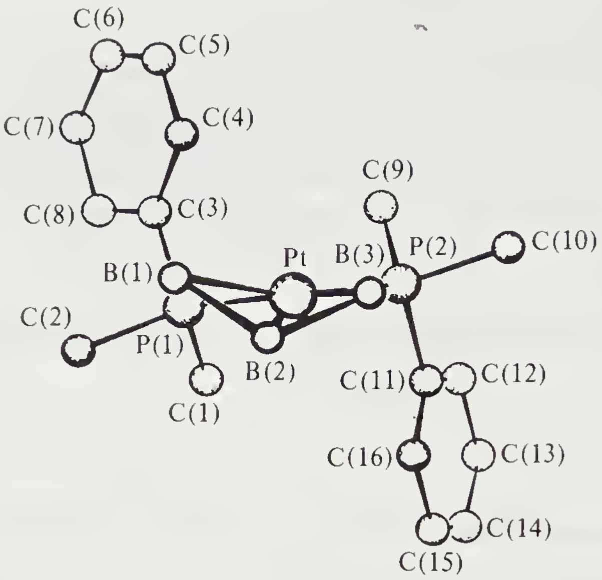


Figure 36 Structure of $(Me_2PhP)_2PtB_3H_7$

thermal reaction of B_5H_9 and $Fe(CO)_5$ (or of B_4H_{10} with $Fe_2(CO)_9$ at −75 °C);[93a] in this case an $Fe(CO)_3$ unit occupies the apex in the B_5H_9-like square pyramid (Figure 37). The view that 1-$(CO)_3FeB_4H_8$ and B_5H_9 have similar electronic structures, with $Fe(CO)_3$ replacing an apex BH unit, is supported by UV photoelectron spectroscopic studies[110] and, to a degree, by MO energy level calculations.[111]

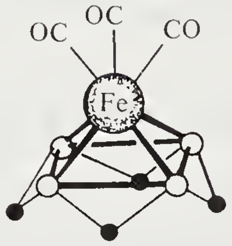


Figure 37 Proposed structure of 1-$(CO)_3FeB_4H_8$

Closely related to 1-$(CO)_3FeB_4H_8$ are the air-stable crystalline cobaltaboranes 1- and 2-$CpCoB_4H_8$,[17] in both of which a BH unit in B_5H_9 is formally replaced by an electronically equivalent (see Section 5.5.2.4) CoCp group. The red 2-isomer is formed in ~5% yield in the reaction of $B_5H_8^-$, $CoCl_2$ and $C_5H_5^-$, which also generates a host of other isolable cobaltaboranes; at 200 °C, the 2-isomer rearranges to yellow 1-$CpCoB_4H_8$ (Figure 38). Both 1-$CpCoB_4H_8$ and its analogue, 1-$(CO)_3FeB_4H_8$, contain the formal $B_4H_8^{2-}$ cyclic planar ligand, isoelectronic with cyclobutadienide, $C_4H_4^{2-}$, and are the first characterized complexes incorporating this ligand. Crystallographic studies have been conducted on both 2-$CpCoB_4H_8$[112a] and 1-$CpCoB_4H_8$.[112b]

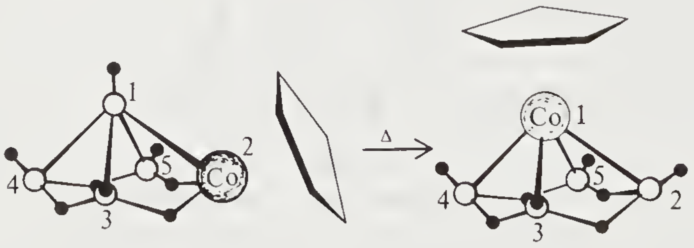


Figure 38 Rearrangement of 2- to 1-$CpCoB_4H_8$[17b]

The chemistry of 2-$CpCoB_4H_8$ has been extensively studied,[69] and this complex is the precursor to numerous other metallaboranes and metallacarboranes. The B—H—Co hydrogens are acidic toward hydride ion, and removal of one such proton gives the 2-$CpCoB_4H_7^-$ ion, analogous to $B_5H_8^-$; reaction of the anion with $CoCl_2$ and NaC_5H_5 generates di-, tri- and tetra-cobalt metallaboranes (see following Sections). Insertion of alkynes into neutral 2-$CpCoB_4H_8$ forms *nido*-cobaltacarboranes, discussed below.[69]

A different type of five-vertex *nido* species is the cupraborane 2-$(Ph_3P)_2CuB_4H_9$, produced in the reaction of $B_4H_9^-$ or $B_5H_{12}^-$ with $(Ph_3P)_3CuCl$.[104] In this species the Cu atom is proposed to occupy a basal vertex in the CuB_4 square pyramid, but the adjacent basal boron atoms and the apex boron are assigned *two* terminal hydrogens each, from NMR evidence; evidently there is no Cu—H bonding interaction in the molecule.

5.5.5 CAGE SYSTEMS WITH SIX OR SEVEN VERTICES

5.5.5.1 Metallacarboranes

Relatively few six-vertex *closo* boron clusters are known, but a very extensive chemistry based on seven-vertex polyhedra has been developed, primarily owing to the ready availability of *nido*-2,3-$C_2B_4H_8$ and its *C,C′*-dialkyl derivatives. Direct insertion of metals into *closo*-1,5-$C_2B_3H_5$ at elevated temperature generates the *closo* (octahedral) species 1,2,4-$CpCoC_2B_3H_5$ and 1,2,4-$(CO)_3FeC_2B_3H_5$; these compounds can accept additional metal groups to give the seven-vertex clusters 1,2,3,5-$Cp_2Co_2C_2B_3H_5$ and 1,2,3,5-$(CO)_6Fe_2C_2B_3H_5$ respectively.[14]

Seven-vertex *closo* (pentagonal bipyramidal) MC_2B_4 and $M_2C_2B_3$ cage systems have been synthesized by a variety of routes, of which the most important are the reactions of metal reagents with neutral and anionic *nido*-carboranes (see Sections 5.5.3.1.1 and 5.5.3.1.2). For example, treatment of *nido*-2,3-$C_2B_4H_8$ with $Fe(CO)_5$ forms yellow-orange *closo*-1,2,3-$(CO)_3FeC_2B_4H_6$, which in turn loses BH to generate *nido*-1,2,3-$(CO)_3FeC_2B_3H_7$, a pale yellow liquid (Figure 17b).[57] An analogous reaction is that of *nido*-2-$MeC_3B_3H_6$ with $Mn(CO)_5$ at 175–200 °C in the vapor phase, which forms yellow $(CO)_3MnMeC_3B_3H_5$ (Figure 2) in 85–90% yield.[9] The main group elements gallium and indium have been inserted into 2,3-$C_2B_4H_8$, producing *closo*-1,2,3-$MeMC_2B_4H_6$ (M = Ga, In) by similar gas-phase syntheses involving metal trialkyls.[10]

Reactions of metal ions with small carborane anions afford seven-vertex metallacarboranes. Treatment of *closo*-2,4-$C_2B_5H_7$ with sodium naphthalenide in THF, followed by addition of $CoCl_2$ and NaC_5H_5 in THF, generates mainly *closo*-1,2,3-$CpCoC_2B_4H_6$ plus higher *closo*-cobaltacarboranes; the formation of the CoC_2B_4 system entails loss of a BH unit, though it probably proceeds *via* a *nido*-$C_2B_5H_7^{2-}$ intermediate (Section 5.5.3.1.2 and equation 6).[82] A similar reaction utilizing $FeCl_2$ gave a mixture of products all of which are substituted derivatives of the *closo* seven-vertex species $CpFe^{III}C_2B_4H_6$ or $CpFe^{II}(H)C_2B_4H_6$. Again, the metal *replaces* BH in the cage rather than merely expanding the polyhedron.[57] In contrast to the cobalt reaction, no polyhedra larger than seven vertices were observed to form.

Of somewhat more general significance are the insertion reactions of the *nido*-2,3-$R_2C_2B_4H_5^-$ anions (R = alkyl or H), which are easily generated from neutral $R_2C_2B_4H_6$ species by bridge-deprotonation with sodium hydride in cold THF. The unprotonated B—B edge on the open face presents a site for metal attack, which initially leads to bridge substitution as shown in Figure 22.[57] Many other examples of main group-[113] and transition metal-bridged[61,113a] derivatives of *nido*-$R_2C_2B_4H_6$ have been reported, including platinum-[79] and mercury-bridged[61] species. Analogous mercury-bridged complexes have been prepared from *nido*-(η-C_5R_5)$CoMe_2C_2B_3H_4^-$, which is derived from the *nido*-2,3-$Me_2C_2B_4H_5^-$ ion by replacement of the apex BH with a Co(η-C_5R_5) group (Figure 39).[114]

The characterized metal-bridged complexes of *nido*-$R_2C_2B_4H_6$ carboranes are coordinatively saturated with respect to the metal atom; ejection of some of the metal-bound ligands by thermal[79a] or photochemical[57] means creates coordinative unsaturation, leading to full incorporation of the metal into the face of the C_2B_4 pyramid with formation of a *closo*-MC_2B_4 pentagonal bipyramidal system (Figure 22). Presumably, metal-bridged complexes also exist as intermediates in the direct synthesis of the *closo*-MC_2B_4 cages from *nido*-$R_2C_2B_4H_5^-$ ions and metal salts, but such intermediates have not been directly observed.

The most important route to seven-vertex *closo* metallacarboranes has been the reaction of a *nido* anion (*e.g.* $C_2B_4H_7^-$ or $Me_2C_2B_4H_5^-$) with a metal halide (equations 29–31).[4a,4d,12b,115]

$$\text{2,3-}C_2B_4H_7^- + CoCl_2 + C_5H_5^- \xrightarrow[\text{ii, H}^+,\ O_2]{\text{i, THF}} \underset{60\%}{CpCoC_2B_4H_6} \qquad (29)$$

$$2,3\text{-}C_2B_4H_7^- + (Ph_2PCH_2)_2NiCl_2 \xrightarrow{THF} \underset{17\%}{(Ph_2PCH_2)_2NiC_2B_4H_6} \tag{30}$$

$$2,3\text{-}C_2B_4H_7^- + SnCl_2 \text{ or } PbBr_2 \xrightarrow{THF} \underset{5\text{–}10\%}{SnC_2B_4H_6 \text{ or } PbC_2B_4H_6} \tag{31}$$

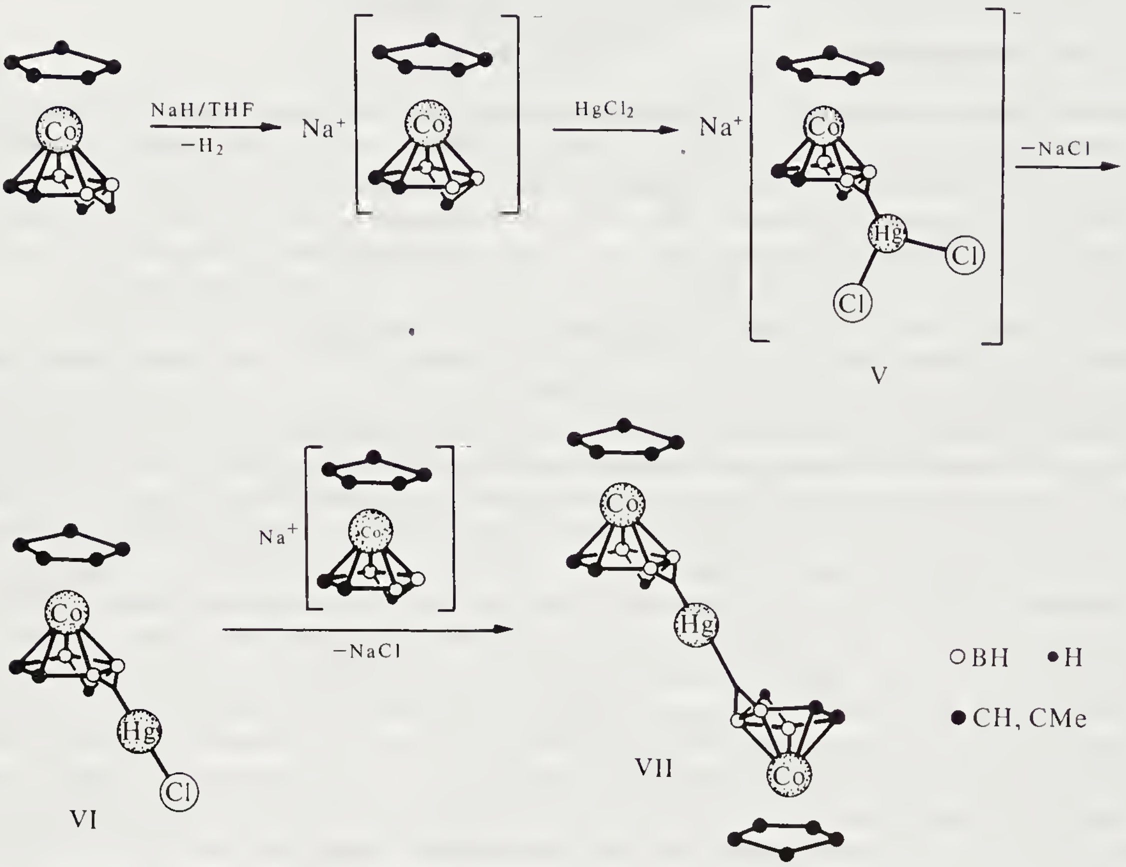


Figure 39 Synthesis of mercury-bridged cobaltacarborane complexes. The structures of VI and VII are established from X-ray studies; that of V is proposed

Similarly, linked-cage bis(cobaltacarboranes) have been prepared by insertion into the $[Me_2C_2B_4H_4]_2^{2-}$ dianion (Figure 30).[58]

In the proposed structures of the tin and lead metallacarboranes (equation 31), the metal has no *exo*-polyhedral ligands but presumably directs an unshared electron pair outward from the cage.[115] In the absence of a 'capping' ligand such as $C_5H_5^-$, bis(carboranyl) transition metal sandwich complexes can be obtained (equations 32, 33).[116] In these compounds, one or both of the B—H—B bridge hydrogens on the carborane ligands are retained in the metal complex and are associated with the metal atom, probably capping one or more M—B—B triangular faces.[4c,116,117]

$$2,3\text{-}Me_2C_2B_4H_5^- + CoCl_2 \xrightarrow{THF} (Me_2C_2B_4H_4)_2CoH \tag{32}$$

$$2,3\text{-}Me_2C_2B_4H_5^- + FeCl_2 \xrightarrow{THF} (Me_2C_2B_4H_4)_2FeH_2 \tag{33}$$

The structure of the bis(carboranyl)iron complex formed in equation (33) has been established crystallographically (Figure 40).[118] As shown, the $Me_2C_2B_4H_4^{2-}$ ligands are mutually staggered in a manner almost identical to that of the two halves of the $Me_4C_4B_8H_8$ carborane which is formed by oxidative fusion of the iron and cobalt complexes (Figure 41).[4c,116,117] Oxidative ligand fusion, discussed briefly in Section 5.5.3.1, is not restricted to complexes of the $R_2C_2B_4H_4^{2-}$ ligand; it has been observed in mixed-ligand complexes such as $(Me_2B_4H_4)FeH_2(Me_2C_2B_7H_7)$ (which generates $Me_4C_4B_{11}H_{11}$),[106] and in *nido*-cobaltacarboranes (Figure 29). The fusion process in principle offers a route to very large (supra-icosahedral) cage systems, but as yet it has not been successfully demonstrated with the dicarbollide ($C_2B_9H_{11}^{2-}$) or other large ligands.

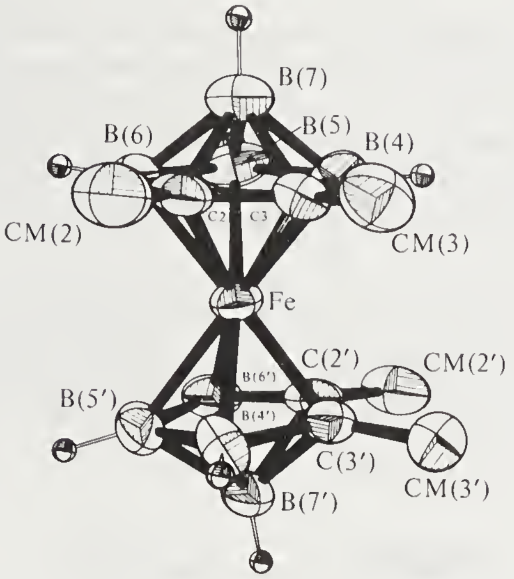


Figure 40 Structure of (2,3-$Me_2C_2B_4H_4)_2FeH_2$. The metal-bound hydrogen atoms, not shown, are believed to reside on the FeB_2 triangular faces

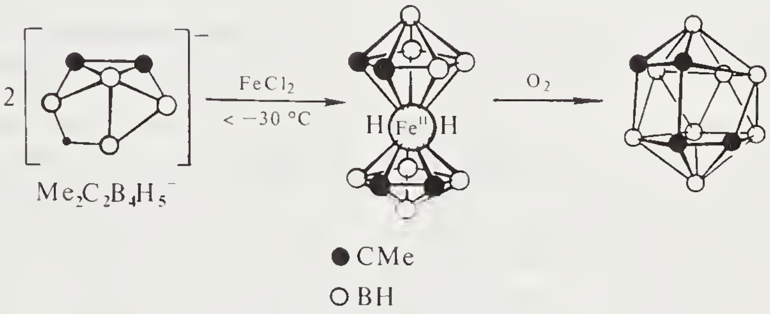


Figure 41 Formation of (2,3-$Me_2C_2B_4H_4)_2FeH_2$ and oxidative fusion to give $Me_4C_4B_8H_8$

The ligand fusion reaction, so far as is known, is restricted to transition metal complexes containing *two* carborane or borane ligands coordinated to a common metal atom ('*commo*' complexes). The seven-vertex *commo*-metallacarboranes also exhibit other novel stereochemical behavior which is not paralleled in the monocarboranyl metal complexes such as $CpCoC_2B_4H_6$.[4c] For example, insertion of CpCo into $(Me_2C_2B_4H_4)_2FeH_2$ gives the structurally unique species shown in Figure 42a,[34,119] while insertion of Sn or Ge produces compounds of the formula $(Me_2C_2B_4H_4)_2FeM$ (M = Sn, Ge) whose proposed structure is represented in Figure 42b.[119] The cobalt species $(Me_2C_2B_4H_4)_2CoH$ similarly undergoes further incorporation of cobalt to give di- and tri-cobalt species such as *nido,closo*-$(Me_2C_2B_3H_5)CoH(Me_2C_2B_4H_4)$ (Figure 12 and Section 5.5.2.4)[40,117]

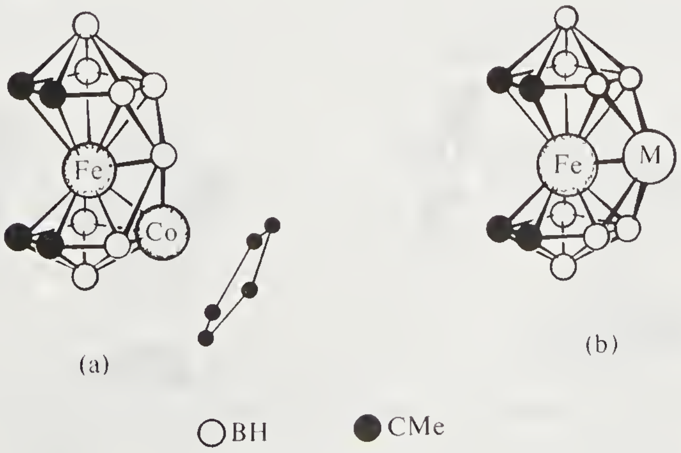


Figure 42 (a) Structure of $CpCoFeMe_4C_4B_8H_8$; (b) proposed structure of $MFeMe_4C_4B_8H_8$ (M = Ge or Sn)

The seven-vertex *closo* species having only *one* carborane ligand exhibit, in general, more predictable chemistry than the bis(carboranyl) complexes. In most of the MC_2B_4 *closo* systems the *exo*-polyhedral ligand on the metal is $C_5H_5^-$ or, less frequently, carbonyl or phosphine groups. Controlled degradation of *closo*-1,2,3-$CpCoC_2B_4H_6$ by strong bases opens the cage by removal of the apex BH group, giving a *nido* system, $CpCoC_2B_3H_7$, which is isoelectronic with 2,3-$C_2B_4H_8$ and can be similarly deprotonated to produce the $CpCoC_2B_3H_6^-$ ion. Insertion of a second $CpCo^{2+}$ moiety into the anion, with loss of H^+, generates the 'triple-decker sandwich' dicobalt complex 1,7,2,3-$Cp_2Co_2C_2B_3H_5$ (Figure 43).[12] This latter species can be viewed both as a seven-vertex $Co_2C_2B_3$ *closo* system with the required 16 skeletal electrons (see Section 5.5.2.4), and as a sandwich comprising two $C_5H_5^-$ ligands, two Co^{3+} ions and a central $C_2B_3H_5^{4-}$ ring which is isoelectronic with $C_5H_5^-$ (the $C_2B_3H_5^{4-}$ unit, however, has no independent existence in solution).[120] An identical sequence has been demonstrated for the *C*-monomethyl and *C,C'*-dimethyl analogues of these cobalt species.[12b]

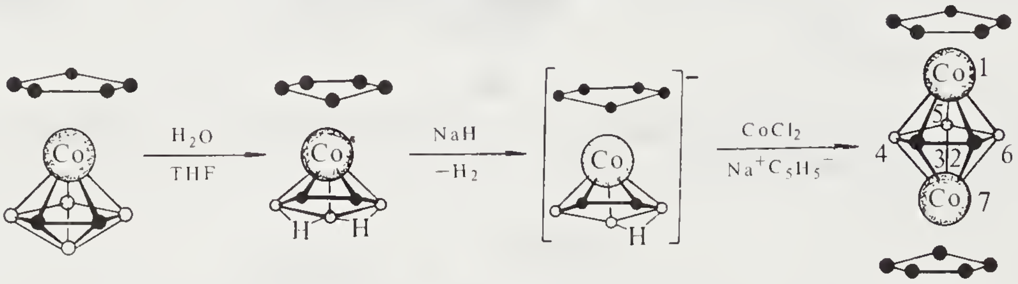


Figure 43 Sequence illustrating cage degradation of 1,2,3-$CpCoC_2B_4H_6$ to *nido*-1,2,3-$CpCoC_2B_3H_7$, bridge deprotonation, and insertion of a second cobalt to give the triple-decked complex 1,7,2,3-$Cp_2Co_2C_2B_3H_5$

Thermal rearrangement of 1,7,2,3-$Cp_2Co_2C_2B_3H_5$ at temperatures above 200 °C produces, in sequence, three new isomers, the final product being the 1,7,2,4 'triple-decker' sandwich in which the carbon atoms in the central C_2B_3 ring occupy nonadjacent vertices (Figure 25a).[77a] The two isolable intermediates, the 1,2,4,5- and 1,2,3,5-systems, have adjacent metal atoms, one of which occupies an equatorial (low-coordinate) vertex; as shown in the Figure, the first step in the isomerization requires an unusual migration of cobalt from a high- to low-coordinate site (see Section 5.5.3.1.7). X-ray analyses have confirmed the 1,7,2,3, 1,7,2,4 and 1,2,4,5 cage geometries,[12a,121,122] and the four isomers have been examined in detail *via* NMR[120] and electrochemical[123] studies. These investigations have shown that the two triple-decker isomers (1,7,2,3 and 1,7,2,4) are markedly different, with the former exhibiting strong localized bonding between the (adjacent) carbons in the C_2B_3 ring.

Various $Cp_2Co_2C_2B_3H_5$ isomers have also been obtained by other routes; thus treatment of *closo*-1,6-$C_2B_4H_6$ with sodium naphthalenide, $CoCl_2$ and $Na^+C_5H_5^-$ gives the 1,7,2,4-isomer in low yield,[12b] and the reaction of $CpCo(CO)_2$, or cobalt vapor, with cyclopentadiene, butyne and B_5H_9 produces small amounts of the 1,7,2,3-system together with other mono- and di-cobalt products.[75]

Other *closo*-$M_2C_2B_3$ polyhedral systems have been characterized as well. The reaction of the previously mentioned bis(carboranyl)iron dihydride complex $(2,3\text{-}Me_2C_2B_4H_4)_2FeH_2$ with $CoCl_2$ and $C_5H_5^-$ in ethanolic KOH produces, *inter alia*, the mixed-metal cobaltaferracarboranes depicted in Figure 44.[119] The 1,2,4,5-$Cp_2CoFe(H)Me_2C_2B_3H_3$ structure, confirmed crystallographically,[122] is an isoelectronic analogue of 1,2,4,5-$Cp_2Co_2C_2B_3H_5$ described above. A surprising product of the $CoCl_2/B_5H_9/C_5H_5^-$ reaction[17b] (see following Section) is the dicobalt species shown in Figure 23b. In this molecule,[70] a C_5H_4 ring system has been partially incorporated into a cobalt–boron cage, forming a $Co_2C_2B_3$ polyhedron which is, in fact, a 1,3-propenylene-disubstituted derivative of the previously described triple-decker 1,7,2,3-$Cp_2Co_2C_2B_3H_5$.

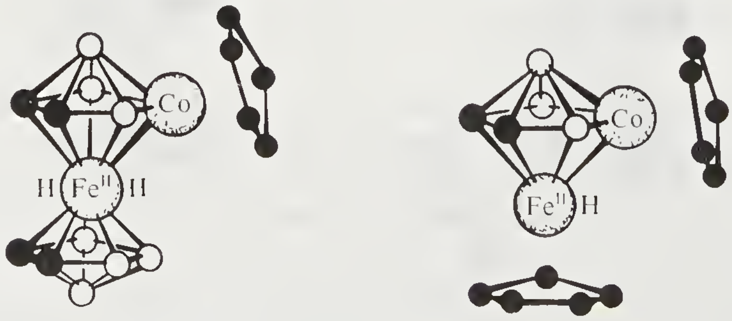


Figure 44 Proposed structure of $CpCoMe_2C_2B_3H_3Fe(H)_2Me_2C_2B_4H_4$ (left) and established structure of 1,2,4,5-$Cp_2Fe(H)CoMe_2C_2B_3H_5$ (right); the location of the metal-bound hydrogen has not been confirmed, but is proposed from NMR evidence

The planar 2,3-$C_2B_3H_5^{4-}$ 'ligand', which has a formal existence in the 1,7,2,3-$Cp_2Co_2C_2B_3H_5$ triple-decker complex discussed above, can accept two protons as B—H—B bridges to give the formal 2,3-$C_2B_3H_7^{2-}$ ligand; transition metal complexes such as 1,2,3-$(CO)_3FeC_2B_3H_7$[57] and 1,2,3-$CpCoC_2B_3H_7$[12b] can be regarded both as complexes of $C_2B_3H_7^{2-}$ and as six-vertex *nido* cages. As already noted, these species can be obtained by removal of the apex BH from the corresponding *closo*-MC_2B_4 cage, but the cobalt compound and its *C*-alkyl derivatives have also been synthesized by an entirely different route, namely the insertion of alkynes into 2-$CpCoB_4H_8$ (Figure 23a).[69]

Since 2,3-$C_2B_3H_7^{2-}$ is isoelectronic with $C_5H_5^-$, the nature of the ring–metal binding in $(CO)_3FeC_2B_3H_7$ has been investigated by MO methods[124] and compared with $CpFe(CO)_3^+$; the ferracarborane is concluded to be largely ionic, though this result is difficult to reconcile with the physical and chemical properties of the complex. X-ray crystal structures of $(CO)_3FeC_2B_3H_7$[125] (Figure 17b) and $(Me_2C_2B_3H_5)CoH(Me_2C_2B_4H_4)$[40] (*via* a cobaltocenium derivative, Figure 12) have confirmed the planarity of the C_2B_3 ring system.

A structurally anomalous six-vertex *nido*-ferracarborane, $(CO)_3FeC_4BH_5$, was mentioned in Section 5.5.3.1.5. Still another kind of structural peculiarity has been observed in the seven-vertex platinacarboranes, 1,2,3- and 1,2,4-$(Et_3P)_2PtR_2C_2B_4H_4$ (R = Me or H).[79a] These compounds, obtained by pyrolysis of the μ-$\{(Et_3P)_2PtH\}R_2C_2B_4H_5$ bridged complexes (see equation 18), have significantly different structures. When R = Me, the 1,2,3-(adjacent-carbon) isomer is obtained, but when R = H, the product is the 1,2,4-isomer; both species are roughly pentagonal bipyramidal, but X-ray studies show that, while the 1,2,4-isomer is *closo* (as expected for a 16-electron, six-vertex cage) the 1,2,3-isomer has *nonbonding* Pt—C distances and hence is relatively open (Figure 45).[79a] Such anomalies are common among metallacarboranes of the heavy metals, as noted earlier in Section 5.5.2.5.

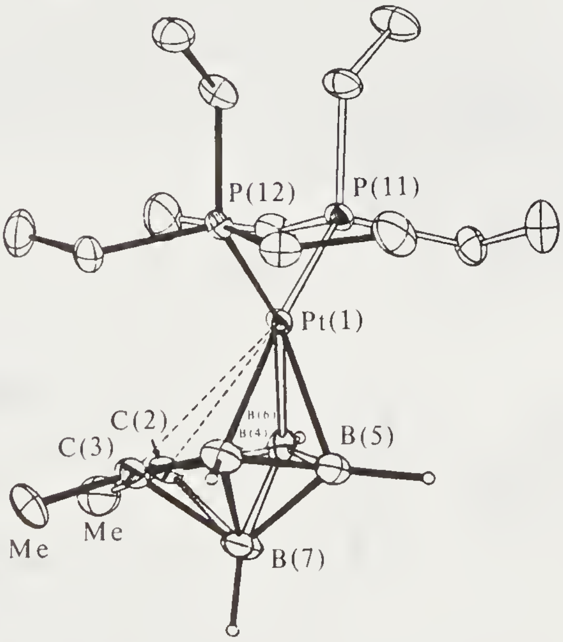


Figure 45 Structure of 1,2,3-$(Et_3P)_2PtMe_2C_2B_4H_4$

5.5.5.2 Metallaboranes

In striking contrast to the large family of seven-vertex pentagonal bipyramidal metallacarboranes, there are no known examples of *closo*-metallaborane species having this geometry. There are, however, a few six-vertex *closo* (octahedral) metallaboranes, including 1,2-$Cp_2Co_2B_4H_6$, 1,2,3-$Cp_3Co_3B_3H_5$, some *B*-cyclopentyl derivatives of these, and η-C_5Me_5 analogues of the cyclopentadienyl species. The only *mono*metallic compound in this class is $(CO)_3FeB_5H_3(CO)_2$, a red liquid obtained in the thermal reaction of B_5H_9 with $Fe(CO)_5$ (Figure 33).[93b] The violet, crystalline $Cp_2Co_2B_4H_6$ and brown crystalline $Cp_3Co_3B_3H_5$ are among the low-yield products of the previously mentioned reaction of $B_5H_8^-$, $CoCl_2$ and $C_5H_5^-$;[17b] both species are formed in larger yield by addition of CoCp units to the 2-$CpCoB_4H_7^-$ ion in THF solution.[69] The structures (Figure 46), determined from NMR and X-ray data,[36,126] contain hydrogen atoms bridging Co_2B triangular faces on the *closo* polyhedron. These hydrogens were directly located only in the Co_2B_4 complex.

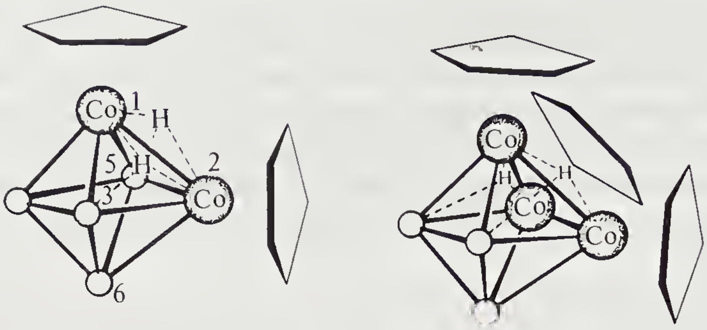


Figure 46 Structures of 1,2-$Cp_2Co_2B_4H_6$ (left) and 1,2,3-$Cp_3Co_3B_3H_5$ (right); the bridging hydrogen atoms in the dicobalt species were located and refined in an X-ray study; those in the tricobalt complex are assigned from NMR evidence

The complex $Cp_3Co_3B_4H_4$, a yellow crystalline solid which is also obtained in the $CoCl_2/B_5H_9/C_5H_5^-$ reaction, has a *closo* Co_3B_3 cage whose Co_3 triangular face has been capped by a BH unit (Figure 7). X-ray structure determinations on this species[36] and its pentamethylcyclopentadienyl counterpart, $(\eta\text{-}C_5Me_5)_3Co_3B_4H_4$,[127] disclose that the molecules have nearly identical polyhedral structures despite extreme crowding of the C_5Me_5 rings in the latter complex. These species are 14-electron, seven-vertex ($2n$-electron) systems for which Wade's rules predict capped octahedral structures, as observed (see discussion in Section 5.5.2.4).

A number of six-vertex *nido*-metallaboranes have been described, which have pentagonal pyramidal cage geometries and are structural and electronic analogues of B_6H_{10}. In general, these species are prepared by addition of a metal to B_5H_9 or the $B_5H_8^-$ ion as described in Section 5.5.3.2. In some instances, such as 2-$(CO)_3MnB_5H_{10}$,[94] 2-$(CO)_3FeB_5H_9$ (Figure 33),[93c] and 2-$CpFeB_5H_{10}$,[19] the metal occupies a basal position; in other cases the metal is apical, as in 1-$CpCoB_5H_9$, which is obtained on heating B_5H_9 with $CpCo(CO)_2$.[95a] In the $CpFeB_5H_{10}$ system, the 2-isomer at 180 °C in toluene rearranges to the 1-isomer, which contains a planar $B_5H_{10}^-$ ligand that is isoelectronic with $C_5H_5^-$ (Figure 47).[19] Thus 1-$CpFeB_5H_{10}$ is postulated as a direct structural and electronic analogue of ferrocene, although X-ray data are not yet available.

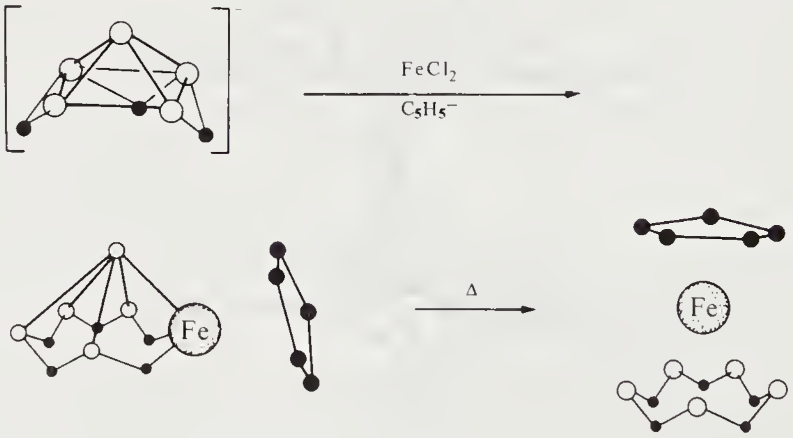


Figure 47 Formation of 2-$CpFeB_5H_{10}$ and rearrangement to 1-$CpFeB_5H_{10}$

The ferraborane 2-$(CO)_3FeB_5H_9$ loses a proton on treatment with potassium hydride, forming the $(CO)_3FeB_5H_8^-$ anion which reacts with bis(triphenylphosphine)copper(I) chloride to form a most unusual species, μ-$\{(Ph_3P)_2Cu\}(CO)_3FeB_5H_8$ (Figure 48a).[128] The unique feature of this structure is a bonding interaction between a terminal B—H hydrogen and the bridging copper atom, which forces the copper into a nearly coplanar orientation with the FeB_4 basal plane.

A variety of transition metal-bridged derivatives of B_5H_9 and B_6H_{10} has been reported. While these are not metallaboranes in a strict sense (since the metal is not part of the cage proper), there is obviously a close structural relationship. Thus the species μ-$(Ph_3P)_2CuB_5H_8$ (Figure 48c)[103] and μ-$(Ph_3P)_2CuB_6H_9$ are obtained by introduction of the copper group into a basal B—B bond in $B_5H_8^-$ and $B_6H_9^-$, respectively. Similar metal-bridged species involving nickel,[129] platinum,[130] rhodium,[130] iridium,[130] iron,[130] magnesium[131] and cadmium[132] have been characterized, including a number of complexes of neutral B_6H_{10}.[130]

A structurally different class of *nido*-metallaboranes consists of the beryllium-containing species $(B_5H_{10})_2Be$, $B_5H_{10}BeBH_4$ and $B_5H_{10}BeCp$ (Figure 49).[133] In these species, incorporation of beryllium into the borane framework is accomplished *via* reactions of 1-halopentaboranes with $Be(BH_4)_2$ or of $B_5H_{10}BeBr$ with $Cs^+B_3H_8^-$.

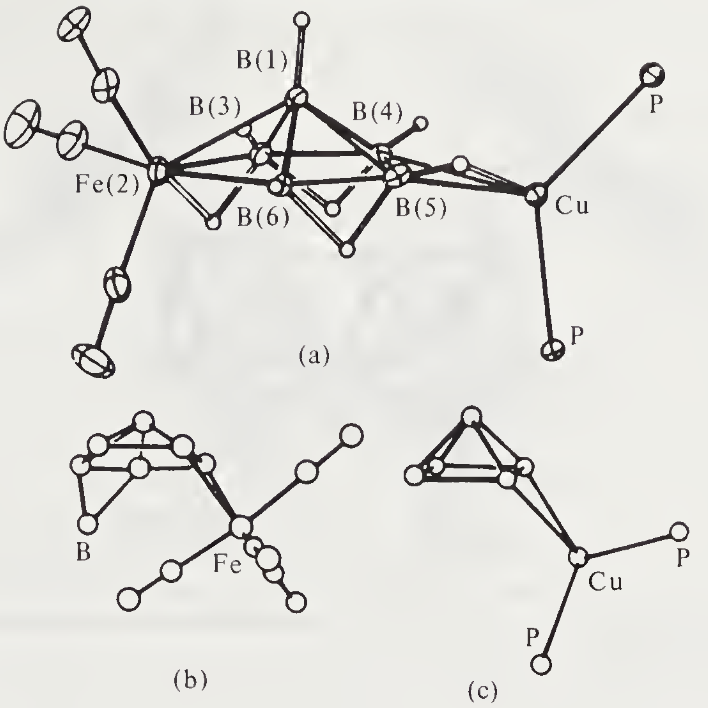


Figure 48 (a) Structure of μ-$(Ph_3P)_2Cu$-$(CO)_3FeB_5H_8$; (b) structure of μ-$(CO)_4FeB_7H_{12}^-$; (c) structure of μ-$(Ph_3P)_2$-CuB_5H_8 [bridging hydrogen atoms omitted in (b) and (c)]

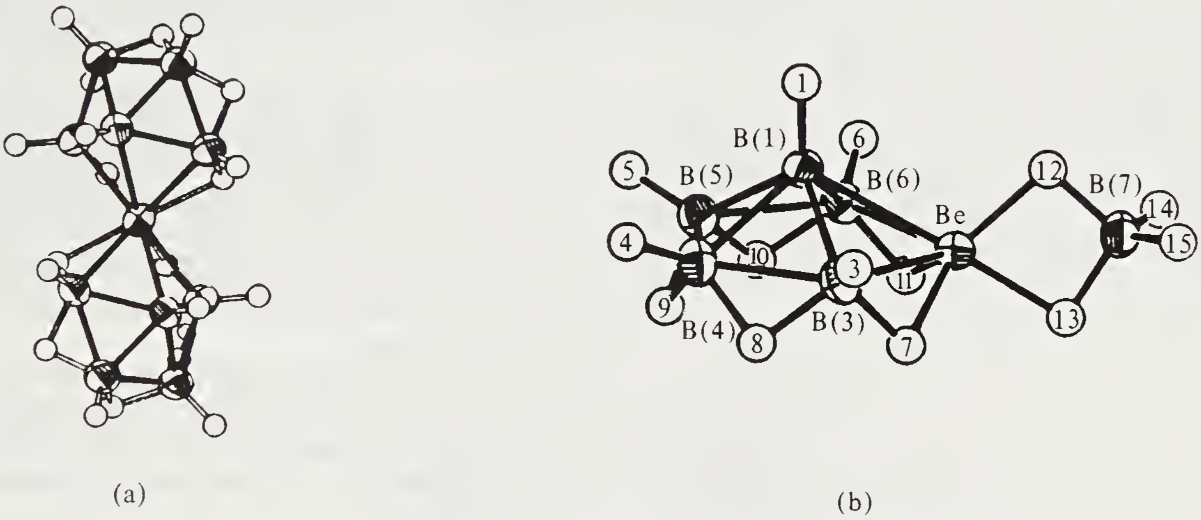


Figure 49 Structures of (a) $(B_5H_{10})_2Be$ and (b) $B_5H_{10}BeBH_4$[133b]

5.5.6 CAGE SYSTEMS WITH EIGHT, NINE OR TEN VERTICES

5.5.6.1 Metallacarboranes

Metallaboron polyhedra of intermediate size have been prepared by a wide variety of methods, but most of these, in essence, involve either insertion of metals into carboranes of 7–9 vertices, or the partial degradation of large (*e.g.* 12-vertex) metallacarboranes. General discussions of these synthetic approaches are given in Section 5.5.3.1; the present treatment will deal with certain species that illustrate the preparative and structural principles involved.

Few eight-vertex metallacarboranes are known. The direct insertion of metals into *closo*-2,4-$C_2B_5H_7$ by thermal reaction with $Fe(CO)_5$ or $CpCo(CO)_2$ gives, respectively, $(CO)_3$-$FeC_2B_5H_7$ and $CpCoC_2B_5H_7$;[14,57] the latter compound is also obtained in low yield by treatment of the $C_2B_5H_7^{2-}$ dianion with $CoCl_2$ and NaC_5H_5.[82] Electron-counting arguments (Section 5.5.2.4) predict regular *closo* structures for these 18-electron cages, and X-ray evidence has confirmed that the related *commo*-cobaltacarborane $(\eta$-$C_5Me_5)_2Co_3Me_4C_4B_8H_7$ contains two eight-vertex 18-electron $Co_2C_2B_4$ *closo* polyhedra fused at a common cobalt vertex (Figure 50).[134] This particular species, obtained as a by-product of the synthesis of 1,2,3-$(\eta$-$C_5Me_5)CoMe_2C_2B_4H_4$ from 2,3-$Me_2C_2B_4H_5^-$ ion, $CoCl_2$ and LiC_5Me_5 in THF solution, has the peculiar feature that the two cages are linked by a direct B—B bond; moreover, the two borons involved have no terminal hydrogen atoms.[134] Another presumed eight-vertex, 18-electron *closo* system is

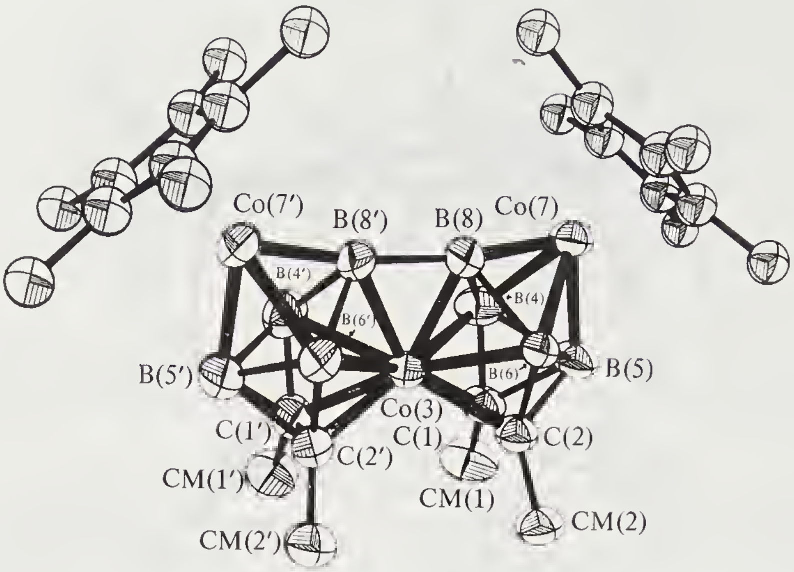


Figure 50 Structure of (η-C_5Me_5)$_2$$Co_3Me_4C_4B_8H_7$. All boron atoms except B(8) and B(8′) have attached terminal hydrogen atoms, not shown; also not shown is a hydrogen bound to the central cobalt, assigned from NMR data but not located in the X-ray study

$CpCoSnMe_2C_2B_4H_4$, prepared by reaction of $SnMe_2C_2B_4H_4$ (Section 5.5.5.1) with CpCo-(CO)$_2$.[115]

The unusual cobaltaferracarborane $CpCoFeMe_4C_4B_8H_8$ (Figure 42a) can be viewed as two eight-vertex capped polyhedra fused along a common edge; in this case the normal eight-vertex *closo* geometry is not observed because there is a shortage of two electrons relative to the 'normal' requirement of $2n + 2$ per cage.[118,119]

Recently the first confirmed example of an eight-vertex open cage metallacarborane, $CpCoPh_4C_4B_3H_3$, was prepared by Sneddon *et al.*[75b] from B_5H_9, diphenylacetylene and cobalt vapor and characterized by X-ray diffraction.[135] Significantly, this molecule is formally cage-isoelectronic with the metallaborane $Cp_4Ni_4B_4H_4$ [since NiCp and CH are each formal three-electron donors to skeletal bonding (Section 5.5.2.4)], yet differs from it dramatically in cage geometry; as discussed in the following section, the Ni_4B_4 cluster is a *closo* (D_{2d}) polyhedron. Like the nickel compound, *arachno*-$CpCoPh_4C_4B_3H_3$ structurally violates the Wade rules,[2,27] which predict *nido* geometry for eight-vertex, 20-electron systems.

Nine- and ten-vertex metallacarboranes of iron, cobalt, nickel or platinum have been synthesized by direct reactions (that is, without prior opening of the cage) of the *closo*-carboranes 2,4-$C_2B_5H_7$, 1,7-$C_2B_6H_8$, 4,5-$C_2B_7H_9$ or their *C*-alkyl derivatives with transition metal reagents. The products incorporate MC_2B_5, $M_2C_2B_5$, $M_3C_2B_5$, MC_2B_6, $M_2C_2B_6$ or MC_2B_7 cage systems, as illustrated by reactions (34),[14] (35),[58] (36),[136] (37)[59] and (38)–(41).[137]

$$C_2B_5H_7 + CpCo(CO)_2 \xrightarrow[\text{gas phase}]{260\,^\circ C}$$

$$\underset{4\%}{CpCoC_2B_4H_6} + \underset{25\%}{CpCoC_2B_5H_7} + \underset{\substack{\text{1,8,5,6-isomer, 25\%}\\ \text{1,7,5,6-isomer, 2\%}}}{Cp_2Co_2C_2B_5H_7} + \underset{\substack{\text{2,3,8,1,6-isomer, 20\%}\\ \text{2,3,4,1,10-isomer, 1\%}}}{Cp_3Co_3C_2B_5H_7} \qquad (34)$$

$$\underset{\text{(mixture of isomers)}}{H_6B_5C_2\text{-}C_2B_5H_6} + CpCo(CO)_2 \longrightarrow \underset{\text{(6 isomers)}}{\text{1,8,5,6-}Cp_2Co_2C_2B_5H_6\text{-}C_2B_5H_6} \qquad (35)$$

$$CpCoMe_2C_2B_4H_4 + Fe(CO)_5 \xrightarrow[n\text{-nonane}]{125\,^\circ C} closo\text{-}\{(CO)_3Fe\}_2CpCoMe_2C_2B_4H_4 \qquad (36)$$

$$C_2B_5H_7 + Pt\{PhCH{=}CH_2(PEt_3)_2\} \longrightarrow closo\text{-}(Et_3P)_2Pt_2C_2B_5H_7 \qquad (37)$$

$$\underset{R\,=\,H,\ Me;\ R'\,=\,Me,\ Et}{R_2C_2B_6H_6 + Pt(trans\text{-stilbene})(PR'_3)_2} \xrightarrow{20\,^\circ C} \underset{\substack{\text{(two isomers: one closed}\\ \text{polyhedral, one open-cage)}}}{(R'_3P)_2PtR_2C_2B_6H_6} \qquad (38)$$

$$\underset{R\,=\,Me;\ R'\,=\,Me,\ Et}{R_2C_2B_6H_6 + Ni(cod)(PR'_3)_2} \xrightarrow{20\,^\circ C} \underset{(closo\text{ only})}{(PR'_3)_2NiR_2C_2B_6H_6} \qquad (39)$$

$$C_2B_7H_9 \quad + \quad Pt(PEt_3)_3 \quad \xrightarrow{20\,^\circ C} \quad (PEt_3)_2PtC_2B_7H_9 \qquad (40)$$

(one isomer; open-cage)

$$R_2C_2B_7H_7 \quad + \quad Ni(cod)PR'_3 \quad \xrightarrow{20\,^\circ C} \quad (PR'_3)_2NiR_2C_2B_7H_7 \qquad (41)$$

$R = H, Me; R' = Me, Et$ (one isomer, open-cage)

The cobaltacarborane products in equations (34) and (35) are all formulated as *closo* species, in agreement with the $2n + 2$ skeletal electron count in each cage. The two isomers of $Cp_2Co_2C_2B_5H_7$, a nine-vertex *closo* system, exhibit the phenomenon, rare in metallaborane chemistry, of *reversible* thermal migration of metal atoms on the polyhedral surface (Figure 25b).[77a] Crystallographic analyses have confirmed both structures shown.[138] Similar equilibria are exhibited by linked-cage carboranyl derivatives of the same two isomers of $Cp_2Co_2C_2B_5H_7$, except that in this case the rearrangement is complicated by the presence of the *closo*-$C_2B_5H_6$ ligand (Figure 27) as described in Section 5.5.3.1.7.[58]

The metal-containing species prepared *via* direct insertion by Stone and coworkers (equations 37–41) exhibit some novel stereochemistry and provide several examples of clear 'violations' of Wade's rules (Section 5.5.2.5). Although the $(Et_3P)_2Pt_2C_2B_5H_7$ complex (equation 37) is a *closo* nine-vertex polyhedron, as expected,[59] the nine-vertex platinacarborane isomers derived from $C_2B_6H_8$ or its *C,C'*-dimethyl derivative consist of an open-cage[139a] and a closed-cage (*closo*)[139b] species (Figure 51b, a).[137] Since these are *formally* 20-electron ($2n + 2$) PtC_2B_6 cages, *closo* geometry is anticipated; the isolation, therefore, of a small quantity of a '*nido*' isomer along with the major (*closo*) isomer is ascribed to kinetic effects and to a tendency of platinum and nickel to contribute only two, rather than three, orbitals of suitable energy to cage bonding in bis(phosphino)platinacarboranes.[47b] The corresponding synthesis of $(Et_3P)_2PtC_2B_7H_9$ (equation 40) generates only one detectable isomer, and it is open-cage (Figure 51c)[139c] in violation of electron-counting arguments. Similar findings with nickel in place of platinum (equations 39 and 41), have been reported;[137] in addition, reactions of nickel or platinum reagents with the *arachno*-carborane $C_2B_7H_{13}$ or its *C,C'*-dimethyl derivative give open-cage MC_2B_9 species (Figure 17a).[56]

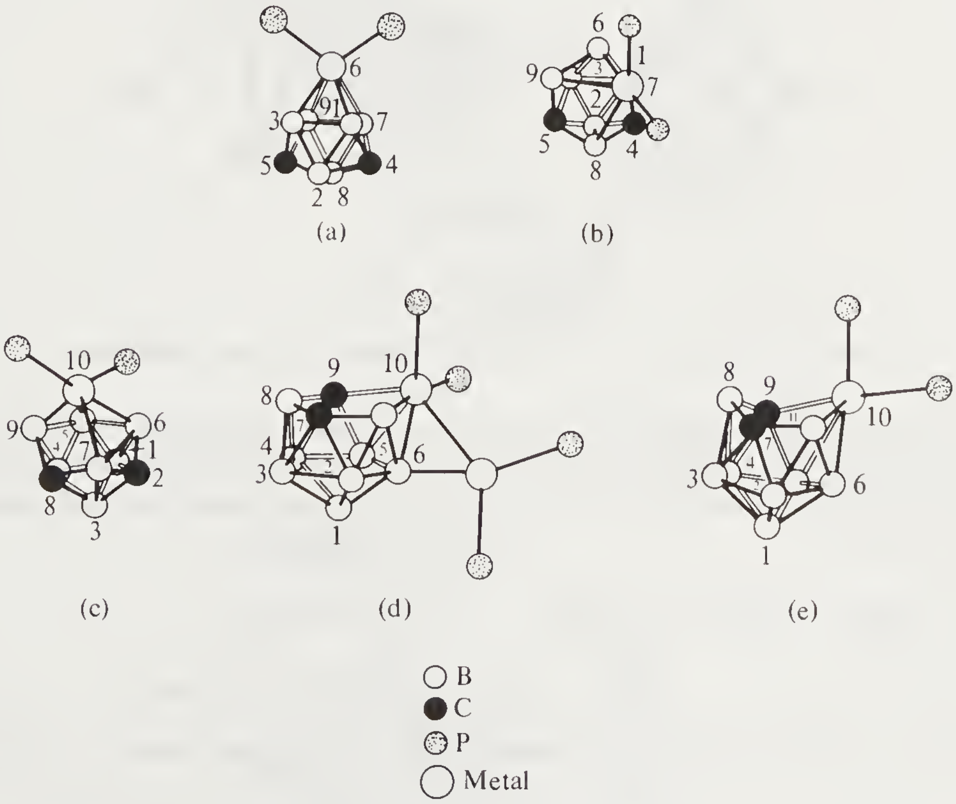


Figure 51 Structures of nickel and platinum metallacarboranes:[137] (a) *closo*-$L_2MC_2(R_2)B_6H_6$ ($L = Et_3P$ or Me_3P; $M = Ni$ or Pt; $R = H$ or Me); (b) *nido*-$L_2MC_2(R_2)B_6H_6$ ($L = Et_3P$ or Me_3P; $M = Pt$; $R = H$ or Me); (c) *nido*-$L_2PtC_2(R_2)B_7H_7$ ($L = Et_3P$ or Me_3P; $M = Ni$ or Pt; $R = H$ or Me); (d) *nido*-μ-$(Me_3P)_2Pt$-$(Me_3P)_2PtC_2B_8H_{10}$; (e) *nido*-$(Me_3P)_2PtC_2B_8H_{10}$

Reactions of *nido*-carborane anions with transition metal reagents (Section 5.5.3.1.2) furnish another useful route to 9- and 10-vertex metallacarboranes. (The polyhedral expansion approach, which is assumed to involve *nido* anionic intermediates formed from *closo*-carboranes, also generates 9- and 10-vertex products as described below.) The $C_2B_7H_{11}^{2-}$ ion and its conjugate acid $C_2B_7H_{12}^-$, which are derived from the neutral carborane $C_2B_7H_{13}$ (Figure 17a) by removal of equatorial methylene protons, are precursors to several MC_2B_7 and MC_2B_6 cage systems (equations 42–44).[140–142] The structures of the $(C_2B_7H_9)_2Co^-$ and $(CO)_3MnC_2B_6H_8^-$ ions have been crystallographically determined (Figure 52).[143,144] In these complexes, as in most metallacarboranes derived from *nido*-carborane anions, the metal and framework carbon atoms occupy adjacent vertices; this is attributable to the tendency of the anions to adopt structures in which the cage carbons are in low-coordinate sites on the open face,[30] which is normally the locus of complexation by the metal.

$$C_2B_7H_{11}^{2-} + BrMn(CO)_5 \xrightarrow[\text{reflux}]{\text{THF}} (CO)_3MnC_2B_6H_8^- \qquad (42)$$

41% (as Et_4N^+ salt)

$$C_2B_7H_{11}^{2-} \xrightarrow{Co^{2+}} Co^0 + H_2 + (C_2B_7H_9)_2Co^- \qquad (43)$$

$$\xrightarrow[C_5H_5^-]{Co^{2+}} CpCoC_2B_7H_9$$

$$C_2B_7H_{12}^- \xrightarrow[\substack{M\,=\,Rh,\,Ir\\ R\,=\,aryl}]{MCl(PR_3)_3} (PR_3)_2M(H)C_2B_7H_9 \qquad (44)$$

$$\xrightarrow{RuHCl(PPh_3)_3} (PR_3)_2RuC_2B_7H_9$$

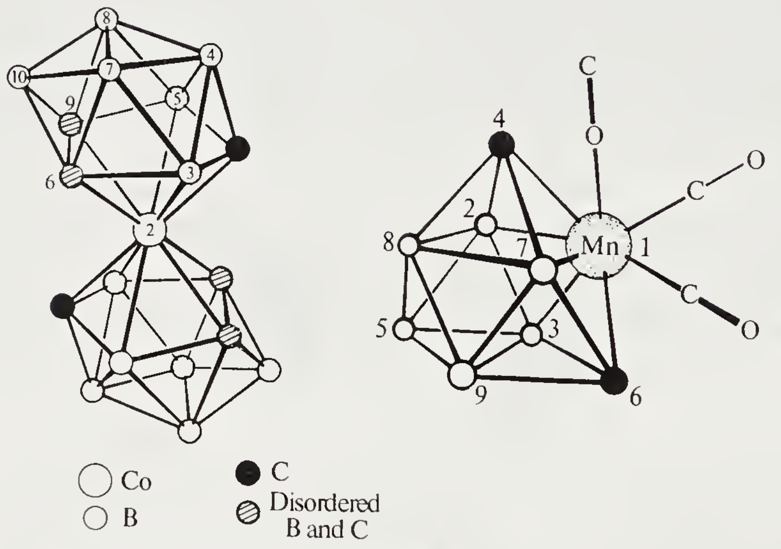


Figure 52 Structures of the $(C_2B_7H_9)_2Co^-$ and $(CO)_3MnC_2B_6H_8^-$ ions

The synthetic approach of polyhedral expansion (Section 5.5.3.1.8) has also been employed to generate 9- and 10-vertex metallacarboranes from intermediate *closo*-carboranes (equations 45–49).[82,145,146] In this technique a presumed *nido*-dianion is formed but is not isolated prior to addition of the metal.

$$2,4\text{-}C_2B_5H_7 \xrightarrow[C_{10}H_8]{Na} [C_2B_5H_7^{2-}] \xrightarrow[C_5H_5^-]{CoCl_2} 1,2,4\text{-}CpCoC_2B_4H_6 +$$

25% (other products 1–2% each)

$$CpCoC_2B_5H_7 + CpCoC_2B_6H_8 + Cp_2Co_2C_2B_4H_6 + Cp_2Co_2C_2B_5H_7 + Cp_2Co_2C_2B_6H_8 \qquad (45)$$

$$1,7\text{-}C_2B_6H_8 \xrightarrow[C_{10}H_8]{Na} \xrightarrow[C_5H_5^-]{CoCl_2} CpCoC_2B_6H_8 + Cp_2Co_2C_2B_6H_8 \qquad (46)$$

4% 7%

$$4,5\text{-}C_2B_7H_9 \xrightarrow[C_{10}H_8]{Na} \xrightarrow[C_5H_5^-]{CoCl_2} \underset{12\%}{CpCoC_2B_6H_8} + \underset{9\%}{CpCoC_2B_7H_9} \qquad (47)$$

$$1,7\text{-}C_2B_6H_8 \xrightarrow[C_{10}H_8]{Na} \xrightarrow[C_5H_5^-]{FeCl_2} \underset{(2\text{ isomers, }18\%)}{CpFeC_2B_6H_8} \qquad (48)$$

$$4,5\text{-}C_2B_7H_9 \xrightarrow[C_{10}H_8]{Na} \xrightarrow[C_5H_5^-]{FeCl_2} \underset{(2\text{ isomers, }10\%)}{CpFeC_2B_6H_8} + \underset{5\%}{Cp_2Fe_2C_2B_6H_8} + \underset{6\%}{CpFeC_2B_8H_{10}} \qquad (49)$$

All of the metallacarborane products in reactions (45)–(47) contain formal ($2n + 2$)-electron cages and have been assigned *closo* structures. As shown, these reactions tend to produce a mixture of 'expanded' polyhedra (systems larger than the original carborane) as well as other products in which the metal replaces boron and the number of vertices is unchanged. This is typical of the 'polyhedral expansion' reaction as applied to the smaller carboranes; with larger carborane substrates, especially $C_2B_9H_{11}^{2-}$, the expansion proceeds more cleanly with little or no loss of boron (Sections 5.5.7–5.5.9).

The ferracarboranes formed in reactions (48) and (49) are somewhat exceptional. The $CpFeC_2B_6H_8$ isomers contain formal Fe(III) and are paramagnetic, hence are formally assigned only $2n + 1$ skeletal electrons but are nonetheless believed to have *closo* structures, based on NMR spectra of the corresponding reduced Fe(II) species.[145] The proposed geometry of 4,1,8-$CpFeC_2B_6H_8$ (Figure 53) contains iron in a low-coordinate vertex of the tricapped trigonal prism.[145] The diiron species obtained in reaction (49) is a formal $2n$-electron system and adopts the unique geometry shown in Figure 54, in which the metal atoms are within bonding distance of each other.[146] While there are a number of ways to describe, or qualitatively account for, this observed structure, a useful approach is to regard the $Fe_2C_2B_6$ cage as a capped-tricapped trigonal prism; this would be consistent with the general rule that $2n$-electron systems adopt the geometry of a *closo* ($n - 1$)-vertex polyhedron with the remaining atom capping one of the faces (Section 5.5.2.4).

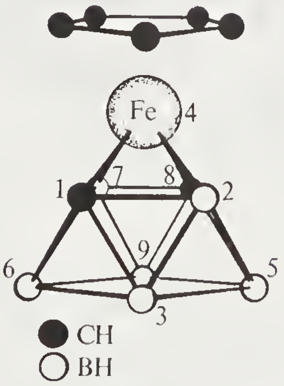


Figure 53 Proposed structure of 4,1,8-$CpFeC_2B_6H_8$

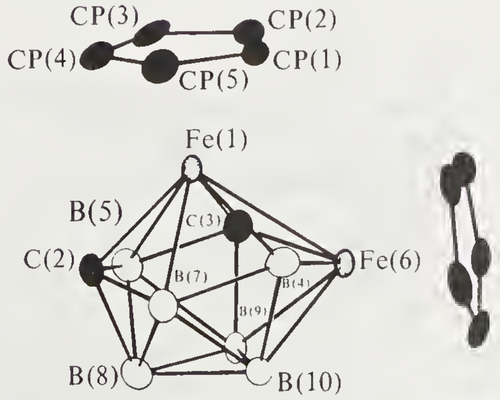


Figure 54 Structure of $Cp_2Fe_2C_2B_6H_8$

The principle of polyhedral expansion can be applied to *nido*-carboranes as well, as illustrated by the insertion of nickel into 2-CB_5H_9 *via* treatment with sodium amalgam followed by nickelocene (equation 13). Several isomers of a nine-vertex trinickel metallacarborane, $Cp_3Ni_3CB_5H_6$,[66] are known. The established structure[66] of one of the isomers (Figure 55) is *nido*, in conformity with the $(2n + 4)$-electron cage system, and is isostructural with the metallaborane $Cp_4Ni_4B_5H_5$, described below.

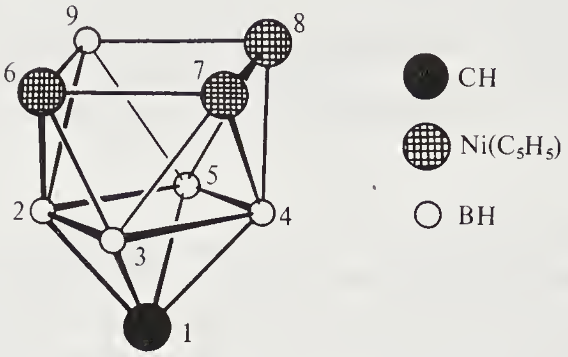


Figure 55 Structure of $Cp_3Ni_3CB_5H_6$

The polyhedral contraction technique (Section 5.5.3.1.8) also yields 9- and 10-vertex metallacarboranes, *via* partial degradation of larger (usually icosahedral) metallacarboranes in basic media,[84] as illustrated by the conversion of 1,2,3-$CpCoC_2B_9H_{11}$ to $CpCoC_2B_8H_{10}$ and $CpCoC_2B_7H_9$ (equation 21). Further degradation of $CpCoC_2B_8H_{10}$ by $FeCl_3$ in ethanol produces a *nido* species, $CpCoC_2B_7H_{11}$, whose structure (Figure 56) has been established by X-ray diffraction.[147] In these examples only one or two BH units are removed from the polyhedron, but the degradation of the 13-vertex system $CpCoC_2B_{10}H_{12}$ (Section 5.5.9) in ethanolic KOH eliminates *four* skeletal atoms (carbon and three boron) to generate a nine-vertex monocarbon species, $CpCoCB_7H_8^-$, in 65% yield.[148] The cage structure (Figure 57)[149] is a *closo* polyhedron,

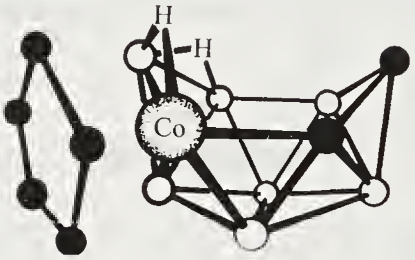


Figure 56 Structure of $CpCoC_2B_7H_{11}$

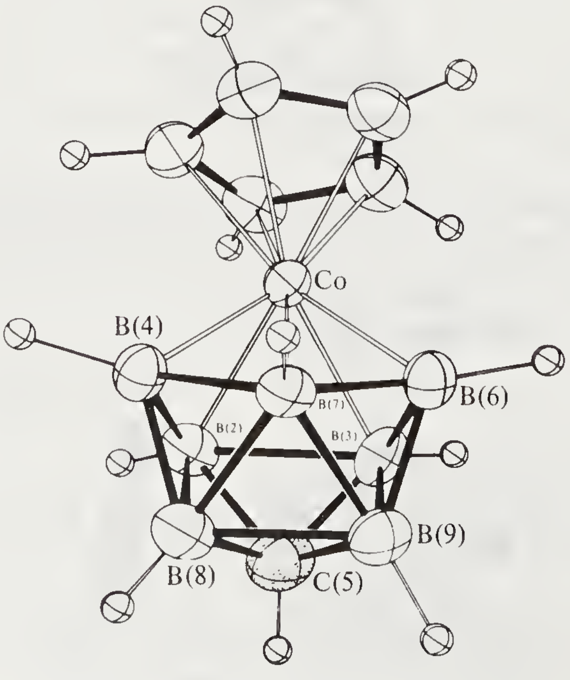


Figure 57 Structure of the $CpCoCB_7H_8^-$ ion

as expected for a nine-vertex, 20-electron system. The parent and C-methylated $CpCoCB_7H_8^-$ ions undergo oxidation to neutral $CpCoCB_7H_8$ and the C-methyl derivative, respectively, which contain formal cobalt(IV). The neutral species are unstable at room temperature, even in the absence of light and air.[148]

The $CpCoCB_7H_8^-$ ion can be expanded *via* the sodium naphthalenide treatment followed by reaction with $NiBr_2{\cdot}2C_2H_4(OMe)_2$ and NaC_5H_5 to give four isomers of a mixed-metal system, $Cp_2CoNiCB_7H_8$.[77b] On heating the principal isomer (I) at 300 °C, rearrangement to other isomers occurs as shown in Figure 25c. The structure of IV has been confirmed crystallographically, with a Co—Ni distance of 2.449(1) Å.[150]

Other than the methods of metal insertion into neutral and anionic carboranes, described above, the only other generally applicable technique that has been utilized in the synthesis of intermediate metallacarboranes is thermal isomerization (Section 5.5.3.1.7).[58,77,138] There are, however, reports of other syntheses that cannot as yet be described as general, but may have significance for future investigation. The reaction of 2-butyne with the *nido*-ferraborane $1\text{-}(CO)_3FeB_4H_8$ yields a small quantity of a partly characterized species formulated as $(CO)_3FeMe_4C_4B_4H_4$, which decomposes to form a stable tetracarbon carborane, $Me_4C_4B_4H_4$.[151] This observation represents perhaps the first direct synthesis of a carborane from a metallaborane and an alkyne, although *metalla*carboranes had previously been prepared by alkyne insertion into *nido*-cobaltaboranes.[69] A new (1,7,2,5) isomer of $Cp_2Co_2C_2B_5H_7$ was produced (as the C,C′-dimethyl derivative) from the reaction of B_5H_9, C_5H_6, 2-butyne, and cobalt vapor,[75] and the treatment of the *commo*-ferracarborane $(2,3\text{-}Me_2C_2B_4H_4)_2FeH_2$ (Figure 40) with CO gas at 200 °C gave $2,1,4\text{-}(CO)_3FeMe_2C_2B_7H_7$, a 10-vertex *closo* polyhedron (Figure 58) in a surprising 76% yield.[119]

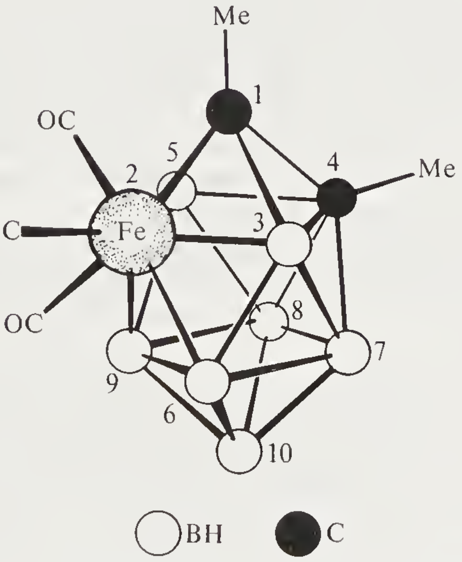


Figure 58 Proposed structure of $2,1,4\text{-}(CO)_3FeMe_2C_2B_7H_7$

For the most part, the substitution chemistry of the 8- to 10-vertex metallacarboranes has not been examined in detail. However, $2,1,6\text{-}CpCoC_2B_7H_9$ undergoes bromination in CCl_4 to give di- and tri-bromo derivatives, while acylation occurs exclusively at boron; in contrast to the metallocenes, acetyl substitution does not take place at the C_5H_5 ring.[152]

5.5.6.2 Metallaboranes

The principal borane substrates that have been utilized in the preparation of 8- to 10-vertex metallaboranes are $B_9H_{13}^{2-}$, $B_9H_{14}^-$ and $B_9H_{12}L^-$ (L = Lewis base), derived from $B_{10}H_{14}$; surprisingly, B_5H_9 and the $B_5H_8^-$ ion have also played an important role. The only known eight-vertex *closo*-metallaboranes (exclusive of metallacarboranes) are the previously mentioned species $Cp_4Co_4B_4H_4$,[17b,153] $Cp_4Ni_4B_4H_4$[21] and $Cp_3Co_3B_5H_5$.[95b] The Co_4B_4 and Ni_4B_4 clusters are the only tetrametallic boron cage compounds, and are structurally important species. As shown in Figure 59, both complexes have *closo* geometries with idealized D_{2d} symmetry, but they differ in that the metal atoms occupy the high-coordinate vertices in the cobalt system and the low-coordinate vertices in the nickel compound. *Both species violate the Wade skeletal electron rules* (Section 5.5.2.4) in that the cobalt complex has 16 electrons ($2n$) while the nickel compound has 20 ($2n + 4$), despite which both molecules exhibit undistorted *closo* geometry as proved by X-ray

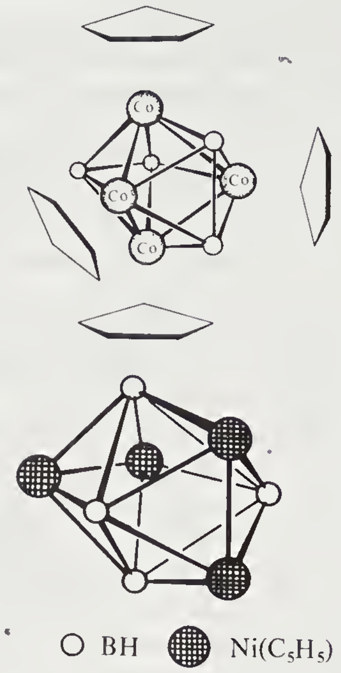


Figure 59 Structures of $Cp_4Co_4B_4H_4$ (top) and $Cp_4Ni_4B_4H_4$ (bottom)

diffraction studies.[21,153] This intriguing structural problem has been discussed in qualitative terms and viewed in the context of eight-vertex polyhedra in general;[153] recently a quantitative MO treatment has provided an elegant insight into the observed structures by viewing each molecule as interlocking distorted B_4 and M_4 tetrahedra.[154] The green tetracobalt complex was isolated in very low yield from the reaction of $CoCl_2$, $B_5H_8^-$ and $C_5H_5^-$ in cold THF,[17b] while the brown tetranickel compound was produced in somewhat larger amounts (~17%) from the treatment of $B_5H_8^-$ with nickelocene in the presence of sodium naphthalenide;[21] the same reaction gives the green nine-vertex *nido* species $Cp_4Ni_4B_5H_5$, whose structure is analogous to that of $Cp_3Ni_3CB_5H_6$ (Figure 55) with NiCp replacing the apex CH unit.

A related compound, $Cp_3Co_3B_5H_5$, has been obtained by co-condensation of B_5H_9, C_5H_6 and cobalt vapor,[95b] and is proposed to have a *closo* geometry like that of its isoelectronic analogue $Cp_4Co_4B_4H_4$. A σ-cyclopentyl derivative of this molecule was isolated from the same reaction.[95b]

A unique metallaborane containing eight heavy atoms is μ-$(CO)_4FeB_7H_{12}^-$, which consists of a pyramidal B_6H_{10} framework in which one B—H—B bridge has been replaced by a bridging BH_3 unit and another by an $Fe(CO)_4$ moiety.[155] This species is generated by reaction of B_6H_{10} with $Fe_2(CO)_9$ to form neutral μ-$(CO)_4FeB_6H_{10}$, which on reaction with potassium hydride yields the μ-$(CO)_4FeB_6H_9^-$ anion; the latter complex on treatment with B_2H_6 produces μ-$(CO)_4FeB_7H_{12}^-$.

Nine-vertex metallaboranes are rare. Other than $Cp_4Ni_4B_5H_5$, mentioned above, the only published example at this writing is $(Et_3P)_2PtB_8H_{12}$, a *nido* species obtained by degradation of $(Et_3P)_2PtB_9H_{11}L$ (see below; L = Lewis base) in alcohol.[100] Another platinaborane, $(EtMe_2P)_2PtB_8H_{12}$, has been synthesized by Greenwood and co-workers from the reactions of $B_9H_{14}^-$ or $B_9H_{13}SMe_2$ with $(PhMe_2P)_2PtCl_2$;[156] deprotonation and subsequent addition of more platinum reagent gives *arachno*-$\{(PhMe_2P)_2Pt\}_2B_8H_{10}$.

A rather large family of 10-vertex *nido*-metallaboranes now exists, most of these species having an MB_9 or M_2B_8 framework analogous to $B_{10}H_{14}$. A straightforward synthesis[157a] is based on metal insertion into $B_9H_{14}^-$ (equation 50). The structure of a *B*-substituted derivative of the manganaborane product[157b] is depicted in Figure 60. Traces of a 2-THF-substituted derivative were also obtained; this species can be produced in good yield on oxidation of the parent anion in THF. The rhenium analogue, 6-$(CO)_3ReB_9H_{13}^-$, has been prepared similarly from $Re(CO)_5Br$.[157a]

$$B_9H_{14}^- + BrMn(CO)_5 \xrightarrow{R_2O} 6\text{-}(CO)_3MnB_9H_{13}^- + 2CO + HBr \qquad (50)$$

It is apparent from Figure 60 that these complexes closely correspond to a $B_{10}H_{14}$ basket in which a BH unit at the 6 (or 9) vertex has been replaced by an electronically equivalent (two-electron donor) $(CO)_3Mn^-$ group, and a detailed comparison of X-ray data on $B_{10}H_{14}$ and the manganaborane confirms this impression.

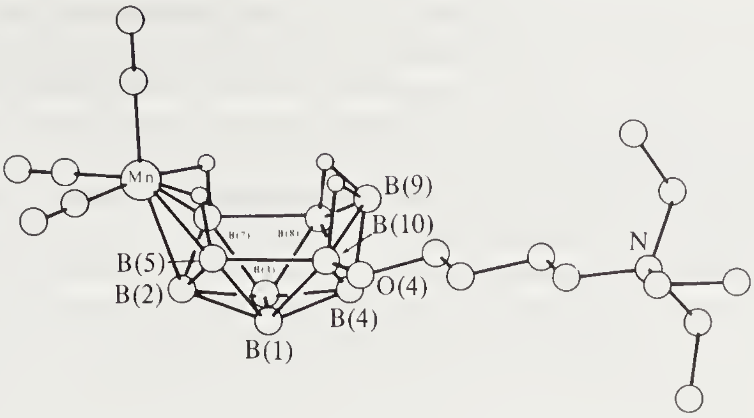


Figure 60 Structure of 10-$Et_3N(CH_2)_4O$-6-$(CO)_3MnB_9H_{12}$

The manganaborane structure in Figure 60 is analogous to that proposed earlier for the *nido*-platinaborane $(Et_3P)_2PtB_9H_{11}L$, which was obtained by reaction of *trans*-$(Et_3P)_2PtClH$ with the $B_9H_{12}^-$ ion in the presence of a donor, L, which can be an amine, nitrile, phosphine or sulfide.[100]

Several cobaltaboranes based on $B_{10}H_{14}$ are known, in which the metal(s) occupy any of several cage locations. These were isolated from reactions involving $B_9H_{14}^-$, $B_5H_8^-$ or B_5H_9 (equations 51–53).[17,105,95a] Yields in reactions (51) and (53) are low (1–2%) but the pentamethylcyclopentadienyl complexes in reaction (52) are obtained in about 10% yield. X-ray structure determinations on 5-$CpCoB_9H_{13}$ (Figure 9),[37] 6-(η-C_5Me_5)CoB_9H_{13}, and the 5,7- and 6,9-isomers of (η-C_5Me_5)$_2Co_2B_8H_{12}$ (Figure 61)[105] establish the $B_{10}H_{14}$-like cage geometry and, again, reveal remarkably close similarity to the structural parameters of $B_{10}H_{14}$ itself. It is worth noting that in all known metallaborane analogues of $B_{10}H_{14}$, the bridging hydrogen atoms retain the same locations.

$$B_5H_8^- + CoCl_2 + C_5H_5^- \xrightarrow{THF}$$

$$5\text{-}CpCoB_9H_{13} + \text{several other cobaltaboranes} \qquad (51)$$

(minor product) (see Sections 5.5.1.2 and 5.5.3.2.2)

$$B_9H_{14}^- + CoCl_2 + C_5Me_5^- \xrightarrow{THF}$$

$$6\text{-}(\eta\text{-}C_5R_5)CoB_9H_{13} + 5,7\text{-}(\eta\text{-}C_5R_5)_2Co_2B_8H_{12} + 6,9\text{-}(\eta\text{-}C_5R_5)_2Co_2B_8H_{12} \qquad (52)$$

(R = Me) (major products)

$$B_5H_9 + CpCo(CO)_2 \xrightarrow{225\ °C/75\ °C} 2\text{-}CpCoB_9H_{13} + 1\text{-}CpCoB_5H_9 \qquad (53)$$

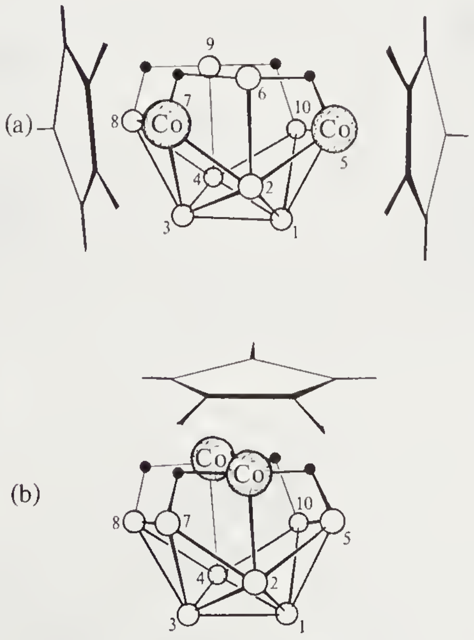


Figure 61 Structures of 5,7- and 6,9-$(PCp)_2Co_2B_8H_{12}$; a C_5Me_5 ring has been omitted for clarity in the lower drawing

The *nido* 10-vertex platinaheteroboranes 9,9′-$(Ph_3P)_2$-6,9-$SPtB_8H_{10}$[96] and 9,9′-$(Ph_3P)_2$-6,9-$NPtB_8H_{11}$[97] have been mentioned in Section 5.5.3.2. Their structures are analogous to those in Figures 60 and 61 with the 6,9 vertices occupied by sulfur (or nitrogen) and platinum, respectively. Again, the X-ray-determined *nido* cage geometries are in conformity with the electron-counting rules previously discussed.

The only *closo*-metallaboranes in the 9- to 10-vertex range are 1- and 2-$CpNiB_9H_9^-$ and their *B*-perchloro counterparts.[92] The parent species are formed, together with larger nickelaboranes, in the reaction of nickelocene with *nido*-$B_9H_{12}^-$ or *closo*-$B_9H_9^{2-}$ (equations 54, 55). Figure 62 presents schematically the formation and proposed structures of these complexes; as shown, isomerization of the 2-isomer converts it to 1-$CpNiB_9H_9$. The perchloro derivatives, prepared by treatment with Cl_2 in acetonitrile, are also thermally interconvertible, the 2-isomer converting to 1-$CpNiB_9Cl_9$ rapidly at 130 °C.[92]

$$B_9H_{12}^- + Cp_2Ni \xrightarrow[MeCN]{Na/Hg} \underset{7\%}{1\text{-}CpNiB_9H_9^-} + \underset{18\%}{2\text{-}CpNiB_9H_9^-} \qquad (54)$$

$$B_9H_9^{2-} + (CpNiCO)_2 \xrightarrow{MeCN} \underset{18\%}{1\text{-}CpNiB_9H_9^-} + \underset{20\%}{2\text{-}CpNiB_9H_9^-} \qquad (55)$$

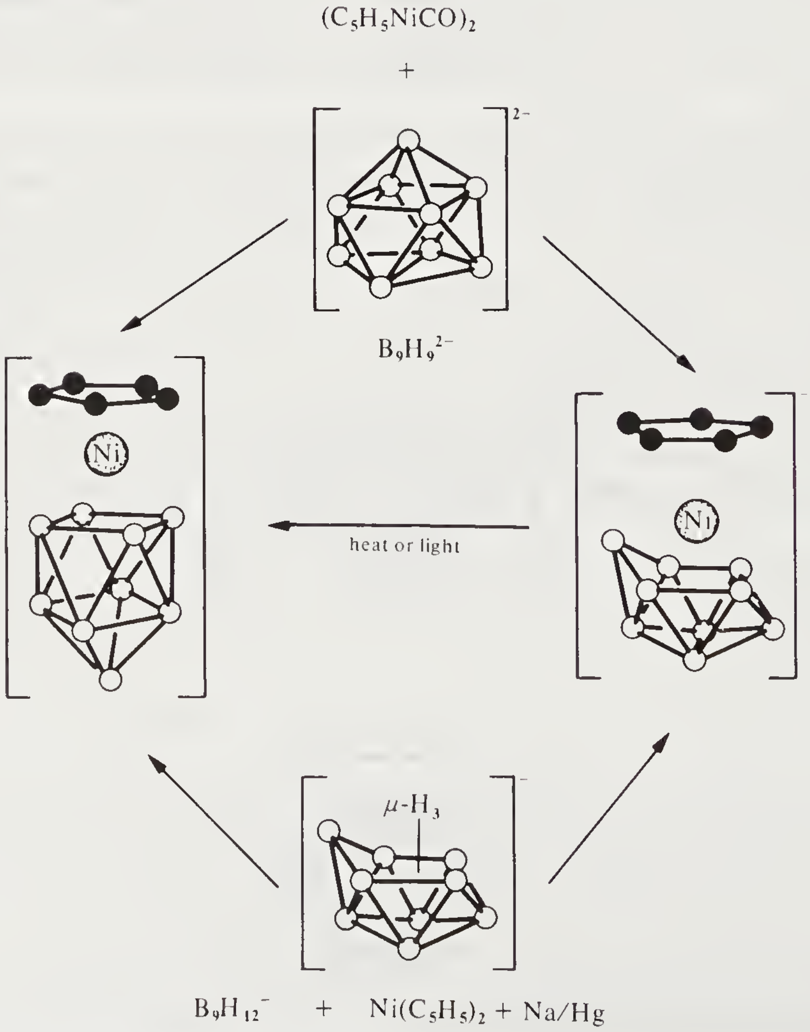


Figure 62 Synthesis of 1- and 2-$CpNiB_9H_9^-$

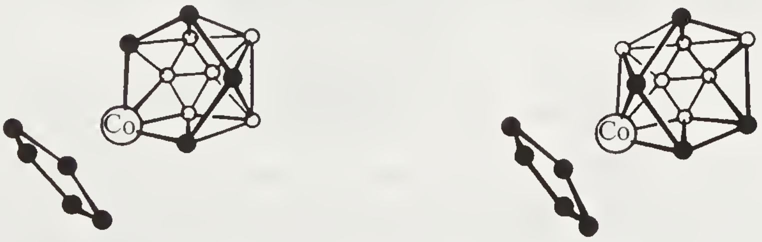
5.5.7 CAGE SYSTEMS WITH ELEVEN VERTICES

5.5.7.1 Metallacarboranes

The common polyhedral shapes to be expected for 11-atom cages are the *closo*-octadecahedron (Figure 3h) for $(2n + 2)$-electron systems, and the *nido* icosahedral fragment, derived by removal of one vertex from a 12-vertex *closo* polyhedron, for $(2n + 4)$-electron systems. With few exceptions, the known 11-vertex metallacarboranes and metallaboranes fall into these two classes. The synthetic approaches are similar to those employed for previously described classes of clusters, and consist mainly of direct metal insertion into neutral carboranes, treatment of *nido*-carborane anions with ionic metal reagents, thermal rearrangement, and polyhedral expansion and contraction (Section 5.5.3.1).

The direct insertion of platinum into *closo*-1,8-$C_2B_8H_{10}$, *via* treatment of that carborane with PMe_3 and bis(cyclooctadiene)platinum(0) in solution at room temperature, gave the unexpected, structurally novel product μ-$(PMe_3)_2Pt$-10,7,9-$(PMe_3)_2PtC_2B_8H_{10}$, in which the *exo*-polyhedral metal atom bridges a Pt—B edge of the open 11-vertex cage (Figure 51d).[137,59] The hydrogen atom originally on B(6) was not located, but presumably occupies a bridging position on the open face. On treatment of this complex with activated charcoal, the *exo*-polyhedral metal group is removed to yield the unsubstituted 11-vertex *nido* species 10,7,9-$(PMe_3)_2PtC_2B_8H_{10}$ (Figure 51e).[137,59] As with some other platinum compounds described above, both of these species formally violate the skeletal electron-pair theory, which would assign $2n + 2$ electrons to the cage and hence predict a *closo* geometry; the distortion is tentatively attributed to unequal *d*-orbital contributions to the cage by the platinum atom.[137]

Treatment of neutral $Me_4C_4B_8H_8$ with $CpCo(CO)_2$ in THF solution under UV light has been shown to produce two isomers of 11-vertex $CpCoMe_4C_4B_6H_6$ and one isomer of a 12-vertex $CpCoMe_4C_4B_7H_7$, with net loss of two and one BH units, respectively.[77f] The CoC_4B_6 isomers were proposed to have 11-vertex icosahedral-fragment structures with the four skeletal carbon atoms on the open face,[77f] and recent X-ray studies[80] of isomers I and II (Figure 63) have confirmed both assignments.



Isomer II Isomer I

Figure 63 Structure of $CpCoMe_4C_4B_6H_6$, isomers I and II

Metal insertion into 10-vertex carborane anions produces, as expected, 11-vertex metallacarboranes. Reactions of the *nido*-5,6-$C_2B_8H_{11}^-$ ion with rhodium and iridium reagents generate *closo*- and *nido*-metallacarborane products (Figure 21).[64] With iridium, only *closo* species are obtained (see equation 10, above), while rhodium reagents produce *nido*-metallacarboranes (equation 56).[64] The $L_2RhC_2B_8H_{11}$ and $L_3RhC_2B_8H_{11}$ products (Figure 21) contain formal Rh(I); however, the metal valence shells contain 16 electrons in the former case and 18 in the latter, and this difference is reflected in their chemistry. The formation of all the species in Figure 21 and equations (10) and (56) can be viewed as oxidative additions. In solution, *nido*-$(PEt_3)_3RhC_2B_8H_{11}$ undergoes reversible dissociation of triethylphosphine; the product then partially isomerizes to a *closo* species (equation 57). The dynamic processes involve facile, reversible cage opening and reversible transfer of hydride from cage to metal, and are potentially useful in catalysis.[64]

$$C_2B_8H_{11}^- \quad + \quad RhClL_3 \quad \longrightarrow \quad \textit{nido}\text{-}9,7,8\text{-}L_2RhC_2B_8H_{11} \quad + \quad \textit{nido}\text{-}9,7,8\text{-}L_3RhC_2B_8H_{11} \qquad (56)$$

$$\mathrm{L = PPh_3,\ P(\textit{p}\text{-}Tol)_3} \qquad\qquad \mathrm{L = AsMe_2Ph,\ PMe_2Ph,\ PMe_3,\ AsMe_3,\ SbMe_3,\ PEt_3}$$

$$\textit{nido}\text{-}(PEt_3)_3RhC_2B_8H_{11} \quad \rightleftharpoons \quad PEt_3 \quad + \quad \textit{nido}\text{-}9,7,8\text{-}(PEt_3)_2RhC_2B_8H_{11} \qquad (57)$$

$$\textit{closo}\text{-}1,2,4\text{-}(PEt_3)_2(H)RhC_2B_8H_{10} \quad \xleftarrow{\quad} \text{ on standing}$$

The same carborane anion on treatment with $RuHCl(PPh_3)_3$ forms *closo*-1,1,3-$(PPh_3)_3$-1*H*-1,2,4-$RuC_2B_8H_9$, in which a triphenylphosphine unit displaces a terminal B—H hydrogen from the carborane cage.[64] Similar reactions of $C_2B_8H_{11}^-$ with (triphenylphosphine) metal halides of copper, silver and gold give the metallacarboranes $Ph_3PMC_2B_8H_{11}$ (M = Au, Cu) and $(Ph_3P)_2AgC_2B_8H_{11}$.[158] The last compound loses a phosphine ligand on recrystallization, forming $Ph_3PAgC_2B_8H_{11}$, which has been shown by X-ray crystallography to contain weak intermolecular B—H—Ag bridges; the molecule itself has an *arachno* cage structure in which the silver atom is coordinated to just three boron atoms, and the two carbons are on the open face.[158]

Analogous metal insertions with the monocarborane anion $CB_9H_{12}^-$ yield 1,2-$CpMCB_9H_{10}^-$ *closo*-metallacarboranes of iron and cobalt (see equation 14).[67] An X-ray structure determination of the iron complex established the geometry as a *closo* 11-vertex polyhedron (Figure 3h) with the metal atom occupying the unique 1-coordinate vertex and carbon in an adjacent 2-coordinate location.[159a] A related synthesis[38] involving $Me_3N{\cdot}CB_9H_{11}$ (analogous to $CB_9H_{12}^-$ with Me_3N replacing H^-) produced *closo*-$CpCo(Me_3N)CB_9H_9$, in which the metal, in contrast to the iron compound mentioned above, occupies the 2-vertex in the polyhedron (equation 15 and Figure 10). Curiously, this molecule is fluxional in solution at 70 °C.[38] When $Me_3NCB_9H_{11}$ is treated with $NaSe_x$, the *nido* species $Me_3NCSeB_9H_9$ is formed. In accordance with its $2n + 4$ skeletal electrons, the proposed structure is an open-faced 11-vertex icosahedral fragment with the Se and C atoms in nonadjacent vertices on the open face. A closely related selenacarborane, 10,7,8-$SeC_2B_8H_{10}$, has been prepared from the 7,8-$C_2B_9H_{12}^-$ ion.[159b]

Polyhedral expansion of *closo*-1,8- and -1,6-$C_2B_8H_{10}$, *via* cage-opening followed by metal ion insertion as described above (Section 5.5.3.1.8), readily yields 11-vertex metallacarboranes (equation 58).[145] The product of this reaction has a *closo* 11-vertex geometry analogous to that of the cobalt species shown in Figure 25e (isomer II). The corresponding synthesis of 1,2,3-$CpCoC_2B_8H_{10}$ from 1,6-$C_2B_8H_{10}$ is complex, and generates 10- and 12-vertex products including $CpCoC_2B_7H_9$, $Cp_2Co_2C_2B_8H_{10}$, the bis(carboranyl) species $(C_2B_8H_{10})_2Co^-$ and other compounds, in addition to the expected CoC_2B_8 system.[145] At −80 °C, the yield of $CpCoC_2B_8H_{10}$ is low, and the main products are a pair of $Cp_2Co_2C_2B_8H_{10}$ isomers and a $CpCo(C_2B_8H_{10})$-$Co(C_2B_8H_{10})^-$ anion which contains both *closo* 11-vertex CoC_2B_8 and *closo* 12-vertex $Co_2C_2B_8$ cages linked by a cobalt atom common to both.[160]

$$closo\text{-}1,6\text{-}C_2B_8H_{10} \xrightarrow[C_{10}H_8]{Na} \xrightarrow[NaC_5H_5]{FeCl_2} 1,2,3\text{-}CpFeC_2B_8H_{10} \qquad (58)$$

Interestingly, when 1,10-$C_2B_8H_{10}$ is employed in a similar reaction in place of the 1,6-isomer, the main product is 1,2,3-$CpCoC_2B_8H_{10}$, identical to that from the 1,6-$C_2B_8H_{10}$ reaction.[145] The same species can also be prepared from the $C_2B_8H_{10}^{2-}$ ion, methanolic KOH, $CoCl_2$ and cyclopentadiene.[161]

Another general route to 11-vertex *closo*-metallacarboranes is the polyhedral contraction (Section 5.5.3.1.8) of *closo* 12-vertex polyhedra such as $CpCoC_2B_9H_{11}$, as illustrated above in equation (21).[84,162] Similar treatment of the biscarboranyl anion $(1,2\text{-}C_2B_9H_{11})_2Co^-$ produces $(1,2\text{-}C_2B_9H_{11})Co(2,4\text{-}C_2B_8H_{10})^-$, which contains 11- and 12-vertex *closo* polyhedra fused at a common metal atom.[84] Reaction of this compound with pyridine opens the C_2B_8 ligand (*via* contribution of two electrons to the cage by pyridine) to give a red adduct, $(C_2B_9H_{11})$-$Co(C_2B_8H_{10}{\cdot}NC_5H_5)^-$, whose X-ray-determined structure[163] is shown in Figure 64. The neutral complex 1,2,4-$CpCoC_2B_8H_{10}$ can also be opened with pyridine to generate an adduct whose cage geometry is proposed to be analogous to that in Figure 64, with $C_5H_5^-$ replacing the $C_2B_9H_{11}^{2-}$ ligand (Figure 65).[162] These open-cage pyridine adducts can be re-closed by oxidation with $FeCl_3$ (equations 59, 60).[162]

$$nido\text{-}CpCoC_2B_8H_{10}{\cdot}NC_5H_5 \xrightarrow{FeCl_3} [closo\text{-}CpCoC_2B_8H_9{\cdot}NC_5H_5]^+ \qquad (59)$$

$$[nido\text{-}(C_2B_9H_{11})CoC_2B_8H_{10}{\cdot}NC_5H_5]^- \xrightarrow{FeCl_3} closo\text{-}(C_2B_9H_{11})CoC_2B_8H_9{\cdot}NC_5H_5 \qquad (60)$$

The stereochemistry involved in polyhedral expansion, contraction and rearrangement of 11- and 12-vertex cobaltacarboranes is complex and has been examined in considerable detail (for a summary of this work see ref. 4a, pp. 149–156).[84,162] As is implied by analogy with carborane chemistry, the intermediates in the expansion and contraction processes are assumed to be *nido* species, and this has been confirmed by studies of several reaction systems. The *nido* intermediates can be converted to *closo* species by oxidation and, in some instances, by pyrolysis (with loss of

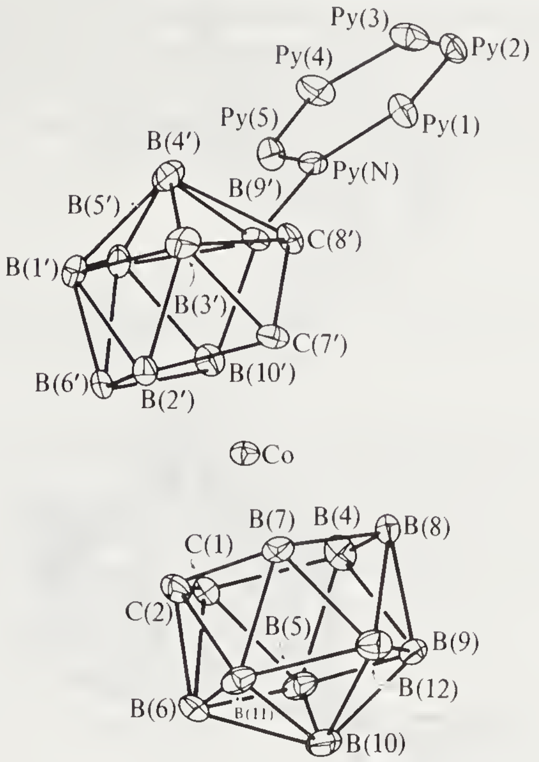


Figure 64 Structure of the $(C_2B_9H_{11})Co(C_2B_8H_{10}{\cdot}NC_5H_5)^-$ ion

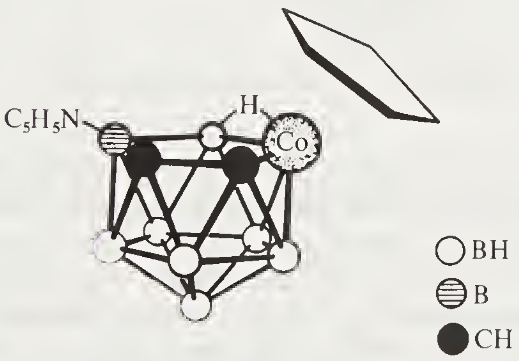


Figure 65 Proposed structure of $CpCoC_2B_8H_{10}{\cdot}NC_5H_5$

H_2) (equation 61).[162] The *nido*-$CpCoC_2B_8H_{12}$ complex in this equation has both B—H—B and B—H—Co hydrogen bridges and is electronically analogous to the pyridine derivative in Figure 65, except that the latter species has only a single (B—H—Co) bridging proton, as shown.

$$\begin{tikzcd}
3,1,2\text{-}CpCoC_2B_9H_{11} \arrow[r, "OH^-"] & \begin{array}{c}[9,7,8\text{-}CpCoC_2B_8H_{11}]^- \\ \textit{nido}\end{array} \arrow[dl, shift left, "HCl"'] \arrow[d, "H_2O_2,\ OH^-"] \\
\begin{array}{c}9,7,8\text{-}CpCoC_2B_8H_{12} \\ \textit{nido}\end{array} \arrow[ur, shift left, "KOH,\ MeOH"'] \arrow[r, shift left, "H_2O_2,\ OH^-"] \arrow[dr, bend right, "\Delta", "-H_2"'] & \begin{array}{c}1,2,4\text{-}CpCoC_2B_8H_{10} \\ \textit{closo}\end{array} \arrow[l, shift left, "Zn/HCl"] \arrow[d, "\Delta"] \\
 & 1,2,3\text{-}CpCoC_2B_8H_{10}
\end{tikzcd} \tag{61}$$

Similar chemistry has been developed for the biscarboranyl $(C_2B_9H_{11})_2Co^-$ system. One can intercept the *nido* intermediates with cobalt ions and produce dimetallic products; thus in the base degradation of either 3,1,2-$CpCoC_2B_9H_{11}$ or [3-(1,2-$C_2B_9H_{11})_2Co]^-$ in the presence of Co^{2+} ion, products incorporating icosahedral $Co_2C_2B_8$ cages are obtained (requiring loss of BH).[162]

The polyhedral expansion technique can also be applied to 10-vertex *closo*-metallacarboranes, giving 11-vertex $M_2C_2B_7$ systems. Thus treatment of 2,1,6-$CpCoC_2B_7H_9$ with sodium naphthalenide followed by $CoCl_2$ and NaC_5H_5 gives a mixture of 10- to 12-vertex products including several isomers of $Cp_2Co_2C_2B_7H_9$;[164] if $FeCl_2$ is employed in place of $CoCl_2$, the product is a mixed-metal species, $Cp_2CoFeC_2B_7H_9$ (Figure 66).[165]

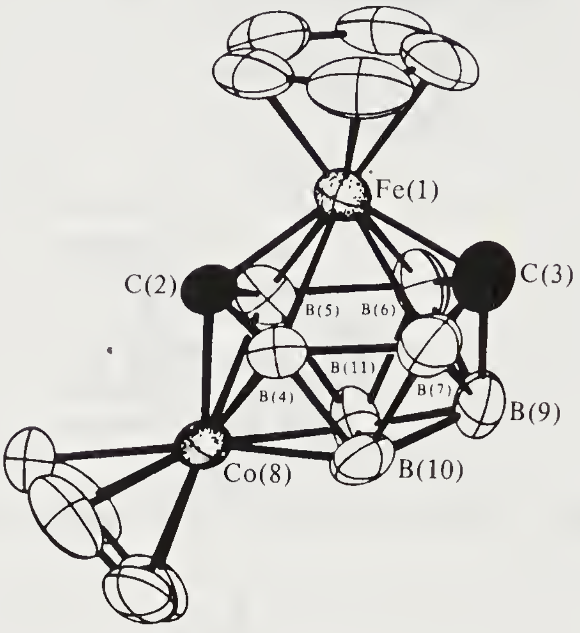


Figure 66 Structure of $Cp_2CoFeC_2B_7H_9$

Thermal rearrangements of 11-vertex metallacarboranes afford new isomers, and also provide some insight into the thermodynamic preferences of metal and carbon atoms in these systems. In general, the observations are in accord with findings for other metallacarboranes (Section 5.5.3.1.7). Thus 1,2,4-$CpCoC_2B_8H_{10}$ is converted to the thermally more stable 1,2,3-isomer in which the carbons occupy nonadjacent vertices; on extended heating, metal atom transfer occurs, forming numerous isomers of the icosahedral $Cp_2Co_2C_2B_8H_{10}$ system.[87] The 1,2,4 → 1,2,3 rearrangement of the $CpCoMe_2C_2B_8H_8$ system has been shown to produce an isolable intermediate identified as the 10,2,3-isomer.[77e] Similar isomerizations occur in the dicobalt 1,6,2,4-$Cp_2Co_2C_2B_7H_9$ 11-vertex system, which first produces the 1,4,2,3-isomer by migration of carbon to nonadjacent locations, and ultimately forms the 1,10,2,3-isomer by migration of cobalt (Figure 25d). Still other isomers have been found in this reaction system,[77c,166] suggesting multiple pathways for rearrangement.

5.5.7.2 Metallaboranes

An extensive family of 11-vertex metallaborane complexes derived from $B_{10}H_{14}$ has been characterized, as described in several reviews[5] and in Sections 5.5.1.2 and 5.5.3.2 of the present chapter. Some of the syntheses involve direct reactions of decaborane with metal reagents, as in equations (1) and (62); with Group III alkyls, both deprotonation and metal insertion into the framework take place (equation 62).[91] With a 1 : 1 ratio of reactants, a second indium complex, $MeInB_{10}H_{12}$, is obtained, while the corresponding thallium reaction produces $Me_2Tl^+B_{10}H_{13}^-$. Figure 67 presents the proposed structure[91] for the $Me_2InB_{10}H_{12}^-$ ion; the $Me_2TlB_{10}H_{12}^-$ species has been assigned a different geometry in which the Me_2Tl group forms a *dihapto* bridge across the B(6)—B(9) edge of the B_{10} cage. Treatment of $Me_2Tl^+[Me_2TlB_{10}H_{12}]^-$ with MeHgCl generates the $MeHgB_{10}H_{12}^-$ ion, an isoelectronic analogue of $MeInB_{10}H_{12}$.

$$2MMe_3 + B_{10}H_{14} \xrightarrow{\text{solvent}} Me_2M^+[Me_2MB_{10}H_{12}]^- + 2CH_4 \qquad (62)$$

$$M = \text{In, Tl} \qquad \text{solvent} = C_6H_6,\ Et_2O$$

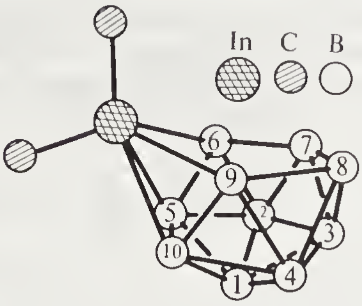


Figure 67 Proposed structure of the $Me_2InB_{10}H_{12}^-$ ion

Neutral $B_{10}H_{14}$ also reacts directly with zinc and cadmium dialkyls (equation 1),[5a,16] with platinum chlorohydrides,[98] with $(Et_3P)_3Pt$,[102] with nickelocene[92] and with selenium and tellurium reagents,[159b,167] to give 11-vertex *nido*-metallaboranes (equations 63–66). The cadmium species is a unique dimeric complex in which two metals bridge two B_{10} units.[16c] The proposed structures of the nickel complexes in reaction (64) are shown in Figures 32 and 34; similar *nido* 11-vertex structures have been assigned to the other species in reactions (63)–(66), all of which are 26-electron *nido* systems, isoelectronic with $B_{11}H_{11}^{4-}$ and $C_2B_9H_{11}^{2-}$.

$$B_{10}H_{14} \quad + \quad (Et_3P)_2PtHCl \xrightarrow{C_6H_6} (Et_3P)_2PtB_{10}H_{12} \quad + \quad (Et_3P)_2PtCl_2 \quad + \quad H_2 \tag{63}$$

$$B_{10}H_{14} \quad + \quad Cp_2Ni \xrightarrow[1\ h]{\text{glyme}} \underset{\textit{nido}}{CpNiB_{10}H_{13}} \underset{H^+}{\overset{OH^-}{\rightleftarrows}} \underset{\textit{nido}}{CpNiB_{10}H_{12}^-}$$

$$\xrightarrow[\text{prolonged}]{\text{glyme}} (B_{10}H_{12})_2Ni^{2-} \tag{64}$$

$$B_{10}H_{14} \quad + \quad Na_2X_4 \xrightarrow[H_2O]{NH_3} XB_{10}H_{11}^- \xrightarrow{H^+} XB_{10}H_{12} \tag{65}$$

$$X = Se,\ Te$$

$$B_{10}H_{14} \quad + \quad Na_2SeO_3{\cdot}5H_2O \xrightarrow{H_2O} 7,8\text{-}Se_2B_9H_9 \tag{66}$$

Neutral Grignard reagents of decaborane, $B_{10}H_{13}MgX$, have been employed to prepare $Hg(B_{10}H_{12})_2^{2-}$. Analogous $M(B_{10}H_{12})_2^{2-}$ complexes in which M is zinc or cadmium have been prepared by hydrolysis of the solvated $M(B_{10}H_{12})_2{\cdot}L_2$ (L = diethyl ether or THF) species;[168] the structure of the $Zn(B_{10}H_{12})_2^{2-}$ dianion (Figure 31)[169] differs significantly from that of $Ni(B_{10}H_{12})_2^{2-}$ (Figure 34),[170] in that the two ligands are bound in a *trans* configuration in the latter species but are mutually rotated by only 90° in the former. The cadmium and mercury complexes are similar to that of zinc.[169]

The more common synthetic route to MB_{10}-type metallaboranes is *via* the $B_{10}H_{13}^-$ anion, which is readily obtained by deprotonation of $B_{10}H_{14}$ with amines, metal hydrides or other strong bases. Reactions of metal halides with $B_{10}H_{13}^-$ in THF give species of the type $M(B_{10}H_{12})_2^{2-}$ or $L_nMB_{10}H_{12}$ (L = phosphino or carbonyl groups and M = Co, Ni, Pd, Pt, Rh or Ir), as given in equation (25) above.[98] Neutral products formulated as $L_2MB_{10}H_{12}$, where M is palladium or platinum and L is a triorganophosphine, are also formed (equation 27); still another type, $L_3M(B_{10}H_{12})^-$, where L is a phosphine or CO and M is cobalt, rhodium or iridium, can be obtained (equation 26).[98] The proposed geometries of the MB_{10} *nido* cages in these complexes are similar to those shown in Figures 31 and 34. The species $(Me_2PhP)_2PtB_{10}H_{12}$ is fluxional in solution, the L_2Pt group rotating with respect to the $B_{10}H_{12}$ ligand; it has been suggested that such behavior may be general in this class of platinaborane.[171]

Other routes to MB_{10}-type metallaboranes are known. Treatment of the $B_{10}H_{13}^-$ ion with $CoX_2(pyridine)_2$ (X = Cl or Br) gives paramagnetic *nido* complexes of the form $X_2(py)$-$CoB_{10}H_{11}py$, in which one pyridine ligand is coordinated to cobalt and the other to the borane cage on the open face adjacent to cobalt.[172] The salt $Cs_2B_{10}H_{14}$ reacts with $CoCl_2$ or $NiCl_2$ to yield $M(B_{10}H_{12})_2^{2-}$ complexes,[173] and platinum can be inserted directly into the *closo*-$B_{10}H_{10}^{2-}$

ion, opening the cage to produce *nido*-metallaboranes (equation 67).[102] A minor product of the reaction between $B_5H_8^-$, $FeCl_2$ and $C_5H_5^-$ (Section 5.5.3.2.2) is 2-$CpFeB_{10}H_{15}$, whose proposed structure (Figure 68) is again a *nido* 11-vertex FeB_{10} cage, but with the metal occupying an unusual vertex in the 2-position *off* the open face.[19]

$$B_{10}H_{10}{}^{2-} \quad + \quad (LL)PtCl_2 \quad \xrightarrow[CHCl_3]{EtOH} \quad (LL)PtB_{10}H_{11}OEt \qquad (67)$$

several isomers

LL = 1,2-bis(diphenylphosphino)ethane

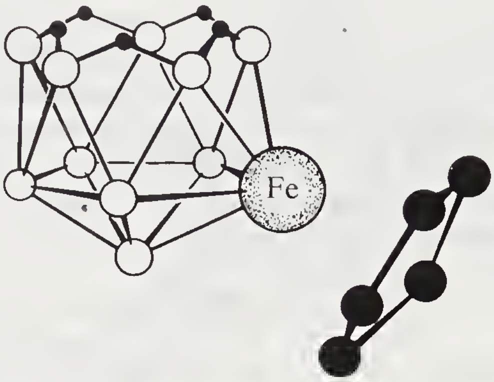


Figure 68 Proposed structure of 2-$CpFeB_{10}H_{15}$

The phosphino ligands in *nido*-$(Ph_3P)_2PdB_{10}H_{12}$ can be readily exchanged for other groups such as CN^-, $S_2C_2(CN)_2^{2-}$ and *o*-phenanthroline, and exchange on $(Ph_3P)_2(CO)IrB_{10}H_{12}$ gives analogous species containing the $S_2C_2(CN)_2^{2-}$ ligand.[99e]

MB_{10} *nido*-metallaboranes incorporating main group metals can be prepared from B_{10} anions by routes similar to those described above; thus the reaction of $B_{10}H_{13}^-$ with Me_3SnCl or Me_3GeBr forms the corresponding $Me_3MB_{10}H_{12}$ species, whose postulated structures are analogous to that of the isoelectronic cage system $Me_2InB_{10}H_{12}^-$ (Figure 67).[174] Yet another type of MB_{10} cage consists of the transition metal complexes derived from the isomeric $B_{18}H_{20}^{2-}$ ions, which in turn are obtained by deprotonation of *n*- or *i*-$B_{18}H_{22}$. The complexes have the form $L_nMB_{18}H_{20}$ (L = CO or phosphino groups), and the proposed geometry is shown in Figure 69.[101]

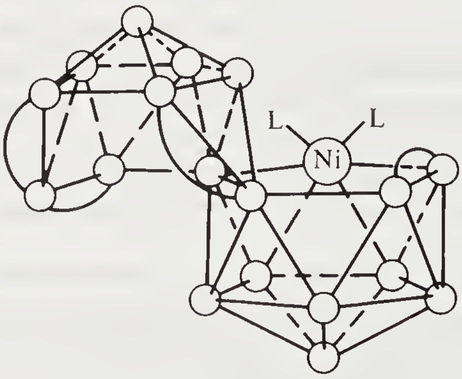


Figure 69 Proposed structure of $L_2NiB_{18}H_{20}$ complexes (L = CO or phosphine)

Metallaboranes of 11 vertices containing the *nido*-$SB_9H_9^{2-}$ and *arachno*-$SB_9H_{11}^{2-}$ ions, which are isoelectronic analogues of $B_9H_{13}^{2-}$ and $B_9H_{15}^{2-}$, respectively, have been prepared. Treatment of $Li_2SB_9H_9$ with $(Ph_3P)_2PdCl_2$ in THF solution forms yellow $(Ph_3P)_2PdSB_9H_9$, whose proposed *closo* geometry is shown in Figure 70.[99b] It is useful to note that this 11-vertex, 24-electron ($2n$ + 2) system, with 2-electron contributions from the boron and palladium atoms and four from sulfur, conforms to the skeletal electron-counting rules discussed in Section 5.5.2.4. If two additional electrons are introduced, one expects cage-opening to give a *nido* system; indeed, complexes of the type $M(SB_9H_{11})_2^{2-}$ (M = Ni or Pd) have been assigned *nido* geometries (Figure 71). These latter species are prepared by reactions of $LiCsSB_9H_{11}$ with the metal acetylacetonate (attempts to make the platinum analogue resulted in reduction of the metal salt).[99b]

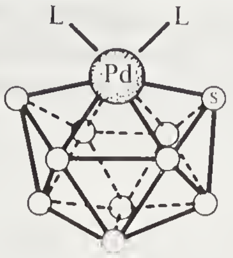


Figure 70 Proposed structure of $L_2PdSB_9H_9$ (L = Ph_3P)

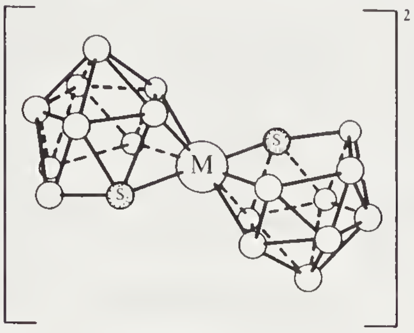


Figure 71 Proposed structure of the $M(SB_9H_{11})_2^{2-}$ ions (M = Ni, Pd); bridging hydrogen atoms on the open faces are not shown

The $SB_9H_{12}^-$ ion, which may be regarded as a protonated form of $SB_9H_{11}^{2-}$, on treatment with potassium polyselenide forms $SeSB_9H_9$, an 11-vertex, 26-electron species whose proposed *nido* structure is shown in Figure 72.[43b] Addition of a CpCo unit to this molecule gives a unique 12-vertex structure, analogous to that depicted in Figure 14 (type 7).

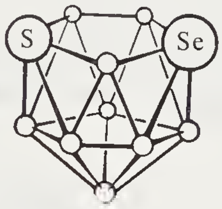


Figure 72 Proposed structure of $SeSB_9H_9$

5.5.8 CAGE SYSTEMS WITH TWELVE VERTICES

5.5.8.1 Metallacarboranes

A vast chemistry based on *closo*-MC_2B_9 polyhedra and other icosahedral systems has been developed following the original report of $CpFeC_2B_9H_{11}$ (Figure 1) by Hawthorne and co-workers in 1965.[3] Since much of this work has been previously summarized in various reviews,[4] and space limitations preclude a full detailed account here, the present coverage will focus on aspects having general significance, with certain reactions and structures selected to illustrate the more important principles.

5.5.8.1.1 Two-carbon cages

Most of the known 12-vertex metallacarboranes incorporate MC_2B_9 systems and are derived from *o*- or *m*-carborane (1,2- or 1,7-$C_2B_{10}H_{12}$) by base-extraction of boron to create the *nido* 11-vertex $C_2B_9H_{12}^-$ or $C_2B_9H_{11}^{2-}$ (dicarbollide) ions (Figure 19), into which a metal ion can be inserted to complete the MC_2B_9 icosahedron.[175] This technique is described briefly in Section 5.5.3.1.2, above. When conducted in aqueous media, the protonated form of the anion ($C_2B_9H_{12}^-$) is in equilibrium with the dicarbollide ion; in nonaqueous media, the 'extra' proton is removed prior to metal insertion (equations 68, 69). Addition of the metal reagent is usually conducted without prior isolation of the $C_2B_9H_{11}^{2-}$ salt; both bis(dicarbollide) and mixed-ligand complexes (Figures 1 and 73) can be prepared in this way (equations 70–76).[175]

$$\text{1,2- or 1,7-}C_2B_9H_{12}^- + OH^- \rightleftarrows C_2B_9H_{11}^{2-} + H_2O \tag{68}$$

$$\text{1,2- or 1,7-}C_2B_9H_{12}^- + H^- \xrightarrow{\text{THF}} C_2B_9H_{11}^{2-} + H_2 \tag{69}$$

$$\tfrac{3}{2}Co^{2+} + 2C_2B_9H_{11}^{2-} \xrightarrow{\text{THF}} (C_2B_9H_{11})_2Co^- + \tfrac{1}{2}Co^0 \tag{70}$$

$$Co^{2+} + 2C_2B_9H_{12}^- \xrightarrow[\text{NaOH}]{\text{hot aq.}} (C_2B_9H_{11})_2Co^{2-} \xrightarrow{\text{air}} (C_2B_9H_{11})_2Co^- + Co^0 \tag{71}$$

$$C_5H_5^- + C_2B_9H_{11}^{2-} + CrCl_3 \longrightarrow CpCrC_2B_9H_{11} + 3Cl^- \tag{72}$$

$$\begin{array}{l} C_2B_9H_{11}^{2-} + M(CO)_6 \xrightarrow[\text{M = Cr, Mo, W}]{h\nu} (CO)_3MC_2B_9H_{11}^{2-} + 3CO \\ \qquad\qquad H(CO)_3MC_2B_9H_{11}^- \xleftarrow{\text{HCl}} \end{array} \tag{73}$$

$$\begin{array}{l} BrM(CO)_5 + C_2B_9H_{11}^{2-} \longrightarrow \sigma\text{-}\{(CO)_5M\}C_2B_9H_{11}^- + Br^- \\ \qquad \text{3,1,2-}(CO)_3MC_2B_9H_{11}^- + 2CO \xleftarrow[\text{THF}]{\text{reflux}} \\ \qquad\qquad M = Mn, Re \end{array} \tag{74}$$

$$\begin{array}{l} C_2B_9H_{11}^{2-} + FeCl_2 \xrightarrow{\text{THF}} (C_2B_9H_{11})_2Fe^{2-} \underset{\text{Na}}{\overset{O_2}{\rightleftarrows}} (C_2B_9H_{11})_2Fe^- \\ \qquad C_2B_9H_{12}^- + FeCl_2 \xrightarrow{OH^-} \nearrow \end{array} \tag{75}$$

$$C_5H_5^- + C_2B_9H_{11}^{2-} + FeCl_2 \xrightarrow[\text{reflux}]{\text{THF}} CpFe^{III}C_2B_9H_{11} \xrightarrow{\text{Na/Hg}} CpFe^{II}C_2B_9H_{11}^- \tag{76}$$

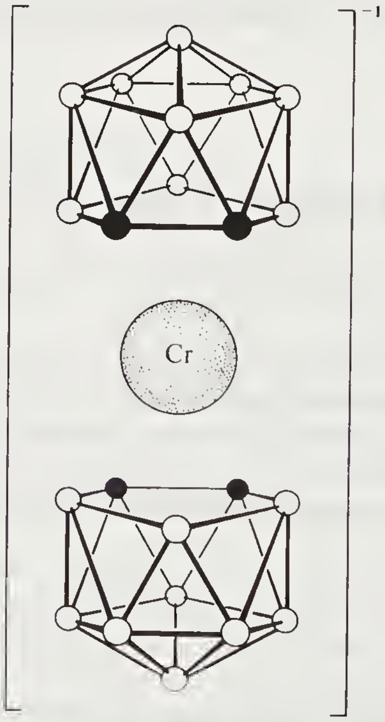


Figure 73 Structure of the $Cr(1,2\text{-}Me_2C_2B_9H_9)_2^-$ ion[230]

The insertion of metal and non-metal atoms into the dicarbollide ions is extremely versatile, primarily for two reasons: (1) the 1,2- and 1,7-$C_2B_9H_{11}^{2-}$ ions are stable species which can survive fairly rigorous reaction conditions (*e.g.* strong bases or reflux temperatures), and (2) completion of the icosahedron is, in general, strongly favored in both a thermodynamic and a kinetic sense.

The products, such as the species depicted in Figures 1 and 73, are usually highly air-stable, robust materials, obtained as colored crystalline solids (however, in contrast, the metal tricarbonyl complexes in equation (73) are highly air sensitive). In an improved technique, cyclopentadienylmetal dicarbollyl complexes can be prepared directly from *o*-carborane and C_5H_6 by generation of $C_2B_9H_{12}^-$ *in situ* (equation 77).[176]

$$1,2\text{-}C_2B_{10}H_{12} \xrightarrow[\text{MeOH}]{\text{alkaline}} C_2B_9H_{12}^- \xrightarrow[C_5H_6]{CoCl_2} CpCoC_2B_9H_{11} \xrightarrow[CoCl_2]{KOH} Cp_2Co_2C_2B_8H_{10} \tag{77}$$

Substituted derivatives of the $C_2B_9H_{11}^{2-}$ and $C_2B_9H_{12}^-$ ions undergo analogous reactions to give the corresponding metallacarboranes; for example, complexation of the benzodicarbollide ion, which contains an *exo*-polyhedral —CH=CH—CH=CH— linkage to the carboranyl carbon atoms, occurs with manganese, cobalt and nickel reagents.[177] Treatment of $C_2B_9H_{12}^-$ ions with hydride transition metal reagents forms hydridometallacarboranes.[178] Species such as the ruthenacarborane formed in reaction (78) exhibit activity as catalysts for the homogeneous hydrogenation and isomerization of alkenes, as described below.

$$7,8\text{- or }7,9\text{-}C_2B_9H_{12}^- \ + \ (Ph_3P)_3RuHCl \longrightarrow \underset{(3,1,2\text{- or }3,1,7\text{-isomer})}{(Ph_3P)_2RuH_2C_2B_9H_{11}} \tag{78}$$

Insertion into the $C_2B_9H_{11}^{2-}$ and $C_2B_9H_{12}^-$ ions is not limited to transition metals; reaction with halides of Group III, IV or V affords main group metallacarboranes such as $GeC_2B_9H_{11}$ and its tin and lead congeners[68] (equation 16), $EtAlC_2B_9H_{11}$[179] and others. With respect to the lanthanide and actinide elements, only one structurally characterized metallacarborane exists: treatment of the $7,8\text{-}C_2B_9H_{11}^{2-}$ ion with UCl_4 forms the uranacarborane $U(C_2B_9H_{11})_2Cl_2^{2-}$; this species reacts with C_8H_8 to give uranocene.[180]

The base degradation/metal insertion technique can also be applied to icosahedral MC_2B_9 systems, to remove a BH unit and insert a second metal atom, forming $M_2C_2B_8$ cages. In this way, 'chains' of 12-vertex polyhedra fused at the metal vertices have been prepared (Figure 74).[175d]

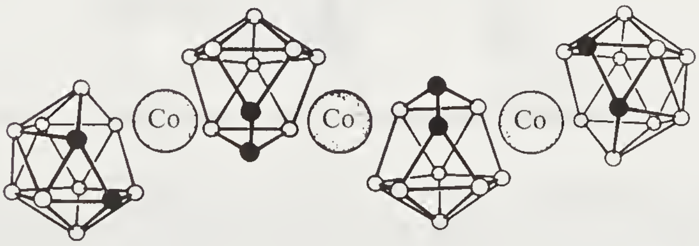


Figure 74 Structure of the $\{(C_2B_9H_{11})Co(C_2B_8H_{10})\}_2Co^{3-}$ ion[246]

Most of the other general synthetic routes to metallacarboranes outlined in Section 5.5.3.1 have also been successfully applied to 12-vertex systems. Thus the polyhedral expansion of 11-vertex carboranes or metallacarboranes generates, respectively, MC_2B_9 and $M_2C_2B_8$ products (equations 79, 80).[145,164] Reaction (79) is not a particularly attractive route since $C_2B_9H_{11}$ itself is normally obtained by degradation of $C_2B_{10}H_{12}$.[6] The product of reaction (80) has been shown to have metal atoms in adjacent vertices in the cage (Figure 75),[181] reflecting the tendency of carborane polyhedra to open in such a way that the 'hole' is adjacent to skeletal carbon atoms; subsequent metal insertion normally occurs at these sites. If a metallacarborane substrate is employed, di- and even tri-metallic species can be obtained (equation 81).[164] Another general technique, described above, is that of direct insertion of metals into the cage without prior opening of the polyhedron; when applied to *closo*-$R_2C_2B_9H_9$ species[13,47a] this gives 12-vertex *closo*-metallacarboranes (equation 82).

$$closo\text{-}C_2B_9H_{11} \xrightarrow{2e^-} C_2B_9H_{11}^{2-} \xrightarrow[C_5H_5^-]{CoCl_2} CpCoC_2B_9H_{11} \tag{79}$$

$$1,2,3\text{-}CpCoC_2B_8H_{10} \xrightarrow{2e^-} CpCoC_2B_8H_{10}^{2-} \xrightarrow[C_5H_5^-]{CoCl_2} Cp_2Co_2C_2B_8H_{10} \tag{80}$$

$$CpCoC_2B_7H_9 \xrightarrow[C_{10}H_8]{Na} \xrightarrow[C_5H_5^-]{CoCl_2} \underset{22\%}{Cp_2Co_2C_2B_7H_9} + \underset{3\%}{Cp_3Co_3C_2B_7H_9} \qquad (81)$$

$$Me_2C_2B_9H_9 + Pt(PEt_3)_3 \longrightarrow (Et_3P)_3PtMe_2C_2B_9H_9 \qquad (82)$$

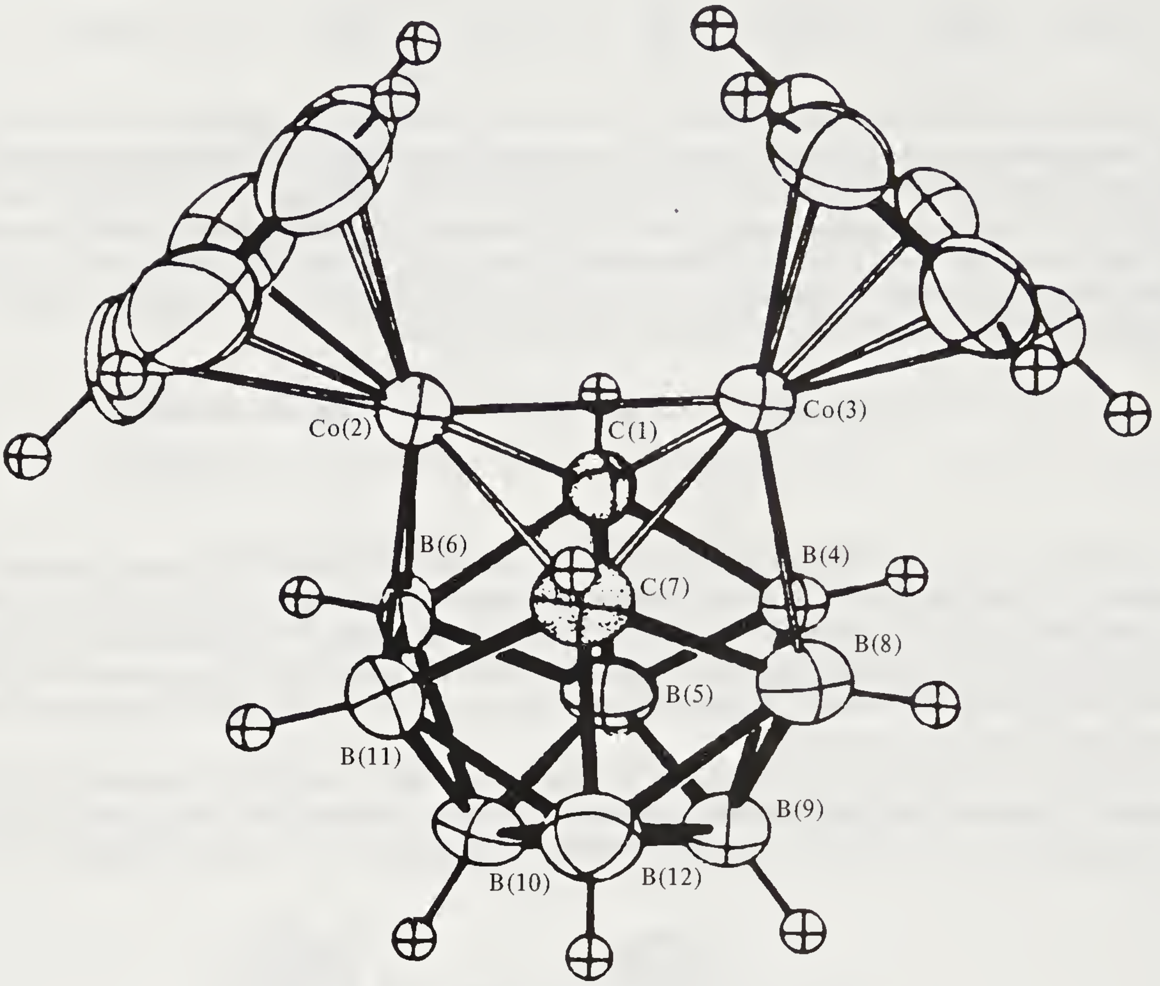


Figure 75 Structure of 2,3,1,7-$Cp_2Co_2B_8H_{10}$

Metal replacement, as in the treatment of $Tl^+[TlR^1R^2C_2B_9H_9]^-$ (R^1, R^2 = H or Me) with $CoCl_2$ or $FeCl_2$, affords FeC_2B_9 or CoC_2B_9 cages, the skeletal thallium atom being displaced in the process.[13a,86] This method has been demonstrated only with thallium species thus far.

The physical and chemical properties of icosahedral dicarbon metallacarboranes have been extensively studied by Hawthorne and coworkers as well as by other groups;[4a,b,e,175] the following discussion summarizes some of the more important general observations.

(*i*) *Cage stability*

The 7,8- and 7,9-$C_2B_9H_{11}^{2-}$ ions compare favorably with $C_5H_5^-$ in their ability to form stable complexes with transition and main group metal ions, so much so that some dicarbollide complexes [*e.g.* $(C_2B_9H_{11})_2Cu^-$][182] have no isolable $C_5H_5^-$ analogue. The copper(III) complex just cited also illustrates the fact that the $C_2B_9H_{11}^{2-}$ ions, to a far greater extent than $C_5H_5^-$, can stabilize high metal oxidation states; this is apparent, for example, in the chemistry of nickel dicarbollyls,[175a,183] which involves oxidation states of +2, +3 and +4.

$$[(C_2B_9H_{11})_2Ni^{II}]^{2-} \xrightleftharpoons[Na/Hg]{O_2} [(C_2B_9H_{11})_2Ni^{III}]^- \xrightleftharpoons[Cd]{Fe^{3+}} (C_2B_9H_{11})_2Ni^{IV} \qquad (83)$$

(*ii*) *Geometric and electronic structure*

Skeletal electron-counting rules predict a *closo* icosahedral structure for 26-electron, 12-vertex cage systems such as $CpCoC_2B_9H_{11}$ and $(Ph_3P)_2NiC_2B_9H_{11}$ in which the metal-ligand group is a formal two-electron donor (see Section 5.5.2.4). Species which contain only 24 or 25 electrons also usually adopt regular *closo* geometry, so strongly favored is the icosahedron; an example is the paramagnetic, 25-electron $CpFeC_2B_9H_{11}$ (Figure 1), which contains formal iron(III). However, electron-rich 12-vertex systems, *i.e.* those containing in excess of 26 skeletal electrons, exhibit cage distortion of a peculiar type: the metal atom is laterally shifted (by 0.1–0.3 Å) from the center of the C_2B_3 bonding face of the $C_2B_9H_{11}^{2-}$ ligand, usually such that the metal–boron distances are shorter than the metal–carbon vectors.[175b] This 'slip-distortion' is exhibited by $(1,2\text{-}C_2B_9H_{11})_2M$ complexes in which the metal ion has more than six *d*-electrons [e.g. Ni(II), Cu(II), Cu(III), Au(II), Au(III), Pd(II)], illustrated in Figure 76. The nature of this effect has been widely explored by experimental and theoretical techniques,[53,182,184] with somewhat divergent interpretations of the electronic factors underlying the distortion. Recent work[53b,184d,184e] suggests that both the oxidation state of the metal and the nature of substituents attached to the open pentagonal face of the carborane ligand affect the degree and type of the slippage. In essence, MO studies[184e] show that the distortions are dictated by a requirement of maximum overlap between the metal and ligand bonding orbitals (HOMO and LUMO, respectively).

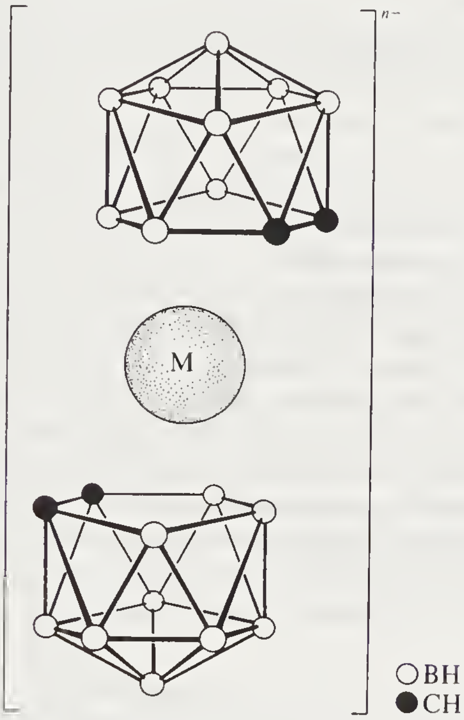


Figure 76 Structure of slip-distorted $(C_2B_9H_{11})_2M^{n-}$ complexes[182]

Structure determinations on $C_2B_9H_{11}^{2-}$ metal complexes establish that the metallacarborane cage adopts a more open geometry as the electron density on the metal increases. Thus, in comparison with the icosahedral structure of species having d^0 to d^6 metals, and the 'slipped' structures adopted by complexes of d^7 and d^8 metals (described above), the geometry of $(Ph_3P)HgC_2B_9H_{11}$, containing d^{10} mercury, is shown in Figure 77; mercury is strongly bonded to only one cage atom with very weak interactions toward the others.[48,51] The $3,1,2\text{-}TlC_2B_9H_{11}^-$ ion[48] represents perhaps the 'extreme' case, with a fully saturated $d^{10}s^2$ metal and very long Tl–cage distances, suggesting an ion pair, $Tl^+C_2B_9H_{11}^{2-}$. The implication of weak thallium–cage bonding is consistent with the facile displacement of thallium by other metals as discussed earlier.

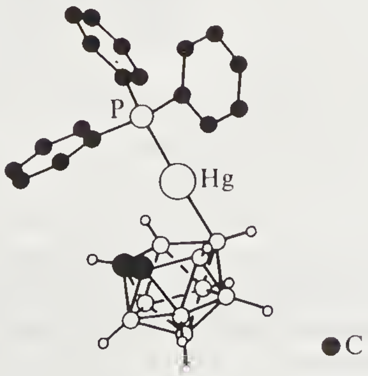


Figure 77 Structure of $Ph_3P\text{-}HgC_2B_9H_{11}$

Even in 26-electron, 12-vertex cages, which conform to the $(2n + 2)$-electron requirement for icosahedral geometry, significant distortion is often observed in metallacarboranes of the heavier transition elements, particularly palladium, platinum and gold (see also Section 5.5.6.1).[47,51,53,185] Mingos[47b] attributes this effect to unequal bonding capabilities of the metal $5d_{xz}$ and $5d_{yz}$ orbitals with respect to the C_2B_3 face of the carborane ligand.

The electronic structure and properties of icosahedral metallacarboranes have been examined in some detail *via* NMR,[186] magnetic,[187] NQR[188] and theoretical[47b,189] methods. The $C_2B_9H_{11}^{2-}$ ligands exhibit a high degree of electron delocalization[186b] and the NQR data reveal that the electron configuration of the metal atom is very similar in Cp_2Co, 3,1,2-$CpCoC_2B_9H_{11}$ and $(1,2\text{-}C_2B_9H_{11})_2Co^-$. However, the commonly invoked comparison between the sandwich complexes of $C_2B_9H_{11}^{2-}$ and those of $C_5H_5^-$, while qualitatively correct, has its limitations: MO studies[189] indicate that ligand σ-orbitals are much more important in metal–ligand bonding in the dicarbollide complexes than in the metallocenes.

(*iii*) *Substitution on the cage*

Introduction of substituent groups at BH or CH locations in icosahedral metallocarboranes can be accomplished, in general, by methods similar to those developed for the $C_2B_{10}H_{12}$ carboranes.[6] These include metallation at carbon *via* treatment with *n*-butyllithium[190a] and electrophilic halogenation at boron locations.[175a,190b] Many *C*-substituted metallacarboranes have also been prepared directly from substituted $C_2B_9H_{11}^{2-}$ or $C_2B_9H_{12}^-$ derivatives.[4a]

Introduction of substituents other than halogens at boron positions on the cage is more difficult, but treatment of $CpCoC_2B_9H_{11}$ with sulfur over $AlCl_3$ affords 8- and 9-mercapto derivatives; the corresponding reaction of $(1,2\text{-}C_2B_9H_{11})_2Co^-$ yields 8,8′-HS-Co$(1,2\text{-}C_2B_9H_{10})_2$, a species in which the two cages are bridged by sulfur.[191] A structurally analogous complex containing a bridging S_2CH unit (Figure 78) is produced by treatment of the cobaltacarborane anion with carbon disulfide and HCl over $AlCl_3$ (equation 84).[192] Similar compounds in which the bridging group is HCO_2, $MeCO_2$, MeS, *o*-C_6H_4, MeO, EtO, MeSe, MeTe, NH_2, NHMe or NMe_2 have been prepared;[191–193] in all cases the cages are linked *via* the 8,8′ boron atoms (as in Figure 78), these being the most negative sites and hence the preferred points for electrophilic attack. The bridging carbon atom in the HCS_2-bridged species is an electron-deficient carbonium ion center and is easily reduced to the —S—CH_2—S— bridged species; similarly, the —$MeCO_2$— complex is readily hydrolyzed in refluxing aqueous ethanol, producing a diol.[192b]

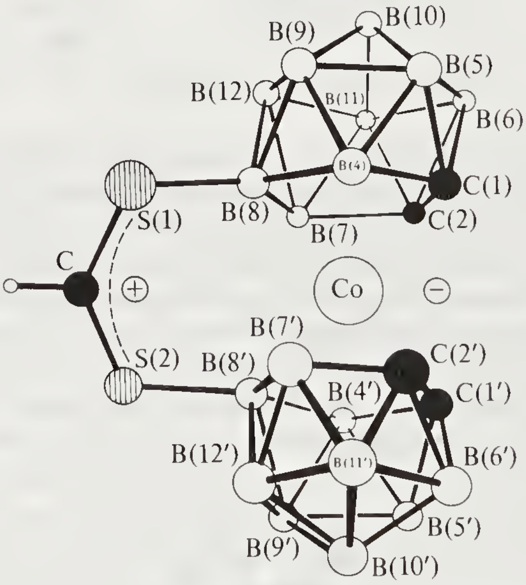


Figure 78 Structure of 8,8′-HCS_2-$(1,2\text{-}C_2B_9H_{10})_2Co$

$$(1,2\text{-}C_2B_9H_{11})_2Co^+ \quad + \quad CS_2 \quad + \quad H^+ \quad \longrightarrow \quad (1,2\text{-}C_2B_9H_{10})_2CoS_2CH \quad + \quad H_2 \qquad (84)$$

Friedel–Crafts acetylation of 3,1,2-$CpCoC_2B_9H_{11}$ also occurs at B(8), generating the acetyl, chloro and hydroxy derivatives.[194] *B*(6)-Substituted derivatives, on the other hand, can be obtained from 3-NH_2-1,2-$C_2B_{10}H_{11}$ by conversion to the $NH_2C_2B_9H_{11}^-$ ion and complexation with $CoCl_2$ and C_5H_6 in a strongly basic solvent.[195]

B-Substituted complexes are also prepared from protonated complexes as described below.

(*iv*) *Reactions at the C_5H_5 ring*

Russian workers have prepared derivatives of 3,1,2-$CpCoC_2B_9H_{11}$ containing substituents on the cyclopentadienyl group, *via* reaction of the parent complex with Grignards.[196] The acidity of the C_5H_5 protons in the parent species is lower than in Cp_2Co, and H–D exchange in this complex is much faster for the carborane C—H than for the cyclopentadienyl C—H protons.[197] Both types of hydrogens, however, form hydrogen bonds with Me_2SO.[198] Reactions of $CpCoC_2B_9H_{11}$ and 3,6,1,2-$Cp_2Co_2C_2B_8H_{10}$ with organolithium reagents also effect substitution on the ring.[199]

Insertion of boron into the C_5H_5 ring has been observed; when 3,1,2-$CpCoC_2B_9H_{11}$ is reduced with sodium and subsequently treated with $PhBCl_2$, the main product is a phenylboranato complex, 3,1,2-(η^6-$C_6H_5BC_5H_5$)$CoC_2B_9H_{11}$.[200]

Protonation of bis(dicarbollyl) transition metal complexes may occur at the C_5H_5 ring, although this is not certain; however, the $(1,2\text{-}C_2B_9H_{11})_2Fe^{II}H^-$ ion, formed by reaction of the dianion with aqueous HCl or $HClO_4$, does not exhibit a high-field proton NMR shift, tending to rule out direct Fe—H bonding.[201] Electrochemical studies have shown that 3,1,2-$CpCoC_2B_9H_{11}$ and its *B*-tribromo derivative protonate at the ring rather than the metal.[202] The protonated iron species reacts readily with dialkyl sulfides to produce *B*-substituted derivatives.[201]

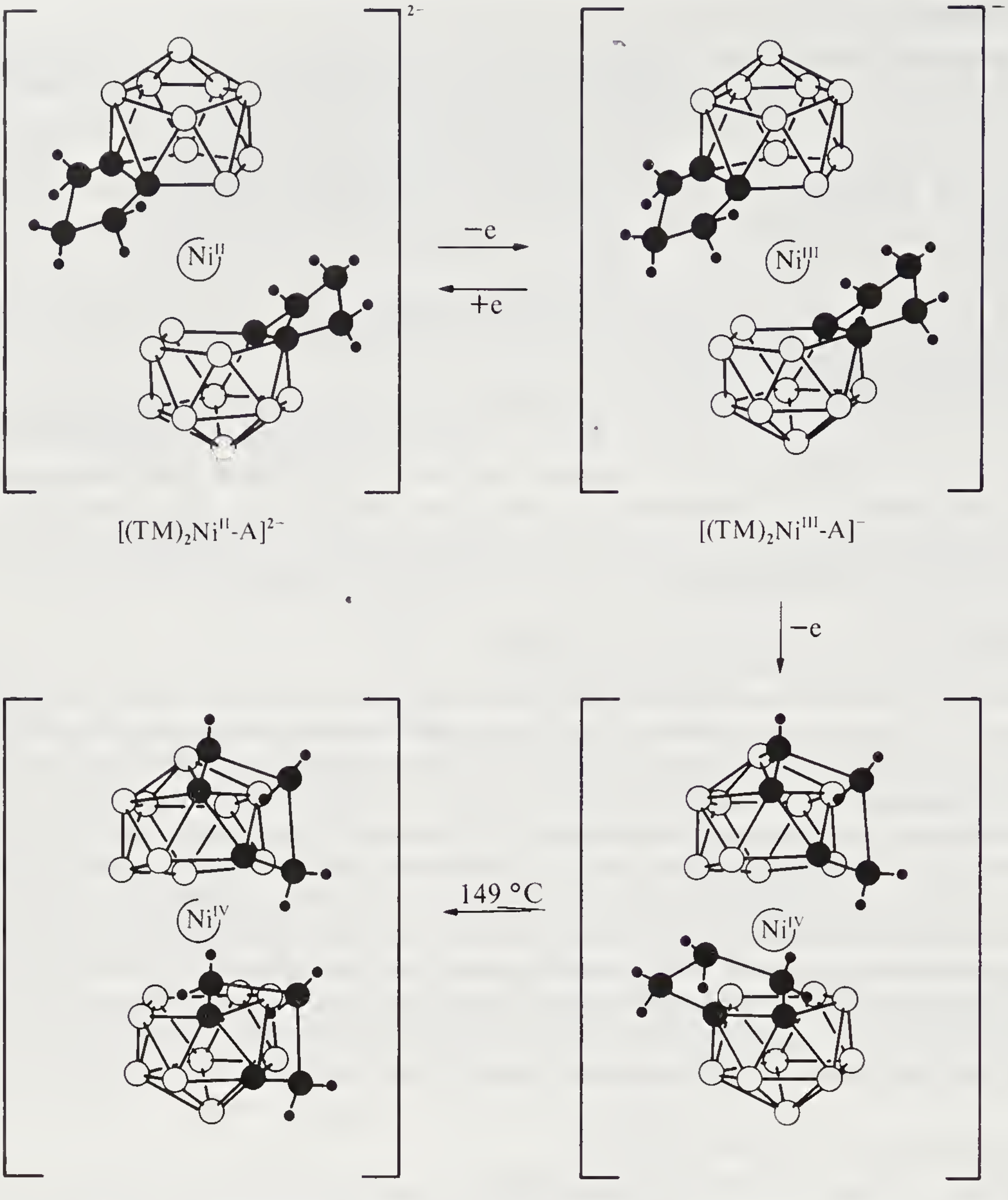
(*v*) *Thermal rearrangement and metal transfer*

A general discussion of metallacarborane isomerization at elevated temperature appears in Section 5.5.3.1.7. Detailed studies of certain icosahedral systems, particularly $CpCoC_2B_9H_{11}$[77g] and $Cp_2Co_2C_2B_8H_{10}$,[77c] reveal complex patterns of interconversion leading to numerous (perhaps all possible) cage isomers, with a clear tendency for the framework carbon atoms to separate (as in the carboranes); there is also a drive to minimize metal–carbon links in the cage. In species with more than one framework metal atom, the nature of the metal–metal interaction is complex, and *general* rules regarding the stability of adjacent-metal *vs.* nonadjacent-metal isomers cannot be given; indeed, examples have been cited of adjacent-metal and nonadjacent-metal isomers in thermal equilibrium with each other (see Section 5.5.6.1 and Figure 25b). High-temperature isomerizations, in which the metal and carbon atoms migrate on the polyhedral surface, are often accompanied by metal atom transfer *between* cages, as in the conversion of 11-vertex *closo*-1,2,3-$CpCoC_2B_8H_{10}$ to several isomers of 12-vertex *closo*-$Cp_2Co_2C_2B_8H_{10}$.[87]

(*vi*) *Isomerization via oxidation/reduction*

In certain 12-vertex metallacarboranes containing metal atoms that are capable of adopting several stable oxidation states, some remarkable structural changes can be induced by chemical or electrochemical redox reactions in conjunction with thermal isomerization. The most extensively studied complexes are of the form $M(C_2B_9H_{11})_2^{n-}$ where M is nickel or palladium and n is 2, 1 or 0, corresponding to the formal metal oxidation states II, III and IV, respectively.[183,203] Three different types of cage geometry, designated A, B and C, are observed in the nickel systems. Type A species have the slipped structure shown in Figure 76, those of type B have a 1,2-1′,7′ geometry in which one carbon atom in one ligand has moved away from the open face (but is still linked to the other carbon), and the type C complexes adopt a 1,7-1′,7′ configuration with one carbon in *each* ligand off the open face (*i.e.* in the 7-vertex). In each of these classes the metal can adopt any of the three available oxidation states, as demonstrated by detailed investigation[183,203] of the bis(*C*,*C*′-dimethyl) or *C*,*C*′-trimethylene derivatives. A sequence involving the latter system is shown in Figure 79, where all three structural classes (A, B, C) are represented. In these trimethylene-substituted species the stereochemistry is somewhat simplified by the fact that the cage carbons are constrained to adjacent vertices. When the carbons are not ‘tied together’, as in the parent or *C*,*C*′-dimethyl derivatives, many more isomers are possible in principle, since the carbons can migrate away from each other; however, the *C*,*C*′-dimethyl species in fact exhibit completely analogous behavior to that of the trimethylene derivatives.

Neutral $Ni^{IV}(1,2\text{-}C_2B_9H_{11})_2$ is an unusual metallacarborane in that it (1) adopts the nonslipped cisoid geometry[204] shown in Figure 80, with cage carbons in the two ligands in close proximity, and (2) exhibits extraordinarily strong acidity in its cage C—H protons. The nonslipped structure is as expected for $(2n + 2)$-electron polyhedra, but the cisoid arrangement (also found for the palladium analogue) contrasts with the usual transoid geometry of $M(C_2B_9H_{11})_2^{n-}$ complexes (Figure 73). The high carbon acidity is attributed to the +4 oxidation state of nickel, which attracts electron density from the carborane ligands. A further consequence of the high oxidation state is a strong inductive electron-withdrawing ($-I$) effect (comparable with that of CN) towards



$[(TM)_2Ni^{II}\text{-}A]^{2-}$

$[(TM)_2Ni^{III}\text{-}A]^{-}$

(±)- and *meso*-$[(TM)_2Ni^{IV}\text{-}C]^0$

(±)-$[(TM)_2Ni^{IV}\text{-}B]^0$

Figure 79 Interconversions of bis(1,2-μ-trimethylene) derivatives of $(1,2\text{-}C_2B_9H_{11})_2Ni^{n-}$ ions[203]

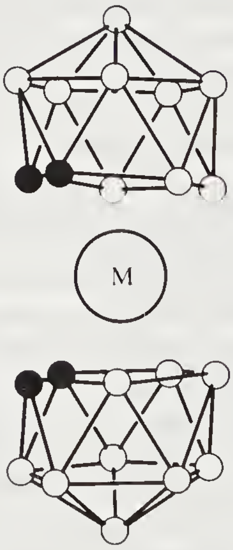


Figure 80 Structure of $Ni^{IV}(1,2\text{-}C_2B_9H_{11})_2$

C-bonded substituents; in contrast, the isoelectronic Fe(II) and Co(III) complexes exhibit large $+I$ effects.

Detailed discussions of these and other aspects of nickel and palladium carborane stereochemistry can be found elsewhere.[175b,183,203]

(*vii*) *Hydridometallacarboranes and catalysis*

Icosahedral metallacarboranes containing MH or MH_2 groups, where M is rhodium, ruthenium or iridium, have been shown to catalyze homogeneously the hydrogenation and isomerization of alkenes, hydrosilylation of ketones, and conversion of unsaturated alcohols to aldehydes and ketones, in some cases with rates and selectivity comparable with, or exceeding, those of conventional catalyst systems.[205] A general route to complexes of this type utilizes the reaction of the 7,8- or 7,9-$C_2B_9H_{12}^-$ ion with transition metal reagents which may or may not contain hydride ligands themselves (equations 78 and 85).[178,205a,206] The transfer of a hydrogen ligand from a carborane substrate to the metal, as in equation (85), was first demonstrated in iron complexes of the $C_2B_4H_7^-$ ion (Figure 22),[11,57] although the latter species contain face-bridging, rather than terminal, hydride ligands. As confirmed in an X-ray study[207] of 3,1,2-$(Ph_3P)_2Rh(H)C_2B_9H_{11}$, the hydride ligand occupies a terminal coordination site on rhodium with an Rh—H bond length of 1.54(9) Å. The ruthenium dihydride complex (3,1,2-isomer) in equation (78) loses H_2 reversibly on heating; CO and HCl also displace the hydride ligands, as shown in equation (86).[178] Similarly, 3,1,2-$(Ph_3P)_2Rh(H)C_2B_9H_{11}$ reacts with H_2SO_4 or HNO_3 to form complexes having metal–oxygen bonds (equation 87).[208]

$$(Ph_3P)_3Rh^+ \quad + \quad C_2B_9H_{12}^- \xrightarrow[60\ °C]{MeOH} (Ph_3P)_2Rh(H)C_2B_9H_{11} \qquad (85)$$

$$\begin{tikzcd}
(Ph_3P)_2RuH_2C_2B_9H_{11} \arrow[r, shift left, "160\ °C"] \arrow[d, "HCl"'] \arrow[dr, "CO"] & (Ph_3P)_2RuC_2B_9H_{11} + H_2 \arrow[l, shift left, "25\ °C"] \\
(Ph_3P)_2Ru(H)(Cl)C_2B_9H_{11} & (Ph_3P)_2Ru(CO)C_2B_9H_{11}
\end{tikzcd} \qquad (86)$$

$$\begin{tikzcd}
(Ph_3P)_2Rh(H)C_2B_9H_{11} + H_2SO_4 \arrow[r, "CH_2Cl_2"] & 3,1,2\text{-}(Ph_3P)_2(HSO_4)RhC_2B_9H_{11} + H_2 \arrow[l, bend left, "H_2\ (1\ atm)"]
\end{tikzcd} \qquad (87)$$

A different synthesis of a metallacarborane hydride, though not yet shown to have general applicability, involves the thermal interchange of a metal phosphino ligand and a BH hydrogen atom in 3,1,2-$(Ph_3P)_2NiC_2B_9H_{11}$ to form 8-Ph_3P-3,1,2-$(Ph_3P)Ni(H)C_2B_9H_{11}$ (Section 5.5.3.1.7);[78] the product is a rare example of a hydridometallacarborane of a *first-row* transition metal. The catalytic activity of the hydridometallacarboranes is reflected in their ability to promote deuterium exchange in boranes, carboranes and metallacarboranes.[205a,206] The exchange is believed to proceed *via* oxidative addition of B—H bonds to the catalyst *via* reversible dissociation of a phosphine ligand to give a coordinatively unsaturated mono(triphenylphosphine) species (equation 88).[206] A monoligand complex, $(Ph_3P)Rh(H)C_2B_9H_{11}$, has been isolated[209] from the reaction of $C_2B_9H_{11}^{2-}$ ion with $(Ph_3P)_3RhCl$, but the major product[15] of this reaction is a dimer, $[(Ph_3P)RhC_2B_9H_{11}]_2$, whose structure is shown in Figure 81. The dimer catalyzes the homogeneous hydrogenation of alkenes (as does the monomer) and may represent an oxidative intermediate in the oxidative addition of a terminal B—H bond to the metal.[15]

$$(Ph_3P)_2M(H)C_2B_9H_{11} \rightleftharpoons (Ph_3P)M(H)C_2B_9H_{11} \quad + \quad PPh_3 \qquad (88)$$

Polystyrene-based polymers incorporating the $(Ph_3P)_2Rh(H)C_2B_9H_{10}$ icosahedral system have been synthesized by various methods and shown to be effective *heterogeneous* catalysts for alkene isomerization and hydrogenation.[63]

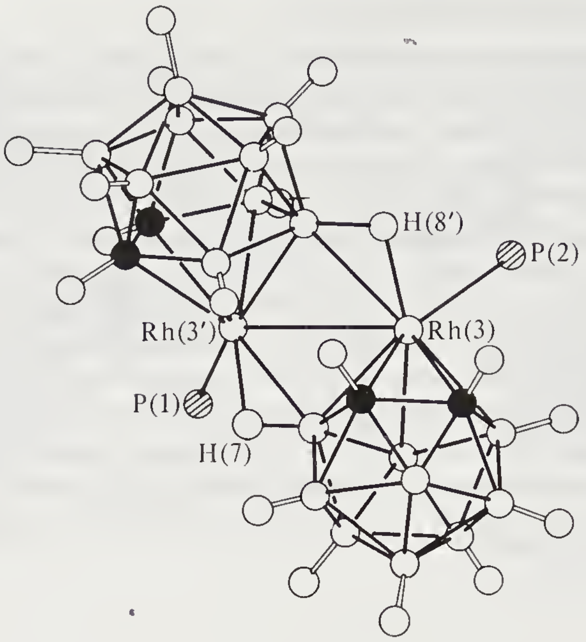


Figure 81 Structure of $[Ph_3PRhC_2B_9H_{11}]_2$

5.5.8.1.2 One-carbon cages

The carbollide ion, $CB_{10}H_{11}^{3-}$, is an isoelectronic analogue of the dicarbollide ion, $C_2B_9H_{11}^{2-}$, and has a similar open-cage (*nido*) structure into which a metal ion can be inserted to complete the icosahedron. Addition of one or two protons to $CB_{10}H_{11}^{3-}$ (*e.g.* in B—H—B bridging locations on the open face) gives $CB_{10}H_{12}^{2-}$ and $CB_{10}H_{13}^-$ respectively, which are counterparts of $C_2B_9H_{12}^-$ and $C_2B_9H_{13}$. Directly related to these are the species $R_3N{\cdot}CB_{10}H_{12}$ (R = H or alkyl), which are *formally* derived from $CB_{10}H_{13}^-$ by replacement of H^- with NR_3.

The synthetic routes to these monocarbon carboranes are totally different from those of the dicarbon systems, although the methods for insertion of metals into them to create metallacarboranes are similar. All of the 11-vertex *nido*-monocarboranes are derived from cyano derivatives of decaborane(14), in the course of which the cyano carbon atom is incorporated into the cage framework (equations 89–91).[210,73]

$$B_{10}H_{14} \;+\; 2CN^- \xrightarrow[-HCN]{H_2O} B_{10}H_{13}CN^{2-} \xrightarrow[\text{ion exchange}]{2H^+} B_{10}H_{12}CNH_3 \qquad (89)$$

$$B_{10}H_{14} \;+\; RNC \longrightarrow B_{10}H_{12}CNH_2R \qquad (90)$$

$$(R = Me, Et, Pr^n, Bu^t)$$

$$B_{10}H_{12}CNH_3 \xrightarrow[NaOH]{Me_2SO_4} B_{10}H_{12}CNMe_3 \xrightarrow{Na/THF}$$

$$CB_{10}H_{11}{}^{3-}\ (\text{THF adduct}) \xrightarrow{H_2O} CB_{10}H_{13}{}^- \qquad (91)$$

Metallacarboranes can be obtained from the $R_3N{\cdot}CB_{10}H_{12}$ species as well as the $CB_{10}H_{11}^{3-}$ and $CB_{10}H_{13}^-$ ions by reaction with metal salts,[210a,210b,211] as in the examples shown in equations (92) and (93). The products of these reactions are icosahedral cages, isoelectronic with $CpCoC_2B_9H_{11}$ with the metal coordinated to a CB_4 face; at 450 °C the nickel compound rearranges to 1,7 and 1,12 (*meta* and *para*) isomers.[211d]

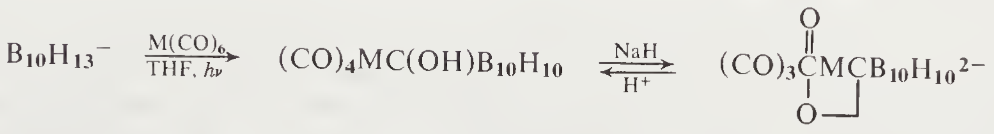
$$CB_{10}H_{13}{}^- \xrightarrow[EtOH]{KOH} \xrightarrow[CoCl_2]{C_5H_6} \xrightarrow{O_2} CpCoCB_{10}H_{11}{}^- \qquad (92)$$

$$B_{10}H_{12}C{\cdot}NMe_3 \xrightarrow[THF]{Na} \xrightarrow[NiBr_2]{NaC_5H_5} \xrightarrow{O_2} CpNiCB_{10}H_{11} \qquad (93)$$

Another approach to monocarbon metallacarborane synthesis utilizes direct metal insertion into the *closo*-$CB_{10}H_{11}^-$ ion and *closo*-$Me_3N{\cdot}CB_{10}H_{10}$, which are analogues of *closo*-$C_2B_9H_{11}$.[47d] Thus, reaction of these species with organometallic reagents of nickel, palladium or platinum, *e.g.*

$Ni(cyclooctadiene)(Bu^tNC)_2$ or $Pt(\textit{trans}\text{-stilbene})(Et_3P)_2$, yields products formulated as $L_2MCB_{10}H_{11}$ or $L_2MC(NMe_3)B_{10}H_{10}$ which are generally icosahedral; however, where M is palladium or platinum, distortion from icosahedral symmetry has been observed in the form of a long (2.60 Å) metal–carbon interaction (see Sections 5.5.2.5 and 5.5.8.1.1, above).

Still other routes to MCB_{10} cages, not yet shown to be of general utility, have been demonstrated. Photolysis of the decaborane derivative $6\text{-}\{CpFe(CO)_2\}B_{10}H_{13}$ generates icosahedral $1,2\text{-}CpFeC(L)B_{10}H_{10}$, where L is a solvent molecule (THF or Et_2O) (see Figure 24).[72] In the previously mentioned reaction of molybdenum, chromium or tungsten hexacarbonyls with the $B_{10}H_{13}^{-}$ ion, a carbonyl group is incorporated together with a metal atom into the B_{10} cage to generate a 12-vertex *closo*-MCB_{10} system (equation 94).[73] Both of the icosahedral complexes in this reaction are converted by aqueous bases to *nido*-metallaboranes of the type $(CO)_4MB_{10}H_{12}^{2-}$, *via* removal of the cage carbon atom.



$$B_{10}H_{13}^{-} \xrightarrow[\text{THF, } h\nu]{M(CO)_6} (CO)_4MC(OH)B_{10}H_{10} \underset{H^+}{\overset{NaH}{\rightleftarrows}} (CO)_3\overset{\overset{O}{\|}}{C}M\underset{\llcorner O \lrcorner}{C}B_{10}H_{10}^{2-} \qquad (94)$$

$$M = Cr, Mo, W$$

Formal replacement of BH with CoCp in $CpCoCB_{10}H_{11}^{-}$ (equation 92) would create a dimetallic system, $Cp_2Co_2CB_9H_{10}^{-}$. Such a complex has been prepared and characterized by X-ray diffraction, and found to have icosahedral geometry with the metal and carbon atoms forming one triangular face.[212] Alternatively, one can replace BH with a main group element such as phosphorus or arsenic to generate $MXCB_9$ cage systems where M is a transition metal and X is the main group heteroatom. Such species are prepared from the icosahedral 1,2- or $1,7\text{-}XCB_{10}H_{11}$ compounds[213] (X = P, As) by base degradation to remove one boron, producing an $XCB_9H_{11}^{-}$ open-cage ion (analogous to $C_2B_9H_{12}^{-}$);[213b] deprotonation with sodium hydride yields 1,2- or $1,7\text{-}XCB_9H_{10}^{2-}$, direct counterparts of the 1,2- and $1,7\text{-}C_2B_9H_{11}^{2-}$ (dicarbollide) ions.[214] Complexation of the $PCB_9H_{10}^{2-}$ or $AsCB_9H_{10}^{2-}$ ions, or their derivatives, with transition metals is straightforward and largely parallels that of the dicarbollides (equations 95, 96). The X-ray-determined structure[214] of the *P,P′*-dimethyl derivative of the iron complex is depicted in Figure 82. The 'bare' phosphorus atoms in the dianion can coordinate to electron-acceptors such as Me^+; thus treatment of

$$1,7\text{-}PCB_9H_{10}^{2-} + BrMn(CO)_5 \xrightarrow[\text{reflux}\\ -2CO]{THF} 2,1,7\text{-}(CO)_3MnPCB_9H_{10}^{-} + Br^{-} \qquad (95)$$

$$1,2\text{- or } 1,7\text{-}PCB_9H_{10}^{2-} + FeCl_2 \xrightarrow{THF} (PCB_9H_{10})_2Fe^{2-} \qquad (96)$$

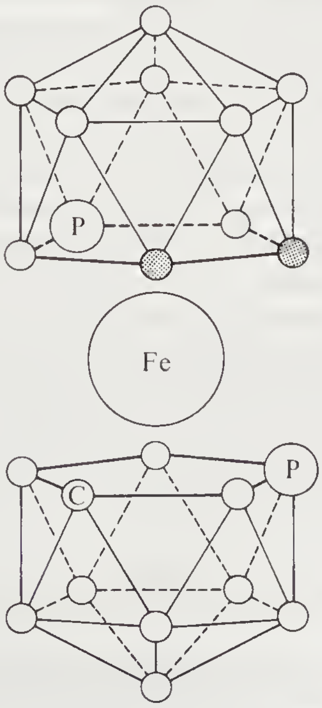


Figure 82 Structure of $(MePCB_9H_{10})_2Fe$; shaded atoms are disordered carbon/boron positions

$(PCB_9H_{10})_2Fe^{2-}$ with methyl iodide forms neutral $(MePCB_9H_{10})_2Fe$. Reaction of the latter complex with sodium hydride removes one methyl group to give the $(MePCB_9H_{10})Fe(PCB_9H_{10})^-$ monoanion.[215] Similarly, $(1,7\text{-}XCB_9H_{10})_2Fe^{2-}$ (X = P, As) ions react with Group VIB carbonyls to form σ-complexes containing *exo*-polyhedral metal–phosphorus linkages (equation 97).[216] Analogous compounds of manganese, cobalt and nickel have been prepared,[214–218] as have cyclopentadienyl metal complexes such as 3,1,2-$CpCoAsCB_9H_{10}$ in which the three heteroatoms form a triangular face.[213c]

$$(1,7\text{-}XCB_9H_{10})_2Fe^{2-} \quad + \quad M(CO)_6 \quad \xrightarrow{h\nu} \quad [(CO)_5M{-}XCB_9H_{10}]_2Fe^{2-} \qquad (97)$$

$$X = P, As; M = Cr, Mo, W$$

5.5.8.1.3 Four-carbon cages

An extensive series of 12-vertex metallacarborane cage systems of the MC_4B_7 and $M_2C_4B_6$ types has been characterized,[4c,41,42,43a,43c,60,77f] whose preparation and structures are very different from those of the mono- and di-carbon systems described above. In contrast to the latter group, the four-carbon species are mostly 'electron-rich' (more than $2n + 2$ framework electrons) and adopt open-cage (*nido* or *arachno*) geometries. X-ray studies on many of these compounds have disclosed novel types of cluster shapes, in some of which the framework carbon atoms occupy unusual, kinetically stabilized sites. Figure 14 depicts the various types of 12-vertex, 28-electron (formally *nido*) systems thus far known, most of which are four carbon carboranes (Section 5.5.2.4).

The tetracarbon species have been prepared by (1) direct insertion of metal groups into $Me_4C_4B_8H_8$ (Figure 5) with loss of BH, (2) reaction of the $Me_4C_4B_8H_8^{2-}$ dianion with metal ions (again with loss of BH), and (3) oxidative fusion of small metallacarborane anions; all three reaction types are frequently complex, with several competing processes which generate mixtures of products in low to moderate individual yields.[4c] For example, photolytic reaction of $CpCo(CO)_2$ with $Me_4C_4B_8H_8$ in THF gave $CpCoMe_4C_4B_7H_7$ (isomer I) together with isomers of an 11-vertex system, $CpCoMe_4C_4B_6H_6$.[77f] The structure of isomer I and its thermal rearrangement product, isomer III,[80] are shown in Figure 28 (isomer II, representing yet another structural type,[43a] is illustrated in Figure 6). Of these three known isomers of $CpCoMe_4C_4B_7H_7$, the thermodynamically preferred structure is that of III, a *nido* 12-vertex cage with all four framework carbon atoms on the open face, one of which is separated from the others; this implies that, despite the tendency of carbons to separate from each other on thermal rearrangement (see Section 5.5.3.1.7), the drive to occupy low-coordinate vertices is predominant in this instance.[80]

Metal insertion into the $Me_4C_4B_8H_8^{2-}$ dianion is typified by the formation of $CpFeMe_4C_4B_7H_8$ together with several 14-vertex products (equation 12).[60] A crystallographic study of this complex established the structure shown in Figure 14 (type 5), in which one CMe unit occupies a high-coordinate vertex distant from the other carbons; a mechanism to account for this particular cage geometry has been proposed.[219] Similarly, treatment of the $Me_4C_4B_8H_8^{2-}$ ion with nickel and cobalt reagents generates still other 12-vertex cage systems.[60,77f]

Fusion of two pyramidal 1,2,3-$CpCoMe_2C_2B_3H_4^-$ ions (derived from the neutral complex by bridge-deprotonation with sodium hydride) *via* equation (98) forms the 12-vertex species $Cp_2Co_2Me_4C_4B_6H_6$, isomer V (Figure 29).[41,88] This process is formally analogous to the oxidative fusion of two metal-complexed $Me_2C_2B_4H_4^{2-}$ ligands to give $Me_4C_4B_8H_8$, as described in Section 5.5.5.1 and 5.5.3.1.10, and the structure of the cobaltacarborane product (V) shown in Figure 29 clearly reflects the face-to-face fusion of two CoC_2B_4 units. However, in contrast to $Me_4C_4B_8H_8$ (Figure 5), the C(3)—C(7) interaction is distinctly nonbonding (2.79 Å), indicating that the presence of two CoCp groups ties up sufficient electron density in local Co—C interactions such that the central C—C link is weakened to the point of scission.[41] The same effect is observed even when only *one* apex BH is replaced, as in $CpCoMe_4C_4B_7H_7$, isomer I (Figure 28).[42] This problem has also been examined theoretically by Lipscomb,[220] who approaches these systems from a localized three-center bond point of view.

$$2CpCoMe_2C_2B_3H_4^- \xrightarrow{O_2} Cp_2Co_2Me_4C_4B_6H_6 \qquad (98)$$

Curiously, fusion of the non-methylated (parent) species 1,2,3-$CpCoC_2B_3H_7^-$ under similar conditions yields not one but *three* isomers of $Cp_2Co_2C_4B_6H_{10}$, all of which belong to different structural classes (Figure 83);[88] one of these is isostructural with the single isomer of Cp_2-

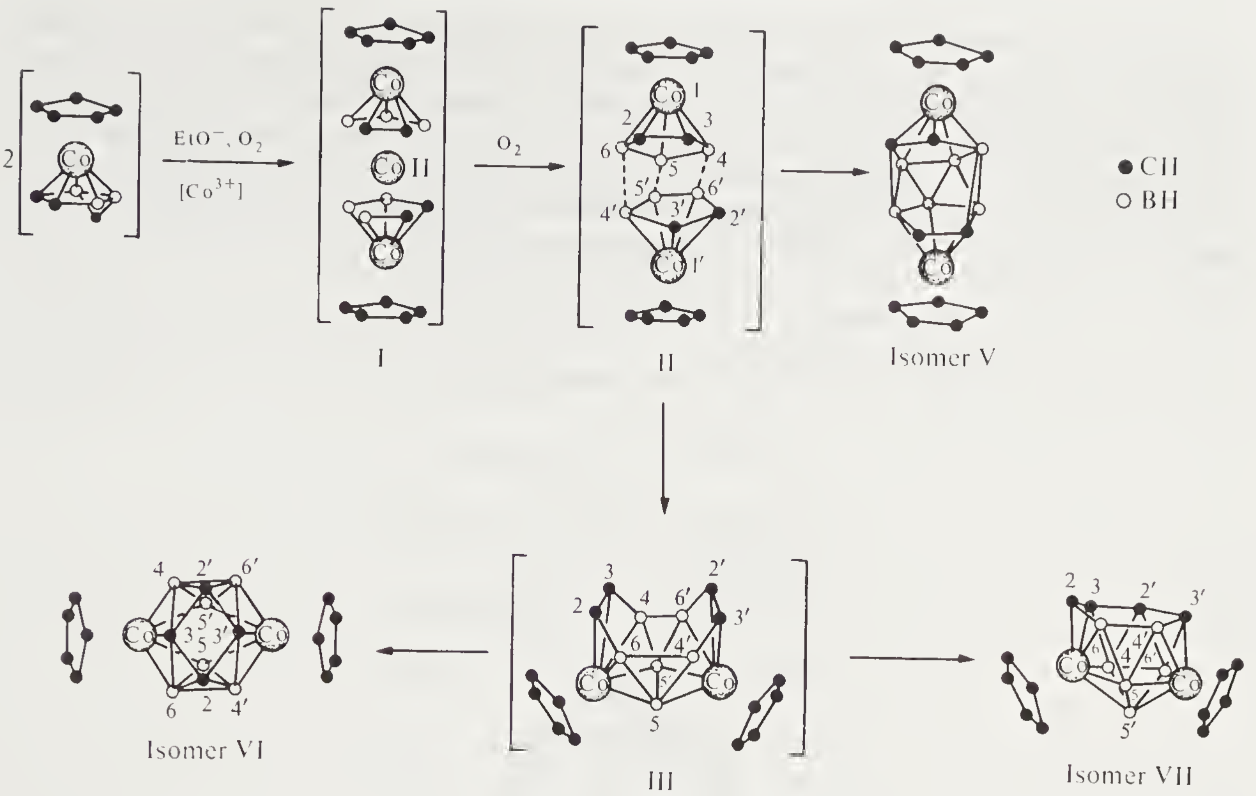


Figure 83 Proposed mechanism for formation of $Cp_2Co_2C_4B_6H_{10}$ isomers. Structures of isomers V and VII are established; that of VI is proposed from NMR evidence[41]

$Co_2Me_4C_4B_6H_6$ that is obtained on fusion of the $CpCoMe_2C_2B_3H_5^-$ ion, described above. A possible mechanism[41] accounting for the formation of the three products is presented in Figure 83.

5.5.8.2 Metallaboranes

The prototype 12-vertex borane is the icosahedral $B_{12}H_{12}^{2-}$ ion, a $(2n+2)$-electron *closo* system. Formal replacement of one or more BH units with other two-electron donors, or of BH^- units with three-electron donors, should retain the 12-vertex, 26-skeletal electron system and hence the icosahedral geometry; however, heteroatoms that cause the skeletal bonding electron count to exceed 26 are expected to produce distortion or opening of the cage. Thus far, most 12-vertex metallaboranes are of the closed icosahedral type and are prepared by insertion of a metal into a *nido* 11-vertex borane or heteroborane substrate; the *closo* anions $B_{11}H_{11}^{2-}$ and $B_{10}H_{10}^{2-}$ have also been successfully employed in the synthesis of nickelaboranes (equations 99–101).[92] The icosahedral NiB_{11} and Ni_2B_{10} systems formed in reactions (99) and (100) are isoelectronic analogues of the carboranes $CB_{10}H_{11}^-$ and $1,2\text{-}C_2B_{10}H_{12}$ (*o*-carborane), respectively, thereby illustrating the formal electronic equivalence of CH and NiCp units [Section 5.5.2.4 (Table 1)]. Insertion of selenium or tellurium similarly forms icosahedral 26-electron species, a 'bare' Se or Ge atom effectively replacing BH^{2-} in the $B_{12}H_{12}^{2-}$ system (equation 102).[221]

$$\textit{nido}\text{-}B_{11}H_{13}{}^{2-} \quad + \quad Cp_2Ni \quad \xrightarrow[\text{MeCN}]{\text{Na/Hg}} \quad \textit{closo}\text{-}CpNiB_{11}H_{11}{}^- \tag{99}$$

$$\textit{closo}\text{-}B_{11}H_{11}{}^{2-} \quad + \quad CpNi(CO)_2 \quad \xrightarrow{\text{THF}} \nearrow$$

$$\textit{closo}\text{-}B_{10}H_{10}{}^{2-} \quad + \quad Cp_2Ni \quad \xrightarrow{1,2\text{-}(MeO)_2C_2H_4} \quad \textit{closo}\text{-}1,2\text{-}Cp_2Ni_2B_{10}H_{10} \tag{100}$$

$$\textit{nido}\text{-}CpNiB_{10}H_{12} \quad + \quad Cp_2Co \quad \xrightarrow{1,2\text{-}(MeO)_2C_2H_4} \quad \textit{closo}\text{-}1,2\text{-}Cp_2CoNiB_{10}H_{10}{}^- \tag{101}$$

$$\textit{nido}\text{-}B_{11}H_{14}{}^- \quad \xrightarrow{\text{NaHSeO}_3\text{ or TeO}_2} \quad MB_{11}H_{11} \tag{102}$$

(M = Se or Te)

A variety of 12-vertex metallaheteroboranes has been prepared by insertion of transition metals into neutral or anionic 11-vertex phospha-, arsena-, stiba-, thia-, selena- and tellura-boranes. A commonly employed substrate is the *nido*-$SB_{10}H_{10}^{2-}$ (thiollyl) ion, which is isoelectronic with $C_2B_9H_{11}^{2-}$ (dicarbollide) and mimics its behavior in complexation with metals (equation 103).[222] The products are all assigned icosahedral cage structures similar to that depicted for the bis(thiaborane)cobalt complex in Figure 84. Analogously, the protonated species $SB_{10}H_{11}^-$ complexes with rhodium to give *closo*-$(Ph_3P)_2Rh(H)SB_{10}H_{10}$.[99c]

$$(SB_{10}H_{10})^{2-} \xrightarrow{FeCl_2} (SB_{10}H_{10})_2Fe^{2-}$$

$$\xrightarrow{CoCl_2} (SB_{10}H_{10})_2Co^-$$

$$\xrightarrow{CoCl_2,\ C_5H_5^-} CpCoSB_{10}H_{10}$$

$$\xrightarrow{(Et_3P)_2PtCl_2} (Et_3P)_2PtSB_{10}H_{10}$$

$$\xrightarrow{(CO)_5ReCl} (CO)_3ReSB_{10}H_{10}^- \qquad (103)$$

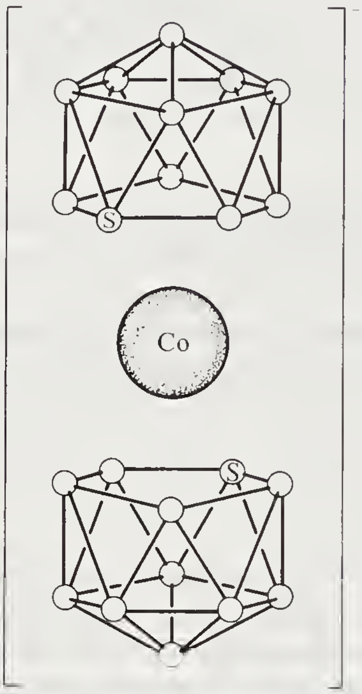


Figure 84 Proposed structure of the $Co(SB_{10}H_{10})_2^-$ ion;[222] the same geometry has been established for the $Fe(SB_{10}H_{10})^{2-}$ ion[248]

Treatment of the 11-vertex *nido* species $SeB_{10}H_{12}$ or $TeB_{10}H_{12}$ with $CoCl_2$ in aqueous KOH yields $(MB_{10}H_{10})_2Co^-$ (M = Se, Te), which are analogues of the $(SB_{10}H_{10})_2Co^-$ ion in Figure 84; the corresponding $CpCoMB_{10}H_{10}$ species, as well as iron analogues, have also been characterized.[167] The reactions of *nido*-$Se_2B_9H_9$ and *nido*-$SSeB_9H_9$ with KOH followed by cyclopentadiene and cobalt(II) chloride take a different course, producing respectively the 12-vertex *nido* species $CpCoSe_2B_9H_9$ and $CpCoSSeB_9H_9$, which are 28-electron $(2n + 4)$ systems; the X-ray-determined structure of the diselenium product is shown in Figure 14 (type 7).[43b] With the diselenium reagent, a 26-electron *closo* system, $Cp_2Co_2SeB_9H_9$, is also formed.

Metallaheteroboranes containing Group V atoms have been obtained by several routes. The reaction of *nido*-$PhPB_{10}H_{11}^-$ (itself prepared by treatment of $B_{10}H_{13}^-$ ion with $PhPCl_2$) with $(CO)_5MnBr$ and sodium hydride in THF forms the $(CO)_3MnPPhB_{10}H_{10}^-$ ion, which is proposed to have a *closo* structure with adjacent manganese and phosphorus atoms.[223] Here $Mn(CO)_3^-$ and PPh are formal two- and four-electron donors respectively, equivalent to two CH units; hence the molecule is analogous to $C_2B_{10}H_{12}$. Related cobalt complexes can be obtained similarly (equation 104).[99d] The unsubstituted $CpCoPB_{10}H_{10}^-$ complexes can be alkylated at the 'bare' phosphorus atom to form $CpCoP(R)B_{10}H_{10}$ species.

$$RPB_{10}H_{12} + CoCl_2 + C_5H_6 + KOH \xrightarrow{EtOH} CpCoP(R)B_{10}H_{10} + CpCoPB_{10}H_{10}^-$$

$$R = Me,\ Et,\ Pr^n,\ Bu^t \qquad (104)$$

The *nido* anion $AsB_{10}H_{12}^-$ and its methyl-substituted derivative readily form transition metal complexes, *e.g.* equations (105) and (106). Related systems containing *two* arsenic atoms can be prepared from the $As_2B_9H_{10}^-$ ion or from neutral 1,2-$As_2B_{10}H_{10}$ (equation 107).[99d] Finally, electronically analogous *closo* 12-vertex diantimony or mixed arsenic–antimony complexes have been obtained[99d] from the icosahedral species $SbAsB_{10}H_{10}$, $Sb_2B_{10}H_{10}$ and the $SbB_{11}H_{11}^-$ ion; the characterized products include $CpCoAsSbB_9H_9$ and $CpCoSb_2B_9H_9$. All of these arsenic- and antimony-containing systems are formally assigned 26 skeletal bonding electrons to which neutral As or Sb atoms contribute three electrons (Section 5.5.2.4), and accordingly are proposed to have closed icosahedral cage geometry. In most cases the main group and transition metal atoms will occupy adjacent vertices, by virtue of the strong tendency of main group atoms to adopt locations on the open face of the precursor 11-vertex *nido* species into which the transition metal is inserted.

$$AsB_{10}H_{12}^- \xrightarrow[\text{NaOH, aq.}]{CoCl_2} Co(AsB_{10}H_{10})_2^{3-}$$

$$\searrow \xrightarrow[\text{NaOH, aq.}]{NiCl_2} Ni(AsB_{10}H_{10})_2^{2-} \qquad (105)$$

$$MeAsB_{10}H_{12} \xrightarrow[CoCl_2]{C_5H_6} \xrightarrow[\text{EtOH}]{\text{KOH}} CpCoAsB_{10}H_{10}^- \qquad (106)$$

$$As_2B_9H_{10}^- \xrightarrow[\text{Et}_3\text{N, THF}]{CoCl_2,\ C_5H_6} CpCoAs_2B_9H_9$$

$$\searrow \xrightarrow[\text{NaOH, aq.}]{CoCl_2} Co(As_2B_9H_9)_2^{\ -} \qquad (107)$$

5.5.9 CAGE SYSTEMS WITH THIRTEEN OR FOURTEEN VERTICES

5.5.9.1 Two-carbon Cages

At this writing, all known and structurally characterized boron clusters of more than 12 framework atoms are metallacarboranes, and all of these are derived from the $C_2B_{10}H_{12}$ or $R_4C_4B_8H_8$ (R = Me or Et) carborane systems. The synthetic routes employed are similar to those described earlier for smaller metallacarboranes, in most cases employing the 'polyhedral expansion' principle. Thus the $C_2B_{10}H_{12}$ icosahedral cage can be opened by reduction with sodium, forming a $C_2B_{10}H_{12}^{2-}$ ion (whose detailed structure as an uncomplexed free species is still not known); insertion of a metal cation yields a 13-vertex MC_2B_{10} system, as in equation (20).[65,83] When capping ligands such as $C_5H_5^-$ are absent, bis(carboranyl) complexes of the $C_2B_{10}H_{12}^{2-}$ ligand are obtained (equation 108). The 13-vertex *closo* polyhedral geometry[224] exhibited by these species is typified by the structure of the $[1,6\text{-}Me_2C_2B_{10}H_{10}]_2Ti^{2-}$ dianion shown in Figure 85. In some cases, fluxional behavior in solution is indicated by ^{11}B NMR evidence, as in the species 4,1,7-

$$C_2B_{10}H_{12}^{2-} \xrightarrow{M^{n}} (C_2B_{10}H_{12})_2M^{n-4} \qquad (108)$$

M = Fe, Co, Ni, Ti, V, Cr, Mn, Zr, Hf; n = 2, 3 or 4

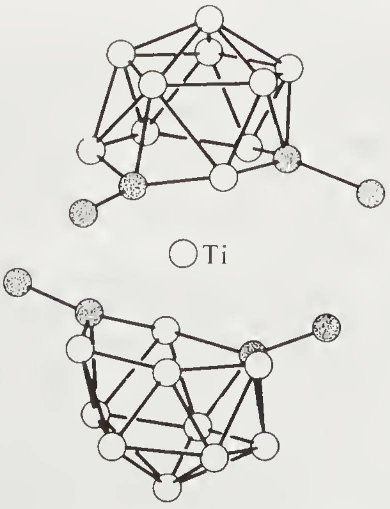


Figure 85 Structure of the $(1,6\text{-}Me_2C_2B_{10}H_{10})_2Ti^{2-}$ ion

$CpCoC_2B_{10}H_{12}$ which, at −30 °C or above, undergoes rapid equilibration between enantiomeric forms such that the time-averaged geometry contains a mirror plane; at −90 °C, however, the asymmetric static geometry (Figure 86)[77h] is observed.[83]

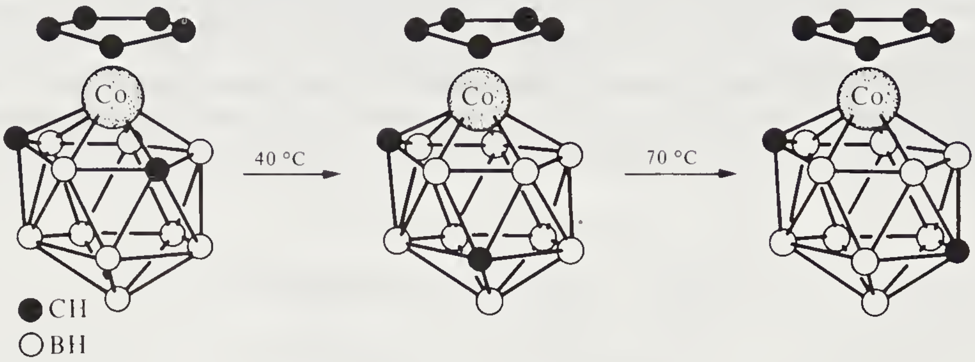


Figure 86 Rearrangement of $CpCoC_2B_{10}H_{12}$ isomers

Application of the expansion technique to MC_2B_9 polyhedral cage systems affords dimetallic $M_2C_2B_9$ 13-vertex species. Thus reduction of 3,1,2-$CpCoC_2B_9H_{11}$ to the (presumed) dianion followed by treatment with $CoCl_2$ and $C_5H_5^-$ forms $Cp_2Co_2C_2B_9H_{11}$.[164] A similarly prepared species, $Cp_2Fe_2C_2B_9H_{11}$, formally is a 26-electron cage and is therefore electron hyperdeficient;[225] partial X-ray data suggest that the iron atoms occupy nonadjacent vertices in the polyhedron, but the indicated Fe—Fe distance of ~3.20 Å would be remarkably short for a nonbonded interaction.

When the cage reduction/metal insertion sequence is conducted on the 13-vertex system 4,1,13-$CpCoC_2B_{10}H_{12}$, the products are two isomeric 14-vertex $Cp_2Co_2C_2B_{10}H_{12}$ complexes.[226] The proposed geometry of these cages is the bicapped hexagonal antiprism; X-ray confirmation of these particular species has not been reported, but this is in fact the established structure of an electronically analogous system, $Cp_2Fe_2Me_4C_4B_8H_8$, isomer VIII (see below).

Another route to dimetallic 13-vertex cages utilizes the previously described base-degradation method in which one BH unit is extracted and replaced by a metal ion (equation 109).[227] This method can be used to prepare mixed-metal complexes such as $Cp_2CoFeC_2B_9H_{11}$. Such degradations evidently occur by multiple pathways since several isomers are obtained.

$$CpCoC_2B_{10}H_{12} \xrightarrow[EtOH]{KOH} \xrightarrow[C_5H_6]{MCl_2} Cp_2M_2C_2B_9H_{11} \qquad (109)$$

$$M = Co, Fe$$

The thermal rearrangement of the 13-vertex *closo* system $CpCoC_2B_{10}H_{12}$ and its *C,C*-dimethyl derivative has been examined in detail,[77h] establishing that the previously noted tendency of the skeletal carbon atoms to separate from each other and from the metal (Section 5.5.3.1.7) holds true here also. The *C*-monomethyl derivative, however, differs from the parent and dimethyl complexes in that it is not fluxional at room temperature. A proposed scheme for the rearrangement of the parent species is shown in Figure 86.

Extremely facile isomerizations of $(1,2\text{-}C_2B_{10}H_{12})_2M^{n-}$ complexes (M = Co, Ni, Fe) have been noted.[228] At temperatures as low as 20 °C, the carborane ligands undergo rearrangement in which the carbon atoms separate; oxidation of these complexes by O_2, $KMnO_4$ or other agents generates mixtures of the neutral carboranes 1,2-, 1,7- and 1,12-$C_2B_{10}H_{12}$. The product ratio is extremely sensitive to reaction conditions, particularly temperature and time elapsed between metallacarborane formation and oxidative degradation to form carboranes. The ease of rearrangement of these complexes stands in sharp contrast to the thermal isomerization of 1,2-$C_2B_{10}H_{12}$ to the 1,7- and 1,12-isomers, which requires temperatures in excess of 425 and 600 °C, respectively.[6]

5.5.9.2 Four-carbon Cages

Metallacarboranes of 13 and 14 vertices have been prepared by insertion of transition metals into $Me_4C_4B_8H_8$ or the $Me_4C_4B_8H_8^{2-}$ ion. The stereochemistry exhibited by most of these species is strikingly different from that of the metal complexes of $C_2B_{10}H_{12}^{2-}$ and its *C*-alkyl derivatives, described above; the difference arises from the presence of four CMe units in the framework, which has both electronic and steric consequences as will be shown. Neutral $Me_4C_4B_8H_8$, a white, volatile, air-stable solid with a distorted icosahedral cage geometry (Figure 5), reacts with molybdenum or tungsten hexacarbonyls in refluxing heptane to give the respective 13-vertex $(CO)_3M$-$Me_4C_4B_8H_8$ species, which have not yet been structurally characterized (equation 3).[60] (Direct reaction with $CpCo(CO)_2$, on the other hand, is accompanied by loss of BH units, giving 11- and 12-vertex $CpCoMe_4C_4B_nH_n$ ($n = 6, 7$) products, but no 13-vertex species[77f,80]). The $Me_4C_4B_8H_8^{2-}$ dianion, readily generated by reduction of the neutral carborane with sodium naphthalenide, reacts with metal salts in THF in the presence of the $C_5H_5^-$ ion to produce 13- and 14-vertex neutral species (as well as smaller cage systems); thus with $FeCl_2$ at least four isomers of 14-vertex $Cp_2Fe_2Me_4C_4B_8H_8$ species are obtained (equation 12).[60] Similar treatment[77f] with $CoCl_2$ (Figure 87) gave only a single (detectable) isomer of 13-vertex $CpCoMe_4C_4B_8H_8$ together with 12-vertex $CpCoMe_4C_4B_7H_7$ (isomer II) and a cobaltocenium-substituted zwitterionic product, σ-$[(\eta\text{-}C_5H_5)Co(\eta\text{-}C_5H_4)]^+$—$Me_4C_4B_8H_8^-$, whose X-ray-determined structure[219] (Figure 87) is assumed to reflect closely that of the $Me_4C_4B_8H_8^{2-}$ ion itself.

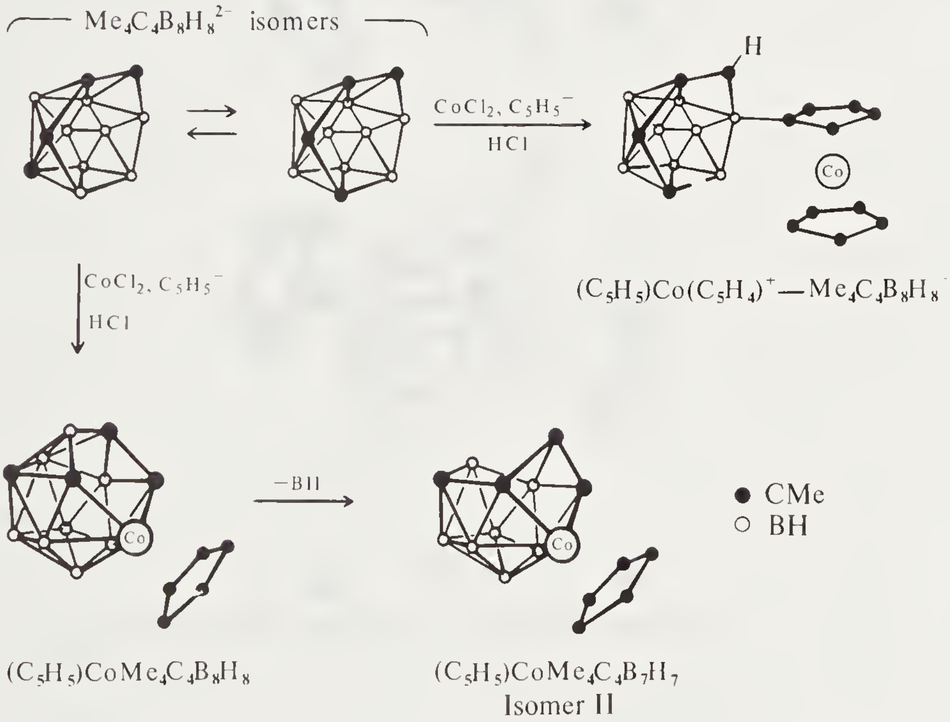


Figure 87 Proposed scheme for the formation of the cobaltocenium-substituted derivative of the $Me_4C_4B_8H_8^{2-}$ dianion. The structure of the $CpCo(C_5H_4)^+$-$Me_4C_4B_8H_8^-$ and $CpCoMe_4C_4B_7H_7$ products are established,[219,43a] as is that of a nickel analogue of the $CpCoMe_4C_4B_8H_8$ intermediate shown;[43a] the geometries shown for the $Me_4C_4B_8H_8^{2-}$ isomers are postulated[43a]

It is probable that the $Me_4C_4B_8H_8^{2-}$ ion, in THF solution at room temperature, exists as an equilibrium mixture of two or more isomers. This appears to be the only satisfactory explanation of the formation of several different $Fe_2C_4B_8$ cage systems in the reaction with $FeCl_2$ and NaC_5H_5 noted above; two of these $Cp_2Fe_2Me_4C_4B_8H_8$ products have been structurally characterized[49] and found to have different cage geometries that are *not directly interconvertible by any straightforward process*. These structures, designated as isomers I and II (Figure 88), are therefore assumed to originate from insertion of iron into different isomeric forms of the $Me_4C_4B_8H_8^{2-}$ ion; a possible mechanistic pathway leading to the observed products has recently been published.[219]

Application of electron-counting rules (Section 5.5.2.4) to $Cp_2Fe_2Me_4C_4B_8H_8$ leads to a prediction of *closo* geometry, since there are 30 skeletal electrons (the relative contributions of FeCp, CMe and BH being 1, 3 and 2) in a 14-vertex skeleton, corresponding to a $(2n + 2)$-electron system. The expected 'ideal' geometry for a 14-vertex *closo* system is a bicapped hexagonal antiprism, but neither isomer has such a structure; indeed, these cages are not even *closo*, I and II having five- and four-sided open faces respectively (Figure 88). At elevated temperatures, both isomers rearrange to a common structure (isomer V), which in turn ultimately converts to the expected *closo* structure, isomer VIII (Figure 26).[4c,49] This isomerization sequence differs markedly from those normally observed for *dicarbon* metallacarboranes (Section 5.5.3.1.7), in which carbon and metal atoms migrate on a polyhedral surface but *the same gross cage geometry is maintained throughout*; in the rearrangements in Figure 26, three structural classes are represented (*i.e.* I and V; II; VII and VIII), characterized by distinctly different connectivities and polyhedral shapes. Isomers I, II and V are kinetically stabilized at ambient temperature, and are locked into highly irregular geometries; only under vigorously energetic conditions (*e.g.* 300 °C) is the thermodynamically preferred geometry, VIII, attainable. The highly symmetric (ideal D_{2d}) cage structure of VIII has been confirmed crystallographically.[229]

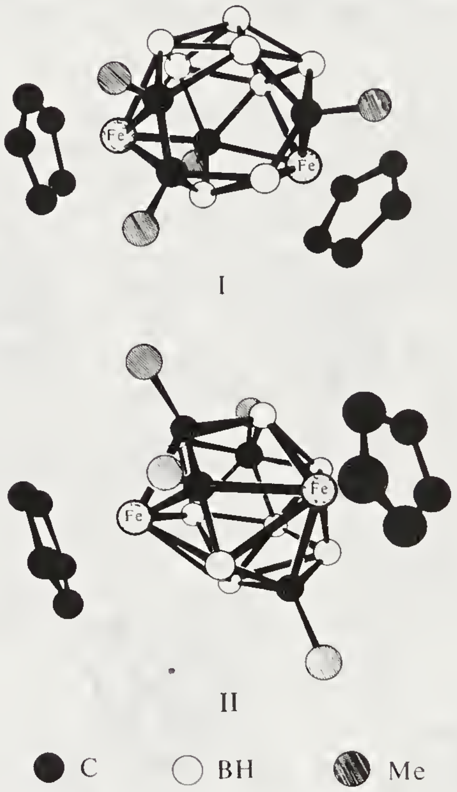


Figure 88 Structures of $Cp_2Fe_2Me_4C_4B_8H_8$ isomers[49]

The tendency of four-carbon metallacarboranes to adopt open, unconventional cage structures (also observed in 11- and 12-vertex systems as described above) can be ascribed largely to the presence of localized bonding interactions in the vicinity of the carbon atoms, and to the natural proclivity of carbon to seek low-coordinate vertices. In other words, as the framework carbon content increases, one may expect to find greater resemblance to hydrocarbon-like (*i.e.* localized) as opposed to borane-like (delocalized) frameworks.

Thirteen-vertex metallacarboranes have also been obtained on treatment of the $Me_4C_4B_8H_8^{2-}$ ion with $(Ph_2PCH_2)_2NiCl_2$ at room temperature.[60] Three air-stable isomers of $(Ph_2PCH_2)_2Ni\text{-}Me_4C_4B_8H_8$ are obtained, one of which has been structurally characterized by X-ray diffraction.[43a] The cage geometry (Figure 89) is, interestingly, a 13-vertex *nido* framework (*i.e.* a 14-vertex *closo* polyhedron from which one vertex has been removed); this is exactly what one would predict

Table 2 Metallacarboranes Characterized by X-ray Diffraction[r]

Compound[a]	*Cage geometry*[b]	*Selected cage bond lengths* (Å)	*Figure*	*Ref.*
6-Vertex systems				
1,2,3-$(CO)_3FeC_2B_3H_7$	PPy	C—C 1.410(4)	17b	125
$(2,3\text{-}Me_2C_2B_3H_5)Co(2,3\text{-}Me_2C_2B_4H_3)\text{-}5\text{-}C_5H_4CoCp$	PPy	C—C 1.418(9)[c]	12	40
7-Vertex systems				
		Iron		
$H_2Fe(2,3\text{-}Me_2C_2B_4H_4)_2$	PB	C—C 1.484(4)	40	118
		Iron–Cobalt		
1,2,4,5-$Cp_2FeCoMe_2C_2B_3H_4$	PB	Fe—Co 2.560(1) C—C 1.443(5)	44	122
		Cobalt		
1,2,3-$CpCoMe_2C_2B_4H_4$	PB	C—C 1.461(2)	43	231
$(2,3\text{-}Me_2C_2B_3H_5)Co(2,3\text{-}Me_2C_2B_4H_3)\text{-}5\text{-}C_5H_4CoCp$	PB	C—C 1.489(9)[d]	12	40
μ-HgCl-1,2,3-$PCpCoMe_2C_2B_3H_4$	BPPy	C—C 1.35(2)	39	114
μ,μ'-Hg-$(CpCOMe_2C_2B_3H_4)_2$	BPPy	C—C 1.43(1)	39	114
1,2,4,5-$Cp_2Co_2C_2B_3H_3$	PB	Co—Co 2.495(1) C—C 1.450(9)	25a	122
1,7,2,3-$Cp_2Co_2C_2B_3H_4$-2-Me	PB	C—C 1.441(7)	43	12a
1,7,2,4-$Cp_2Co_2C_2B_3H_4$-2-Me	PB		25a	121
1,7,2,3-$Cp_2Co_2C_2B_3H_3$-1,3-C_3H_4	PB	C—C 1.485(4)	23b	70
		Gallium		
1,2,3-$MeGaC_2B_4H_6$	PB	C—C 1.47(4)		10b
		Platinum		
1,2,3-$(Et_3P)_2PtMe_2C_2B_4H_4$	DPB	C—C 1.427(10)	45	79a
μ-$Pt(H)(Et_3P)_2$-2,3-$C_2B_4H_7$	BPPy	C—B/C 1.478(12)		79a, 79b
8-Vertex systems				
$CpCoFeMe_4C_4B_8H_8$	CPB	Fe—Co 2.480(1) C—C 1.453(8), 1.447(9)	42a	34
$(PCp)_2Co_3Me_4C_4B_8H_7$	Dod	C—C 1.453(4), 1.442(5)	50	134
$CpCoPh_4C_4B_3H_3$	*arachno*	C—C 1.379(5), 1.419(5)		135
9-Vertex systems				
		Manganese		
1,4,6-$(CO)_3MnC_2B_6H_8^-$	TTP		52	144
		Cobalt		
3,4-$CpCoCB_7H_8^-$	TTP		57	149
1,7,5,6-$Cp_2Co_2C_2B_5H_7$	TTP	Co—Co 2.444(3)	25b	138
1,8,5,6-$Cp_2Co_2C_2B_5H_7$	TTP		25b	138
		Nickel		
1,6,7,8-$Cp_3Ni_3CB_5H_6$	CSA	Ni—Ni 2.4040(5)	55	66
		Platinum		
4,5,6-$(Me_3P)_2PtC_2B_6H_8$	TTP		51a	139b
4,5,6-$(Me_3P)_2PtMe_2C_2B_6H_6$	TTP		51a	139b
$(Et_3P)_2PtMe_2C_2B_6H_6$	*nido*[e]		51b	139a
1,7,4,5-$(Et_3P)_2Pt_2C_2B_5H_7$	TTP	Pt—Pt 3.051(4)		59
10-Vertex systems				
1,6,2,3-$Cp_2Fe_2C_2B_6H_8$	BSA[f]	Fe—Fe 2.571(1)	54	146
8,6,7-$CpCoC_2B_7H_{11}$	*nido*[g]	C—C 1.452(5)	56	147
$Co(1,6\text{-}C_2B_7H_9)_2^-$	BSA		52	143
2,6,1,10-$Cp_2Co_2C_2B_6H_8$	BSA	Co—Co 2.489(1)		238
6,7,1-$Cp_2CoNiCB_7H_8$	BSA	Co—Ni 2.449(1)	25c	150
6,5,9-$(Me_3P)_2NiMe_2C_2B_7H_9$	*nido*[g]		17a	56
9,2,7-$(Et_3P)_2PtMe_2C_2B_7H_7$	*nido*[h]		51c	139c
11-Vertex systems				
1,2-$CpFeCB_9H_{10}^-$	*closo*[i]			159
1,8,2,3-$Cp_2FeCoC_2B_7H_9$	*closo*[i]		66	165b
2,6-$CpCoCB_9H_9$-2-NMe_3	*closo*[i]		10	38

Table 2 (*continued*)

Compound[a]	*Cage geometry*[b]	*Selected cage bond lengths* (Å)	*Figure*	*Ref.*
9,7,8,10,11-$\mathrm{CpCoMe_4C_4B_6H_6}$	CPA	C—C 1.518(4)	63	80
2,7,8,10,11-$\mathrm{CpCoMe_4C_4B_6H_6}$	CPA	C—C 1.564(6), 1.559(6)	63	80
$\mathrm{CpCo(C_2B_8H_{10})Co(C_2B_8H_{10})^-}$	*closo*[i]			160
$\mathrm{(C_2B_9H_{11})Co(C_2B_8H_{10})\text{-}NC_5H_5^-}$	CPA	C—C 1.598(13), 1.504(12)	64	163
10,7,9-$\mathrm{(Me_3P)_2PtC_2B_8H_{10}}$-$\mu$(6,10)-$\mathrm{(Me_3P)_2Pt}$	CPA	Pt—Pt 2.820(2)	51d	59
$\mathrm{(Ph_3P)AgC_2B_8H_{11}}$	CPA[j]			158
10,7,9-$\mathrm{(Me_3P)_2PtC_2B_8H_{10}}$	CPA		51e	59
12-Vertex systems				
		Aluminum		
3,1,2-$\mathrm{EtAlC_2B_9H_{11}}$	I			240
μ-$\mathrm{Me_2Al}$-1,2-$\mathrm{C_2B_9H_{12}}$	MBO			244
		Chromium		
$\mathrm{Cr(1,2\text{-}Me_2C_2B_9H_9)_2^-}$	I	C—C 1.64(1)	73	230
		Iron		
3,1,2-$\mathrm{CpFe^{III}C_2B_9H_{11}}$		C—C 1.58	1	234
$\mathrm{CpFeC_2B_9H_{10}}$-8-$\mathrm{OCOCF_3}$	I			251
$\mathrm{(CO)_4Fe_2^I(1,2\text{-}C_2B_9H_{11})_2^{2-}}$	I	Fe—Fe 2.591(5) C—C 1.61(2), 1.64(2)		236
$\mathrm{CpFeMe_4C_4B_7H_8}$	*nido*	C—C 1.454(3), 1.616(3)	14 (type 5)	60
$\mathrm{CpFeCB_{10}H_{10}}$-*C*-$\mathrm{OEt_2}$	I		24	72
$\mathrm{Fe(1,7\text{-}MePCB_9H_{10})_2}$	I		82	214
		Cobalt		
3,1,2-$\mathrm{CpCoC_2B_9H_{10}}$-8-OAc	I			194
3,1,2-$\mathrm{CpCoC_2B_9H_{10}}$-8-Ac	I			194
$\mathrm{Co(1,2\text{-}C_2B_9H_{11})_2^-}$	I	C—C 1.624(5)		237, 254
$\mathrm{Co(1,2\text{-}C_2B_9H_8Br_3)_2^-}$	I	C—C 1.66(2)		239
$\mathrm{Co(1,2\text{-}C_2B_9H_{10})_2}$-$\mu$(8,8′)$\mathrm{OCH_3}$	I			250
$\mathrm{Co(1,2\text{-}C_2B_9H_{10})_2}$-$\mu$(8,8′)$\mathrm{S_2CH}$	I	C—C 1.625(16)	78	192c
$\mathrm{(C_2B_9H_{11})Co(C_2B_8H_{10})\text{-}NC_5H_5^-}$	I	C—C 1.598(13), 1.504(12)	64	163
$\mathrm{CpCoMe_4C_4B_7H_7}$, isomer I	[k]	C—C 1.39, 1.37	28	232
$\mathrm{CpCoMe_4C_4B_7H_6\text{-}OC_2H_5}$, isomer I	[k]	C—C 1.448(5), 1.374(6)	28	42
$\mathrm{CpCoMe_4C_4B_7H_7}$, isomer II	[k]	C—C 1.480(4), 1.567(4), 1.424(4)	6	43a
$\mathrm{CpCoMe_4C_4B_7H_7}$, isomer III	*nido*	C—C 1.431(6)	28	43c
3,1,2-$\mathrm{CpCoAsCB_9H_{10}}$	I	1.609(7)		213c
2,3,1,7-$\mathrm{Cp_2Co_2C_2B_8H_{10}}$	I	Co—Co 2.387(2)	75	181
$\mathrm{CpCo(C_2B_8H_{10})Co(C_2B_8H_{10})^-}$	I			160
3,6,1,2-$\mathrm{(1',2'\text{-}C_2B_9H_{11})_2Co_2C_2B_8H_{10}^{2-}}$	I	C—C 1.613(8), 1.561(7)		245
$\mathrm{[(1,2\text{-}C_2B_9H_{11})Co(1,2\text{-}C_2B_8H_{10})]_2Co^{3-}}$	I	C—C 1.60	74	246
1,2,3-$\mathrm{Cp_2Co_2CB_9H_{10}^-}$	I	Co—Co 2.430(2)		212
$\mathrm{Cp_2Co_2Me_4C_4B_6H_6}$, isomer V	[k]	C—C 1.425(4)	13	41
$\mathrm{Cp_2Co_2C_4B_6H_{10}}$, isomer VII	*nido*	C—C 1.423(8)	13	88
$\mathrm{CpCo(Et_3P)_2PtC_2B_8H_{10}}$	I			13b
		Nickel		
$\mathrm{Ni^{II}(1,7\text{-}C_2B_9H_{11})_2^{2-}}$	SI		76	243
$\mathrm{Ni^{III}(1,2\text{-}C_2B_9H_{11})_2^-}$	I	C—C 1.589(10)	79	242
$\mathrm{Ni^{IV}(1,2\text{-}C_2B_9H_{11})_2}$	I	C—C 1.601(2), 1.610(2)	80	204
1,2,1′,7′-$\mathrm{Ni^{IV}(Me_2C_2B_9H_9)_2}$	I	C(1)—C(2) 1.636(13), C(1′)—C(7′) 1.717(15)	79	247
		Copper		
$\mathrm{Cu^{II}(1,2\text{-}C_2B_9H_{11})_2^{2-}}$	SI		76	184a
$\mathrm{Cu^{III}(1,2\text{-}C_2B_9H_{11})_2^-}$	SI	C—C 1.45(3), 1.52(3)	76	184a

Table 2 (*continued*)

Compound[a]	*Cage geometry*[b]	*Selected cage bond lengths* (Å)	*Figure*	*Ref.*
		Molybdenum		
$(CO)_3(\overline{CO)Mo(CO}B_{10}H_{10})^{2-}$	I			73
		Ruthenium		
$2,1,7\text{-}(Ph_3P)_2H_2RuC_2B_9H_{11}$	I			178
		Rhodium		
$3,1,2\text{-}(Ph_3P)_2HRhC_2B_9H_{11}$	I	Rh—H 1.54(9)		207
$3,1,2\text{-}(Ph_3P)_2(HSO_4)RhC_2B_9H_{11}$	I	C—C 1.682(17)		208a
$3,1,2\text{-}(Ph_3P)_2(NO_3)RhC_2B_9H_{11}$	I	C—C 1.88(7)		208b
$3,1,2\text{-}(Ph_3P)(CO)RhC_2B_9H_{10}\text{-}4\text{-}NC_5H_5$	I	C—C 1.630(7)		241
$[3,1,2\text{-}(Ph_3P)RhC_2B_9H_{11}]_2$	I[m]	Rh—Rh 2.763(1) Rh—H 1.77(6), 1.78(6)	81	15
		Palladium		
$3,1,2\text{-}(Ph_4C_4)PdMe_2C_2B_9H_9$	I			175a
$3,1,2\text{-}\{C_2H_4(NMe_2)_2\}PdC_2B_9H_{11}$	SI			47e
$3,1,2\text{-}(Me_3P)_2PdC_2B_9H_{11}$	I			47e
$2,1\text{-}(Bu^tNC)_2PdCB_{10}H_{10}\text{-}1\text{-}NMe_3$	I[f]			47d
		Rhenium		
$3,1,2\text{-}(CO)_3ReC_2B_9H_{11}^-$	I	C—C 1.61(2)		233
		Platinum		
$3,1,2\text{-}(Et_3P)_2PtC_2B_9H_{11}$	SI	C—C 1.529(10)		53a
$2,1,7\text{-}(PhMe_2P)_2PtMe_2C_2B_9H_9$	SI			235
$CpCo(Et_3P)_2PtC_2B_8H_{10}$	I			13b
		Gold		
$3,1,2\text{-}(S_2CNEt_2)AuC_2B_9H_{11}$	SI	C—C 1.46(2)		185
$Au^{III}(1,2\text{-}C_2B_9H_{11})_2^-$	SI	C—C 1.50(1)		184d
		Mercury		
$\sigma\text{-}(Ph_3P)Hg\text{-}1,2\text{-}C_2B_9H_{11}$	[n]	C—C 1.54(1)	77	51
		Thallium		
$Tl^+(1,2\text{-}C_2B_9H_{11})^{2-}$	[p]			48
		Uranium		
$Cl_2U(1,2\text{-}C_2B_9H_{11})_2^{2-}$	I			180
13-Vertex systems				
		Titanium		
$Ti(Me_2C_2B_{10}H_{10})_2^{2-}$	*closo*[q]		85	224b
		Cobalt		
$4,1,7\text{-}CpCoC_2B_{10}H_{12}$	*closo*[q]		86	224a
		Nickel		
$(Ph_2PCH_2)_2NiMe_4C_4B_8H_8$	*nido*	C(3)—C(9) 1.672(4), C(7)—C(13) 1.517(5)	89	43a
14-Vertex systems				
$Cp_2Fe_2Me_4C_4B_8H_8$				
isomer I	*nido*[k]	C—C 1.459(2)	88	49
isomer II	*nido*[k]	C—C 1.447(4)	88	49
isomer V	*nido*[k]		26	49
isomer VIII	*closo* (BCHA)		26	229

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[a] Within each category, compounds are listed in order of increasing atomic number of the cage metal atom; abbreviations: Cp = $\eta^5\text{-}C_5H_5$; PCp = $\eta^5\text{-}C_5Me_5$. [b] PPy = pentagonal pyramid; BPPy = metal-bridged pentagonal pyramid; PB = pentagonal bipyramid; DPB = distorted pentagonal bipyramid; CPB = capped pentagonal bipyramid; Dod = dodecahedron; TTP = tricapped trigonal prism; CSA = capped square antiprism; BSA = bicapped square antiprism; CPA = capped pentagonal antiprism; MBO = metal bridged open cage; I = icosahedron; SI = slip-distorted icosahedron (see text); BCHA = bicapped hexagonal antiprism. [c] C—C distance in open (*nido*) cage. [d] C—C distance in *closo* 7-vertex cage. [e] Opened tricapped trigonal prism. [f] Distorted. [g] $B_{10}H_{14}$-like open basket. [h] Opened bicapped square antiprism. [i] See Figure 3h. [j] Crystallizes as dimer with intermolecular B—H—Ag bridges. [k] Irregular open-cage structure. [m] Cages linked by Rh—Rh and two Rh—H—B bonds. [n] σ-Hg complex of *nido*-$C_2B_9H_{11}^{2-}$. [p] Ion pair. [q] See Figure 3j. [r] See refs. 252–257 for recent work, details of which could not be included.

Table 3 Metallaboranes Characterized by X-ray Diffraction[g]

Compound[a]	*Cage geometry*[b]	*Selected cage bond lengths* (Å)	*Figure*	*Ref.*
4-Vertex systems				
$(Me_2PhP)_2PtB_3H_7$	D		36	107d
5-Vertex systems				
$1,2(CO)_6Fe_2B_3H_7$	SP	Fe—Fe 2.559(2)	11	39
$2\text{-}CpCoB_4H_8$	SP		38	112a
$1\text{-}CpCoB_4H_8$	SP		38	112b
6-Vertex systems				
$CpBeB_5H_8$	MBO			133c
$Be(B_5H_{10})_2$	PPy		49a	133b
$(B_5H_{10})Be(BH_4)$	PPy		49b	133b
$1,2\text{-}Cp_2Co_2B_4H_6$	O	Co—Co 2.557(1)	46	126
$1,2,3\text{-}Cp_3Co_3B_3H_5$	O	Co—Co 2.488(1), 2.472(1)	46	36
$\mu\text{-}(Ph_3P)_2Cu\text{-}B_5H_8$	MBO		48c	103b
7-Vertex systems				
$\mu\text{-}(THF)_2Mg\text{-}(B_6H_9)_2$	MBO			131
$1,2,3\text{-}Cp_3Co_3B_4H_4$	CO	Co—Co 2.444(1) 2.435(1)	7	36
$1,2,3\text{-}(PCp)_3Co_3B_4H_4$	CO	Co—Co 2.493(9) 2.501(9) 2.498(9)	7	127
$1,2,3\text{-}Cp_3Co_3B_3H_3\text{-}\mu_3\text{-}CO$	CO			259
$\mu\text{-}(Ph_3P)_2Cu\text{-}2\text{-}(CO)_3FeB_5H_8$	MBO		48a	128
$Cl_2Pt(B_6H_{10})_2$	MBO			130b
8-Vertex systems				
$\mu\text{-}(CO)_4Fe\text{-}B_7H_{12}^-$	MBO		48b	155
$Cp_4Co_4B_4H_4$	Dod	Co—Co 2.478(1)[d]	59	153
$Cp_4Ni_4B_4H_4$	Dod	Ni—Ni 2.354(1)	59	21
9-Vertex systems				
$1,6,7,8\text{-}Cp_4Ni_4B_5H_5$	CSA	Ni—Ni 2.387(6)	[c]	232
10-Vertex systems				
$6\text{-}(CO)_3MnB_9H_{12}\text{-}5\text{-}O(CH_2)_4$	[e]			157a
$6\text{-}(CO)_3MnB_9H_{12}\text{-}2\text{-}O(CH_2)_4$	[e]			249
$6\text{-}(CO)_3MnB_9H_{12}\text{-}10\text{-}O(CH_2)_4NEt_3$	[e]		60	157b
$5\text{-}CpCoB_9H_{13}$	[e]		9	37
$6\text{-}(PCp)CoB_9H_{13}$	[e]			105b
$6,9\text{-}(PCp)_2Co_2B_8H_{12}$	[e]		61b	105b
$5,7\text{-}(PCp)_2Co_2B_8H_{12}$	[e]		61a	105b
$9,6\text{-}(Ph_3P)_2PtNB_8H_{11}$	[e]			97
$9.6\text{-}(Ph_3P)_2PtSB_8H_{10}$	[e]			96
$8\text{-}OEt\text{-}9,6\text{-}(Ph_3P)_2PtSB_8H_9$	[e]			96
11-Vertex systems				
$Ni(B_{10}H_{12})_2^{2-}$	CPA		34	170
$Zn(B_{10}H_{12})_2^{2-}$	CPA		31	169
$(Et_3P)_2HPtSB_9H_{10}$	CPA	Pt—S 2.43		100
12-Vertex systems				
$Fe(SB_{10}H_{10})_2^{2-}$	I		84	248
$CpCoSe_2B_9H_9$	[f]	Co—Se 2.435(1) 2.378(1)	14 (type 7)	43b

[a] Within each category, compounds are listed in order of increasing atomic number of the cage metal atom; abbreviations: Cp = η^5-C_5H_5; PCp = η^5-C_5Me_5. [b] D = dihedral; PPy = pentagonal pyramid; MBO = metal-bridged open cage; O = octahedron; SP = square pyramid; BSPy = metal-bridged square pyramid; CO = capped octahedron; DPB = distorted pentagonal bipyramid; Dod = dodecahedron; CSA = capped square antiprism; CPA = capped pentagonal antiprism. [c] Structure is analogous to $Cp_3Ni_3CB_5H_6$ (Figure 55). [d] Mean of six independent values. [e] $B_{10}H_{14}$-like basket. [f] Irregular open-cage structure (see Figure 14). [g] See refs. 257, 258 and 260 for recent work, details of which could not be included.

for a $(2n + 4)$-electron cage system of 13 vertices. An analogous structure has been proposed for the isoelectronic complex $CpCoMe_4C_4B_8H_8$ (Figure 87),^{77f} and it is significant that loss of a BH unit from that species, with accompanying small atomic movements in the framework, generates the observed $CpCoMe_4C_4B_7H_7$ product, as shown in the same Figure. The proposed mechanism is based on characterized product structures but has not been confirmed by direct evidence.

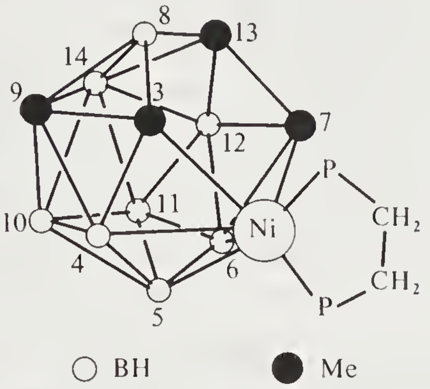

Figure 89 Structure of $(Ph_2PCH_2)_2NiMe_4C_4B_8H_8$

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5.6

Heterocarboranes

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5.6.1 INTRODUCTION

This chapter surveys the chemistry and structure of heterocarboranes, where the term hetero is defined as the main group elements (*e.g.* Be, Mg, Al, Ge, P, S, *etc.*).

The reported syntheses of $B_{10}H_{10}^{2-}$ in 1959[1] and of $B_{12}H_{12}^{2-}$ a year later[2] were major turning points in the study of the larger boron hydride molecules. These closed-cage dianions possessed remarkable chemical stability compared with the lower boron hydrides (*e.g.* B_2H_6 and B_5H_9). This allowed extensive reactivity studies of these anions employing standard chemical methods used for compounds which are not air sensitive.

The first published account of polyhedral heteroboranes concerned the syntheses of the carboranes $C_2H_2B_3H_3$ and $C_2H_2B_5H_5$.[3] In this report it was demonstrated that replacement of two B^- units (from the parent $B_5H_5^{2-}$ and $B_7H_7^{2-}$ ions) with two isoelectronic C atoms was possible. In 1963 the synthesis of the icosahedral carborane $C_2H_2B_{10}H_{10}$, isoelectronic with $B_{12}H_{12}^{2-}$, was reported by two industrial groups.[4,5] The chemistry of the carboranes (see Chapter 5.4 of this work) and the related metallacarboranes (see Chapter 5.5) has been studied extensively.

The first heterocarborane reported was 1,2-$PCHB_{10}H_{10}$,[6] which is an icosahedral molecule isoelectronic with $C_2H_2B_{10}H_{10}$. Since then several hundred derivatives which incorporate almost all the main group elements have been prepared. The discussion of the chemistry and structures of these compounds is subdivided by the periodic groups for convenience.

5.6.2 DERIVATIVES CONTAINING GROUP IIA ELEMENTS

Diethyl- or dimethyl-beryllium diethyl etherate reacted with 7,8-$C_2H_2B_9H_{11}$ (the two carbon atoms are adjacent to one another on the open face of this cage structure) in benzene/ether at room temperature to form 1 equivalent of alkane. A second equivalent of alkane was evolved during removal of the solvent at 50 °C, forming crystalline $Et_2O{\cdot}BeC_2H_2B_9H_9$.[7,8] This compound was very sensitive to moist air and hydrolyzed with the formation of 7,8-$C_2H_2B_9H_{10}^-$. Treatment of the ether complex with trimethylamine formed $Me_3N{\cdot}BeC_2H_2B_9H_9$, which was much more stable to moist air than the ether complex. Potassium hydroxide in ethanol degraded the trimethylamine complex to form 7,8-$C_2H_2B_9H_{10}^-$. These beryllium derivatives are thought to have a *closo* icosahedral structure like $C_2H_2B_{10}H_{10}$. The ether or trimethylamine is believed to be coordinated to the beryllium atom.

5.6.3 DERIVATIVES CONTAINING GROUP IIIA ELEMENTS

In the gas phase at 180–215 °C, trimethylgallium reacted with 2,3-$C_2H_2B_4H_6$ to form the *closo* molecule $MeGaC_2H_2B_4H_4$ in 20% yield.[9] A similar reaction involving trimethylindium at a temperature of 95–110 °C formed $MeInC_2H_2B_4H_4$ in 50% yield.[10] A single-crystal X-ray study of the gallacarborane[10] established the molecular geometry illustrated in Figure 1. The gross structure is that of a pentagonal bipyramid with the MeGa group occupying an apex position. The adjacent carbon atoms are in the five-membered equatorial ring. It should be noted that the gallium atom is closer to the boron atoms than to the carbon atoms in the equatorial ring and that the Ga—Me axis is tilted 23° with respect to the perpendicular to the equatorial plane. It has been suggested that the distortions are due to the interaction of the gallium *d*-orbitals with the cage framework orbitals.[10] At greater than 100 °C, both the gallium and indium compounds decompose with the formation of 2,3-$C_2H_2B_4H_6$ and each cage is destroyed by elemental bromine under Friedel–Crafts conditions. The gallium derivative was attacked at room temperature by excess HCl to form 2,3-$C_2H_2B_4H_6$. A bridge-substituted gallium carborane and a probable aluminum-bridged derivative have been prepared by insertion of the dialkyl metal group into the $C_2H_2B_4H_5^-$ ion according to equation (1).[11]

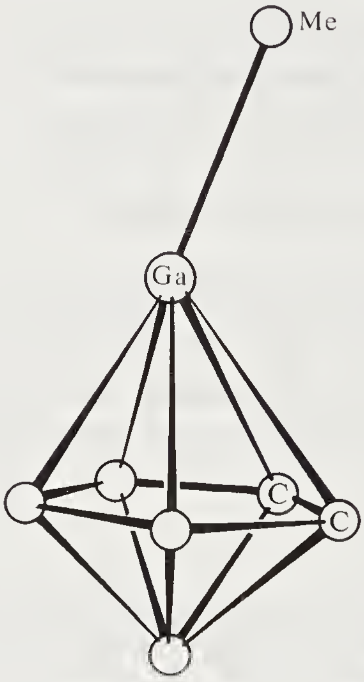

Figure 1 Structure of $MeGaC_2H_2B_4H_4$

$$2,3\text{-}C_2H_2B_4H_5^- + Me_2MCl \longrightarrow Me_2MC_2H_2B_4H_5 + Cl^- \qquad (1)$$

(M = Al or Ga)

Mixing 7,8-$C_2H_2B_9H_{11}$ with triethylaluminum in benzene at room temperature generated ethane and formed $Et_2AlC_2H_2B_9H_{10}$ in good yield.[12] Reflux of the benzene solution caused slow (25 h) evolution of more ethane and the formation of the icosahedral derivative $EtAlC_2H_2B_9H_9$.[12] A single-crystal X-ray study[13] demonstrated that the Et_2Al group was in a bridging position on the open face of the C_2B_9 icosahedral fragment (see Figure 2). An X-ray study of the *closo* molecule has also been reported.[14] Variable temperature ^{11}B NMR spectra of the bridged derivative showed that the molecule is undergoing rapid exchange at room temperature, presumably involving the Et_2Al group and the bridging hydrogen. The gallium derivative, $EtGaC_2H_2B_9H_9$, was produced by the same reaction sequence used for the aluminum compound.[12] The *closo* aluminum and gallium carboranes, formed above, isomerize when they are sublimed through a glass wool filled hot tube at 400 °C. In addition, a portion of the gallium compound decomposes with elimination of the EtGa unit and formation of *closo*-$C_2H_2B_9H_9$. Controlled hydrolysis of the isomerized aluminacarborane formed $7,9\text{-}C_2H_2B_9H_{10}^-$. This result suggests that the carbon atoms have moved from adjacent to non-adjacent positions in the *closo* structure during isomerization. When $3\text{-}(EtAl)\text{-}1,2\text{-}C_2H_2B_9H_9$ was dissolved in THF the crystalline complex $EtAlC_2H_2B_9H_9{\cdot}(THF)_2$ was obtained. This compound was also formed by the reaction given in equation (2).[15] It is well known that trialkylaluminum compounds expand their coordination sphere to form 1:1 and 2:1 complexes with Lewis bases.[16]

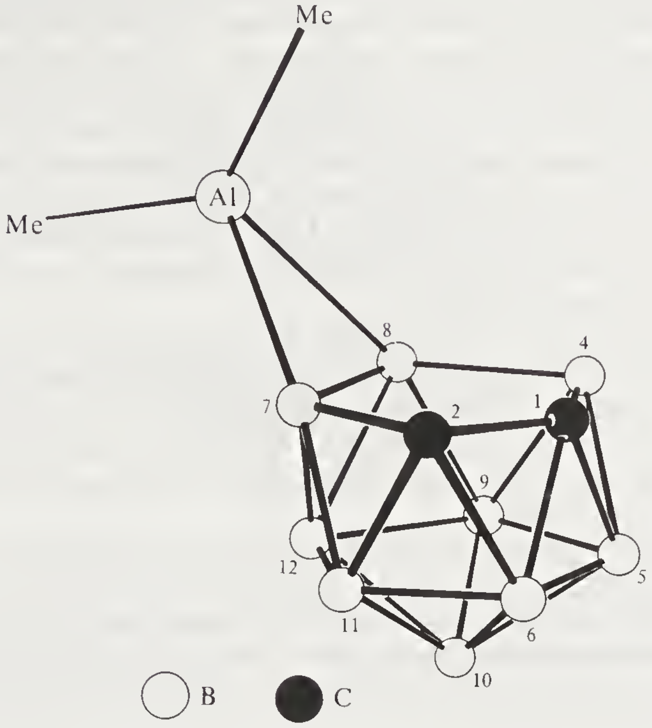

Figure 2 Structure of $Me_2AlC_2H_2B_9H_{10}$

$$Na_2(7,8\text{-}C_2H_2B_9H_9) \quad + \quad EtAlCl_2 \xrightarrow{THF} EtAlC_2H_2B_9H_9{\cdot}(THF)_2 \quad + \quad 2NaCl \qquad (2)$$

When the $7,8\text{-}C_2H_2B_9H_{10}^-$ ion reacted with excess thallium(I) acetate in aqueous alkaline solution, $Tl_2[C_2H_2B_9H_9]$ precipitated from solution.[17] This salt appears to be stable to moisture and air and is useful for the synthesis of some metallacarborane compounds. It resembles TlCp somewhat in its properties which is very useful for the synthesis of cyclopentadienyl metal compounds. One of the two thallium ions is readily replaced by other large cations to form salts such as $[Ph_3PMe][Tl][C_2H_2B_9H_9]$. An X-ray structure of this material has been determined.[18] The thallium atom is symmetrically located over the open face of the $7,8\text{-}C_2H_2B_9H_9^{2-}$ ion. However, the thallium-to-cage atom distances considerably exceed the sum of the covalent radii so that the $TlC_2H_2B_9H_9$ unit is probably an ion pair. The yellow color of the salt suggests some charge transfer in the ion pair, however. Treatment of $Tl_2[7,8\text{-}MeCCHB_9H_9]$ with acetic acid or heating the salt at 300 °C formed thallium metal and $Tl[7,8\text{-}MeCCHB_9H_{10}]$.[19] It is possible that the thallium atom in this compound occupies a bridging position, as was found in the structure of the isoelectronic molecule $Et_2AlC_2H_2B_9H_{10}$ (see Figure 2).[13] Further heating of the monothallium compound formed the *closo* carborane $MeCCHB_9H_9$.

5.6.4 DERIVATIVES CONTAINING GROUP IVA ELEMENTS

Germanium diiodide, tin(II) chloride or lead acetate were reacted with $7,8\text{-}C_2H_2B_9H_9^{2-}$ ion to form the compounds $1,2,3\text{-}GeC_2H_2B_9H_9$, $1,2,3\text{-}SnC_2H_2B_9H_9$ or $1,2,3\text{-}PbC_2H_2B_9H_9$ respectively.[20,21] In a similar manner the $7,9\text{-}C_2H_2B_9H_9^{2-}$ ion (the carbon atoms are on the open face of the cage but are not adjacent) reacted with germanium diiodide to form 1,2,7-$C_2H_2GeB_9H_9$. Treatment of these compounds with ethanolic KOH easily removes the metal atom and forms the corresponding $C_2H_2B_9H_{10}^-$ ion. The stannacarborane 1,2,7-$C_2H_2SnB_9H_9$, obtained by reaction of 7,9-$C_2H_2B_9H_9^{2-}$ with tin(II) chloride, is thermally unstable and decomposes to form *closo*-$C_2H_2B_9H_9$ (in good yield) and tin metal.[22] These compounds are assumed to be *closo* icosahedral molecules containing unsubstituted Ge(II), Sn(II) or Pb(II) units within the cage framework. No X-ray study of the unsubstituted compounds has been reported, probably due to the known propensity of these nearly spherical molecules to be disordered in the solid state. The ^{119}Sn Mössbauer resonance of 1,2,3-$SnC_2H_2B_9H_9$ at 77 K was found well above that of β-tin.[23] The isomer shift of β-tin is considered as the dividing line between Sn(II) and Sn(IV) compounds with tin(II) derivatives being above this value.

Insertion of Ge(II) into 7,8- or 7,9-$ECHB_9H_9^{2-}$ (E = P or As) by reactions similar to those given above formed 1,2,3- and 1,2,7-$GeECHB_9H_9$ in which three different non-boron atoms are part of the polyhedral framework.[24] Thermal rearrangement of 1,2,7-$GePCHB_9H_9$ formed a new isomer which was isolated in pure form by GLC. The relative positions of the germanium, phosphorus and carbon atoms are not known, although the distribution of the heteroatoms is such that the overall molecule is less polar.

Addition of GeI_2, $SnCl_2$ or $PbBr_2$ to a THF solution of $Na[C_2H_2B_4H_5]$ formed $GeC_2H_2B_4H_4$, $SnC_2H_2B_4H_4$ or $PbC_2H_2B_4H_4$ in low yield.[25] The germanium derivative was thermally unstable and was not isolated; the product was detected in the mass spectrum. The tin and lead derivatives were isolated and fully characterized. The proposed *closo* polyhedral structure for these compounds is given in Figure 3. Reaction of $Sn(MeC)_2B_4H_4$ with (η-C_5H_5)$Co(CO)_2$ in a hot–cold reactor maintained at 150 °C and 70 °C formed a low yield of (η-C_5H_5)$CoSn(MeC)_2B_4H_4$.[25] This compound decomposes in solution with the formation of tin and 1-(η-C_5H_5)Co-2,3-$(MeC)_2B_4H_4$.

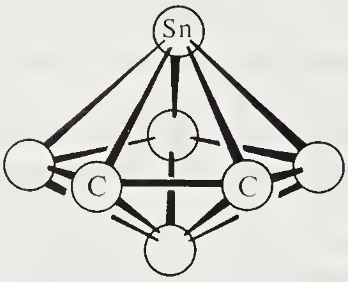

Figure 3 Proposed structure of $SnC_2H_2B_4H_4$

The carborane 2,4-$C_2H_2B_5H_5$ can be reduced with sodium naphthalide in THF to form $Na_2[C_2H_2B_5H_5]$. Reaction of this sodium salt with $SnCl_2$ formed mainly tin metal and 2,4-$C_2H_2B_5H_5$; however, traces of $SnC_2H_2B_5H_5$ were observed in the mass spectrum.[25]

The *closo* anion 1,2-$B_{10}H_{10}CHGe^-$ was formed by reaction of $Na_3B_{10}H_{10}CH(THF)_2$ with $GeCl_4$ at 0 °C.[26] Reaction of this anion with methyl iodide formed sublimable 1,2-$B_{10}H_{10}CHGeMe$ in moderate yield. The neutral compound can be stored as a solid in air for several months with negligible decomposition. When 1,2-$B_{10}H_{10}CHGeMe$ was treated with piperidine as solvent at reflux, demethylation to form 1,2-$B_{10}H_{10}CHGe^-$ occurred. In addition, some of the material underwent germanium atom abstraction to form the $B_{10}H_{12}CH^-$ ion.[27] Attempted thermal isomerization of 1,2-$B_{10}H_{10}CHGeMe$ at 450 °C and Na[1,2-$B_{10}H_{10}CHGe$] at 475 °C leads only to extensive decomposition. The germacarborane anion was observed to function as a two-electron ligand, as illustrated in equations (3) and (4).[26,28] It has been proposed that the germacarborane is bonded to the metals in the complexes by way of the germanium atom.

$$Me_4N[1,2\text{-}B_{10}H_{10}CHGe] \quad + \quad Cr(CO)_6 \quad \xrightarrow{\text{THF (photolysis)}} \quad Me_4N[1,2\text{-}B_{10}H_{10}CHGeCr(CO)_5] \qquad (3)$$

$$Na[1,2\text{-}B_{10}H_{10}CHGe] \quad + \quad [(\eta\text{-}C_5H_5)Fe(CO)_2(\text{cyclohexene})]PF_6 \quad \longrightarrow \quad (\eta\text{-}C_5H_5)Fe(CO)_2GeCHB_{10}H_{10} \qquad (4)$$

The anion $(Me_2C_2B_4H_4)_2FeH^-$ reacted with MCl_2 (M = Ge or Sn) to form the unusual multielement compound $MFeMe_4C_4B_8H_8$.[29] The simplicity of the ^1H and ^{11}B NMR spectra of the tin derivative suggests that it may be fluxional in solution. The proposed structure for the germanium derivative is given in Figure 4.

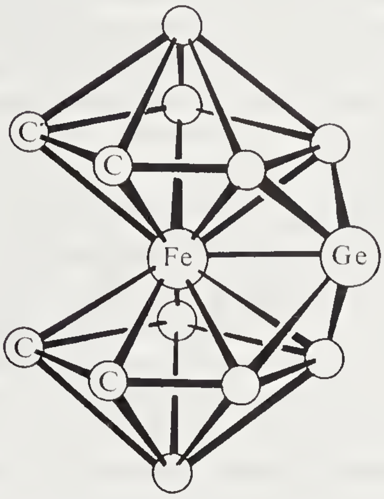

Figure 4 Proposed strucure of $GeFeC_4Me_4B_8H_8$

When $Na[2,3\text{-}C_2H_2B_4H_5]$ was reacted with Me_3SiCl, a bridge-substituted product, shown in Figure 5, was formed.[30] This is a general reaction and many derivatives containing silicon, germanium, tin and lead groups are known (see Table 1 for typical examples). The compound $(\mu\text{-}GeMe_3)\text{-}2,3\text{-}C_2H_2B_4H_5$ isomerized at slightly above room temperature to give a terminally bound trimethylgermyl compound. The germyl group is probably attached to a boron atom on the open face of the structure adjacent to a carbon atom (see Figure 5). The compounds $(\mu\text{-}SnMe_3)\text{-}2,3\text{-}C_2H_2B_4H_5$ and $(\mu\text{-}PbMe_3)\text{-}2,3\text{-}C_2H_2B_4H_5$ do not thermally isomerize at 220 °C and 120 °C respectively (at these temperatures they decompose).[31]

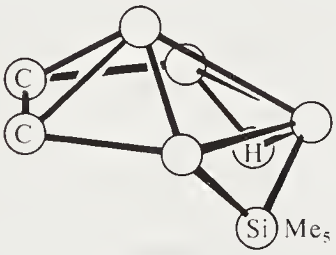

Figure 5 Structure of $\mu\text{-}(Me_3Si)\text{-}2,3\text{-}C_2H_2B_4H_5$

Table 1 Typical $(\mu\text{-}MR_n)C_2H_2B_4H_5$ Derivatives

Compound	*Ref.*
$(\mu\text{-}SiH_3)\text{-}2,3\text{-}C_2H_2B_4H_5$	1
$(\mu\text{-}GeHe_3)\text{-}2,3\text{-}C_2H_3B_4H_5$	1
$(\mu\text{-}GeMe_3)\text{-}2,3\text{-}C_2H_2B_4H_5$	1
$(\mu\text{-}SnMe_3)\text{-}2,3\text{-}C_2H_2B_4H_5$	2
$(\mu\text{-}PbMe_3)\text{-}2,3\text{-}C_2H_2B_4H_5$	2
$(\mu\text{-}SiH_2)(2,3\text{-}C_2H_2B_4H_5)_2$	2

1. M. L. Thompson and R. N. Grimes, *Inorg. Chem.*, 1972, **11**, 1925.
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5.6.5 DERIVATIVES CONTAINING GROUP VA ELEMENTS

5.6.5.1 Monocarbon Derivatives

The first icosahedral molecules prepared in this group were $1,2\text{-}PCHB_{10}H_{10}$[35] and the corresponding arsa and stiba derivatives. Reaction of $Na_3B_{10}H_{10}CH{\cdot}(THF)_n$ with PCl_3, $AsCl_3$ or SbI_3 formed $1,2\text{-}PCHB_{10}H_{10}$ (45% yield), $1,2\text{-}AsCHB_{10}H_{10}$ (25% yield) and $1,2\text{-}SbCHB_{10}H_{10}$ (41%

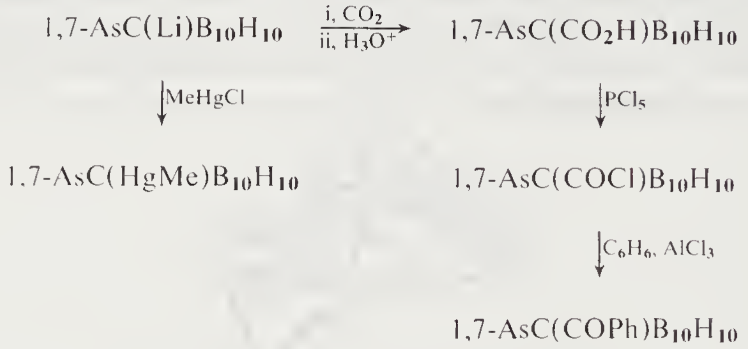
yield) respectively.[36–38] As with isoelectronic 1,2-$C_2H_2B_{10}H_{10}$, the phospha-, arsa- and stibacarboranes undergo thermal rearrangement to the 1,7- and 1,12-isomers. All the isomers of the phospha- and arsa-carboranes can be readily prepared. Heating 1,2-$SbCHB_{10}H_{10}$ at 450 °C for 13 h in a sealed tube gave decomposition products and a 20% yield of 1,7-$SbCHB_{10}H_{10}$.[38] The 1,12-isomer of stibacarborane was detected by gas chromatography but was not isolated.

The reactivity of all three isomers of both phospha- and arsa-carboranes in aluminum chloride catalyzed halogenation reactions has been extensively investigated.[39] Comparison of relative ease of monochlorination gave the following results:

$$1,2\text{-}AsCHB_{10}H_{10} > 1,2\text{-}C_2H_2B_{10}H_{10} > 1,2\text{-}PCHB_{10}H_{10}$$
$$1,7\text{-}AsCHB_{10}H_{10} > 1,7\text{-}C_2H_2B_{10}H_{10} \approx 1,7\text{-}PCHB_{10}H_{10}$$
$$1,12\text{-}AsCHB_{10}H_{10} > 1,12\text{-}PCHB_{10}H_{10} > 1,12\text{-}C_2H_2B_{10}H_{10}$$

In all cases the ease of electrophilic substitution decreased in the order 1,2- > 1,7- > 1,12-isomer. In one case, the electrophilic dichlorination product of 1,7-$PCHB_{10}H_{10}$, the X-ray crystal structure was determined.[47] The compound was found to have a distorted icosahedral structure.

Treatment of 1,2-$PCHB_{10}H_{10}$ with excess Bu^nLi in ether–benzene at −30 °C rapidly formed $Li_3[CHB_{10}H_{10}]$ and Bu^n_3P.[40] However, when a similar reaction was run with the 1,7- and 1,12-phosphacarborane (or the corresponding arsacarborane isomers), metalation of the C—H bond occurred to give 1,7-$PC(Li)B_{10}H_{10}$ and 1,12-$PC(Li)B_{10}H_{10}$ respectively. The lithio derivatives have been used as a starting point to prepare several *C*-substituted compounds, as illustrated in Scheme 1.[41,42] Reaction of the 1,2- or 1,7-isomers of phospha- or arsa-carborane with neat piperidine at reflux resulted in boron abstraction to give 7,8- and 7,9-$ECHB_9H_{10}^-$ (E = P or As) respectively in good yield.[38] Treatment of 1,2-$SbCHB_{10}H_{10}$ with dilute piperidine in benzene solution at reflux formed 7,8-$SbCHB_9H_{10}^-$; however, the use of neat piperidine in this reaction produced mainly $CHB_{10}H_{12}^-$. Other nucleophilic reagents such as sodium ethoxide or alcoholic KOH caused abstraction of the heteroatom or a boron atom, resulting in a mixture of products as illustrated by equation (5).[40]



Scheme 1

$$1,7\text{-}PCHB_{10}H_{10} \quad + \quad NaOEt \quad \xrightarrow[\text{reflux}]{\text{ethanol}} \quad 2\text{-}CHB_{10}H_{12}^- \quad + \quad 7,9\text{-}PCHB_9H_{10}^- \qquad (5)$$

The 1,12-isomer of either the phospha- or arsa-carboranes was reduced with sodium (employing naphthalene as an electron carrier) to an $ECHB_{10}H_{10}^{2-}$ ion (E = P or As). Oxidation of the dianion with $CuCl_2$ formed only 1,7-$ECHB_{10}H_{10}$.[43] A rearrangement of the icosahedron had taken place during this two-step sequence. Reduction of 1,12- $AsCHB_{10}H_{10}$ with sodium in liquid ammonia and subsequent acid hydrolysis formed a new carborane, 1-$CHB_{10}H_{12}^-$, in which the carbon atom is located on the opposite side of the *nido* cage from the open face.[44] Thus all three possible isomers of $CHB_{10}H_{12}^-$ have been prepared.

Polarographic reduction of isomeric arsa- and phospha-carboranes disclosed that the electron affinity of the cage system increases when a CH unit in a carborane is replaced by either an arsenic or a phosphorus atom.[45] In another study it was determined that the acidity of the CH group (as measured by the rate of exchange of hydrogen between ammonia and $PCDB_{10}H_{10}$, for example) increases in the order 1,7-$C_2H_2B_{10}H_{10}$ < 1,7-$AsCHB_{10}H_{10}$ < 1,7-$PCHB_{10}H_{10}$.[46]

Other *nido* 12-atom derivatives which are isoelectronic with $AsCHB_{10}H_{10}^{2-}$ have recently been prepared. Reaction of $Me_3NCB_{10}H_{12}$ with sodium hydride in THF followed by $PhAsCl_2$ formed *nido*-$Me_3NC(AsPh)B_{10}H_{10}$ in low yield.[57] A single-crystal X-ray structure determination (Figure

6) of the corresponding phosphacarborane suggests that the 'PPh' unit bridges two boron atoms

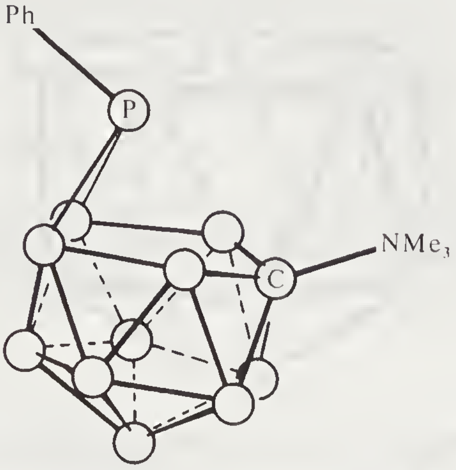


Figure 6 Structure of $Me_3NC(PPh)B_{10}H_{10}$

in the open face of the $Me_3NCB_{10}H_{10}$ 11-atom icosahedral fragment.[58]

5.6.5.2 Monocarbon Derivatives containing Transition Metals

Treatment of 7,8- or 7,9-$ECHB_9H_{10}^-$ (E = P or As) with sodium hydride removes the bridging hydrogen to form 7,8- or 7,9-$ECHB_9H_9^{2-}$, which are analogs of 7,8- and 7,9-$C_2H_2B_9H_9^{2-}$. These dianions are capable of accepting a transition metal atom into the open face of the heterocarborane to complete the icosahedral structure. A review of the transition metal phospha- and arsa-metallocarboranes has recently appeared.[48] Manganese, iron, cobalt and nickel complexes of 7,8- and 7,9-$ECHB_9H_9^{2-}$ (E = P or As) have been prepared.[49–53] In general the 7,9-$ECHB_9H_9^{2-}$ ions appear to give a higher yield of the various metal complexes than the 7,8-dianions. The iron complex $[(7,9\text{-}PCHB_9H_9)_2Fe]^{2-}$ when treated with methyl iodide formed neutral (7,9-$MePCHB_9H_9)_2Fe$ and an X-ray study of this compound has been reported which demonstrated that the methyl groups were bonded to the phosphorus atoms.[51] Attempts to involve the phosphorus lone pair electrons of 1,2-$PCHB_{10}H_{10}$ in chemical bonding (*e.g.* quaternization with methyl iodide) have not been successful.[35] However, the 7,9-$ECHB_9H_{10}^-$ (E = P or As) ions readily react with methyl iodide to form 7,9-$MeECHB_9H_{10}$. These phospha- and arsa-carborane derivatives can also function as two-electron donor ligands in many transition metal complexes. The photochemical reaction of $(7,9\text{-}AsCHB_9H_9)_2Fe^{2-}$ with $Cr(CO)_6$ in THF led to the formation of $[(CO)_5\text{-}Cr(AsCHB_9H_9)]_2Fe^{2-}$.[54] It is proposed that each heterocarborane ligand is π-bonded to the iron atom and σ-bonded through the arsenic atom to a $Cr(CO)_5$ unit. Other σ-bonded complexes such as $[7,8\text{-}B_9H_{10}CHAsMo(CO)_5]^-$, $[(7,8\text{-}B_9H_{10}CHP)Mn_2(CO)_9]^-$ and $(\eta\text{-}C_7H_7)Mo\text{-}(CO)_2(7,8\text{-}PCHB_9H_{10})$ have also been reported.[44,55,56]

5.6.5.3 Dicarbon Derivatives

Treatment of 7,8-$C_2H_2B_9H_{10}^-$ with nitrous acid in water at 0 °C formed $HNC_2H_2B_8H_8$ and $H_2NC_2H_2B_8H_9$ in moderate yield.[32,33] These are the only two azacarboranes reported to date. Alkylation of $HNC_2H_2B_8H_8$ with $PhCH_2Br$ in the presence of KOH in Et_2O solvent formed $PhCH_2NC_2H_2B_8H_8$. The structure of this compound was determined by X-ray methods (see Figure 7) and is an icosahedron missing one boron vertex.[34] The two carbon atoms and the nitrogen atom are on the open face of the cage. The ^{11}B NMR spectra of $HNC_2H_2B_8H_8$ and the isoelectronic thia- and selena-carboranes ($SC_2H_2B_8H_8$ and $SeC_2H_2B_8H_8$) are strikingly similar, suggesting the same structure for all three. The second azacarborane is believed to be a derivative of 5,6-$C_2H_2B_8H_{10}$ in which a bridging hydrogen is replaced by a bridging NH_2 group.

A compound of the formula $PhAsC_2H_2B_9H_9$ has been prepared from $Na_2[C_2H_2B_9H_9]$ and $PhAsCl_2$ in THF.[59] A variable temperature ^1H NMR study showed that the CH protons became nonequivalent below −40 °C, suggesting that the molecule has a fluxional *nido* structure similar to that of $Me_2AlC_2H_2B_9H_9$. Another method of synthesis of $RAsC_2H_2B_9H_9$ derivatives (R = Ph, Me or Bu^n) involves reaction of $Tl_2[7,8\text{-}C_2H_2B_9H_9]$ with $RAsCl_2$.[60] Treatment of $PhAsC_2H_2B_9H_9$ with Br_2 cleaved the phenyl–arsenic bond and formed $BrAsC_2H_2B_9H_9$. The

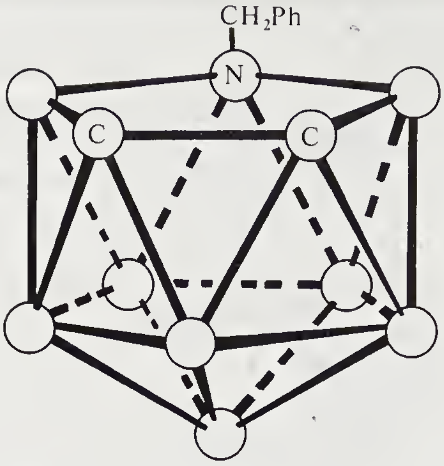


Figure 7 Structure of $PhCH_2NC_2H_2B_8H_8$

arsacarboranes degraded rapidly with ethanolic KOH to form $K[7,8\text{-}C_2H_2B_9H_{10}]$. When bromodimethylarsine was reacted with $Li[7,8\text{-}C_2H_2B_9H_{10}]$ in hot benzene, both $7,8\text{-}C_2H_2B_9H_{11}$ and $(Me_2As)_2C_2H_2B_9H_9$ were formed.[60] The latter substituted compound probably has one bridging Me_2As group and one Me_2As group terminally bound to a boron atom of the cage. This molecule is considered to be a disubstituted $7,8\text{-}C_2H_2B_9H_{11}$ derivative. This derivative reacted with KOH in ethanol to form $Me_2AsC_2H_2B_9H_{10}(OEt)$. Available data suggest that the ethoxide group displaced the terminally bound Me_2As group.

Reaction of $C_2H_4B_7H_9$ with arsenic triiodide and triethylamine formed $As_2C_2H_2B_7H_7$ in moderate yield.[61] The molecule has $n + 2$ pairs of valence electrons, suggesting that it has a *nido* 11-atom structure (see Figure 8). This new type of molecule is isoelectronic with $C_4H_8B_7H_7$, a member of the tetracarbon carborane series. The C_4B_7 molecule has not been isolated; however, MC_4B_7 (M = Fe or Co) metallacarborane derivatives have been reported.[62-64] Photolysis of $(\eta\text{-}C_5H_5)Co(CO)_2$ and $As_2C_2H_2B_7H_7$ in THF formed $(\eta\text{-}C_5H_5)Co(As_2C_2H_2B_7H_7)$ in low yield.[61]

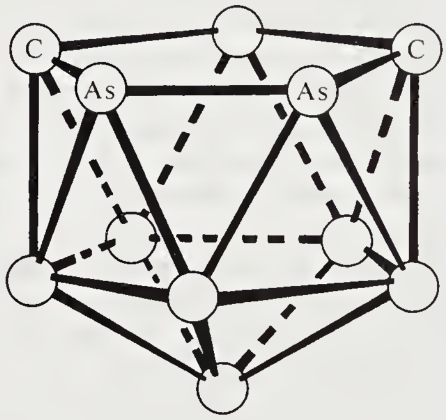


Figure 8 Proposed structure of $As_2C_2H_2B_7H_7$

5.6.6 DERIVATIVES CONTAINING GROUP VIA ELEMENTS

The first heterocarborane reported which contained a Group VIA element was $SC_2H_2B_8H_8$ and this compound was obtained by the reaction shown in equation (6).[33] The redox reaction

$$7,8\text{-}C_2H_2B_9H_{10}^- \xrightarrow{HCl,\ H_2O,\ KHSO_3} SC_2H_2B_8H_8 \qquad (6)$$

between boron hydride derivatives and element oxide reagents appears to be a general method for the synthesis of heteroboranes containing N, As, S, Se or Te in the cage structure.[32,65,66] The compound $SeC_2H_2B_8H_8$, prepared from $7,8\text{-}C_2H_2B_9H_{10}^-$ and $KHSeO_3$, has an ^{11}B NMR spectrum very similar to that of the corresponding thia- and aza-carborane derivatives.[33,66] A different degradative insertion reaction was employed to form the interesting compound $SCH_2B_7H_9$ (see equation 7).[67] On the basis of very similar ^{11}B NMR spectra it was proposed that this thiacarborane had a structure like that of $C_2H_2B_7H_{11}$ in which a 'CH_2' unit was replaced by an isoelectronic 'S' unit.

$$C_2H_2B_{10}H_{11}^- \xrightarrow{HCl,\ H_2O,\ KHSO_3} SCH_2B_7H_9 \tag{7}$$

Treatment of $C_2H_4B_7H_9$ with polyselenide ion in aqueous base, followed by acidification, formed $SeCH_2CHB_7H_8$.[68] The ^1H NMR spectrum strongly suggest that there is a 'CH_2' group in the molecule. The proposed *arachno* structure for this molecule is shown in Figure 9. Reaction of $Me_3NCB_9H_{11}$ with $(Se)_n^{2-}$ also resulted in selenium insertion to form $Me_3NCSeB_9H_9$.[69]

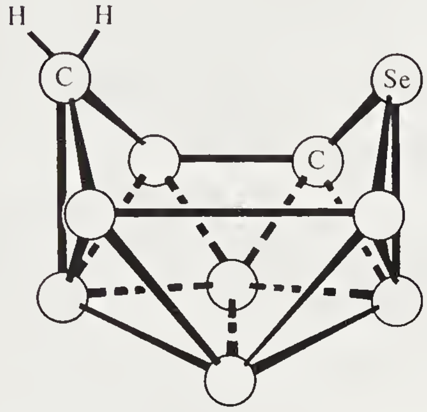


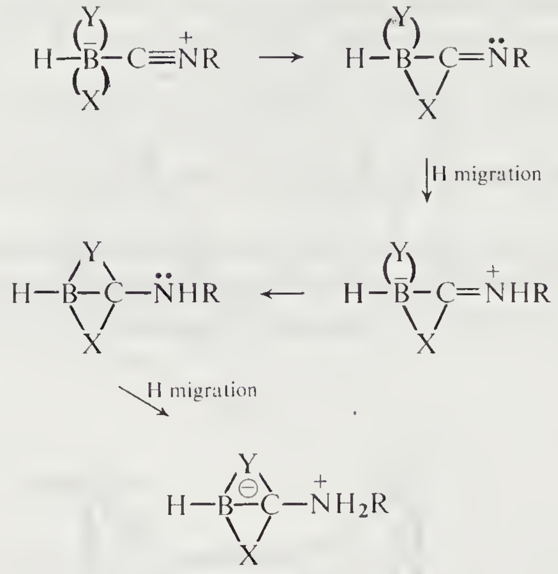
Figure 9 Proposed structure of $SeCH_2CHB_7H_8$

Moderately good synthetic methods for the synthesis of thia- and selena-carboranes have recently been discovered, as illustrated in Scheme 2.[70]

$$\begin{tikzcd}
SB_9H_{11} + CNBu^t \arrow[r] \arrow[d, "NaCN"] & Bu^tH_2NCSB_9H_9 \arrow[d, "\text{i, } NaH/THF;\ \text{ii, } Me_2SO_4"] \\
Na(SB_9H_{11}CN) \arrow[d, "Me_3SiBr"] & Bu^tNMe_2CSB_9H_9 \\
SB_9H_{11}(CNSiMe_3) \arrow[r, "reflux", "C_6H_6"'] & Me_3SiNH_2CSB_9H_9 \arrow[d, "H_2O/OH^-"] \\
 & H_3NCSB_9H_9
\end{tikzcd}$$

Scheme 2

The initial formation of an acid–base complex (*i.e.* $SB_9H_{11}CNR$) may be one of the requirements for this carbon insertion reaction. For the first time, the acid–base complex $SB_9H_{11}(CNSiMe_3)$ has been isolated and characterized prior to further reaction to insert the carbon into the borane cage.[70] A possible generalized mechanism for this type of reaction is illustrated in Scheme 3. The unit (**A**) is a generalized representation for the borane cage which indicates that the central boron atom is multiply bonded to other X and Y portions of the cage structure. This mechanism is an intramolecular version of the reaction sequence proposed in the reaction of BH_3 with alkyl isocyanides.[71] The compound $Me_3NCSeB_9H_9$ described above[69] and



Scheme 3

the thiacarboranes prepared by the isocyanide route have similar *nido* structures, as evidenced by their very similar ^{11}B NMR spectra.

(A)

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6

Aluminum

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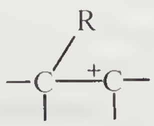
6.1 INTRODUCTION AND OVERVIEW

6.1.1 Historical Development

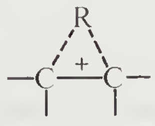
Since aluminum is the most abundant metal in the earth's crust (7.5%) and its organometallic derivatives were first prepared over 120 years ago, one might wonder why the high reactivity and utility of organoaluminum compounds went unnoticed for over a century. Already in 1859 ethylaluminum sesquiiodide (a 1 : 1 mixture of $EtAlI_2$ and Et_2AlI) was obtained by Hallwachs and Schafarik from ethyl iodide and aluminum metal,[1] and in 1865 Buckton and Odling reported the synthesis of aluminum alkyls from mercury alkyls and aluminum metal.[2] Both preparative methods proved to be applicable to the synthesis of many other organometallic compounds, such as those of zinc and, much later, magnesium (Grignard, 1900) and lithium (Ziegler, 1930). Yet the organometallic compounds of all three of these metals were recognized as valuable reagents in organic chemistry long before those of aluminum. Not until the classic studies of Ziegler in the early 1950s did the potential of organoaluminum reagents for organic synthesis and polymerization come to light. Why did organoaluminum chemistry lie dormant so long? The reason lies not merely in their accessibility, for methods for their synthesis were at hand. The more likely reason was the choice of *ether media* when the reactions of aluminum alkyls or aryls had been examined prior to 1950. Chemists had become accustomed to preparing organo-magnesium and -lithium reagents in diethyl ether and had observed an accelerating influence of this solvent on subsequent reactions. Accordingly, reactivity comparisons of organoaluminum reagents with those of other metals were often conducted in ether. Rather than accelerating the reactions of R_3Al, ether is now known to retard additions of R_3Al to alkenes and alkynes (carbalumination).[3] Mechanistic studies have demonstrated that the rate-determining step of such additions involves the attack of the unsolvated, monomeric R_3Al on the unsaturated carbon–carbon linkage. In ether, on the other hand, the stoichiometric solvate $R_3Al{\cdot}OEt_2$ is formed and the aluminum reagent thereby loses its electrophilic reactivity. Thus, ether is responsible for retarding not only carbalumination but, indeed, the whole development of organoaluminum chemistry.

Even though the importance of their Lewis acidity on reactivity had been overlooked, organoaluminum compounds have received some attention as possible intermediates in Friedel–Crafts alkylation reactions.[4] From time to time, alkyl- and aryl-aluminum chlorides have been proposed as precursors to the final products, since alkylaluminum chlorides can be substituted for aluminum chloride as a catalyst[5] and organic chlorides (alkyl and acyl) do react with $RAlCl_2$ reagents to form coupled products[6] R—R′ and R—CO—R′. However, present opinion does not consider organoaluminum compounds as important intermediates in ordinary Friedel–Crafts reactions. But in processes involving the simultaneous action of aluminum chloride and aluminum metal on mixtures of an alkene and alkyl halide, as first studied by Hall and Nash,[7] organoaluminum compounds do exist in the unhydrolyzed product.[8]

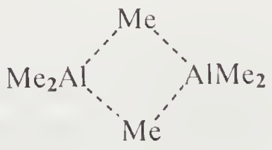
One of the most unusual properties of aluminum alkyls is structural rather than chemical, and this is their dimeric character. Such autocomplexation in alkylaluminum halides, as in aluminum chloride itself, is readily interpreted in terms of coordinative bridging of chloride ligands. But when trimethylaluminum was shown in 1941 to exist as $(Me_3Al)_2$ units in solution and in the vapor state,[9] existing valence theory was inadequate to account for the nature of the bonding. Lively speculation was unleashed, ranging from proposals of ethane-like structures having Al—Al bonds to those suggesting bridging methyl groups involving Al—H—CH_2 bonds. The appeal of some kind of Al—H bonding has persisted[10] even after X-ray crystal analysis (see Figure 2) had verified the bridging methyl, three-centered Al—C—Al arrangement for the solid state.[11,12] The theory of the three-center, two-electron bond was then formulated to explain the bonding in R_3Al dimers, as well as that in diborane and other associated organometallic compounds.[13] Rundle's contributions to our understanding of such electron-deficient, multicenter bonding have proved to be of enduring excellence. It should be noted that such multicenter bonding has also been relevant to another area of great interest, namely that of carbenium ion rearrangements and nonclassical carbenium ions.[14] An alkyl group undergoing a 1,2-shift (**1**) and a nonclassical representation of a carbenium ion (**2**) have an electronic similarity to the bridging methyl in (**3**).



(**1**)



(**2**)



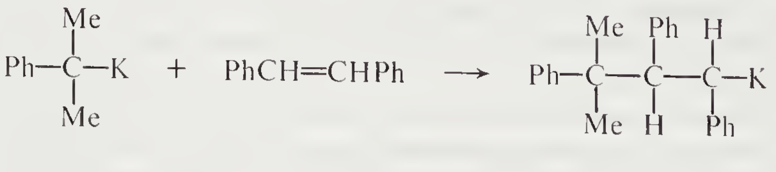
(**3**)

Although such structural studies awakened some interest in organoaluminum compounds in the years following the Second World War, it was the masterly chemical investigations of Karl Ziegler and his group at the Max Planck Institute for Coal Research at Mülheim that aroused international attention. The rapidity with which his research won recognition can be measured by the dates of his first publications on aluminum compounds (1952)[3,15] and the bestowal of the Nobel Prize (1963, jointly with G. Natta).[16] During the intervening decade the newly founded 'Ziegler Chemistry' attracted the keen curiosity of every major chemical firm in the world. In reflecting on how he arrived at the pinnacle of such unexpected prominence, Ziegler retraced the sequence of research studies that led him to organoaluminum chemistry and thereby to his astonishing discoveries. Since this background is both instructive and inspiring, it is a story that bears repeating here.[17]

As a young chemist Ziegler had launched a research program to synthesize and study the behavior of trivalent carbon compounds (organic free radicals). In the course of such experimentation he had occasion to employ organoalkali metal reagents, many of which had been developed by Schlenk and Bergmann,[18] to generate free radicals according to equation (1). Depending upon the nature of R groups in (**4**) and (**6**), stable free radicals could be generated in a systematic manner.[19] Also, certain R groups yielded an organometallic derivative (**4**) (R, R′ = Me, R″ = Ph) capable of adding across the C=C bond in stilbene (equation 2). Ziegler noted that the product (**7**) was also organometallic and could conceivably add to a second mole of the alkene, if not hindered by steric factors.[20] Indeed, the repetitive insertion of alkenic substrate into carbon–metal bonds was subsequently invoked by Ziegler in elucidating the mechanism for the polymerization of butadiene by sodium.[21] The interest in organoalkali metal reactions with alkenes was extended to lithium when in 1930 Ziegler developed a general preparation of RLi and ArLi directly from the organic halides and lithium metal and showed that such reagents add to C=C bonds in fulvenes and in butadiene readily.[22,23] Then in the course of purifying these more readily accessible lithium alkyls, Ziegler observed that attempted distillation of ethyllithium led to decomposition (equation 3). In accounting for the formation of the higher even-numbered alkenes (**8**), Ziegler postulated that the ethyllithium might have added to ethylene to form butyllithium, in a manner analogous to that displayed in his earlier studies with other alkenes (equation 2). The butyllithium, in turn, could lose LiH to form 1-butene or insert another ethylene to form hexyllithium. Analogous reactions could then produce the higher alkenes.[24] What now aroused his curiosity was whether preformed lithium hydride could be added to ethylene under pressure (the reverse of equation 3) and thereby bring about the catalytic oligomerization of this available alkene to higher α-alkenes. Although this experiment proved unsatisfactory, the recently discovered complex hydride $LiAlH_4$ (Schlesinger, Finholt and Bond, 1947)[25] did react with ethylene at 200 °C to yield such α-alkenes (equation 4).[26] Careful analysis showed that the actual oligomerization

$$R'-\overset{R}{\underset{R''}{C}}-M + Me-\overset{Me}{\underset{Br}{C}}-\overset{Me}{\underset{Br}{C}}-Me \xrightarrow[-C_6H_{12}]{-MBr} 2R'-\overset{R}{\underset{R''}{C}} \rightleftarrows R'-\overset{R}{\underset{R''}{C}}-\overset{R}{\underset{R''}{C}}-R' \qquad (1)$$

(**4**) (**5**) (**6**)



$$Ph-\overset{Me}{\underset{Me}{C}}-K + PhCH{=}CHPh \longrightarrow Ph-\overset{Me}{\underset{Me}{C}}-\overset{Ph}{\underset{H}{C}}-\overset{H}{\underset{Ph}{C}}-K \qquad (2)$$

(**7**)

$$EtLi \xrightarrow{\Delta} LiH + CH_2{=}CH_2 + RCH{=}CH_2 \qquad (3)$$

(**8**)

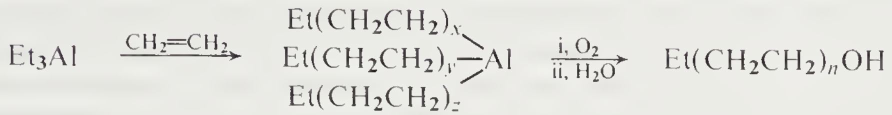
$R = Et, Bu, C_6H_{13}$, *etc.*

$$LiAlH_4 + 4CH_2{=}CH_2 \xrightarrow[\text{pressure}]{\Delta} LiAlEt_4 \longrightarrow RCH{=}CH_2 \qquad (4)$$

(**9**) (**8**)

catalyst was the lithium tetraethylaluminate (**9**) formed *in situ*. Thus, an organoaluminum reagent was shown for the first time to be more synthetically useful than its lithium counterpart, EtLi. Drawing the logical conclusion, Ziegler and Gellert then tested the reactivity of both lithium-free aluminum hydride AlH_3 and triethylaluminum towards ethylene. To their gratification, they found that both rapidly oligomerize ethylene to α-alkenes at temperatures of 100 °C (equation 5).[27] With this discovery, aluminum alkyls gained a unique and commanding role in hydrocarbon chemistry and technology. For not only could aluminum alkyls function catalytically, but they could also react stoichiometrically with ethylene to yield mixtures of higher R_3Al derivatives (**10**) that could be air oxidized and then hydrolyzed to produce straight-chain primary alcohols (**11**) (equation 6).[28]

$$AlH_3 + 3CH_2{=}CH_2 \longrightarrow Et_3Al \longrightarrow RCH{=}CH_2 \qquad (5)$$



$$Et_3Al \xrightarrow{CH_2{=}CH_2} \left.\begin{matrix}Et(CH_2CH_2)_x\\ Et(CH_2CH_2)_y\\ Et(CH_2CH_2)_z\end{matrix}\right\rangle Al \xrightarrow[ii,\ H_2O]{i,\ O_2} Et(CH_2CH_2)_nOH \qquad (6)$$

(**11**)

(**10**)

The implications and potential of this new aluminum chemistry were, by themselves, significant enough to excite widespread industrial interest. Yet nature still had a surprise in store for the Mülheim group. On one occasion when the stoichiometric reaction depicted in equation (6) was being conducted, ethylene insertion was unaccountably retarded and the contents of the autoclave were converted largely to 1-butene, rather than to (**10**) (equation 7).[29] Scrutiny of the anomalous reaction revealed that traces of nickel salts, arising during the cleaning of the autoclave, catalyzed the transfer of AlH_3 from the tributylaluminum intermediate (**12**) to ethylene, thus curtailing the 'growth reaction' of the carbon–carbon chain. Recognition of this 'nickel effect', *i.e.* the catalyzed displacement of one alkene from an aluminum alkyl by a second, unleashed a detailed study of how other transition metal salts would affect the course of organoaluminum–alkene reactions. With growing excitement, Ziegler, Martin and Breil found in 1953 that salts of chromium, zirconium and, most effective of all, titanium did not promote the olefin displacement (equation 7) but rather accelerated tremendously the 'growth reaction' of the carbon–carbon chain (equation 6).[30,31] The result was the efficient, low-pressure production of high-molecular polyethylene (**13**) ($MW = 3 \times 10^6$) (equation 8). Subsequent investigations by Ziegler's group in Mülheim and Natta's group in Milan demonstrated the applicability of such catalysts to the polymerization of α-alkenes and dienes. Natta recognized the importance of stereochemistry in the polymerization of the prochiral α-alkenes and of 1,3-alkadienes. The stereoregularity of the resulting polymers, namely the isotactic, syndiotactic or atactic arrangement of the poly-α-alkenes, was shown to have a profound influence on macroscopic properties, such as melting point, density and tensile strength.[32] These Ziegler–Natta catalysts have revolutionized polymer technology.

$$Et_3Al \xrightarrow{CH_2{=}CH_2} \underset{(\mathbf{12})}{Bu^n{}_3Al} \xrightarrow[Ni]{CH_2{=}CH_2} EtCH{=}CH_2 + Et_3Al \qquad (7)$$

$$CH_2{=}CH_2 \xrightarrow[TiCl_4]{R_3Al} \underset{(\mathbf{13})}{-\!\!(CH_2{-}CH_2)\!\!-_n} \quad n \approx 100\,000 \qquad (8)$$

As will be apparent in this chapter, the consequences of Ziegler's aluminum discoveries to modern chemistry are far-reaching. Not only have they made organoaluminum reagents comparable in importance to those of lithium and magnesium, but they have inspired much research in fundamental organometallic and inorganic chemistry. Many of the findings of such basic research have led to the development of highly successful industrial processes, such as the oligomerization of alkenes,[33] the synthesis of acetic acid from methanol[34] and the stereoselective hydrogenation of unsaturated compounds.[35] The ultimate effect of Ziegler's discoveries, then, has been to transform organometallic chemistry from an arcane science into a mainstay of industrial research.

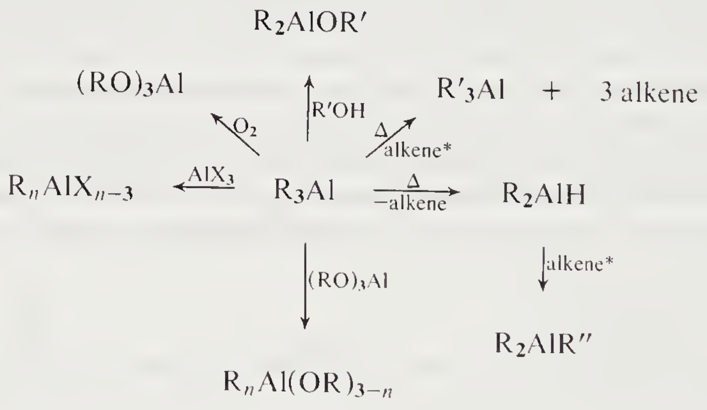
6.1.2 Availability in Research and Industry

Prior to Ziegler's work aluminum alkyls were occasionally the subject of academic research only. The only industrially available compound was aluminum carbide Al_4C_3, made by the union of the elements at 1000 °C. This compound can be viewed as a methanide, since its structure consists of distinctly separate carbon atoms and it hydrolyzes readily to produce methane. But by the late 1950s interest in aluminum alkyls had grown so greatly that commercial production had begun. Most industrial processes are variants of the Ziegler method, which involves the direct union of aluminum metal and hydrogen, in the presence of either R_3Al (equation 9) or alkene (equation 10).[36] If the alkene is too reactive towards R_3Al (*e.g.* ethylene, equation 6), then the method of equation (9) is used, in which R_2AlH is prepared first and then the alkene is added at a lower temperature. For less reactive alkenes such as isobutylene, the one-step method of equation (10) is suitable.

$$2Al + 3H_2 + 4R_3Al \longrightarrow 6R_2AlH \xrightarrow{\text{alkene}} R_3Al \tag{9}$$

$$2Al + 3H_2 + 6CH_2{=}CR_2 \longrightarrow 2(R_2CHCH_2)_3Al \tag{10}$$

Organoaluminum compounds of the type R_nAlZ_{3-n} can often be prepared from R_3Al by methods summarized in Scheme 1. An alternative route to alkylaluminum halides and aluminum alkyls recalls the method first used in 1859 to synthesize aluminum alkyls, namely the direct reaction of an alkyl halide with aluminum (equation 11).[37,38] The sesquihalide mixture (**14**) thereby formed can be separated into its component halides or it can be directly dehalogenated with sodium to yield the aluminum alkyl. This method has particular value for the synthesis of trimethylaluminum and its derivatives, which cannot be prepared by the Ziegler method (equations 9 and 10).



Scheme 1

$$RX + Al \longrightarrow \underbrace{R_2AlX + RAlX_2}_{\textbf{(14)}} \xrightarrow[-NaX]{Na} R_3Al \tag{11}$$

Paralleling this great activity in industrial production of aluminum compounds has been a steady expansion of fundamental research, which has greatly increased the scope of preparative methods. In turn, chemical supply houses now offer a wide variety of unusual aluminum reagents for synthetic and catalytic applications. The present production of these pyrophoric and moisture sensitive compounds has become truly impressive. Already in 1975 the worldwide output of aluminum alkyls was estimated at about 35 to 50 million pounds per year for the open market. Another 200 million pounds annually were being produced by companies as 'captive' intermediates for the intramural preparation of linear alcohols (equation 6) and α-alkenes (equation 5).[39]

6.1.3 Routes to Organoaluminum Compounds

The methods delineated in the previous section are chiefly applicable to the preparation of simple aluminum alkyls and their derivatives on a large scale. Such reactions involve heterogeneous mixtures, pressure equipment and exothermic processes that require safe, efficient heat transfer. Attempts to adapt such reactions to a smaller, laboratory scale require the utmost caution. For example, the reaction of alkyl halides with aluminum metal (equation 11) in an autoclave[40] is most hazardous and conducting the reaction in a glass apparatus requires elaborate precautions.[41] The following methods are more readily adaptable to safe laboratory use, provided that at all times the reaction mixture is protected by an inert atmosphere (anhydrous nitrogen or argon) and that all moisture is excluded.

Firstly, instead of making and using AlH_3, as in equations (9) and (10), one can employ triisobutylaluminum which can be made to transfer AlH_3 to a less volatile alkene either thermally (>100 °C) or with nickel promotion (*cf.* equation 12).[42]

$$(Me_2CHCH_2)_3Al \quad + \quad 3CH_2{=}CHR \quad \xrightarrow[-3C_4H_8]{\Delta} \quad (RCH_2CH_2)_3Al \tag{12}$$

Secondly, the original method of Buckton and Odling can be used to prepare a wide variety of R_3Al types, if the mercury compound is accessible and if both R_2Hg and the resulting R_3Al are not thermolabile (equation 13).[43] An advantage of both these methods is that the resulting aluminum compounds are free of coordinated solvent.

$$3Ph_2Hg \quad + \quad 2Al \quad \xrightarrow{\Delta} \quad 2Ph_3Al \quad + \quad 3Hg \tag{13}$$

Thirdly, aluminum halides can be converted into organometallic compounds by more reactive RM reagents, such as those of sodium, lithium or magnesium. If these reagents must be used in ether solution, then the resulting R_3Al will be formed as an etherate complex. Such coordinated ether may be removable by heat if the aluminum compound is thermostable (equation 14).[44]

$$\underset{\text{(ether)}}{3RMgX} \quad + \quad AlX_3 \quad \xrightarrow[-3MgX_2]{} \quad R_3Al{\cdot}OEt_2 \quad \xrightarrow[-Et_2O]{\Delta} \quad R_3Al \tag{14}$$

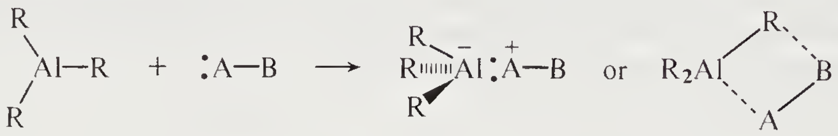
Fourthly, various unsymmetrical aluminum compounds R_2AlR' are obtainable from the organoaluminum halides, which themselves are conveniently prepared from R_3Al and AlX_3 (Scheme 1). Hydrides can be prepared from the chlorides with alkali metal hydrides and these R_2AlH reagents can be added to alkenes or alkynes (equation 15).[45] The chlorides can also be employed in a variant of the third method to produce R_2AlR' (equation 16). In these preparations, elevated temperatures should be avoided, so that disproportionation into R_3Al and R'_3Al does not occur.

$$R_2AlCl \quad \xrightarrow[-LiCl]{LiH} \quad R_2AlH \quad \xrightarrow{CH_2{=}CHR'} \quad R_2AlCH_2CH_2R' \tag{15}$$

$$R_2AlCl \quad + \quad R'Li \quad \xrightarrow[-LiCl]{} \quad R_2AlR' \tag{16}$$

6.1.4 Structure and Physical Properties

Organoaluminum compounds are generally liquid or low-melting, often miscible in hydrocarbon solvents and volatile in high vacuum at moderate temperatures. Such properties are in accord with the presence of covalent rather than ionic carbon–aluminum or hydrogen–aluminum bonds. However, measurements of various colligative properties in solution, such as boiling point elevation and freezing point depression, indicate a general tendency of simple (R_3Al) and mixed (R_nAlZ_{3-n}) units to oligomerize into dimers, trimers or tetramers. As mentioned above, the dimeric nature of trimethylaluminum posed a structural puzzle, whose solution required development of the theory of electron-deficient bonding. Various electronegativity estimates would suggest that the covalent carbon–aluminum bond has considerable polar character: the Pauling method would assign a 20% partial ionic character to this linkage.[46] Although such values have dubious quantitative worth, they do serve to indicate trends among similar bonds. Carbon–aluminum bonds are distinctly less polar than those of magnesium and sodium in Period Two, and are more polar than those of silicon and phosphorus. Such polarity is surely important in contributing both to the electron-deficient bonding of R_3Al units and to the Lewis acidity displayed by R_3Al and R_nAlZ_{3-n} types. It should be noted, however, that monomeric, symmetric R_3Al units would be expected to have an sp^2-hybridized aluminum with the equidistant alkyl groups radiating out from it in a plane (**15**). In such a configuration the effects of any bond polarity should cancel. However, approach of a dipole (**16**) could induce a hybridization change and hence the development of a dipolar configuration for R_3Al. The inducing dipole could be a Lewis base, which has an unshared electron pair, and the resultant would be a classic coordination compound (**17**). Alternatively, AB could be another molecule of R_3Al, which interacts with (**15**) in a mutual dipole-inducing fashion to yield the autocomplex (**18**). In both instances, dipole development aids the reaction (equation 17).



(17)

(**15**) (**16**) (**17**) (**18**)

Since a marked structural change occurs in such hetero- (**17**) or homo-complexation (**18**), it is appropriate here to comment on general electronic and steric factors that determine the stability of such complexes. As a natural extension of the foregoing discussion, it is clear that mixed organoaluminum compounds, such as $RAlCl_2$ and R_2AlOR, will have dipole moments even as monomers and that such dipole-inducing interactions (equation 17) will occur even more readily and completely from an electronic standpoint. Where steric factors do not intervene, the Lewis acidity of aluminum compounds would be expected to decrease in the series $AlCl_3 > RAlCl_2 > R_2AlCl > R_3Al$, and that trend is observed in complexation with alkali metal chlorides.[47]

The role of steric factors on the stability of Group III complexes has been studied in a comprehensive manner by Brown and coworkers.[48] The useful steric distinction is made between F(front)- and B(back)-strains. In the former, recognition is given to the frontal repulsive forces arising from the bonding of a bulky donor to a bulky acceptor, as in $Me_3B{\cdot}NMe_3$, compared with $Me_3B{\cdot}NH_3$. In B-strain, the change in hybridization in going from monomeric Lewis acid (*e.g.* **15**) to complex brings the substituents on R_3Al closer to each other (in (**15**), separation by 120°; in (**17**), separation by about 110°). Depending upon the size of the substituent and the covalent radius of the metal, steric repulsion among the substituents could labilize the complex.

Similar considerations are applicable to bridging complexes such as (**18**), where identical R_3Al units are associated with each other. As a type of F-strain, a large bridging R group should weaken the electron-deficient bonding and destabilize the dimer. This effect is evident in the finding that trimethylaluminum is firmly dimeric,[9] but tri-*t*-butylaluminum is monomeric,[49] in hydrocarbon solution. The role of B-strain in determining the stability of such bridged dimers is less certain, however. In the solid state, the crystal structure of dimeric trimethylaluminum shows an angular separation of the non-bridging methyl groups of 123°, and of the bridging and non-bridging methyl groups of 105°[12] (see Section 6.2.1). Whether such angular changes from the monomeric Me_3Al are mutually compensatory in steric contributions to B-strain is unknown.

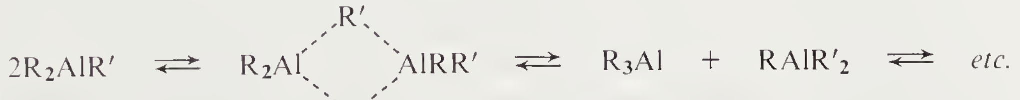
One final consideration in the Lewis acidity of aluminum compounds is the free energy necessary to produce monomeric R_3Al or R_nAlZ_{3-n} from any associated form present (**19**). Obviously the $\Delta G°$ value of equation (18) can play a significant role in determining the strength of Lewis acidity displayed by (**20**), for the same electronic and steric factors that increase the stability of complex (**17**) may also increase the stability of autocomplex (**19**). The firm trimeric character of R_2AlH[50] and the tetrameric nature of Et_2AlF illustrate this point.[51] The complexation of R_2AlH with ether is weaker than that of R_3Al, and solvent-free R_2AlH can readily be isolated from ethereal solution.[26,52]

$$\underset{\mathbf{(19)}}{(R_nAlZ_{3-n})_x} \rightleftarrows \underset{\mathbf{(20)}}{xR_nAlZ_{3-n}} + \Delta G° \qquad (18)$$

Besides such homo- and hetero-complexation, organoaluminum compounds undergo a considerable number of reversible structural changes. The first of these, disproportionation, bears a direct relationship to the autocomplexation depicted in (**3**) and (**18**). In disproportionation, unsymmetrical $R_nAlR'_{3-n}$ and mixed R_nAlZ_{3-n} types are converted into the symmetrical types, R_3Al and R'_3Al or AlZ_3 (equation 19). The reaction equilibrium can lie to the right or to the left, depending upon the nature of R and R′. Most commonly, preferential removal of one of the symmetrical components by volatilization or by preferential complexation with a Lewis base will drive the reaction to the right. For example, the attempted preparation of diphenylaluminum hydride (**21**) in ether eventually leads to triphenylaluminum etherate and polymeric aluminum hydride (equation 20).[53] The relationship between disproportionation and the association of R_3Al units is that both processes involve bridging dimeric structures (equation 21). Whether complete dissociation of dimers (**22**) to monomers (**23**), (**24**), etc. occurs or whether monobridged dimers are the intermediates has been a disputed question.[54]

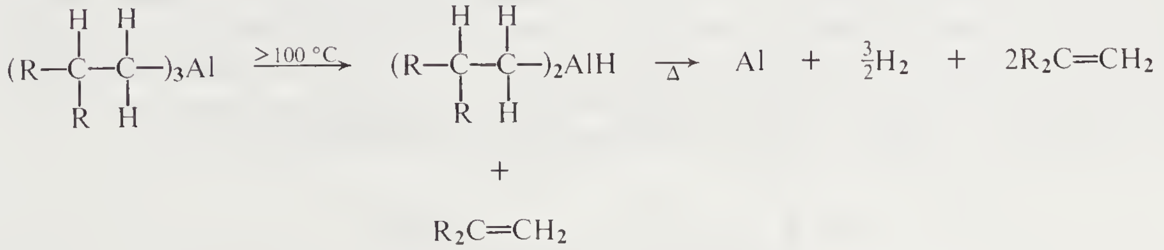
$$3R_2AlR' \rightleftarrows 2R_3Al + R'_3Al \qquad (19)$$

$$Ph_2AlCl \xrightarrow{LiH} \underset{\mathbf{(21)}}{[Ph_2AlH]} \longrightarrow Ph_3Al{\cdot}OEt_2 + (AlH_3)_x \qquad (20)$$



(**23**) (**22**) (**24**) (21)

A second important structural change is the thermal loss of alkene by aluminum alkyls having at least one hydrogen on the β-carbon. Such decomposition can occur stepwise to yield the relatively stable R_2AlH and under forcing conditions leads to the formation of alkene, aluminum metal and hydrogen (equation 22).[36] This extreme outcome represents the reversal of the aluminum alkyl synthesis given in equation (10) above.



$$(R{-}\underset{R}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-})_3Al \xrightarrow{>100\,°C} (R{-}\underset{R}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-})_2AlH + R_2C{=}CH_2 \xrightarrow{\Delta} Al + \tfrac{3}{2}H_2 + 2R_2C{=}CH_2 \qquad (22)$$

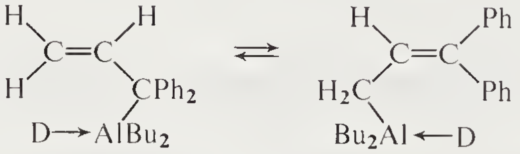
The third structural change, isomerization, can manifest itself in a variety of ways. Closely related to the foregoing alkene elimination is the general tendency of tertiary alkylaluminum and secondary alkylaluminum compounds to isomerize to primary alkylaluminum systems, if structurally possible. Such interconversions most probably involve alkene elimination (*cf.* equation 22) and recombination (hydralumination) to yield the more stable compound (*e.g.* equation 23).[55]

$$R_2C(Et){-}AlR'_2 \rightleftarrows R_2C{=}CHMe + R'_2AlH \longrightarrow R_2CHCH(Me)AlR'_2 \longrightarrow R_2CHCH_2CH_2AlR'_2 \quad (23)$$

Another mode of switching one carbon–aluminum bond into another can occur in allylic and related systems. The temperature dependent NMR spectrum of allyl(diethyl)aluminum in ether solution between −40 and +50 °C may be interpreted in terms of an $ABB'X_2$ spectrum at −40 °C and an AX_4 spectrum above 20 °C. These data are in accord with structure (**25**) interconverting rapidly with structure (**26**) at room temperature (equation 24).[56] There is also evidence from hydrolysis results that the equilibrium in the diisobutyl(diphenylallyl)aluminum system (**27**)–(**28**) lies more in favor of (**28**) when the bulkier Et_3N donor is used in place of Et_2O (equation 25).[57] In addition to such isomerizing rearrangements, there are numerous derivatizing rearrangements where a reagent induces reaction at the other allylic site (*e.g.* equation 26).[58]

(24)

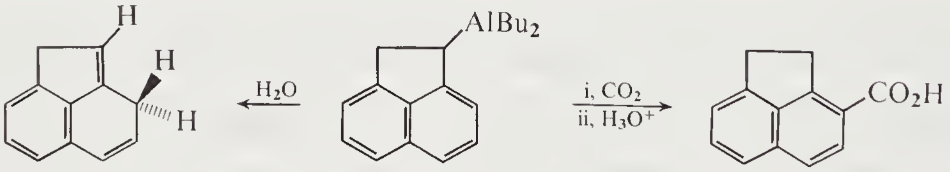
(**25**) (**26**)



(25)

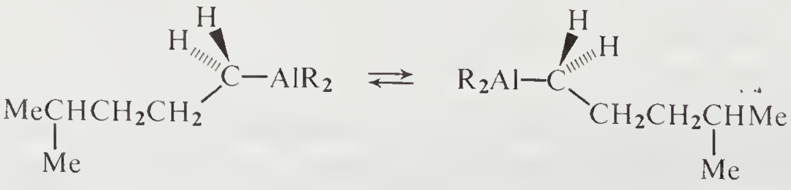
(**27**) (**28**)

D = Et_2O, Et_3N



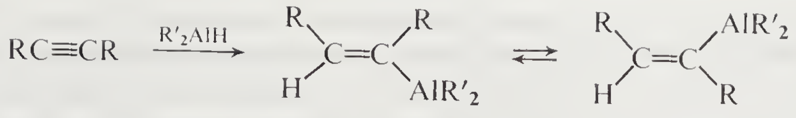
(26)

A further mode of isomerization does not involve a change of site in the carbon–aluminum bond, but rather of stereochemistry. By NMR studies it can be shown that sp^3-hybridized carbon–aluminum bonds can invert at moderate temperatures. At 25 °C tri-2-methylpentylaluminum (**29**, **a** and **b**) (R = i-C_6H_{13}) undergoes inversion with a pre-exchange lifetime of about 11 minutes (equation 27).[59] A less subtle isomerization is the configurational change undergone by sp^2-hybridized carbon–aluminum bonds of vinylaluminum systems. Generally, substituted systems of the type in (**30a**)–(**30b**) are thermodynamically more stable in their (*E*)-form (**30b**). However, many of these compounds can be prepared by the hydralumination of the corresponding alkyne and this process is usually kinetically controlled, so that the (*Z*)-form (**30a**) results (equation 28).[60] The ease with which the (*Z*)-form (**30a**) isomerizes into the (*E*)-form (**30b**) varies greatly with the nature of R: when R,R′ = Ph, the isomerization requires prolonged heating at 100 °C; when R = Ph and R′ = $SiMe_3$, the two forms equilibrate with each other at 0 °C.[61]



(27)

(**29a**) (**29b**)



(30a) (30b)

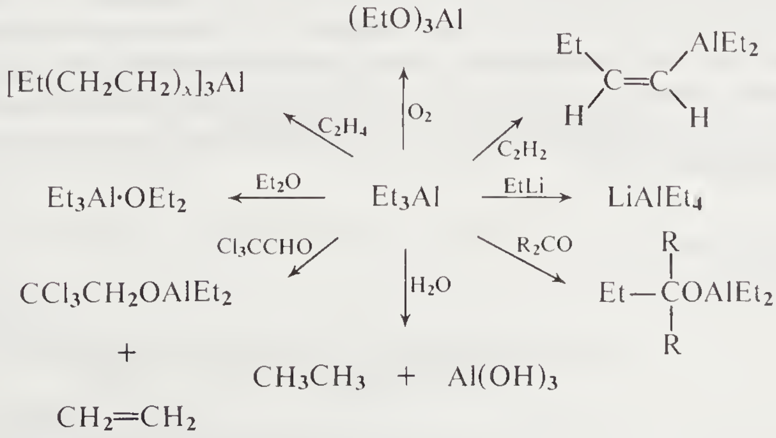
(28)

Finally, since organoaluminum compounds possess polar though covalent bonds and form Lewis complexes with many donors, one might inquire whether ionization and organoaluminum ions have any role in structure or reaction mechanisms. The electrical conductivity of pure R_3Al, R_2AlH and even $RAlX_2$ is so low (about $10^{-8}\ \Omega^{-1}\ cm^{-1}$) that auto-ionization to (**31**) and (**32**) in the sense of equation (29) must be considered negligible.[62] Addition of either neutral donors (D = pyridine, THF or bipyridyl) or anionic donors ($D = F^-$, Cl^- or Br^-) brings about a marked increase in the conductivity to $10^{-3}\ \Omega^{-1}\ cm^{-1}$ and to $10^{-1}\ \Omega^{-1}\ cm^{-1}$, respectively.[63] From these observations one may conclude that the auto-ionization into solvated R_2Al^+ (**31a**) and R_4Al^- (**32**) has been significantly enhanced by complex formation. Similar heterolyses of carbon–aluminum bonds become likely processes in reactions involving strong donors like amines and organoalkali metal compounds, where the resulting complexes $R_3Al{\cdot}NR'_3$ and $M^+AlR_4^-$ could readily dissociate into cationic aluminum and anionic aluminum, respectively.

$$\underset{(\mathbf{31})}{R_2Al^+} + \underset{(\mathbf{32})}{R_4Al^-} \rightleftarrows (R_3Al)_2 \overset{:D}{\rightleftarrows} \underset{(\mathbf{31a})}{R_2Al{:}D^+} + \underset{(\mathbf{32})}{R_4Al^-} \qquad (29)$$

6.1.5 Reactivity Patterns and Reactive Intermediates

Being moderately reactive organometallics, organoaluminum compounds are readily oxidized in air and hydrolyzed by any residual moisture in reaction vessels. Furthermore, being Lewis acids, they form complexes with a wide array of anionic and neutral electron-pair donors (*cf. supra*). As Ziegler's research demonstrated, they also add to both C=C and C≡C linkages much more readily than the generally more reactive organometallic compounds of Groups IA and IIA. On the other hand, aluminum reagents react less uniformly and smoothly with carbonyl substrates, such as ketones and carbon dioxide, than do alkali and alkaline earth organometallic derivatives. In these reactions, often all three carbon–aluminum bonds of R_3Al cannot easily be made to react and R_3Al may, under the reaction conditions, lose alkene (equation 22) to yield R_2AlH. This latter reagent will then produce carbonyl reduction side products. Therefore, the synthetic value of aluminum reagents nicely complements those of lithium and magnesium reagents: the former find their superior applications with unsaturated hydrocarbons, the latter with carbonyl substrates. Using the behavior of triethylaluminum as a paradigm, Scheme 2 illustrates these basic reactions.

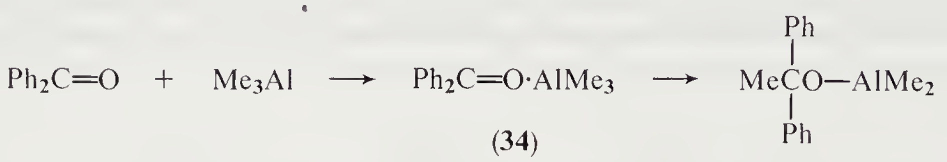


Scheme 2

The common structural feature of all the substrates involved in Scheme 2 is the presence of an unshared or easily polarizable electron pair. The formation and isolation of numerous stable complexes of the type $R_3Al{\cdot}D$ naturally increases the likelihood that similar labile complexes are involved as precursors to many reactions leading to the rupture of carbon–aluminum bonds. The isolation of etherates, $R_3Al{\cdot}OR'_2$ for example, makes it likely that in hydrolysis the hydrate $R_3Al{\cdot}OH_2$ has a fleeting existence. The life time of such an intermediate must be short indeed, for even at −70 °C aluminum alkyls hydrolyze extremely rapidly. In ammonolysis, however, comparable adducts (**33**) can be first formed at lower temperatures and then warmed above room temperature to yield substitution products (equation 30).[48a,64] In a similar way, a yellow complex (**34**) between trimethylaluminum and benzophenone is formed initially, before addition to the carbonyl group occurs (equation 31).[65]

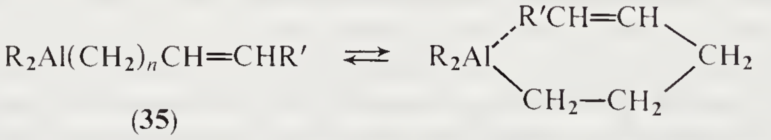
$$\mathrm{Me_3Al} \;+\; \mathrm{R_2NH} \longrightarrow \underset{(\mathbf{33})}{\mathrm{Me_3Al{\cdot}NR_2H}} \xrightarrow[-\mathrm{MeH}]{50\ ^\circ\mathrm{C}} \mathrm{Me_2Al{-}NR_2} \qquad (30)$$

R = H or Me



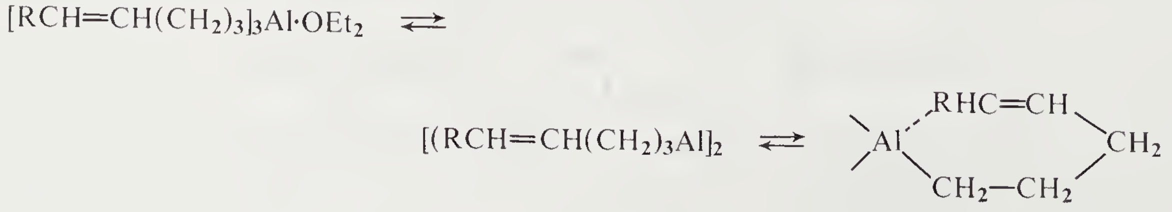
$$\mathrm{Ph_2C{=}O} \;+\; \mathrm{Me_3Al} \longrightarrow \underset{(\mathbf{34})}{\mathrm{Ph_2C{=}O{\cdot}AlMe_3}} \longrightarrow \mathrm{Me}\overset{\mathrm{Ph}}{\underset{\mathrm{Ph}}{\mathrm{C}}}\mathrm{O{-}AlMe_2} \qquad (31)$$

For reactions with alkenes and alkynes where no unshared pairs are available, any preliminary complexation would have to involve the carbon π-electrons. Initial searches for such complexation examined the spectral behavior of a series of alkenyl(dialkyl)aluminum compounds having a varying intramolecular separation between the aluminum center and the alkenic linkage (**35**). Intramolecular coordination (**36**) would bring about changes in the C═C π-electron density and hence in the spectral absorptions (equation 32).[66] When *n* in (**35**) is 4, the C═C stretch in the IR spectrum is shifted to lower frequency by 22 cm^{-1} and the vinylic protons are deshielded in the NMR spectrum, compared with the starting alkene. Such effects were lessened or not observed when $n \neq 4$.



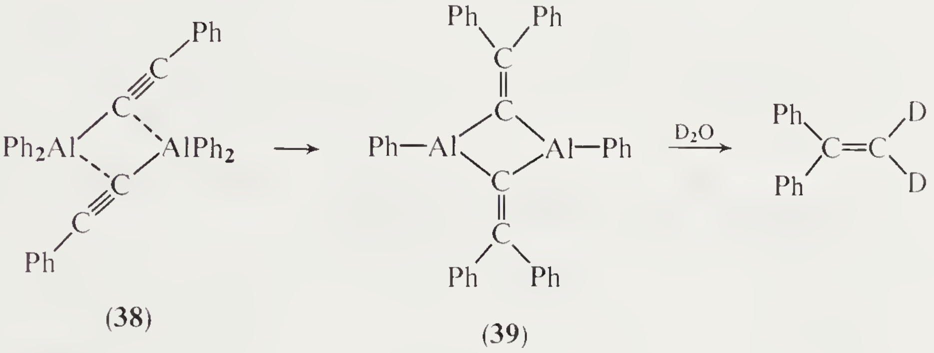
(**35**) (**36**) (32)

To this suggestive work on π-complexation have been added corroborative findings from two different studies. First, a series of trialkenylaluminum compounds was synthesized and their colligative and spectral properties were compared with those of the corresponding trialkylaluminum compounds. Spectral shifts were observed similar to those found in the preceding study. Moreover, when the ether complexes of these alkenylaluminum compounds were prepared, such spectral absorptions showed no special shifts dependent on *n*. Finally, at similar concentrations the trialkenylaluminum members, where *n* = 3 or 4, were found to be monomeric in hydrocarbon solution, while the corresponding trialkyl members were dimeric. All these observations are consistent with the intramolecular coordination depicted in (**36**). Since both dimerization and etherate formation require an available tricoordinate aluminum, these results indicate that coordination, as in (**37**), is stronger than the dimeric bonding of $(RCH{=}CHCH_2CH_2CH_2)_3Al$, but not as strong as etherate formation (equation 33).[67]



(**37**) (33)

In a second study, the X-ray crystal structure of dimeric diphenyl(phenylethynyl)aluminum, resulting from the reaction of phenylacetylene and triphenylaluminum, shows an interesting mode of phenylethynyl bridging[68] (see Section 6.2.1 for the detailed structure). Instead of having the rod-like $PhC\equiv C$ unit almost perpendicular to the Al—Al axis as in the structure of dimeric Ph_3Al, each alkynic unit is definitely bent and inclined toward an aluminum center (**38**). Such bridging geometry suggests that the alkynic group is largely σ-bonded to one aluminum and π-bonded to the other. Warming above its melting point (145 °C) causes carbalumination of the bridging group and hydrolysis yields 1,1-diphenylethylene (equation 34). This interesting dimer takes on special significance in formulating mechanisms for the reaction of organoaluminum compounds with alkynes. Just as the foregoing equilibrium studies show that three-coordinate aluminum can complex with alkenes, structure (**38**) shows that similar complexation can take place with a $C\equiv C$ linkage. Admittedly, such isolated complexes only demonstrate the likelihood of π-complexation between R_3Al and alkenes or alkynes. These findings alone do not permit one to say whether such complexes are preliminary, mechanistically unimportant intermediates (**40**) or whether they are high-energy intermediates (**41**) similar in configuration to the transition state (**42**)for carbalumination (Figure 1). Nevertheless, just as the isolation of stable carbenium ion salts such as $PhC^+BF_4^-$ makes one more confident in postulating high-energy, unisolable carbenium ions, so such studies on π-complexes serve a similar purpose in organoaluminum mechanisms.



(34)

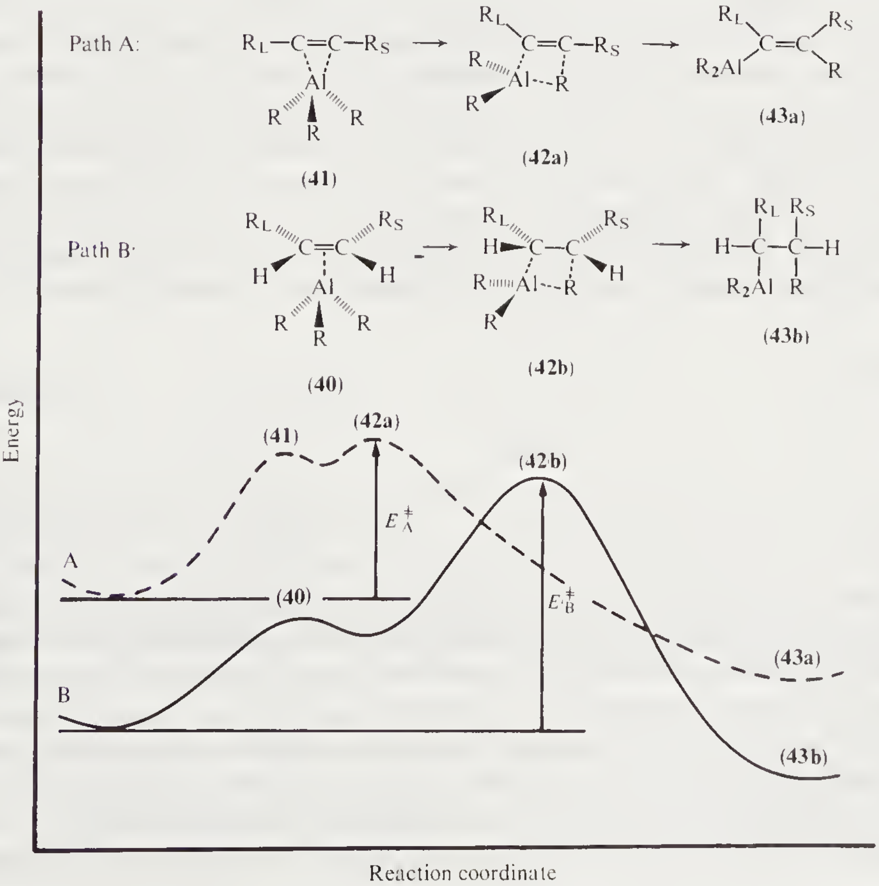
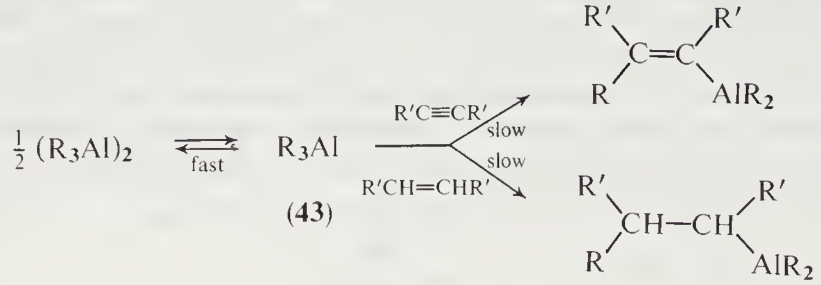


Figure 1 Suggested energy profiles for the carbalumination of alkynes (path A) and alkenes (path B). A similar comparison can be made for the hydralumination of these hydrocarbon types

Kinetic studies of the reactions of R_3Al or R_2AlH compounds with alkenes and alkynes give further insight into the nature of the transition state of such additions. In both carbalumination (equation 35) and hydralumination (equation 36) the rate laws show first order dependence on the hydrocarbon and a fractional order dependence on the aluminum reagent. With dimeric R_3Al in hydrocarbon medium such dependence is essentially one-half order;[3b,69] with trimeric R_2AlH it is one-third order.[45,61] These relationships indicate that the hydrocarbon and the monomeric aluminum reagent are involved in the rate-determining step. Furthermore, solvent studies demonstrate that such monomeric intermediates (**43**) and (**44**) must be unsolvated for maximum ease of addition to carbon–carbon unsaturation. Addition of stoichiometric amounts of Lewis bases, such as tertiary amines or ether[3,53] (*cf.* Section 6.1.1), markedly retards both carbalumination and hydralumination. The combined findings suggest that both processes involve an electrophilic attack by three-coordinate aluminum on the π-electron cloud of the hydrocarbon substrate.



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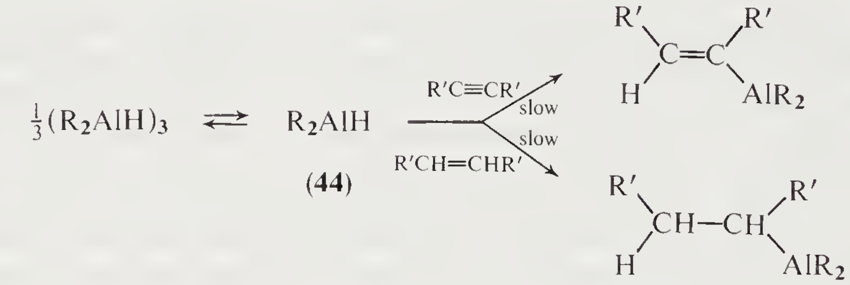
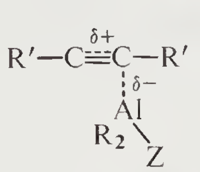
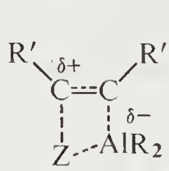


(36)

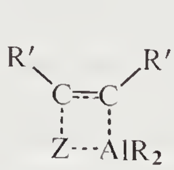
With reference to Figure 1 then, does the transition state for such attack resemble (**40**), a simple π-complex of the type detected in equilibrated systems (*cf.* (**37**) and (**38**)), or has considerable structural distortion occurred to yield a high-energy intermediate (**41**) which may resemble a σ-complex? Moreover, if one recalls the tendency of aluminum centers to form electron-deficient alkyl- and hydride-bridges (*cf.* (**3**)), then a compromise structure between the extremes of (**40**) and (**41**) would be (**45**). The incipient bridging of Z between two electropositive centers would resemble electron-deficient bonding. The greater progress in the new aluminum–carbon bonding than that of the Z—C bonding would avoid the objections that a completely concerted, four-center transition state (**45a**) would encounter from orbital symmetry considerations.[70]



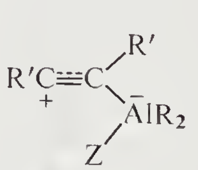
(**40a**)



(**45**)



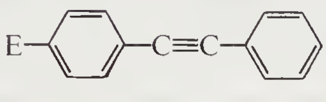
(**45a**)



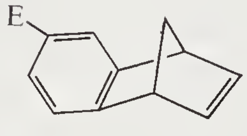
(**41**)

Evidence permitting a choice among transition state models (**40**), (**41**) and (**45**) for carbalumination and hydralumination can be gathered from studies of relative reactivity, stereochemistry and regiochemistry. Each transition state model has certain implicit electronic and steric consequences. Model (**41**) should show the greatest charge separation and hence substituents R′ should have a great electronic influence on ease of reaction, as might be evident from Hammett σ,ρ-relationships. Model (**45**) also has charge separation, but much less than (**41**). Here, the stretching of the Al—Z bond might be manifested by isotope effects, the bending back of the R′ groups, and B-strain. Finally, model (**40**) implies small charge separation, no B-strain, but perhaps some F-strain.

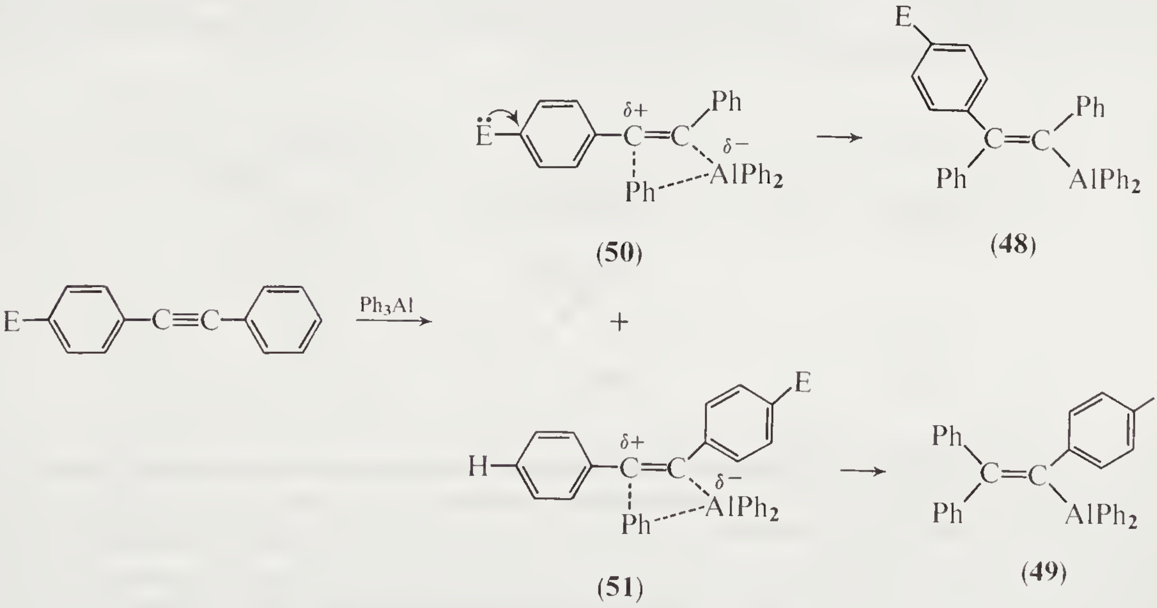
In the carbalumination of alkenes and alkynes with either triethylaluminum[71,72] or triphenylaluminum,[3b,73–75] addition occurs exclusively in a *syn* manner. This stereochemistry is consistent with all three models, (**40**), (**41**) and (**45**). By measuring the rate of carbalumination shown by suitably substituted diphenylacetylenes (**46**)[3b] and benzonorbornadienes (**47**),[74] electronic factors could be evaluated separately from steric factors. In the absence of kinetic complexities due to Lewis basic substituents E (*e.g.* MeO or M$_2$N; *cf. supra*), electron donating substituents (E = Me) accelerate and electron withdrawing substituents retard the addition of Ph_3Al. Moreover, for (**46**) the ratio of regioisomers formed, (**48**) and (**49**), was determined in order to measure the directing influence of the substituents (E = Me_2N, MeO, MeS, Me, Cl, CF_3, $MeSO_2$) (equation 37). The alkynes bearing CF_3 and $MeSO_2$ groups were too unreactive to yield adducts of the type (**48**) and (**49**). For the rest, the ratio of the hydrolyzed products from (**48**) and (**49**) was plotted as their logarithm *versus* Hammett σ-values of the substituents E. A linear correlation having a slope (ρ-value) of -0.713 was thereby observed. A much less satisfactory correlation was obtained when a plot of log (**48**)/(**49**) *versus* Hammett–Brown σ^+-values was attempted. The failure of the product ratio to correlate with σ^+-values and the relatively small absolute value of ρ observed with σ-values both indicate that there is not large charge separation in the transition state. This finding argues against model (**41**). On the other hand, the rate of carbalumination and the small but significant negative ρ show that the *para* electron-donating E groups (Me_2N, MeO, MeS and Me) support the development of some positive charge in the transition state (**50**) of lower energy than (**51**). Model (**45**), accordingly, seems more acceptable than the π-complex model (**40**).



(**46**)

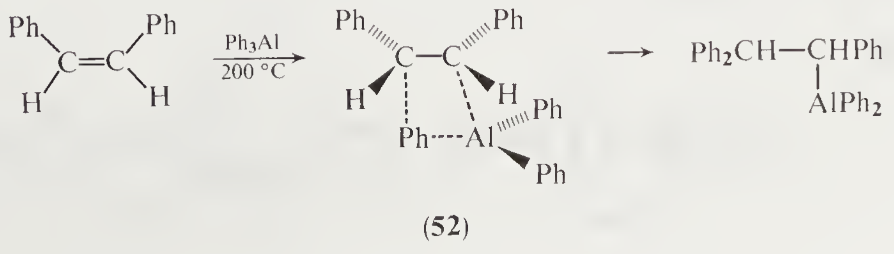


(**47**)



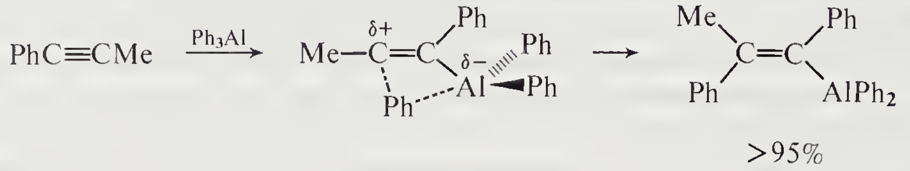
(37)

Although similar considerations seem applicable to the carbalumination of alkenes, it should be noted that generally alkenes are distinctly less reactive than the corresponding alkynes.[73,75] Such relative reactivity would seem anomalous, since alkenes are usually more reactive towards electrophilic agents than alkynes.[76] The reversal with aluminum reagents may stem from the highly ordered transition state (**45**), which for alkenes leads to considerably more F-strain (**52**) than with alkynes (equation 38). Such F-strain is evident even with alkynes and can lead to an almost



(38)

complete reversal of regioselectivity (equations 39 and 40).[77,78] Since the *t*-butyl and methyl groups should exert similar electronic influences, the direction of addition is clearly determined by the F-strain between the bridging phenyl group and the substituent on the alkynic carbon.



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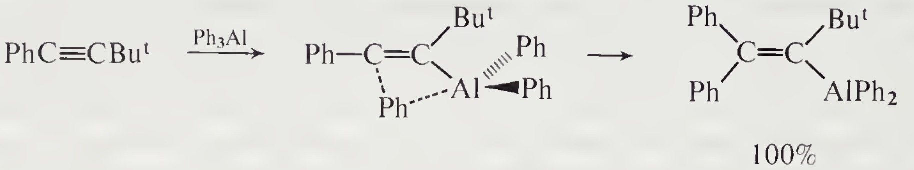
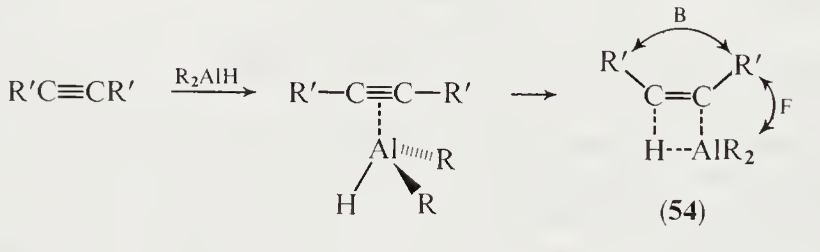


(40)

Evidence gathered from hydralumination studies points to a somewhat different transition state model. If model (**45**) were to obtain, there should be significant stretching of the aluminum–hydrogen bond in this configuration. Yet the observed kinetic isotope effect for hydralumination by *i*-Bu_2AlH (or D) of alkynes is about 1.7.[61] Such a value cannot be considered a primary isotope effect and thus is not consistent with the bridging involved in (**45**). Evidence on the relative reactivity of alkynes is also pertinent: di-*t*-butylacetylene is some 20 times more reactive than di-*n*-butylacetylene at 35 °C.[79] If much change in the alkyne's configuration were to have occurred in the transition state (**54**), the *t*-butyl substituents would have been expected to exert larger rate-retarding F- and B-strain repulsions. However, in an earlier, π-complex-like transition state (**53**), the F- and B-strain contributions could be minimized, yet the greater electron-release of the *t*-butyl group ($\sigma^* = -0.300$) over the *n*-butyl group ($\sigma^* = 0.130$) could still be exerted in enhancing the observed reactivity (equation 41).

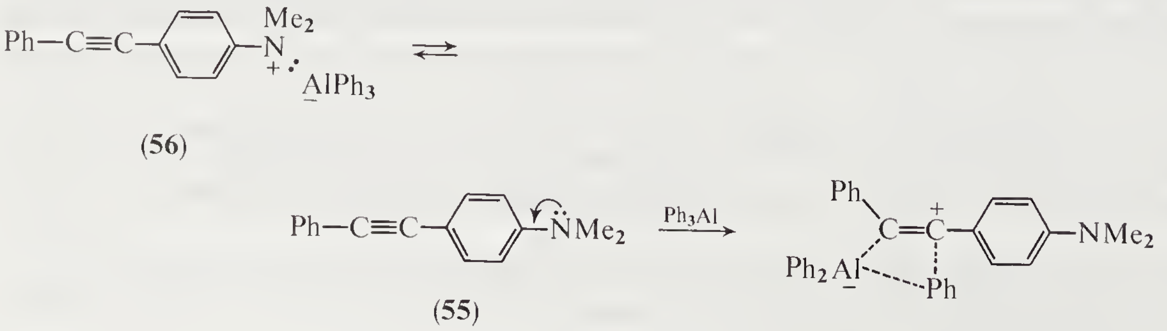


(53)

(54)

(41)

With unsaturated organic substrates bearing unshared electron pairs such as ketones and nitriles, preliminary complexation of the organoaluminum reagent at the Lewis basic site will occur (*cf.* structure (**34**) in equation 31). However, the aluminum–carbon bond in such a complex can exhibit either an enhanced or diminished reactivity. If the coordination in the substrate is not electronically conjugated with or near the final site of reaction, the complexation will simply retard the reaction. In the carbalumination of substituted diphenylacetylenes discussed above (equation 37) for example, the *p*-dimethylamino derivative (**55**) undergoes reaction more slowly than the parent diphenylacetylene because complexation ties up the necessary Ph_3Al monomer (**56**) and simultaneously deactivates the C≡C linkage to electrophilic attack (equation 42).[3b]

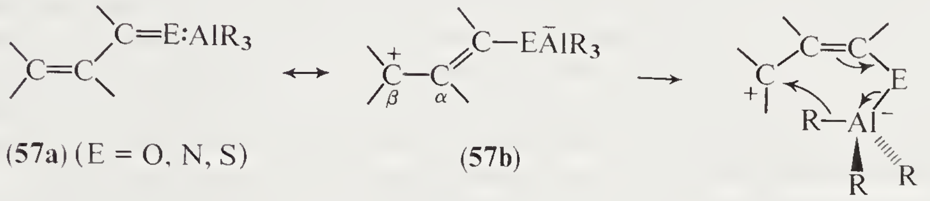


(56)

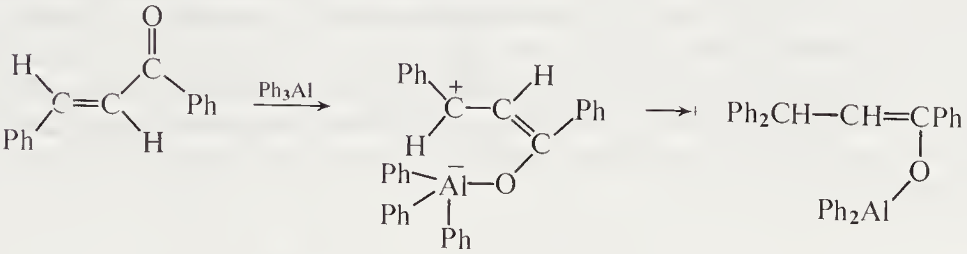
(55)

(42)

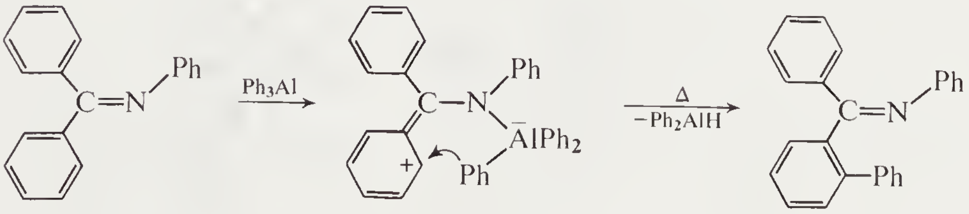
On the other hand, if preliminary coordination brings the carbon–aluminum bond into proximity with the reaction site in the substrate, the reaction rate will be accelerated. Especially favorable for reaction is coordination that brings both reacting centers together and exerts an electronic polarization suitable for reaction. A prominent instance of this situation is the 1,4-addition of organoaluminum reagents to α,β-unsaturated carbonyl substrates and related systems. Coordination at the heteroatom not only makes the β-carbon atom accessible to the carbon–aluminum bond (through a six-membered transition state (**58**)), but induces electronic shifts that make the β-carbon electrophilic and the migrating organic group on aluminum nucleophilic (**57**) (equation 43). Illustrative of such 1,4-carbaluminations are the reactions of benzalacetophenone[80] (equation 44) and of benzophenone anil[81] (equation 45) with triphenylaluminum. These conjugate additions can be viewed as proceeding in a concerted fashion, with electronic reorganization similar to that of a thermally allowed [3,3]-sigmatropic rearrangement.[58] Two reservations should be made explicit, however: (1) before anchimeric assistance such as that depicted in (**58**) is given complete credence, appropriate kinetic measurements should be made to ensure that reaction occurs by an intramolecular reorganization of the suggested complex; and (2) since (**58**) requires that (**57**) be able to adopt a *cisoid* conformation, α,β-unsaturated cyclic ketones should be unable to react by way of (**58**) and would then pursue another pathway.[82] Indeed, evidence has been adduced that such cyclic ketones react with aluminum alkyls principally under the agency of free radical promotion.[83,84]



(**57a**) (E = O, N, S) (**57b**) (**58**) (43)

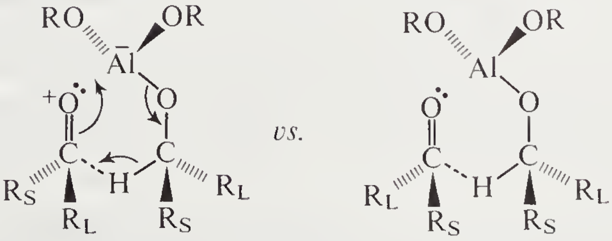


(44)



(45)

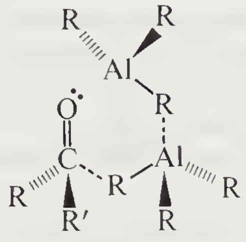
The importance of coordination is evident in many of the alkylation, reduction and enol salt formation processes of carbonyl compounds. Many studies have been performed on the reduction of achiral ketones with optically active aluminum alkoxides or the reduction of chiral ketones by aluminum isopropoxide. The asymmetric induction observed in these reactions is considered to stem from preference for the lower energy transition state (**59**) in a six-membered coordinated complex.[85-87] The buttressing repulsion of the larger groups (R_L) in (**60**) is minimized in (**59**) by pairing them with smaller groups (R_S). Thus, in (**59**) the hydridic hydrogen is brought closer



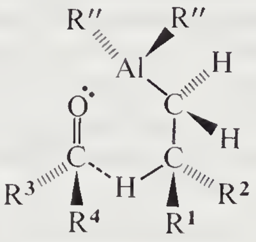
(**59**) (**60**)

to the carbonyl group and the coordination at aluminum establishes the appropriate polarity for hydride transfer.

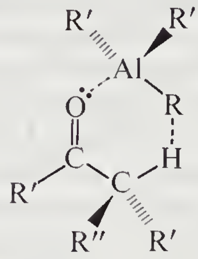
Similar coordination is also pivotal in the reaction of ordinary carbonyl compounds with organoaluminum reagents (*cf.* equation 43). In this case, three reactions are competitive: (1) alkyl transfer from aluminum to carbon (**61**); (2) hydride transfer (**62**), analogous to the Meerwein–Ponndorf–Verley reduction shown in (**59**), for aluminum alkyls having β-hydrogens; and (3) enol salt formation for carbonyl substrates having α-hydrogens on sp^3-hybridized carbon (**63**).



(**61**)



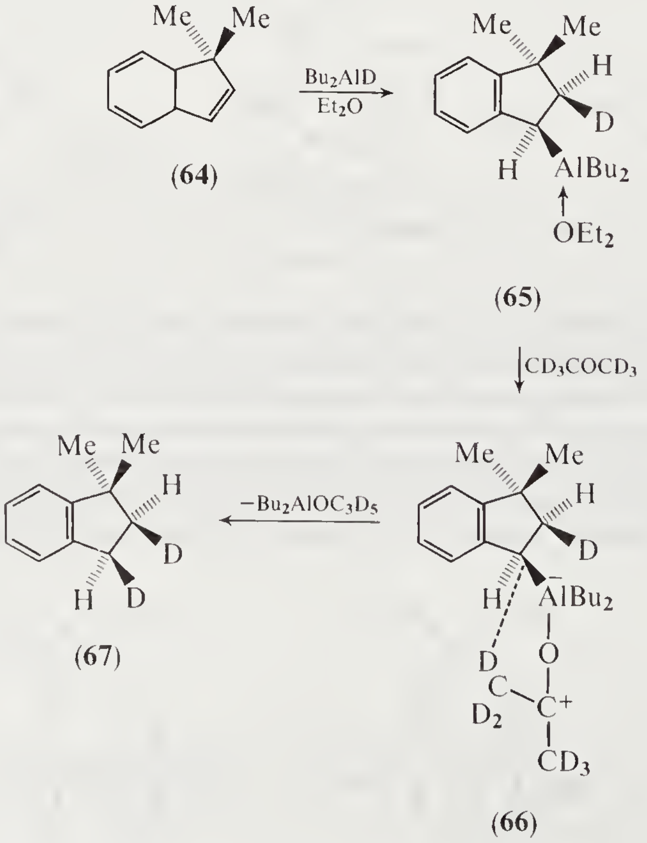
(**62**)



(**63**)

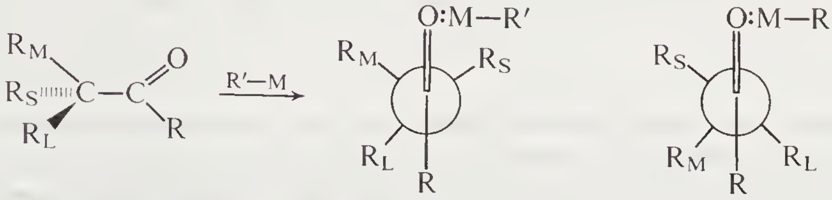
Evidence for a transition state of type (**61**) consists in the detection of complexes between benzophenone and organoaluminum compounds[65,88] and the kinetic rate law observed in hydrocarbon solution at ratios of ketone to R_3Al of 1 : >1.[89,90] Support for transition state (**62**) rests on the use of optically active aluminum compounds ($R'' = CH_2CH(Me)(Et)$ to obtain an enantio-differentiating reduction of phenyl ketones, PhCOR.[91,92] Although optical yields of only 7–13% were obtained with R = Me, Et or Pr, the isobutyl and *t*-butyl ketones gave optical yields of 30–45%. By use of steric arguments analogous to those invoked for (**59**) and (**60**) these findings can be explained satisfactorily in terms of cyclic transition states of type (**62**).

Finally, stereochemical evidence in favor of a cyclic transition state (**63**) for enol salt formation has been gained by the interaction of the racemic indanylaluminum etherate (**65**) (obtained from 1,1-dimethylindene (**64**) and diisobutylaluminum deuteride in the presence of diethyl ether) with acetone-d_6. Insignificant addition of the aluminum reagent to the carbonyl group occurs; instead, the acetone is converted into its enol salt and (**65**) was stereoselectively converted into *cis*-2,3-dideuterio-1,1-dimethylindan (**67**). Cleavage of the indanylaluminum bond with retention of configuration at carbon is best in accord with the coordinated complex transition state shown in (**66**) (Scheme 3).[93]

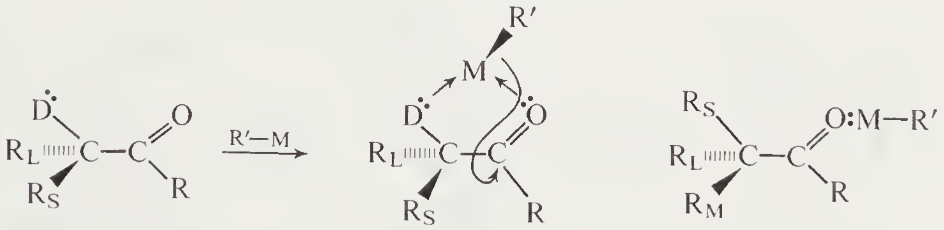


Scheme 3

Before taking up a discussion of other carbonyl reactions, one should recall the considerable body of results obtained from studies of additions to aldehydic and ketonic carbonyl groups directly bonded to chiral carbon centers. From a study of the diastereodifferentiation obtained by additions of RMgX, RLi and LAH to substrates of types (**68**) and (**71**), Cram and coworkers have formulated predictive models[94] that assume complexation of the metal reagent at the carbonyl oxygen (**69**)[95] or complexation both at the carbonyl oxygen and an adjacent Lewis basic center (**72**).[96] The difficulties encountered in rationalizing the diastereomeric product ratios have led Karabatsos to reformulate the first model in terms of (**70**).[97] The arguments in favor of transition state (**70**) are that the preferred conformation of the carbonyl substrate should have the smallest group (R_S) eclipsing the carbonyl oxygen, whether or not R′—M is coordinated ((**73**), where complexed R′—M is directed away from R_S); that such addition reactions are highly exothermic and hence, by Hammond's postulate, should have reactant-like transition states; and that such exothermic reactions should, by the Hammett–Curtin principle,[98] lead to diastereomeric product ratios determined solely by the free energy difference ($\Delta\Delta G^{\ddagger}$) between the two transition states leading to the products; and finally, that the transition state permitting R′ to approach the carbonyl carbon from the flank bearing R_M will have the smaller $\Delta G^{\ddagger}$. By making estimates of the pertinent *gauche* and eclipsed interactions, calculated $\Delta\Delta G^{\ddagger}$ values for the reaction of (**70**) and its diastereomeric transition state were obtained that are in quite good agreement with experimental values.



(**68**) (**69**) (**70**) (46)

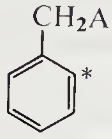


(**71**) (**72**) (**73**) (47)

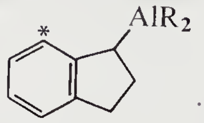
For chiral compounds having donor sites (**71**) (D = OH, NH_2) the chelating transition state (**72**) originally proposed by Cram is confirmed by Karabatsos as being the source of the unusually high diastereomeric product ratios (*e.g.* (**71**), where for R_S = H, R_L = Me, D = NH_2, R = Ph and R′M = *p*-tolylmagnesium bromide, a ratio of 50:1 is obtained).[99]

It should be noted that, in contrast with the Cram models (**69**) and (**72**), the Karabatsos model (**70**) and his interpretation of the chelate ring (**72**) do not require or specify that the R′ group added to the carbonyl be the one originally attached to the coordinated R′—M. In other words, such reactions need not be intramolecular; a second R′—M could attack complex (**70**) or (**72**) (*cf.* (**61**)). Careful kinetic studies will be required before the exact nature of such transition states can be formulated.

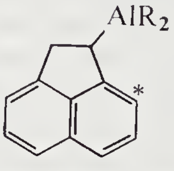
A class of carbonyl reactions of exceptional importance to the question of coordinative assistance is that involving allylic or benzylic aluminum reagents. Reaction of such compounds with carbon dioxide gives exclusively the rearranged carboxylic acid. Structures (**74**–**76**) undergo carbonation with the introduction of the carboxyl group at the asterisked carbon (*cf.* equation 26).[57,58] The locoselectivity (*i.e.* at the allylic terminus) of the carbonation can be best explained by coordination of CO_2 at aluminum (**77**) with the development of fostering polarization (*cf.* (**57**)).



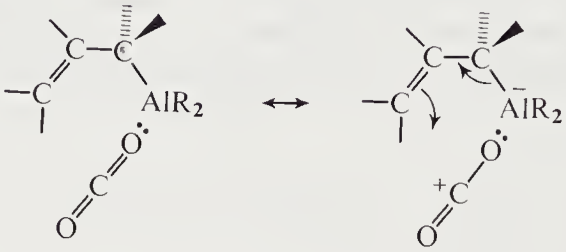
(**74**)



(**75**)

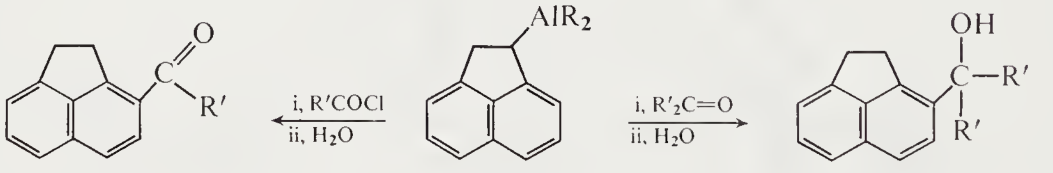


(**76**)

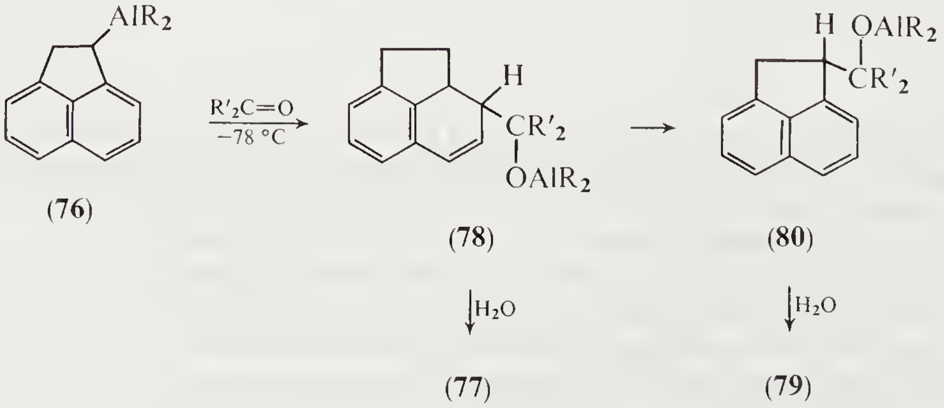


(**77a**) (**77b**)

In a similar fashion, acyl chlorides and ketones react with acenaphthenyl(dialkyl)aluminum (**76**) at −78°C to yield rearranged products, the 3-substituted acenaphthenes (equation 48).[93] The behavior of (**76**) toward ketones, however, is strikingly temperature dependent: when the reaction is conducted at 25 °C, the product is principally the 1-acenaphthenylcarbinol (**79**). This observation demonstrates that the 3-substituted adduct (**78**) is the kinetically controlled product, while the 1-substituted adduct (**80**) is more stable (equation 49).



(**76**) (**77**) (48)

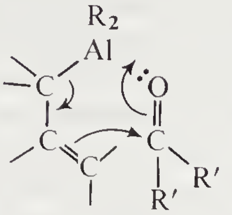


(**76**) (**78**) (**80**) (49)

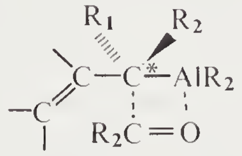
(**77**) (**79**)

The important conclusion that can be drawn from these results, and which may have some generality, is that the kinetic preference for forming (**78**) over (**80**) may stem from the lower $\Delta G^{\ddagger}$

for attaining a six-membered transition state (**81**), compared with a four-membered one (**82**).[58] Configuration (**81**) may be of lower energy because it resembles that for a thermally allowed ($\sigma_s^2 + \sigma_s^2 + \pi_s^2$) process; conversely, structure (**82**) resembles that of a thermally disallowed ($\sigma_s^2 + \pi_s^2$) process.

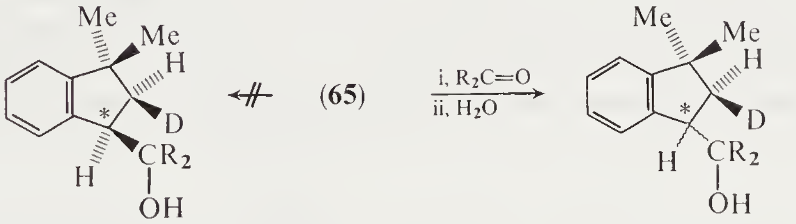


(**81**)



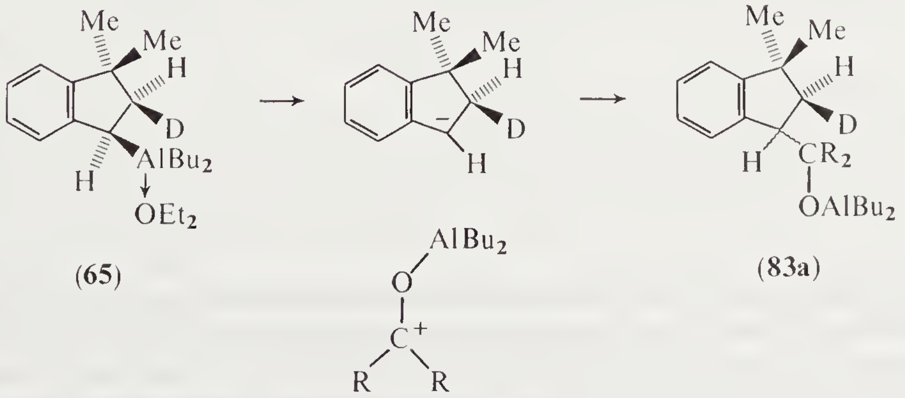
(**82**)

Indeed, in keeping with the disallowed character of a four-centered transition state (with synchronous bond making and bond breaking) is the stereoselectivity of carbonyl insertions into chiral carbon–aluminum bonds. The concerted reaction depicted in (**82**) implies that the configuration at the chiral carbon (*) should be retained in the resulting adduct. When in fact the indanylaluminum compound of known configuration (**65**) is allowed to react with 9-fluorenone, the resulting adduct (**83**) undergoes a complete epimerization (loss) of configuration at the chiral atom (*). Retention of configuration (**84**) was not observed (equation 50).[93] Although the mechanism of configurational loss cannot be discerned with confidence, clearly the indanyl and Bu_2Al fragments must separate first to allow configurational loss, before collapsing to the adduct. Thus, by definition the reaction must be multistep, and not concerted. A possible polar pathway is suggested in equation (51).



(**84**) (**83**)

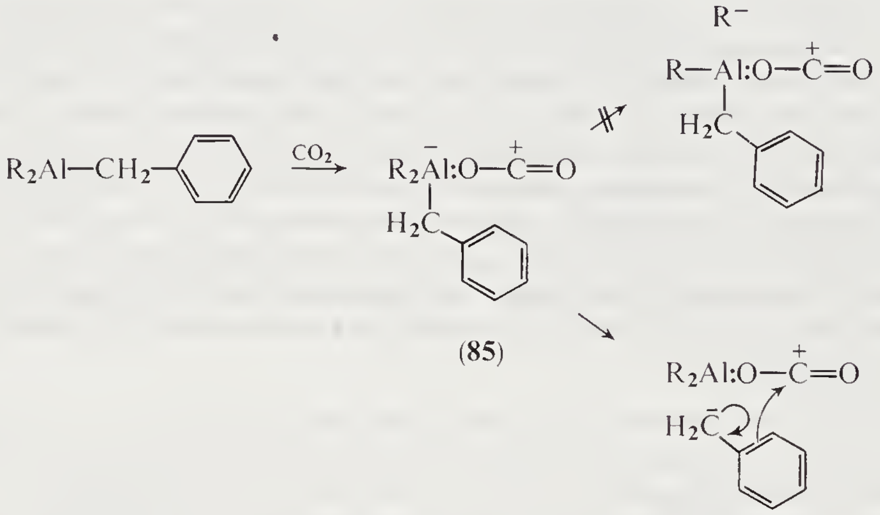
(50)



(**65**) (**83a**)

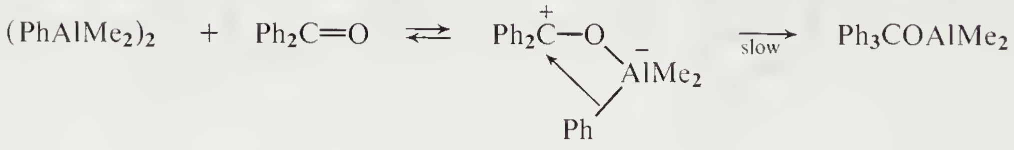
(51)

Not only can preliminary coordination help determine the site of reaction on the carbonyl substrate (1,2- *vs.* 1,4-addition: (**61**) *vs.* (**58**)) or on the aluminum reagents (allyl attack: (**81**) *vs.* (**82**)), but it also helps to explain which group on unsymmetrical reagents $RAlR'_2$ will react preferentially. As Wittig first recognized, complexes between carbonyl derivatives and R_3Al are forms of 'ate' complexes ((**34**) and (**57**)) in which the groups on aluminum are 'loosened anionically'[100] by the build-up of electron density. Hence, that R group on aluminum better able to sustain negative charge will tend to be the more reactive (equation 52). For this reason allylic and benzylic groups (**85**) are more reactive than alkyl groups (*cf.* equations 26, 48 and 52). Similarly, in competitions between alkyl and aryl or vinyl groups in R_2AlAr, the fostering polarization of the 'ate' complex (**86**) not only loosens the more electronegative aryl group anionically, but develops an electrophilic carbonyl carbon. Thus, in the reaction of benzophenone with dimethyl(phenyl)aluminum (a dimer with phenyl bridges),[101] exclusive phenyl–aluminum bond insertion occurs.[102] This specificity can be understood in terms of electrophilic attack by the polarized carbonyl carbon on the π-electron cloud of the phenyl group (assuming (**86**) is involved in the rate determining step (equation 53)). Such selective reactions are reminiscent of Wagner–Meerwein carbenium rearrangements, whereby a 1,2-shift of a phenyl group is also favored over a methyl migration. In a further instance involving an alkyl–vinylic group competition, diisobutyl[(*E*)-stilbenyl]aluminum (**87**) reacts preferentially with CO_2 to give a high yield of the corresponding α-phenylcinnamic acid (equation 54).[103]



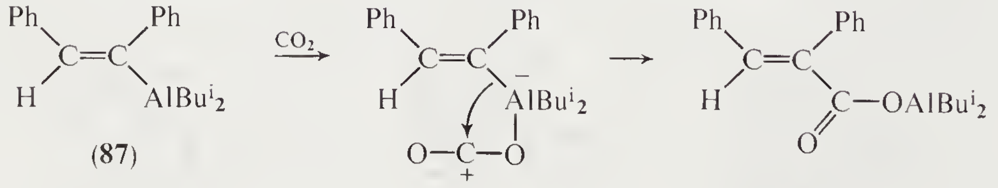
(**85**)

(52)



(**86**)

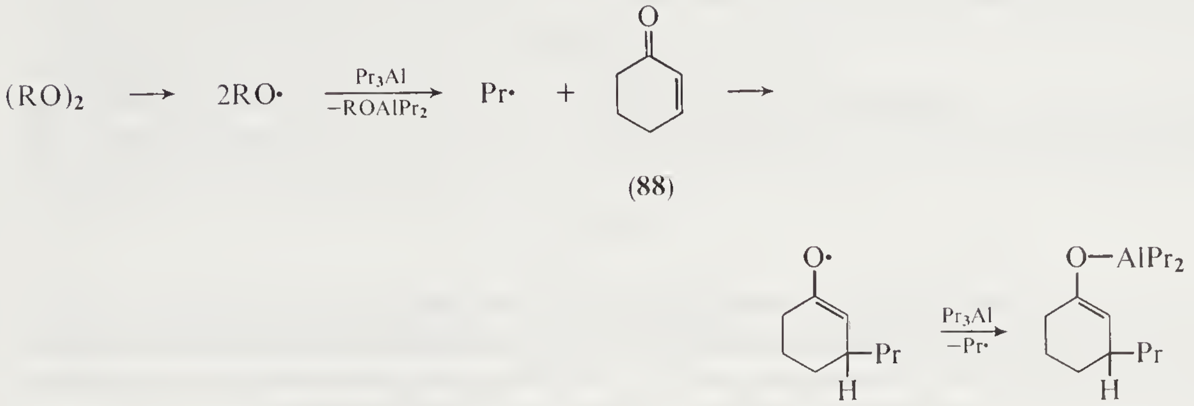
(53)



(**87**)

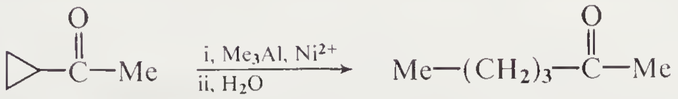
(54)

In all the foregoing reactions of organoaluminum compounds, evidence is adduced for mechanisms proceeding by way of complexation and heterolysis of the C—Al bond. There are also indications that homolytic processes and radical intermediates are important in organoaluminum chemistry. Since the average C—Al bond energy estimated for trimethylaluminum is 273 kJ mol^{-1},[104] such a linkage is moderately resistant to thermal homolysis. In fact, with higher R_3Al types, thermal decomposition usually proceeds by way of dissociation to alkene and R_2AlH (equation 22). However, a number of induced homolyses have been reported for aluminum reactants. As mentioned above (equation 43), concerted 1,4-additions to α,β-unsaturated carbonyl compounds require a *cisoid* configuration. In the case of carbonyl substrates locked in a *transoid* configuration, such as 2-cyclohexenone (**88**), unpromoted alkylation is slow. Yet the 1,4-addition of tri-*n*-propyaluminum is facile, even at −78 °C, if promoted by traces of oxygen or ultraviolet light. Since the presence of the stable galvinoxyl radical inhibits the reaction, a free radical chain mechanism seems to be operative (equation 55).[84] Similarly, catalytic amounts of nickel acetylacetonate accelerate the addition of trimethylaluminum to such α,β-unsaturated ketones, as well as to cyclopropyl ketones (equation 56).[105]



(88)

(55)



(56)

Alkylation of the nickel salt to yield labile Me_2Ni and the decomposition of the latter (Me· + MeNi·) would initiate a free radical chain.

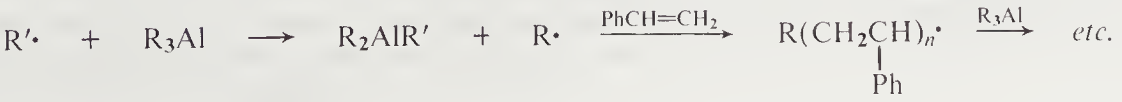
Radical processes are also likely in the reaction of aluminum compounds with oxygen, peroxides or polyhaloalkanes. That all these reactions can occur explosively may indicate the possibility of a free radical chain reaction. The oxygenation of the lower aluminum alkyls occurs with such rapidity that kinetic studies have had to concentrate on the oxidation of the last, less reactive C—Al bond in $RAl(OR)_2$. Oxidation of this compound is retarded by galvinoxyl and hence this step, at least, involves a free radical chain.[106] In this and the preceding steps aluminum peroxides (**90**) are the probable intermediates (equation 57). Just as (**89**) is oxidized by (**90**), so aluminum alkyls or aryls can be oxidized by various diacyl peroxides[107] and dialkyl peroxides[108] Such studies have uncovered evidence that alkyl radicals are generated by the chain transfer step shown in equation (58).[109]

$$\underset{(\mathbf{89})}{R{-}Al(OR)_2} \xrightarrow{O_2} \underset{(\mathbf{90})}{R{-}O{-}O{-}Al(OR)_2} \xrightarrow{RAl(OR)_2} (RO)_3Al \qquad (57)$$

$$RO\cdot + R'_3Al \longrightarrow RO{-}AlR'_2 + R'\cdot \qquad (58)$$

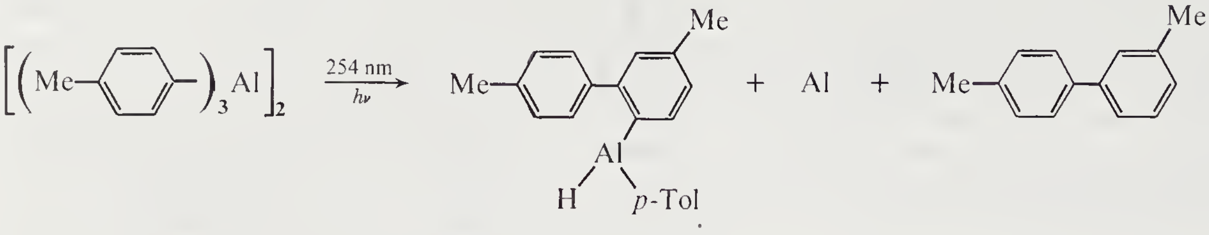
The violent reaction that can occur between aluminum alkyls and carbon tetrachloride seems to involve free radicals, since mixtures of triethylaluminum etherates and this halide initiate the polymerization of vinyl chloride in a free radical manner.[110] The products formed in a controlled reaction are the lower chlorides ($CHCl_3$, CH_2Cl_2 and CH_3Cl), ethyl chloride, ethane, ethylene and C_4 and C_6 hydrocarbons.[111]

It is noteworthy that in the free radical polymerization of styrene, organoaluminum compounds exhibit unusually large chain transfer constants with styryl radicals. While the sizes of the transfer constant at 100 °C are 0.67×10^{-4} and 90×10^{-4} for ethylbenzene and carbon tetrachloride, respectively, those of triethylaluminum and triisobutylaluminum are 17 and 28.5. Since the highly efficient *n*-butanethiol has a value of 22, organoaluminum compounds are among the strongest chain transfer agents known. The nature of the transfer step is concluded to be the generation of an alkyl radical (*cf.* equation 58).[112]



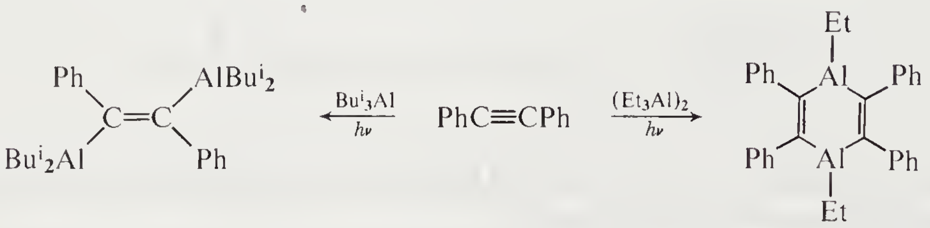
$$R'\cdot + R_3Al \longrightarrow R_2AlR' + R\cdot \xrightarrow{PhCH{=}CH_2} R(CH_2\underset{\substack{|\\ Ph}}{CH})_n\cdot \xrightarrow{R_3Al} etc. \qquad (59)$$

Although free radicals are not easily generated by thermal treatment of R_3Al systems, a number of photochemical reactions could involve homolysis of carbon–aluminum bonds. The unusual rearrangement and decomposition of dimeric aluminum aryls in toluene solution seems to involve efficient radical recombination in the solvent cage, since little radical attack on the solvent is observed (equation 60).[113,114]



(60)

Irradiation of diphenylacetylene in the presence of dimeric triethylaluminum yields a heterocyclic ring (equation 61); a similar irradiation in the presence of monomeric triisobutylaluminum yields the open chain *trans* adduct (equation 61).[115,116] The ethyl groups eliminated in equation (61) are converted into a mixture of ethylene, ethane, butane and hydrogen.



(61)

Many reactions of organoaluminum compounds with active metals such as the electrolysis of organoaluminum complexes and the dehalogenation of alkylaluminum sesquihalides (equation 11) undoubtedly also involve radicals, as will be discussed subsequently.

6.1.6 Industrial Significance

That aluminum organometallic compounds have attained large-scale production and widespread application testifies to their great industrial value, despite the difficulties caused by their air and moisture sensitivity. Many of the commercially important processes are refinements of prototypical reactions discovered and explored by Ziegler. The broadest and most versatile of these is the Ziegler–Natta coordination polymerization process, in which an aluminum alkyl or alkyaluminum halide is combined with a transition metal salt to give catalysts capable of polymerizing ethylene, α-alkenes and 1,3-dienes at low pressures and temperatures in a stereoregular manner.[117] In addition, aluminum alkyls, either alone or with cocatalysts, can produce polyethers from epoxides,[118] aldehydes[119] or vinyl ethers.[120]

A second principal process is the reaction of triethylaluminum with ethylene at 120 °C under a pressure of 100 atm to yield long chain (C_4–C_{30}) trialkylaluminum derivatives ('growth reaction'). These aluminum compounds can either be air oxidized and hydrolyzed to yield a mixture of straight chain alcohols (equation 6)[121,122] or treated with ethylene and a nickel catalyst to provide a mixture of α-alkenes ('displacement reaction', equation 7).[123,124]

A third general process is the preparation of organometallic compounds or organometalloids from aluminum alkyls. One can treat salts of zinc, boron, phosphorus, tin or lead, for example, with the appropriate aluminum reagent to obtain moderate to good yields of metal alkyls (equation 62).[125] Since all carbon–aluminum bonds do not react, the diethylaluminum chloride is recovered and sold as a Ziegler catalyst component.

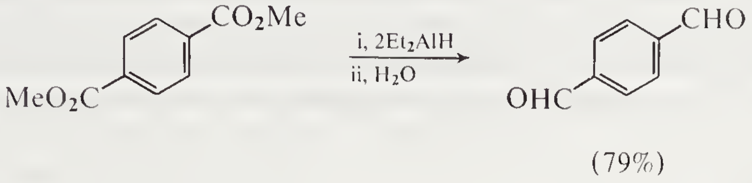
$$2Et_3Al \quad + \quad ZnCl_2 \quad \longrightarrow \quad Et_2Zn \quad + \quad 2Et_2AlCl \tag{62}$$

An alternative approach to lead alkyls is the electrolysis of alkali metal halide complexes of triethylaluminum and the collection of tetraethyllead in the anode compartment (equation 63).[126]

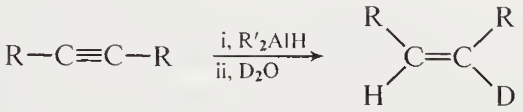
$$4Na^+[Et_3AlF]^- \quad + \quad 3Pb \quad \xrightarrow{\text{electrolysis}} \quad \underset{\text{(anode)}}{3Et_4Pb} \quad + \quad \underset{\text{(cathode)}}{4Al} \quad + \quad 4NaF \tag{63}$$

Fourthly, aluminum alkyls and hydrides have considerable potential in hydrocarbon technology. For example, ethylene can be catalytically dimerized to 1-butene with triethylaluminum and a nickel catalyst.[29] 2-Methyl-1-pentene, an intermediate in the preparation of isoprene for synthetic rubber production, can be prepared by heating propylene with triethylaluminum.[27] Alternatively, π-allylnickel halides and alkylaluminum halides, combined with phosphines, can dimerize propylene into varying ratios of 2-methylpentenes and 2,3-dimethylbutenes.[127] Internal alkenes can be isomerized to α-alkenes by heating with aluminum alkyls.[55]

Finally, organoaluminum reagents have certain attractive advantages for making specific kinds of carbon–carbon and carbon–hydrogen bonds of interest to fine chemical synthesis. Selective reductions of esters to aldehydes (equation 64)[128] and of alkynes to *cis*-alkenes (equation 65)[129] exemplify the controlled reductions attainable.



(64)



(65)

6.1.7 Proper Handling and Storage

Safe experimentation with organoaluminum compounds in the laboratory demands special apparatus, techniques and precautions. Although the essentials of proper procedure will be given in Section 6.8, it is well to have certain caveats in mind at the very beginning. In this way, the reader will appreciate the difficulties of physical measurements, the limitations of possible reactions and the dangers of certain mixtures of reagents.

The spontaneous flammability of many volatile aluminum compounds in air is their most spectacular characteristic. Accordingly, all transfers, storage, measurements and reactions must be done under an anhydrous atmosphere of pure nitrogen or argon. Organoaluminum reagents are excellent scavengers of oxygen, so in manipulating pure R_3Al types, all traces of oxygen must be removed beforehand. Note the following:

1. Work with small quantities of aluminum compounds and organic solvents at a time; set up the apparatus in an area away from flammable solvents;
2. Place the reaction apparatus in a shallow trough able to hold the contents of the ruptured reaction vessel; shield the operator from the apparatus with a transparent plastic screen;
3. Wear a face shield, and goggles, leather gloves and a heavy laboratory coat when working with such reagents to protect oneself from burns;
4. Avoid the presence of water baths and water in the reaction condenser (*cf. infra*); for cooling or warming of the reaction vessel, use cooled hydrocarbon circulated through the condenser or electrically heated oil baths;
5. In case of fire, spread dry sand or vermiculite over the burning mixture, or use a dry powder fire extinguisher designed for metal fires; to avoid unintentional use, extinguishers containing water or carbon tetrachloride should be absent from the work area; and
6. Admixture of aluminum compounds with potential oxidants (peroxides in solvents, metal oxides, polyhalogenated hydrocarbons, nitro compounds, *etc.*) should be avoided or investigated beforehand on a small scale.

The ease or, indeed, violence with which organoaluminum compounds hydrolyze constitutes an equally serious safety hazard. Therefore, the atmosphere and the solvents employed for the storage and reactions of organoaluminum compounds must be scrupulously anhydrous. In fact, in the most exacting work, all traces of active hydrogen compounds, such as phenols, alcohols, thiols, amines of the type RNH_2 and R_2NH and 1-alkynes should be removed from the reaction media. Especially important are the following points:

1. Intentional hydrolyses of organoaluminum reaction mixtures or residual reagents should be conducted in dilute hydrocarbon solution (toluene, xylene or alkane) with efficient stirring and cooling (oil bath, not water bath). Either gradual addition of water droplets or of a higher alcohol should be performed;

2. All accidental sources of water (tubings, drains, cooling water) should be kept distant from reaction and storage areas for organometallic compounds. Vessels and tubes used for transfers should be promptly rinsed after use. If not, residual alkylaluminum compounds may be occluded in pockets by air oxidation. Subsequent hydrolysis may then occur initially slowly and thereafter violently.

Pressure build-up or explosions of organoaluminum reaction or storage vessels can spew the contents out into the atmosphere. Storage vessels should be kept in Schlenk flasks which are set in metal trays or cans having a bed of vermiculite. Storage should be in a cool, dark place away from water and combustibles. Pressure or heat build-up can occur in the following cases, which are particularly hazardous:

1. samples of aluminum hydride or alkylaluminum hydride;
2. mixtures of aluminum reagents and halogenated hydrocarbons (*danger*);
3. active metals (Na, K, Al, *etc.*) and halogenated hydrocarbons or R_nAlX_{3-n}.

A number of commercial suppliers of organometallic aluminum compounds publish brochures describing proper safety and manipulating procedures for transferring these reagents.[130]

6.1.8 Nomenclature

As with other organometallic compounds, those of aluminum can be named by systems derived either from organic chemistry (A) or coordination chemistry (B). In general, the former system is simpler and more suitable for common derivatives not requiring much structural specification. The latter system permits specification of molecular association, solvation and bridging of ligands. In the following paragraphs, the nomenclature rules applicable to various types of aluminum compounds for systems (A) and (B) will be stated and illustrated.

Compounds composed of individual aluminum atoms bonded to the carbon atoms of one or more organic groups and/or to one or more hydrogen atoms are named, in system (A), by citing such groups or hydrogen atoms in alphabetical order, followed by the word 'aluminum'. No space is put between the group names and the word 'aluminum'. The hydrogen attached to the aluminum must be designated by the prefix 'hydrido'. The number of identical groups is indicated by prefixes di, tri, tetra or penta, or by the prefixes bis, tris, tetrakis or pentakis, for complex groups. Thus:

trimethylaluminum	$[Me_3Al]_2$
hydrido(diisobutyl)aluminum	$[Bu^i_2AlH]_3$
ethyl(methyl)phenylaluminum	$[EtMePhAl]_2$
tris(trimethylsilyl)aluminum	$(Me_3Si)_3Al$

In system (B) all groups attached to the central aluminum atom, whether organic, hydrogen, anionic or neutral groups, are listed as prefixes alphabetically, with the foregoing numerical prefixes being used to indicate the number of identical groups. Structure can further be designated as to the following: (1) when a continuous array of atoms in an organic group are bonded to aluminum, the prefix η (read as 'eta' or 'hapto') is used, which can be preceded by arabic numbers indicating the first and last such bonded atoms; and (2) groups bridging between two aluminum atoms are given a prefix of μ. Thus:

di-μ-methyl(tetramethyl)dialuminum (**3**)
butyl(diphenyl)pyridinealuminum $BuPh_2Al{\cdot}NC_5H_5$
1-3-η-cyclopentadienyl(dimethyl)aluminum (**91a**)

(**91a**)

Alternating parentheses are useful in separating a series of different substituents in both systems.

Anionic substituted compounds are named in system (A) by giving the names and numbers of organic groups as prefixes (*cf. supra*), then the word 'aluminum', and finally the anions with endings of 'ide'. In this convention Al—H groupings are considered as anions. The names of radicals and anions are cited, each in alphabetical order. Thus:

phenylaluminum bromide chloride	$PhAl(Br)Cl$
di-*s*-butylaluminum hydride	$\{CH_3CH_2C(Me)H\}_2AlH$
ethyl(phenylethynyl)aluminum ethoxide	$Et(PhC{\equiv}C)AlOEt$

Alternatively, the foregoing compounds can be named as coordination compounds, *i.e.* bromo(chloro)phenylaluminum, di-*s*-butyl(hydrido)aluminum and ethoxy(ethyl)phenylethynylaluminum.

Organoaluminum anions are named by citing all substituents on aluminum as prefixes (system B) and placing them before the root 'aluminate'. The oxidation number can be placed at the end as a Roman numeral (Stock), or the anionic charge can be indicated instead (Ewens–Bassett). Thus:

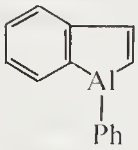
hydridotriphenylaluminate(III)	$[Ph_3AlH]^-$
triisobutyl(methyl)aluminate(1 −)	$[Bu^i_3AlMe]^-$

Alternatively, the first ion can be named under system (A) as triphenylaluminum hydride anion.

Heterocycles bearing aluminum in the ring can be named by replacement nomenclature (system C) or by the extended Hantzsch–Widman nomenclature (system D). In the former method, the name of the corresponding carbocycle is the root name and one or more carbon atoms are pictured as being replaced by aluminum or other heteroatoms. Such replacing atoms are given as prefixes ending in -a and are cited in a given 'seniority' order.[131] Thus:

1-ethyl-1-aluminacyclopentane (**91b**)
1-phenyl-1-aluminaindene (**92**)

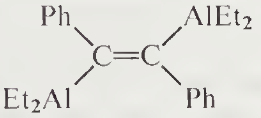
(**91b**)



(**92**)

In the Hantzsch–Widman system the stem 'alumin-' is suffixed with the endings -irene, -ete, -ole, -in, -epin, *etc.*, to designate three-, four-, five-, six- and seven-membered rings, respectively, which have the maximum unsaturation. Completely saturated rings of these corresponding sizes would be named as alumin-irane, -etane, -olane, -ane and -epane. Thus, the compounds (**91b**) and (**92**) would be named as 1-ethylaluminolane and 1-phenylbenzaluminole.

Organoaluminum compounds of a subvalent nature could be named with the oxidation state specified by the Stock convention (diphenylaluminum(II) being $Ph_2Al\cdot$). If one wishes to treat an aluminum-centered group as a substituent, one specifies the groups attached to aluminum as prefixes to the word, 'aluminio'. Thus, the groups Et_2Al and $ClPhAl$ are the diethylaluminio and the chloro(phenyl)aluminio groups; and compound (**93**) would be (*E*)-1,2-bis(diethylaluminio)-1,2-diphenylethene.



(93)

6.1.9 Organization of the Present Treatment

Since a considerable number of special and general reviews on organoaluminum chemistry have been published (refs. 723–742), this author does not strive to present just another detailed account of the structure, synthesis, properties and applications of these compounds. The plan is rather to offer a critical discussion of the present status of our knowledge, to point out important trends in the properties of these compounds and to apply current theory to understanding their structures and reactions. Specific information has been chosen from the literature to illustrate, rather than to exhaust, certain basic viewpoints. Where appropriate, physical and chemical data on individual aluminum compounds are presented in tabular form, so as to permit ready comparison and to reveal significant differences.

In this present section, the reader has been offered an overview of the development and principal aspects of these organoaluminum compounds. However, a rather detailed discussion of the reactivity patterns and possible reactive intermediates in this chemistry has been presented since this will serve as a foundation for many of the following considerations.

Instead of treating the properties of each class of aluminum compound separately (alkyls, hydrides, halides, *etc.*), the following sections treat the properties of all these compounds together under the sequence of these themes: gross molecular structure as mirrored in physical properties; structural changes of a reversible type; detailed molecular structure by spectral means; general methods of preparation; general reactions; uses of aluminum reagents in organic synthesis; and applied aspects, such as industrial use, experimentation and analysis. This unified treatment should display more clearly the ways in which the groups on aluminum alter the structure and reactivity of organoaluminum compounds.

6.2 STRUCTURE AND PHYSICAL PROPERTIES

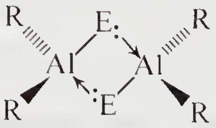
6.2.1 Physical and Colligative Properties

The solubility of organoaluminum compounds in hydrocarbons, their relatively low melting points and boiling points and their low electrical conductivity are more compatible with their structure as covalent molecules than with any ionic aggregation (Tables 1 and 2). Comparison of their physical properties with those of other covalent substances, however, reveals a discrepancy: the aluminum member is less volatile than expected. Thus, for example, trimethylaluminum (MW = 72 and b.p. = 127 °C) boils much higher than tetramethylsilane (MW = 88 and b.p. = 27 °C) or trimethylphosphine (MW = 76 and b.p. = 38 °C). This anomaly, of course, indicates the associated character of the organoaluminum molecular units. The majority of liquid aluminum compounds are mobile (viscosity of $<10^{-2}$ Pa s) and have densities less than unity. Those having a considerable vapor at 20 °C can inflame spontaneously if exposed to air.

The colligative properties of these compounds show their general tendency to exist as dimers, trimers or tetramers in solution (Tables 1 and 2) and even in the vapor state. The trialkylaluminum compounds and alkylaluminum hydrides are associated through bridging alkyl (Figure 2) and bridging hydride (Figure 6) groups, respectively. Only with these bridges is it necessary to invoke the concept of three-center, two-electron bonds (electron deficient bonding) (**94**). With vinyl-, aryl- or acetylenyl-aluminum compounds, the π-electrons of these bridging groups also become involved in the bridge-bonding (**95**), so they are not nearly as 'electron deficient' as alkyl- or hydride-bridged systems. Such π-electron involvement is evident from the slight lengthening of the C(1)—C(2) distance in the bridging phenyl group of triphenylaluminum[132] (Table 3 and Figure 3) and from the inclined geometry of the phenylethynyl group in diphenyl(phenylethynyl)aluminum[68] (Table 4 and Figure 4). The bonding in tricyclopropylaluminum[134] (Figure 5) may resemble that in compounds having unsaturated bridging groups if one views the cyclopropyl groups as having carbon–carbon bonding somewhat intermediate between an alkane and alkene. In either the Coulson[135] or the Walsh[136] view of bonding in cyclopropane, considerable π-character is attributed to the carbon–carbon bonds. From the structure of dimethylaluminum hydride (Figure 6) and from the NMR data indicating bridging cyclopropyl groups in dimeric cyclopropyl(dimethyl)aluminum,[134] it can be concluded that cyclopropyl and hydride bridges are stronger than methyl bridges. (In a similar fashion, the dimeric Me_2AlPh has bridging phenyl groups; *cf. infra.*) As mentioned previously, among alkyl bridging groups steric factors seem dominant in determining bridging strength: hydride ≫ methyl > ethyl > isopropyl > *t*-butyl. However, the superior bridging tendency of unsaturated groups, despite their bulk, is seen in the crystal structure of di-μ-*trans*-3,3-dimethylbut-1-enyl(tetraisobutyl)dialuminum, where the vinyl group is bridged in a manner similar to the phenyl in dimeric Ph_3Al.[137]

(**94**)

E = H, alkyl



(**95**)

E = aryl, 1-alkenyl, 1-alkynyl, cyclopropyl or X, OR′, NR′$_2$

In the case of organoaluminum halides, organoxides and amides (**95**) (E = X, OR′ or NR′$_2$), firm oligomers of the unit R_2AlE are formed, since unshared electron pairs on the heteroatom are available for bridging. For example, the homo-dimer of methylaluminum dichloride has

Table 1 Some Physical Properties of Triorganoaluminum Compounds

Compound	*B.p.* (°C (Torr))	*M.p.* (°C)	*Density* ($g\ cm^{-3}$ (°C))	*Degree of association solution* (*vapor*)	*Ref.*
Me_3Al	127(760)	15	0.743(30)	2(2)	1–5
Et_3Al	62(0.8)	−58	0.835(25)	2	1–3
Pr^n_3Al	85(2)	−84	0.817(30)	2	1, 3
Bu^n_3Al	98(1)	−27	0.816(30)	2	1, 2
Bu^i_3Al	38(0.6)	−6	0.781(25)	1	2, 6
Bu^t_3Al	20(0.001)			1	7
$(CH_2{=}CH)_3Al$	55(1)			2–3	8
Ph_3Al		237		1–2	9–11
$(o\text{-}MeC_6H_4)_3Al$		195			9
$(m\text{-}MeC_6H_4)_3Al$		168			9
$(p\text{-}MeC_6H_4)_3Al\cdot OEt_2$		125		1–2	9
(1-Naphthyl)$_3$Al		256			9
Cp_3Al		60		2	12
$(PhCH_2)_3Al$		118		1	13, 14
$(HC\equiv C)_3Al\cdot OEt_2$		34		1	15
$(MeC\equiv C)_3Al\cdot OEt_2$		78		1	16
$(EtC\equiv C)_3Al\cdot OEt_2$	liq.			1	16
$(Z\text{-}EtCH{=}CH)AlEt_2$[a]	liq.			2	17
$(CH_2{=}CHCH_2)AlEt_2\cdot OEt_2$[a]	liq.			1	18
$(MeC\equiv C)AlEt_2$	103(0.1)			2	19
$(BuC\equiv C)AlPh_2$		87		2	20
$(PhC\equiv C)AlPh_2$		144		2	20, 21

[a] This compound decomposes upon attempted distillation

1. 'Aluminum Alkyls', brochure of Texas Alkyls, Inc., Stauffer Chemical Company, Westport, Conn., 1976.
2. E. G. Hoffmann, *Liebigs Ann. Chem.*, 1960, **629**, 104.
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4. C. H. Henrickson and D. P. Eyman, *Inorg. Chem.*, 1967, **6**, 1461.
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13. R. Köster and G. Bruno, *Liebigs Ann. Chem.*, 1960, **629**, 89.
14. J. J. Eisch and J. M. Biedermann, *J. Organomet. Chem.*, 1971, **30**, 167.
15. G. Wilke and W. Schneider, *Bull. Soc. Chim. Fr.*, 1963, 1462.
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20. J. J. Eisch and W. C. Kaska, *J. Organomet. Chem.*, 1964, **2**, 184.
21. G. D. Stucky, A. M. McPherson, W. E. Rhine, J. J. Eisch and J. L. Considine, *J. Am. Chem. Soc.*, 1974, **96**, 1941.

Table 2 Some Physical Properties of Mixed Organoaluminum Compounds

Compound	*B.p.* (°C (Torr))	*M.p.* (°C)	*Density* ($g\ cm^{-3}$ (°C))	*Degree of association*	*Ref.*
Me_2AlCl	126(760)	−45	0.996(30)	2	1
Me_2AlBr	150(760)			2	2
Me_2AlI	111(50)			2	2
Et_2AlF	106(3)			4	3
Et_2AlCl	127(50)	−85	0.961(25)	2	1
$EtAlCl_2$	115(50)	32	1.207(50)	2	1
Ph_2AlCl		148		2	2, 4
$PhAlCl_2$		95.5		2	2
Me_2AlH	55(9)			3	1
Et_2AlH	77(1)	−60	0.808(20)	3	1
Bu^i_2AlH	114(1)	−80	0.798(25)	3	1
Ph_2AlH		157.5		2.4	5

Table 2 (*continued*)

Compound	*B.p.* (°C (Torr))	*M.p.* (°C)	*Density* (g cm^{-3} (°C))	*Degree of association*	*Ref.*
Et_2AlOMe	76(4)		0.909(40)	3	1
Et_2AlOEt	109(10)	4.5	0.850(30)	2	1
Et_2AlOBu^t	88(0.0001)	70		2	6, 7
$Ph_2AlOCOPh$		160		2	8
Et_2AlNH_2		−57		3	9
$Et_2AlNHMe$	33(0.001)			3	10
Et_2AlNMe_2	66(0.15)	6		2	11
PhAlNPh[a]				4	12, 13

[a] Cubic array of aluminum and nitrogen atoms.

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13. T. R. R. McDonald and W. S. McDonald, *Proc. Chem. Soc.*, 1963, 382.

Table 3 Crystallographic Data for the Dimers of Trimethylaluminum and Triphenylaluminum

	Interatomic distances (pm)		*Angles* (°)
$(Me_3Al)_2$[1]			
Bridge			
Al—C(1)	213.4 ± 1.0	C(3)—Al—C(2)	123.1 ± 0.4
Al—C(1)	215.3 ± 1.2	C(2)—Al—C(1)	107.2 ± 0.5
Terminal			
Al—C(2)	198.3 ± 1.0	C(1′)—Al—C(3)	108.7 ± 0.5
Al—C(3)	195.8 ± 1.1	C(1)—Al—C(1′)	105.3 ± 0.4
Al—Al′	260.0 ± 0.4	C(3)—Al—C(1)	105.1 ± 0.5
Bridge C—H		C(2)—Al—C(1)	106.1 ± 0.5
C(1)—H(1)	105	H(1)—C(1)—H(1)	90
C(1)—H(2)	112	H(1)—C(1)—H(3)	96
C(1)—H(3)	104	H(2)—C(1)—H(3)	120
Terminal C—H		H(1)—C(2)—H(3)	86
C(2)—H(1)	102	H(2)—C(2)—H(3)	100
C(2)—H(2)	103	H(1)—C(3)—H(2)	101
C(2)—H(3)	100	H(1)—C(3)—H(3)	85
C(3)—H(1)	99	H(2)—C(3)—H(3)	88
C(3)—H(2)	92	Al—C(1)—Al′	74.7 ± 0.4
C(3)—H(3)	93	Al′—Al—C(2)	118.2 ± 0.3
		Al′—Al—C(3)	118.7 ± 0.3
$(Ph_3Al)_2$[2]			
Bridge			
Al—C(1)	218.4	C(1)—Al—C(1′)	103.5
Al—C(1)	218.0	Al—C(1)—Al′	76.5
Terminal		Dihedral angle between	
Al—Al′	270	planes C(1)—Al—C(1′)—Al′	
Al—C(2)	195.6	and C(1)-C(6) is 84.4°	
Al—C(3)	196.0		
Bridge C—C			
C(1)—C(2)	142.0	C(2′)—C(1′)—C(6′)	113.7
C(1)—C(6)	142.0	C(1′)—C(2′)—C(3′)	122.3
		C(1′)—C(6′)—C(5′)	124.1

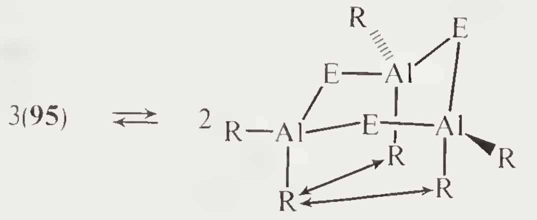
1. R. G. Vranka and E. L. Amma, *J. Am. Chem. Soc.*, 1967, **89**, 3121.
2. J. F. Malone and W. S. McDonald, *Chem. Commun.*, 1967, 444.

Table 4 Crystallographic Data for the Dimers of Tricyclopropylaluminum and Diphenyl(phenylethynyl)aluminum

	Interatomic distances (pm)		*Angles* (*degrees*)
$[(c\text{-}C_3H_5)_3Al]_2$[1]			
Bridge			
Al—C	206.2–209.8 (208.7 av.)		
Al—Al′	261.8		
Terminal			
Al—C	190–195 (193 av.)		
$[Ph_2AlC{\equiv}CPh]_2$[2]			
Bridge			
Al—C(1)	218.4	Al—C—Al′	91.73
Al—C(2)	199.2	Al—C≡C	171.59
C≡C	120.7		
Terminal			
Al—C	194.0		

1. J. W. Moore, D. A. Sanders, P. A. Scherr, M. D. Glick and J. P. Oliver, *J. Am. Chem. Soc.*, 1971, **93**, 1035.
2. G. D. Stucky, A. M. McPherson, W. E. Rhine, J. J. Eisch and J. L. Considine, *J. Am. Chem. Soc.*, 1974, **96**, 1941.

bridging chlorine atoms with an Al—Cl—Al angle of 91° and the terminal chloro–methyl pairs *trans* to each other.[138] The hetero-dimer of Me_3Al with Me_2AlNPh_2, however, has one methyl and one Ph_2N bridge with bridge angles of 77° and 86° for the Al—Me—Al and the Al—N—Al arrays, respectively.[139] The formation of dimers is the most common mode of association, both with triorganoaluminums (**94**) and with mixed organoaluminums (**95**), although trimers or tetramers can be formed with relatively smaller bridging groups (H, F, OMe or NHMe). Such cyclic trimers are proposed to have nonplanar rings,[140] similar to the chair conformation of cyclohexane; smaller bridging groups may cause greater 1,3-nonbonded repulsions in a bridged dimer. With larger R groups, such repulsions may destabilize the trimer (**96**) with respect to the dimer (equation 66).



(66)

(**96**)

6.2.2 Crystallographic Data and Bonding in the Solid Dimer

The structure of dimeric trimethylaluminum in the solid state is that given in Figure 2.[11,12] To account for such a structure for aluminum alkyls, as well as for the dimers or trimers of dialkylaluminum hydrides (Figure 6 gives electron diffraction data for $[Me_2AlH]_2$), the electron deficient bonding has been described in two limiting ways. First, following Rundle,[11] one can assume that the bridge bond arises from the overlap of tetrahedral (sp^3) orbitals from the two aluminum atoms with the tetrahedral orbital of the bridging methyl in $[Me_3Al]_2$ or with the σ-orbital of the hydrogen in $[Me_2AlH]_2$ (**97**). Such a linear combination of atomic orbitals will yield bonding, a non-bonding and an antibonding molecular orbitals; then the bridge bond would result from the two electrons occupying the bonding molecular orbital. This view of the bonding is helpful in understanding the unusually acute Al—C—Al bridge angle, for a better orbital overlap is achieved if the aluminum orbital is not aligned along the Al—C axis, but is directed at the carbon orbital. Further, it is noteworthy that in the ^{13}C NMR spectrum of dimeric trimethylaluminum at −75 °C the $^{13}C\text{–}^{1}H$ coupling constants are 112 Hz and 114 Hz for the bridging and non-bridging methyl groups, respectively.[141a] According to the widely accepted correlation between such coupling constants and carbon hybridization, these results indicate that both methyl groups have the same hybridization, namely sp^3 (CH_4: J_{CH} = 125 Hz).

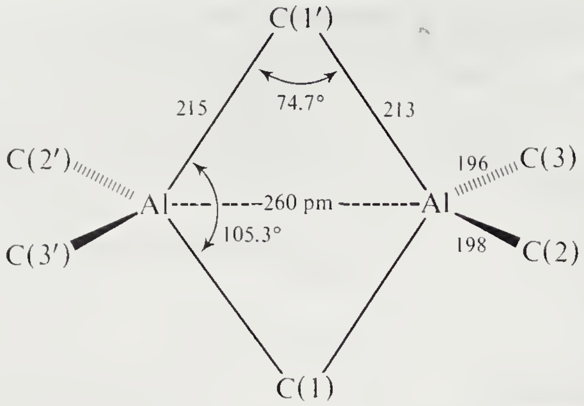
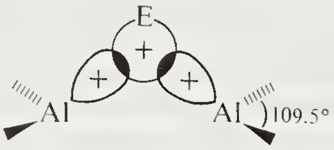


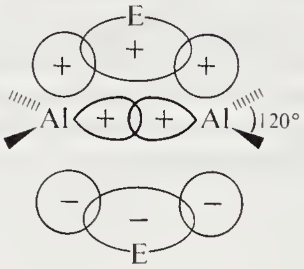
Figure 2 The crystal structure of dimeric trimethylaluminum[12] (hydrogens omitted for clarity)

An alternative bonding picture of the bridge would consider that trigonal (sp^2) orbitals from the two aluminum atoms interact with the non-bridging methyl groups to form a tetramethylethylene-like σ-skeleton and the p-orbitals on the aluminums form a π-orbital. Thus, the interaction of the two $[Me_2Al]^-$ units, as in (**98**), would form bonding σ- and π-orbitals between the aluminum centers. The bridging E groups (E = H, Me) could then be viewed as either methyl or hydrogen cations interacting with the Al—Al π-orbital. The advantage of this model is that the relatively short Al—Al distance (2.60–2.62 Å) is explicable as a Al—Al σ-bond and the relatively wide external C—Al—C angle (123°) as a consequence of sp^2-hybridization of aluminum.



(**97**)

E = Me, H



(**98**)

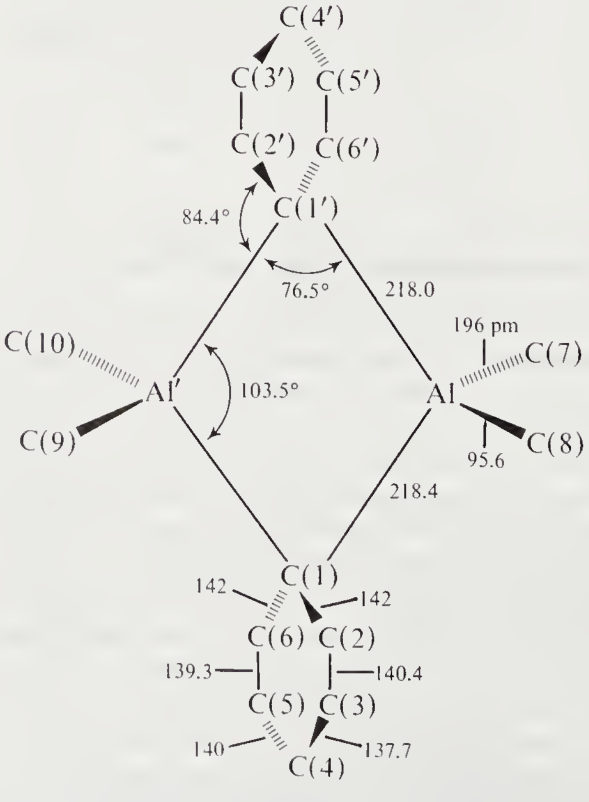
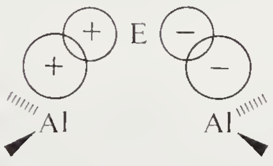


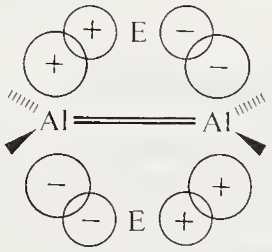
Figure 3 The crystal structure of dimeric triphenylaluminum[132] (hydrogens and some carbons of terminal phenyl groups omitted for clarity)

The actual bonding in dimeric trimethylaluminum is probably intermediate between these two extremes. If the tetrahedral aluminum orbitals in the first description (**97**) also overlap with each other, some Al—Al bonding would arise. Similarly, if the tetrahedral orbital of the bridging methyl group in (**98**) overlaps not only with the π-orbital but also the σ-orbital of the Al—Al linkage, then the bridge-bonding would resemble (**97**). Approximate molecular calculations by Lewis and Rundle[11] and more extensive subsequent calculations[141b,142] both point to the importance of some Al—Al bonding, but the larger contribution to dimerization lies in the Al—C—Al and Al—H—Al interactions.

For dimers having bridges that are not, strictly speaking, electron deficient (E = X, OR, NR$_2$, aryl (Figure 3), vinyl, alkyne and cyclopropyl), one could describe the bonding in terms of coordinate covalence (**95**). Alternatively, however, either of the foregoing models, three-center σ-(**97**) or π-(**98**) bonding, could be invoked if one provides for supplemental bonding. Thus, in (**97**) the empty non-bonding orbital arising from the linear combination of the two aluminum and one E-group orbital could, in (**99**), overlap with the filled *p*- or π-orbital on the bridging group. For (**98**), corresponding to the filled π-orbital of the Al═Al bond, there would be an empty π^*-orbital of proper symmetry to overlap with a filled *p*- or π-orbital on the ligand E (**100**). For the bridging cyclopropyl group, the Walsh model with its array of sp^2-hybridized carbon atoms and its C—C bonds arising from overlapping 2*p*-orbitals would be most readily applicable to (**99**) or (**100**) (Figure 5). With markedly unsymmetrical bridging groups, *i.e.* the phenylethynyl group (Figure 4), the coordination view (**95**) would seem more suitable than either (**99**) or (**100**).



(**99**)



(**100**)

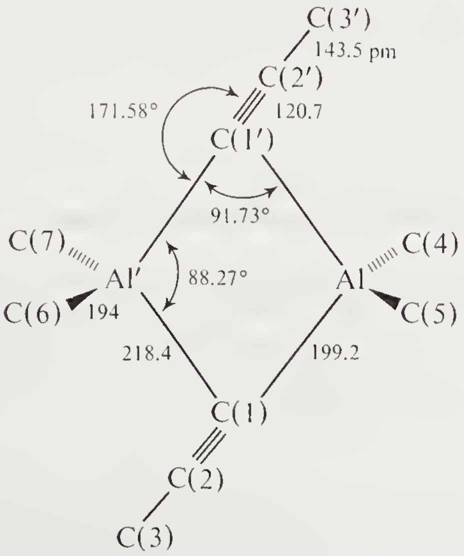


Figure 4 The crystal structure of dimeric diphenyl(phenylethynyl)aluminum[68] (hydrogens and carbons other than the first carbon of each phenyl group [C(3)–C(7)] omitted for clarity)

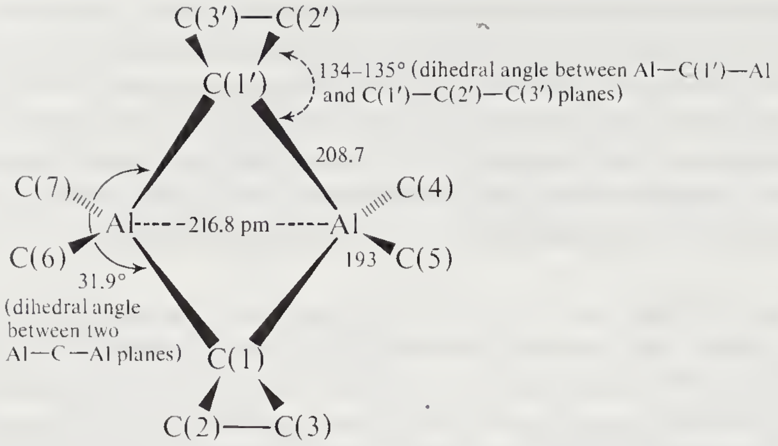


Figure 5 The crystal structure of dimeric tricyclopropylaluminum[134] (hydrogens and some carbons of terminal cyclopropyl groups omitted for clarity)

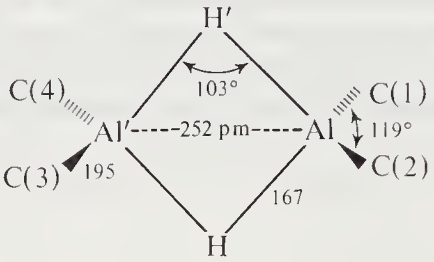


Figure 6 The structure of dimeric dimethylaluminum hydride by electron diffraction[143] (methyl hydrogens omitted for clarity)

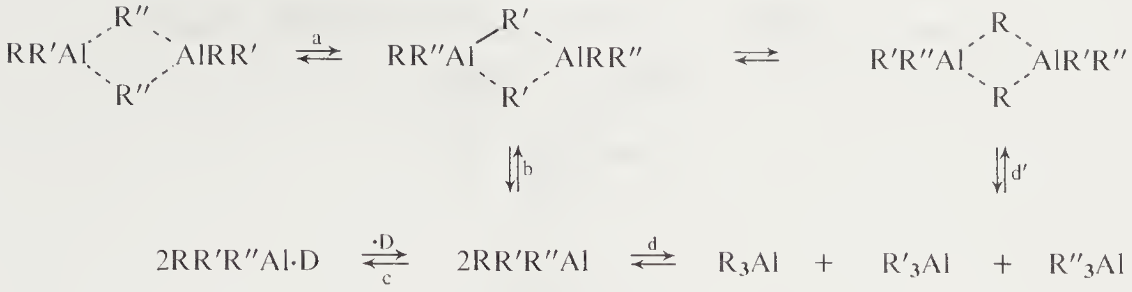
6.2.3 Electron Diffraction Data

Electron diffraction measurements at higher temperatures and lower pressures in the vapor state permit another assessment of molecular association that eliminates structural effects possibly arising from the solid state. Also, electron diffraction yields structural data on less stable members of association equilibria. Data cited in the previous section for dimeric Me_2AlH[143] and trimeric Me_2AlOMe[140] were derived from such measurements. The power of this structural tool is further appreciated from the following recent studies: (a) tetrameric Me_2AlF has been shown to have an eight-membered puckered $(AlF)_4$ ring of low symmetry;[144] (b) exact data have been obtained for dimeric Me_2AlCl showing the non-bridging methylaluminum bond to have more *s*-character ($\angle$C—Al—C = 127°) than in dimeric Me_3Al and the Al—Cl bond considerably longer than the bridging Al—Cl bond in dimeric $AlCl_3$;[145] (c) at 215 °C and 30 Torr trimethylaluminum is completely monomeric and the aluminum and carbon atom skeleton displays D_{3h} symmetry with freely rotating methyl groups;[146] and (d) the dimeric $Me_2AlC{\equiv}CMe$ in the gas phase shows a bridging structure analogous to that shown by dimeric $Ph_2AlC{\equiv}CPh$ in the solid state,[68] thereby confirming that the structure of the latter (Figure 4) is not merely a result of crystal packing forces.[147]

6.2.4 Spectroscopic Investigations of Associated Structures

Variable temperature NMR studies have proved of extraordinary value in following the dynamic equilibria arising in solution from associated organoaluminum compounds. As summarized in Scheme 3, these equilibria include: (a) interchange of bridging and non-bridging groups in RR′R″Al; (b) monomer–oligomer equilibria; (c) monomer complexation with donors; and (d) exchange of groups among aluminum centers.

Pioneering evidence for the presence of bridging and non-bridging methyl groups in dimeric Me_3Al for the solution state was the observation of two sharp proton methyl signals in a 1:2 intensity ratio below −55 °C. The occurrence of the bridging methyl signal at lower magnetic field is compatible with the delocalized electron pair in such a bond.[148,149] Coalescence of the signals at about −35 °C is ascribed to the exchange of the methyl groups between the bridge and terminal positions (process a) through a first order dissociation to monomer (process b, $E^{\ddagger} = 65.5$ kJ mol^{-1}

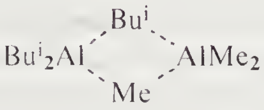


Scheme 3

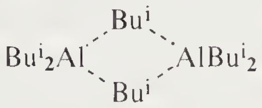
in cyclopentane).[150] That the dimer dissociates ten times faster in toluene than in cyclopentane may indicate that toluene, as a π-base, solvates the transition state of process b and thus lowers $E^{\ddagger}$ (*cf.* process c). Finally, the disproportionation–redistribution equilibrium (formally, process d) probably occurs through various bridging dimers (process d′). Thus, the mixing of dimeric Me_3Al and the largely monomeric Bu^i_3Al in a 1:4 molar equivalent ratio leads to the formation of di-μ-methyl(tetraisobutyl)dialuminum (**101**), as shown by cryoscopic and low temperature NMR measurements (equation 67).[151] This rapid redistribution of alkyl groups occurring upon mixing the components seems to take place *via* mixed associates such as (**102**) and (**103**) for whose existence NMR evidence has been offered. That even triisobutylaluminum, which is monomeric in benzene, can form homo-dimers (**104**) is shown by calorimetric studies of dissolution of the pure aluminum alkyl in alkanes.[149]

(67)

(**101**)


(**102**)

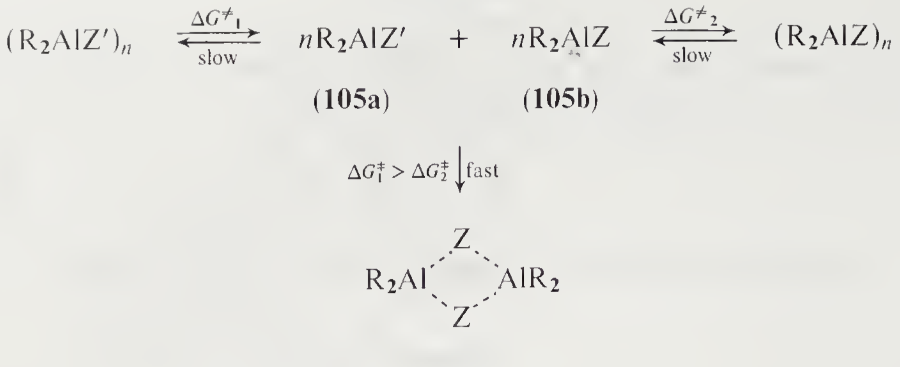

(**103**)


(**104**)

In fact, the thermodynamic driving force for these redistribution reactions of symmetric aluminum compounds R_3Al and AlE_3 is to favor those unsymmetrical products R_nAlE_{3-n} having as many of the strong bridging groups in bridging positions as possible. Examples of this tendency, as verified by NMR measurements, are numerous: (a) the formation of alkyl- and aryl-aluminum halides from R_3Al and AlX_3 (X as better bridge than R);[40,152] (b) the formation of diphenylaluminum hydride (degree of association: 2.4 in C_6H_6) by admixing Ph_3Al and AlH_3 in a 2:1 ratio (H > Ph);[153] (c) the isolation of pure dialkyl(aryl)aluminum compounds from admixing R_3Al and Ar_3Al in a 2:1 ratio, where both NMR and X-ray crystallographic data prove that the aryl groups are in the bridges (Ar > R);[101,154] and (d) the interaction of a 2:1 ratio of R_3Al and $Al(OR')_3$ to yield the dialkylaluminum alkoxides (R′O > R).[40,155]

In this connection, the rate of group exchange between mixed aluminum compounds R_2AlZ and R_2AlZ' (R = Me, Et) is noteworthy. A comprehensive NMR study established the following order of decreasing rates: Me > Et > Cl, Br, I > SMe, OEt > NMe_2, CN, F.[156] Such decreasing ease of exchange seems to be ascribable to the conversely increasing stability of the homo-oligomers from R to F. If the exchange requires the formation of the monomers (**105a** and **105b**), then the highly stable dimers (R_2AlNMe_2) or tetramers (R_2AlF and R_2AlCN) will clearly require a larger activation energy to react with R_2AlZ (Scheme 4). In certain cases, the mixed bridge intermediate (**106**) could be detected by NMR or mass spectral means. Similar studies of group exchange have been conducted with ^{13}C NMR spectroscopy, but complications arising from scalar coupling between ^{27}Al and ^{13}C nuclei must be dealt with by line-shape analysis of spectra obtained at various temperatures.[157]

As noted, a useful technique for detecting associated aluminum compounds is mass spectrometry. However, some aggregates are too weak to be detected. For example, despite the preponderance of the trimethylaluminum dimer in the vapor phase, the mass spectrum at 70 eV revealed no such parent ion and only a weak peak for $Me_5Al_2^+$ (0.2% of the base Me_2Al^+ ion).[158]



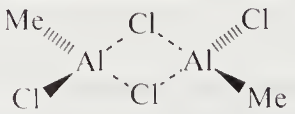
(106)

Scheme 4

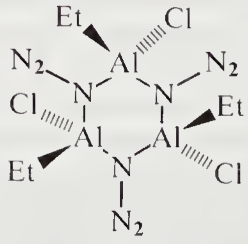
The firm tricyclopropylaluminum dimer, on the other hand, shows a strong mass peak corresponding to $[(C_3H_5)_5Al_2]^+$.[159] Also, the relatively stable dimers and trimers of dimethyl- and diethyl-aluminum hydride[160,161] yielded ions at low source temperatures and reduced ionization voltages, with significant intensities, containing two and three aluminum atoms; for Me_2AlH, a partial sequence of ion abundances is Me_2Al, 100; $Me_3Al_2H_2$, 39.6; Me_4AlH, 3.2; $Me_6Al_3H_2$, 0.3; Me_4Al_3H, 3.2; $Me_5Al_4H_6$, 1.9; and $Me_5Al_5H_9$, 0.3.[160] Under these conditions, even dimeric Me_3Al yields significant peaks for Me_5Al_2 and Me_3Al_2.[161] Likewise, both methylaluminum chlorides yield intense ion fragments clearly derivable from the dimeric forms: for Me_2AlCl; $Me_2Al_2Cl_3$(4.2), $Me_3Al_2Cl_2$(48.4) and Me_4Al_2Cl(1.4); and for $MeAlCl_2$; $MeAl_2Cl_4$ (39.6) and $Me_2Al_2Cl_3$(22) (relative peak intensity in parentheses).[161]

IR and Raman spectral analysis of associated complexes has also proved most informative as to: (a) the stereochemical consequences of bridging; (b) the nature of the bridging group; and (c) the identity of the coordination site, if the ligand has more than one. The first aspect is relevant to the symmetry differences arising from the stereochemistry of substituents in bridged complexes. Thus, the possible *cis–trans* isomerism of dimeric methylaluminum dichloride ((**107**) and (**108**)) can be decided by this measurement. Although the X-ray analysis of the dimer has established the *trans* form (**108**) having centrosymmetric C_{2h} symmetry for the solid state,[138] it was of interest to learn what stereoisomers could exist in solution or in the liquid state. By an examination of all IR and Raman bands and by invocation of the rule of mutual exclusion, it was concluded that all such dimers have structure (**108**).[38,162,163] However, the ease with which halide bridges are disrupted at temperatures above −70 °C[152] means that a small proportion of (**107**) could have escaped detection. On the other hand, the trimer of $EtAl(Cl)N_3$, which was prepared from diethylaluminum chloride and chlorazide, possesses a vibrational spectrum consistent with C_{3v} symmetry. This finding is consistent with an all *cis* disposition of the chloro groups in a six-membered ring (**109**).[164] In a more general application of vibrational spectroscopy, cyclic

(**107**) C_{2v}

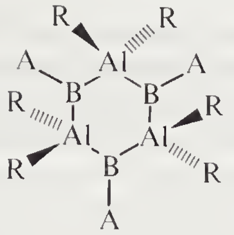


(**108**) C_{2h}



(**109**)

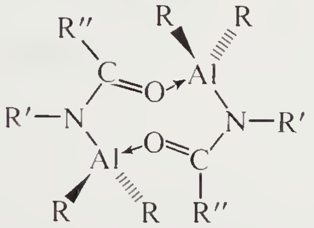
structures (**110**) are deduced for the trimers of diethylaluminum thiocyanate,[165] dimethylaluminum azide[166] and dimethylaluminum methylamide.[167] The methylamide trimer exists in two different forms, which in the solid state have been shown by X-ray crystallography to be chair and skew-boat conformers, respectively.[168]



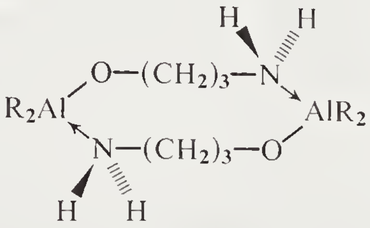
(110)

R = Me, Et
B = S, N, NHMe
A = CN, N_2

With ligands in R_2AlZ having more than one donor site, larger rings may be preferred. The dimeric acylamino derivatives $R_2Al(NRCOR')$ which can result from the reaction of aluminum alkyls with amides[169] or with isocyanates, have IR spectra consistent with the presence of eight-membered rings having centrosymmetric character and with the aluminum atom at the center of a distorted tetrahedron **(111)**. Such a structure has been confirmed by X-ray crystallography.[170] The tendency for eight-membered ring formation seems rather general, for the treatment of trimethylaluminum with either dimethylsulfoxime, Me_2SONH, or dimethylarsinic acid, Me_2AsO_2H, yields dimers similar to that shown in **(111)**.[171] Furthermore, the dimers resulting from aluminum alkyls and either 2-pyridinealdoxime[172] or ethanolamine **(112)**[173] appear to consist of twelve-membered rings. In structure **(112)** it is clear that the oxygen is covalently bound and that the amino nitrogen is coordinated. In **(111)**, however, resonance structures can be written in which the nitrogen and the oxygen centers interchange their covalent and coordinate bonding roles.

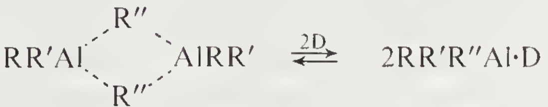


(111)



(112)

The effect of bridging on the vibrational spectral properties of aluminum compounds is a second important application of IR spectroscopy. Such measurements are particularly useful for liquid unsymmetrical compounds such as $RR'R''Al$ and aluminum hydrides. Just as the intramolecular complexation of alkenylaluminum compounds (equations 32 and 33) can be studied by comparing IR C=C stretches for the pure compound with those of its etherate $RR'RAl{\cdot}OEt_2$,[67] so a similar approach can be applied to bridging (equation 68). Bridging of R″ in **(113)** should cause IR spectral shifts compared with those displayed by the monomeric complex **(114)**. With triethylaluminum, for example, etherate formation causes the average valence frequency of the Al—C bond to be lowered by 40 cm^{-1}. Such weakening of the bond can be viewed as a consequence of a diminution of the effective nuclear charge on aluminum (and accordingly, its electronegativity) because of ether coordination.[174] Indeed, the stronger the donor, the greater is the electronegativity of aluminum thought to be lowered.[175] By an NMR study of donor complexes with triethylaluminum, the internal shift of the ethyl protons (δ) was found to become smaller as the donor increased in strength.[176]

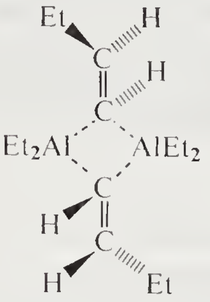


$$RR'Al(\mu\text{-}R'')_2AlRR' \xrightleftharpoons{2D} 2RR'R''Al{\cdot}D \qquad (68)$$

(113) **(114)**

When R″ in **(113)** is hydride, 1-alkenyl or 1-alkynyl, bridging has a striking effect on stretching frequencies. Diethylaluminum hydride, in hydrocarbon and as a neat sample, exhibits its Al—H stretch as a broad band centered at 1777 cm^{-1}, but in THF or triethylamine this frequency sharpens and shifts to 1762 and 1753 cm^{-1}, respectively.[177] Also, (*Z*)-1-butenyl(diethyl)aluminum, which has a degree of association of 2.0–2.5 in benzene, shows its C=C stretching band at 1553 cm^{-1}. This frequency is considerably lowered from that of alkenes of similar structure (1655 cm^{-1}) and from that of the etherate of the butenylaluminum compound (1587 cm^{-1}).[72] Such data indicate that the firmly associated character of this compound may be ascribed to butenyl bridging (*cf.* (**115**), ref. 137). In the case of 1-alkynylaluminum derivatives, these compounds undoubtedly exist as alkynyl-bridged dimers (Figure 4), but their C≡C bond length is not changed over that in the parent alkyne itself. Even the C≡C stretch in diphenyl(phenylethynyl)aluminum or in 1-hexynyl(diphenylaluminum) does not differ by more than 10 cm^{-1} from that in the starting alkynes.[178] There is, however, a shift to higher frequencies upon complexation with ethereal solvents: dimethyl(phenylethynyl)aluminum exhibits its C≡C stretch at 2050 cm^{-1} in benzene and at 2110 cm^{-1} in THF. These observations support the interpretation that bridging weakens the C≡C bond. They also show that comparisons between the spectral behavior of hydrocarbons and aluminum compounds can be deceptive.[179]

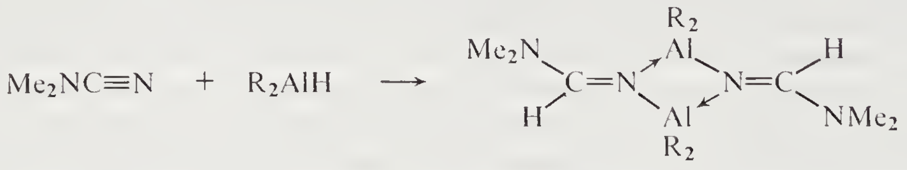
Related to the lowering of the C≡C stretch upon bridging is the intermolecular coordination of organoaluminum compounds with nitriles, such as phenylacetonitrile and benzonitrile.[180] The heats of formation of such complexes (**116**) are found to be proportional to the lowering of the C≡N stretching frequency in their IR spectra.[181] Clearly, resonance structure (**116b**) will be of growing importance as the R groups on aluminum become more electron-withdrawing.



(**115**)

(**116a**) (**116b**)

Finally, vibrational spectroscopy may help to identify the actual coordination site of aluminum in a multidentate ligand. Thus, complexes of trialkylaluminum compounds with *N*,*N*-dimethylcyanamide, $Me_2NC{\equiv}N$, were shown to be coordinated through the cyanide nitrogen by observing that complexation had caused a 50–60 cm^{-1} lowering in the C≡N stretch.[182] When the same cyanamide was reduced with dialkylaluminum hydrides, dimeric (**117**) was obtained whose IR spectrum again permitted the bridging nitrogen to be identified by the lowering of C=N stretch (equation 69). Similar studies show that sulfoxides coordinate through oxygen.[183]



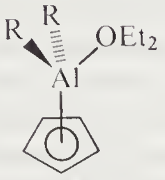
(69)

(**117**)

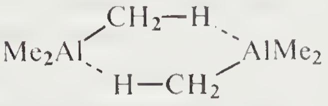
Attempts to assign the coordination site to all-carbon ligands have met with some success. The etherate of diethyl[(*E*)-3-phenyl-2-propen-1-yl]aluminum has a C=C stretch at 1623 cm^{-1}, in keeping with a C=C bond conjugated with a phenyl group. The other allylic isomer would be expected to have its C=C stretch at >1650 cm^{-1}.[56] In addition, analysis of the vibrational bands of the cyclopentadienyl ring in dialkyl(cyclopentadienyl)aluminum compounds, which tend to dimerize in hydrocarbons, are interpreted as being consistent with a pentahapto-C_5H_5 ring for the etherate, $R_2CpAl{\cdot}OEt_2$, (**118**) and with either di- or tri-hapto bonding for the ether-free compound.[184] The ^{13}C NMR spectra of these compounds did not provide reliable criteria for discerning between σ- and π-bonded structures.[185]

In a more subtle uncertainty concerning the bridging site, the crystallographic data for dimeric trimethylaluminum were thought to be consistent with a hydrogen-bridging structure (**119**).[10]

However, this unusual suggestion has received manifold experimental refutation: (a) a complete IR and Raman study;[186] (b) ^{27}Al nuclear quadrupole resonance measurements;[187] and (c) spectrographic measurements actually locating the bridging hydrogens.[188] All such studies confirm the Rundle–Amma picture of the bonding (Figure 2).



(118)



(119)

6.2.5 Thermodynamic Data on the Association Equilibria

The enthalpy of dimerization for gaseous trimethylaluminum has been shown to be −85.68 ± 1.43 kJ mol^{-1},[189] a value agreeing closely with the first reported estimate.[9a] As part of an extensive reassessment and reevaluation of such data, the enthalpy and entropy of dissociation of liquid aluminum alkyl dimers have been measured.[190–194] The $\Delta H_{\mathrm{l}}^{\circ}$ and $\Delta S_{\mathrm{l}}^{\circ}$ values for trimethylaluminum are 81.48 ± 1.28 kJ mol^{-1} (of dimer) and 123.06 ± 1.26 J K^{-1} (per mole of dimer); those for triethylaluminum are 70.98 ± 0.84 kJ mol^{-1} and 134.82 ± 2.52 J K^{-1} mol^{-1}. From such data and vapor pressure studies, the boiling points derived for the pure trimethylaluminum monomer and dimer are 8.1 ± 2.1 and 131.95 ± 0.02 °C.[192] Similar studies for higher alkyls have led to the data listed in Table 5.[194] From such $\Delta H_{\mathrm{l}}^{\circ}$ values, it is evident that there are sharp decreases in the enthalpies of dissociation between Me_3Al and Et_3Al (10.5 kJ mol^{-1}), and between Et_3Al and Pr_3Al (6.3 kJ mol^{-1}). From the propyl homologue the differences between members becomes less than 4.2 kJ mol^{-1}. These changes in $\Delta H_{\mathrm{l}}^{\circ}$ reflect a great increase in steric hindrance to the bridging dimerization early in the homologous series. Correspondingly marked increases in $\Delta S_{\mathrm{l}}^{\circ}$ for the methyl and ethyl members register the considerable rotational restriction that dimerization entails. The feeble increases in $\Delta S_{\mathrm{l}}^{\circ}$ for higher members show that such entropic changes arise principally from the Al—CH_2—CH_2 grouping. Although the dissociation (K_d) of none of these pure alkyls is significant at 25 °C (*e.g.* K_d: of Me_3Al, 1.52×10^{-8}; of $(C_{12}H_{25})_3Al$, 5.13×10^{-4}), at 150 °C trimethylaluminum is 0.8% dissociated, the ethyl member 7%, but the propyl member 23%. Similar studies in hydrocarbon solution naturally show a greater tendency to dissociation. For example, solutions of trimethylaluminum (0.01 mole fraction for all Me_3Al treated as monomer) at 100 °C show the following dissociation of dimer (%): hexadecane, 2.31; mesitylene, 3.48; and benzene, 3.20. The greater dissociation in aromatic solvents speaks for complexation of monomeric Me_3Al with the π-cloud. The enthalpy of such complexation is estimated to be 8.82 kJ mol^{-1} for mesitylene and 7.56 kJ mol^{-1} for benzene.

Table 5 Thermodynamic Data[1] on the Monomer–Dimer Equilibria of Tri-*n*-alkylaluminum Compounds R_3Al

R	$\Delta H_{\mathrm{l}}^{\circ\,a}$ (kJ mol^{-1})	$\Delta S_{\mathrm{l}}^{\circ\,b}$ (J K^{-1} mol^{-1})	K_d at 25 °C[c]	K_d at 150 °C[c]
CH_3	81.48	123.06	1.52×10^{-8}	2.42×10^{-4}
CH_3CH_2	71.11	135.20	4.20×10^{-6}	1.95×10^{-2}
$CH_3CH_2CH_2$	64.72	140.62	1.05×10^{-4}	2.28×10^{-1}
$CH_3(CH_2)_3$	63.04	141.62	2.32×10^{-4}	4.13×10^{-1}
$CH_3(CH_2)_5$	62.08	141.71	3.47×10^{-4}	5.50×10^{-1}
$CH_3(CH_2)_7$	61.66	141.79	4.13×10^{-4}	6.24×10^{-1}
$CH_3(CH_2)_9$	61.36	141.83	4.69×10^{-4}	6.83×10^{-1}
$CH_3(CH_2)_{11}$	61.15	141.88	5.13×10^{-4}	7.29×10^{-1}

[a] $\Delta H_{\mathrm{l}}^{\circ}$ = standard heat of dissociation of one mole of liquid aluminum alkyl dimer. [b] $\Delta S_{\mathrm{l}}^{\circ}$ = standard entropy of dissociation of one mole of liquid aluminum alkyl dimer. [c] K_d = dissociation constant of dimer into monomer.

1. M. B. Smith, *J. Organomet. Chem.*, 1974, **70**, 13.

As the bridging dimer model implies, branching in the alkyl chain near the Al—C bond does have a great effect on association. Such compounds as triisopropylaluminum,[9b] triisobutylaluminum[50] and tri-*t*-butylaluminum[49] are monomeric in benzene solution at about 0 °C. However, careful thermochemical studies have shown that triisobutylaluminum is appreciably associated in the pure state (39.4% at 10 °C and 16.4% at 40 °C) with ΔH°_1 of 34.02 ± 0.42 kJ mol^{-1} and ΔS°_1 of 127.68 ± 1.26 J K^{-1} mol^{-1}.[191]

For arylaluminum compounds similar conditions obtain. Although such compounds tend to be largely dimeric in benzene or cyclohexane solution, the temperature and concentration will be determinant. Thus a 2% solution of triphenylaluminum in benzene gives ebullioscopic data consistent with only an 80% association to dimer.[195] Likewise, tri-*p*-tolylaluminum in benzene solution gives, by either cryoscopic or ebullioscopic measurements, degrees of association ranging from 10 to 90%, depending on concentration and temperature.[196] On the other hand, tribenzylaluminum is reported to be monomeric.[197]

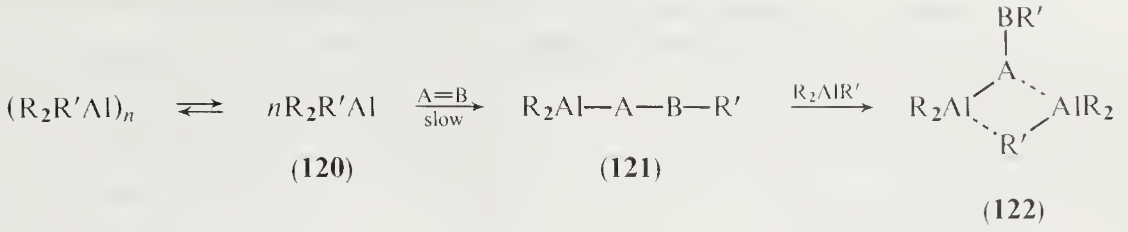
The 1-alkenyl- and 1-alkynyl-aluminum derivatives exist as firm dimers in hydrocarbon solvents,[72,198] as do the cyclopropylaluminum derivatives discussed above. Such firmly bridged dimers may sometimes be dissociated by heat or by complexation with strong Lewis bases. However, such treatment often leads to permanent, irreversible structural change, such as polymerization (alkenyl-, alkynyl-aluminum compounds), disproportionation ($R_2AlZ \rightarrow R_3Al + AlZ_3$) or profound decomposition. These changes can be anticipated in dissociations of mixed organoaluminum derivatives (R_2AlCl, $RAl(OR)_2$, $R_2AlNHMe$, *etc.*) as well.

6.2.6 Structural Types of Stable and Labile Organoaluminum Compounds

As an aid to understanding the equilibria and the reaction mechanisms of organoaluminum chemistry, certain structural factors determining the formation of stable and labile intermediates are now considered.

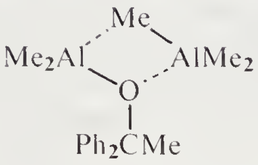
6.2.6.1 Dissociation and association

In the preceding sections the copious information available on oligomeric homo-association is reviewed. Such dimers or trimers often undergo dissociation into monomers (**120**), which generally are the reactive substances in many reactions. Spectroscopic, vapor pressure and electron diffraction measurements have detected or implicated such monomeric forms as equilibrated or transient intermediates in both physical and chemical processes. The fractional kinetic orders observed for the reactions of R_3Al and R_2AlH types with unsaturated hydrocarbons are cited above as evidence supporting the involvement of monomeric alkyl or hydride in the rate-determining step (Section 6.1.5). But the tendency for association of organoaluminum compounds is often so great that the product of such a reaction may capture the reactive monomer in the form of a hetero-associated complex (**122**) and thereby retard the rate of reaction (equation 70). Such behavior is expected to be important whenever the product (**121**) can form bridges similar in strength to those in the starting $R_2R'Al$ compound. Thus, benzophenone reacts rapidly at 25 °C with two moles of trimethylaluminum to form the hetero-associated (**123**)[199] and diisobutylaluminum hydride reacts with alkynes by a kinetic law showing auto-inhibition due to the formation of (**124**).[200–202] The formation of such hetero-bridging is also evident in admixing diisobutylaluminum hydride with either triisobutylaluminum or diisobutylaluminum chloride. By employing the method of continuous variations with the integrated intensity of the Al—H signal, for the first mixture the complexed hydride reaches its maximal value at a 2 : 1 ratio of $Bu^i_3Al : Bu^i_2AlH$ at 35 °C. Similar studies at lower temperatures suggest that 1 : 1 and probably 1 : 2 complexes are more stable below −10 °C and −45 °C, respectively.[203] Likewise, NMR studies on the $Bu^i_2AlH \cdot Bu^i_2AlCl$ pair has uncovered evidence for the equilibration among 2 : 1 (**125**), 1 : 1 (**126**) and 1 : 2 (**127**) complexes.[204] There is NMR evidence that similar mixed bridge associates are also formed between Bu^i_2AlH and certain diisobutyl[(*E*)-vinylic]aluminum systems.[205] The question of a heterolytic dissociation of aluminum oligomers to produce ions has already been addressed (*cf.* equation 29).

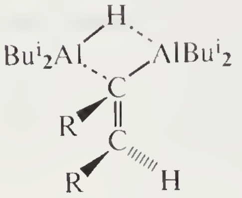


(70)

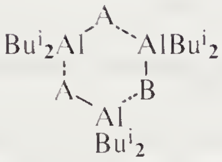
R' = R, H, Cl, OR, *etc.*



(123)



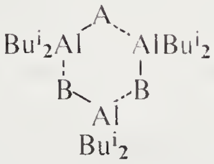
(124)



(125)

A = Bu^i, Cl
B = H

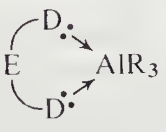
(126)



(127)

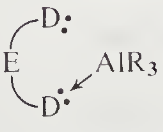
6.2.6.2 Neutral Lewis complexation

Almost every conceivable molecule having unshared electron pairs or even π-electrons can complex with organoaluminum compounds. Besides the many types already mentioned, such as ethers, amines, sulfides and aromatic hydrocarbons, there is spectral evidence that even weak halide donors like methylene chloride[206] and bromo(phenyl)acetylene[207] can complex with trimethylaluminum and diisobutylaluminum hydride, respectively. Selected physical properties for a variety of such complexes are given in Table 6. Complexes involving bidentate Lewis bases **(128)** or dialuminoxanes **(129)** raise the questions of whether five-coordinate aluminum is produced in the former **(128a)** and whether a type of electron-deficient bond **(129a)** is involved in the latter. If the exchange of the aluminum between monodentate sites **(128b)** or **(129b)** is more rapid than the NMR spectral measurement, then averaged absorptions seemingly consistent with **(128a)** and **(129a)** will result. By cooling the sample such exchanges can sometimes be slowed down sufficiently to detect the unsymmetrical complex intermediate. Thus, the NMR spectrum of the 1 : 1 complex between trimethylaluminum and bis(trimethylphosphinimido)dimethylsilane **(129)** at 25 °C exhibits only one absorption arising from the Me_3P group, but that at −60 °C yields two, as **(128b)** would show.[208] Indeed, two nitrogens can be made to coordinate simultaneously

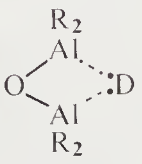


(128a)

or

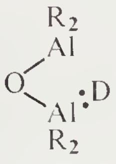


(128b)



(129a)

or



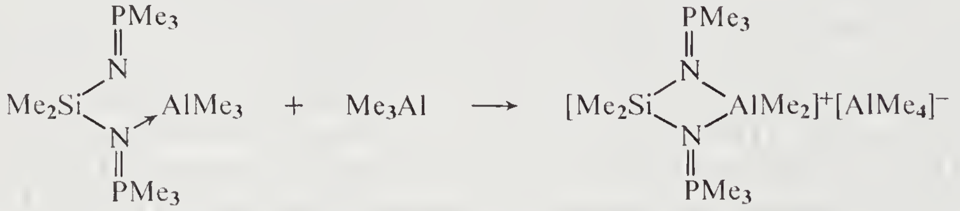
(129b)

Table 6 Some Physical Properties of Selected Neutral Complexes of Organoaluminum Compounds with Lewis Bases

Compound	*B.p.* (°C (Torr))	*M.p.* (°C)	*Ref.*
$Me_3Al{\cdot}OMe_2$	159(760)		1
$(n\text{-}C_3H_7)_3Al{\cdot}OMePh$	105(2)		2
$Ph_3Al{\cdot}OEt_2$		126	3
$Me_3Al{\cdot}NHMe_2$		51	1
$Me_3Al{\cdot}OP(NMe_2)_3$	50(0.001)	88	4
$Me_3Al{\cdot}N{\equiv}CMe$		73	5
$Me_3Al{\cdot}O \leftarrow NMe_3$	142(1)	102	6
$Me_3Al{\cdot}NHPMe_3$		46	7
$Me_3Al{\cdot}N(SiMe_3)PMe_3$	120(1)	80	8
$Et_3Al{\cdot}SMe_2$	60(0.05)		9
$Me_3Al{\cdot}OSMe_2$	108(1)	48	6
$Et_3Al{\cdot}PPr^n_3$	104(0.05)		9
$Et_3Al{\cdot}OPEt_3$	142(1)	−13	10
$Me_2AlCl{\cdot}NMe_3$		124	1
$Me_2AlCl{\cdot}OMe_2$	224(760)		1
$MeAlCl{\cdot}N{\equiv}CMe$		73	5
$Me_2AlH{\cdot}NMe_3$	43(1)	35	11

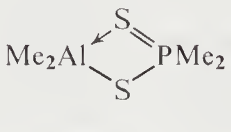
1. N. Davidson and H. C. Brown, *J. Am. Chem. Soc.*, 1942, **64,** 316.
2. G. Geiseler and W. Knothe, *Chem. Ber.*, 1958, **91,** 2446.
3. J. J. Eisch and W. C. Kaska, *J. Am. Chem. Soc.*, 1966, **88,** 2976.
4. H. Lehmkuhl, unpublished studies, cited in H. Lehmkuhl and K. Ziegler, 'Methoden der Organischen Chemie', ed. E. Müller, Thieme Verlag, Stuttgart, 1970, vol. XIII/4.
5. J. R. Jennings, J. E. Lloyd and K. Wade, *J. Chem. Soc.*, 1965, 5083.
6. F. Schindler and H. Schmidbaur, *Chem. Ber.*, 1967, **100,** 3655.
7. H. Schmidbaur and G. Jonas, *Chem. Ber.*, 1968, **101,** 1271.
8. H. Schmidbaur and W. Wolfsberger, *Chem. Ber.*, 1967, **100,** 1000.
9. P. deLoth, *C. R. Hebd. Seances Acad. Sci.*, 1965, **261,** 4758.
10. F. Schindler, H. Schmidbaur and G. Jonas, *Chem. Ber.*, 1965, **98,** 3345.
11. F. M. Peters, B. Bartocha and A. J. Bilbo, *Can. J. Chem.*, 1963, **41,** 1051.

only by ionization (**130**), so resistant is the aluminum to five-coordination (equation 71).[209] Tetraethylaluminoxane forms a 1 : 1 complex with benzonitrile (**129**) (R = Et; D = C_6H_5CN) whose NMR spectrum shows only one type of ethyl signal down to −40 °C. Nevertheless, it is still uncertain whether (**129a**) or (**129b**) is formed.[210]

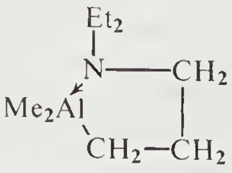


(**129**) (**130**) (71)

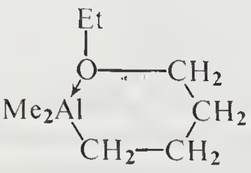
Finally, intramolecular Lewis complexation may stabilize the monomer relative to the dimer. Just as 4-alkenylaluminum compounds tend to be monomeric because of intramolecular π-complexation (equations 32 and 33), so various substituted R_2AlZ whose Z group has donor sites in the γ-, δ- or ϵ-position are monomeric because of intramolecular *n*-complexation (**131**)–(**133**).[211–213]



(**131**)



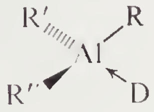
(**132**)



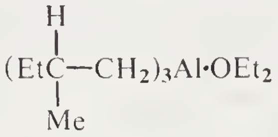
(**133**)

6.2.6.3 *Stability of unsymmetrical and mixed derivatives*

Organoaluminum compounds bearing two or more different groups about the aluminum center generally have a tendency to undergo disproportionation (equation 19). This process is especially facile when the groups on aluminum are weaker bridging groups. Trialkylaluminum compounds of the type RR′R″Al readily form mixtures of R_3Al, $R_2R'Al$, $R_2R''Al\cdots RR'_2Al$, RR''_2Al, *etc.* (Scheme 3), but R_2AlCl and derivatives with C≡CR, CH=CHR, OR, NR_2, SR, *etc.* groups tend to be more stable (Section 6.2.4). Special measures, therefore, must be taken in synthesizing and in employing unsymmetrical RR′R″Al compounds to preserve their integrity. Generally such compounds should be made and handled at moderate temperatures; and the formation of donor complexes with ethers or tertiary amines, RR′R″Al·D, sometimes stabilizes the compound to disproportionation. Although the formation of the etherate stabilizes allyl(diethyl)aluminum towards decomposition,[56] the same donor solvent promotes the disproportionation of dimethyl(phenylethynyl)aluminum.[198] These considerations emphasize the difficulties attending any effort to synthesize and resolve such an optically active compound (**134**), chiral at aluminum. Optically active derivatives chiral at carbon (**135**), however, have been synthesized.[214] Apropos of the stabilizing influence of donors on RR′R″Al, it is noteworthy that (**135**) does not racemize as readily as the ether-free compound.



(**134**)



$$(Et\overset{H}{\underset{Me}{C}}-CH_2)_3Al\cdot OEt_2$$

(**135**)

Conversely, mixed compounds of the type R_2AlZ (where Z is a good bridging group) are generally quite stable to disproportionation, because Z stabilizes the associated form, $(R_2AlZ)_n$. These compounds are therefore most convenient reagents for preparing a wide variety of mixed derivatives, so long as the new group Z′ is also strongly bridging (equation 72). For example, dialkylaluminum bromides or chlorides interact with metal alkoxides, fluorides, azides, hydrides, cyanides, *etc.*, to yield the corresponding derivatives. The preparation and properties of a range of such mixed derivatives are listed in Table 7. Since the highly associated R_2AlZ' products complex only weakly with ether, this donor solvent is often added to aid the displacement. Possibly the reaction proceeds by nucleophilic back-side attack of Z^- on $R_2ClAl\cdot OEt_2$, but the decisive test of such a view would require the availability of optically active compounds like (**134**). In any event, it is likely that transient aluminate anionic intermediates of the type $[R_2AlZZ]^-$ are involved in these metatheses, since isolable complexes like $K[Et_2AlCl_2]$ can be prepared.[215]

$$(R_2AlZ)_n \quad + \quad MZ' \quad \rightleftarrows \quad (R_2AlZ')_{n'} \quad + \quad MZ \tag{72}$$

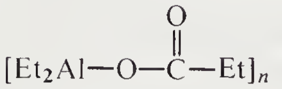
Table 7 Preparation and Properties of Selected Mixed Organoaluminum Compounds

Halide	*Metal salt*	*Product and properties*		*Ref.*
Et_2AlCl	$KOBu^t$	Et_2AlOBu^t	m.p. 78 °C dimeric	1
Et_2AlCl	NaF	Et_2AlF	b.p. 106 °C (3 mmHg) tetrameric	2
Et_2AlCl	NaN_3	Et_2AlN_3	b.p. 63 °C (10^{-3} mmHg) trimeric	3
Bu^i_2AlCl	LiD	Bu^i_2AlD	b.p. 118 °C (6 mmHg) trimeric	4
Me_2AlCl	KCN	Me_2AlCN	m.p. 89 °C tetramer	5
Me_2AlCl	$NaOSiMe_3$	$Me_2AlOSiMe_3$	m.p. 45.5 °C dimer	6

1. K. Ziegler, *Ger. Pat.* 1 162 369 (1961) (*Chem. Abstr.*, 1964, **60**, 15 907).
2. K. Ziegler and R. Köster, *Liebigs Ann. Chem.*, 1957, **608**, 1.
3. M. I. Prince and K. Weiss, *J. Organomet. Chem.*, 1966, **5**, 584.
4. J. J. Eisch and S. G. Rhee, *J. Am. Chem. Soc.*, 1974, **96**, 7276.
5. R. Ehrlich and A. R. Young, *J. Inorg. Nucl. Chem.*, 1966, **28**, 674.
6. H. Schmidbaur, *J. Organomet. Chem.*, 1963, **1**, 28.

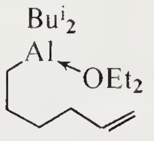
6.2.6.4 Compatibility of functional groups

The reactivity of organoaluminum compounds towards protons, oxidizing agents, C—C unsaturated linkages and carbonyl groups has already been outlined (Scheme 2). Accordingly, any compound having a C—Al bond and one of these functional groups must be considered as metastable and possibly labile. Such intermediates may range in stability from the undetectable, transitory Et_2AlOH, presumably formed by the hydrolysis of Et_3Al, to the isolable $Me_3Al{\cdot}NMe_2H$, formed from the alkyl and secondary amine and decomposing at 110 °C with methane evolution. Furthermore, careful addition of triethylaluminum to an excess of carbon dioxide yields diethylaluminum propionate (**136**),[216] which is highly associated and is stable up to 100 °C with absence of triethylaluminum. The autocomplexation stabilizes the carboxylate function against further carbalumination. Likewise, in the presence of ether diisobutylaluminum hydride adds to 1,5-hexadiene to yield (**137**). This stable complex undergoes cyclization to (**138**) when the ether is removed by a stronger Lewis acid.[217] In this instance, intermolecular complexation stabilizes the 5-hexenylaluminum intermediate.

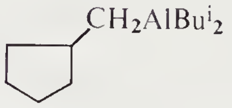

$[Et_2Al{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Et]_n$

(136)

$n = 2$–4



(137)

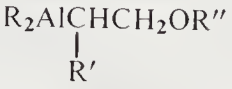


(138)

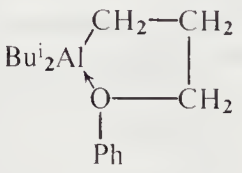
The relatively greater bond energies of Al—Z, Al—O and Al—N bonds, compared with Al—C bonds (bond energy of ≈273 kJ), favors various α-, β- and γ-eliminations of R_2AlZ from structures (**139**)–(**141**), respectively. Compound (**139**), which behaves as a cyclopropanating agent towards alkenes, is isolable as its etherate complex.[218] Structure (**140**) is the probable intermediate in the reduction of vinyl ethers $CHR'{=}CHOR$ to alkenes by R_2AlH.[219] Finally, intermediate (**141**), formed from allyl phenyl ether and Bu^i_2AlH, yields cyclopropane when heated to 100 °C.[220] The uncontrollable, often explosive reaction of aluminum metal or alkyls with organic halides is a more compelling instance of the 'incompatibility' of Al—C and C—X bonds.[221]

Et_2AlCH_2X

(139)


$R_2Al\underset{\displaystyle R'}{\underset{|}{C}}HCH_2OR''$

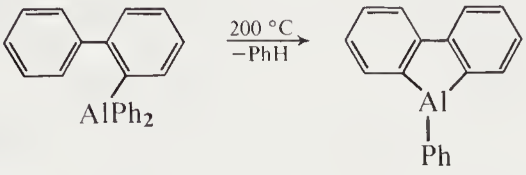
(140)



(141)

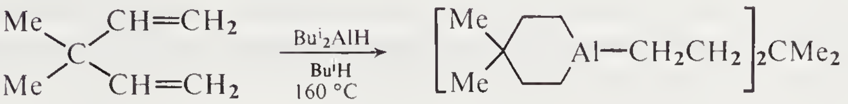
6.2.6.5 Aluminum-containing rings

Just as reactivity relationships of aluminum compounds often suggest the importance of cyclic transition states (Section 6.1.5), so there is a wide array of reactions where isolable heterocyclic aluminum intermediates are formed. Two of the first examples of aluminacarbocyclic systems, (**142**)[222] and (**143**),[223] have been generated as shown in equations (73) and (74). The thermal stability of these unsymmetrical aluminum compounds (*cf.* Section 6.2.6.3) is undoubtedly enhanced by the cyclic structure. Disproportionations involving C—Al ring bonds are suppressed, apparently because such bonds cannot as readily engage in bridging. The formation of such rings seems to follow the same trends as for carbocyclization: five- and six-membered rings are favored. That such heterocycles can be isolated supports the likelihood of their being reactive intermediates in other reactions, such as the stereospecific cyclization of 1-allylcyclohexene (**144**) to *cis*-hydrindan by alkylaluminum hydrides (Scheme 5). Thus, diisobutylaluminum hydride adds to (**144**) yielding (**145**) in a highly loco- and regio-selective manner. Heating causes the evolution of isobutene (**146**) and, because of the proximity of the remaining C═C bond to the Al—H bond, hydralumination (**147**) in a *syn* addition of the internal C═C bond in a distereo-differentiating process. Subsequently, *syn* dehydralumination to produce (**148**) and *syn* carbalumination to form (**149**) provide the precursor to *cis*-hydrindan.[224]



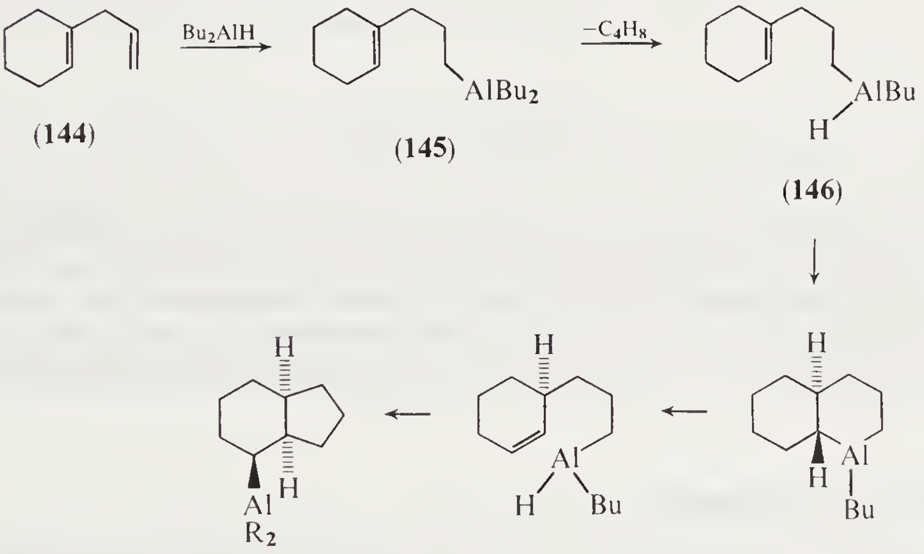
(73)

(**142**)



(74)

(**143**)



(**144**) (**145**) (**146**) (**147**) (**148**) (**149**)

Scheme 5

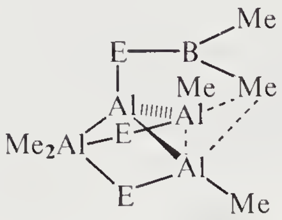
6.2.6.6 *Subvalent aluminum or aluminum–metal bonds*

Although the relative importance of the aluminum–aluminum bonding in dimeric trimethylaluminum may never gain a consensus, in recent years evidence favoring the existence of intermediates having such bonding has been obtained. A number of systems are thought to contain aluminum–aluminum or aluminum–boron bonds on the basis of spectral and chemical information. One of the first reported examples is the yellow solid isolated from the reaction of tetrakisdimethylaminodiborane with trimethylaluminum (equation 75). The complex (**150**) is suggested

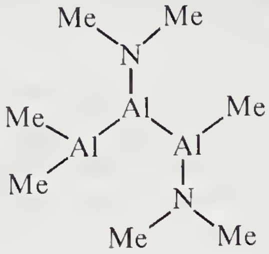
$$3B_2[NMe_2]_4 + 4[Me_3Al]_2 \longrightarrow 5Me_2BNMe_2 + 2[Me_2AlNMe_2]_2 + Me_6[Me_2N]_3Al_4B \qquad (75)$$

(**150**)

to have a tetrahedral array of aluminum atoms, three of which are bridged by dimethylamino groups, the fourth being attached to an $Me_2B—NMe_2$ moiety. The NMR non-equivalence of the methyl groups in Me_2B is ascribed to a four-center (Al, B, Al), four-electron bond (**151**).[225] When a 4 : 1 ratio of trimethylaluminum to borane is used, then a product containing the trialuminum system is isolated, possibly (**152**) or one of its isomers.[226]



(**151**) E = Me_2N



(**152**)

Likewise, the treatment of alkylaluminum chlorides bearing bulky or donor ligands with potassium metal gives a viscous product (**153**) thought to contain Al—Al bonds, because treatment with *O*-deuteriomethanol yields D_2 (equation 76).[227]

$$2RR'AlCl \quad + \quad 2K \quad \longrightarrow \quad \underset{(\mathbf{153})}{[RR'Al{-}AlRR']} \quad + \quad 2KCl \qquad (76)$$

R = Bu^i
R′ = Bu^i, Bu^iO, Me_2N

Just as in such chemically induced homolyses, so also in photochemical bond homolysis the generation of subvalent aluminum (RAl or R_2Al) is a likely first step. Whether such radicals will decompose to aluminum metal and R_3Al or whether they will couple to form Al—Al bonds depends on their thermal and chemical stability. In several photochemical studies there is evidence that intermediates like RAl, R_2Al or R_2AlAlR_2 can be chemically trapped before they decompose (equations 60 and 61).

6.2.6.7 Anionic Lewis complexes

The autoionization of an aluminum alkyl, especially in the presence of strong donors, has already been considered (*cf.* equations 29 and 71). The formation of anionic aluminum complexes is commonly encountered whenever substances of an ionic or highly polar character react with organoaluminum reagents. Thus, metal hydrides, halides, alkoxides, cyanides, alkyls and many similar salts form metal tetrasubstituted aluminates (**154** or **155**) (equation 77). Depending upon the reagents, either 1 : 1 or 1 : 2 complexes can result. These salt-like complexes have measurable but reduced electrical conductivities ($0.01–10 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$) and relatively low melting points and solubility in aromatic hydrocarbons. Table 8 presents a sampling of known complexes and their properties.

$$M^+Z^- \quad + \quad RR'R''Al \quad \longrightarrow \quad \underset{(\mathbf{154})}{M[RR'R''AlZ]} \text{ or } \underset{(\mathbf{155})}{M[(RR'R''Al)_2Z]} \qquad (77)$$

Especially important in reaction mechanisms are those cases where a covalent molecule A—B undergoes heterolysis with the formation of aluminate intermediates. A recent kinetic study of the methylation of *t*-butyl halides by trimethylaluminum (equation 79) shows that the activation energy is ~42 kJ mol^{-1} in methyl chloride and 67 kJ mol^{-1} in cyclopentane. The halide solvent is suggested to aid disruption of the dimer, and the *t*-butyl halide is heterolyzed with aluminate formation (equation 78).[228]

$$(Me_3Al)_2 \quad + \quad 2MeCl \quad \rightleftharpoons \quad 2Me_3Al{\cdot}ClMe \tag{78}$$

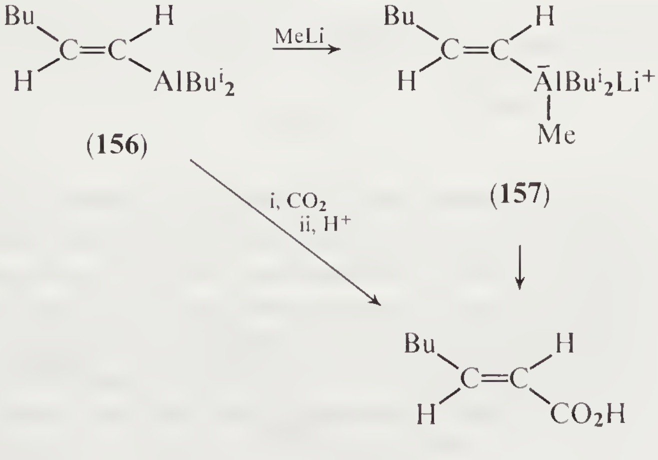
$$Me_3Al{\cdot}ClMe \quad \xrightarrow[-MeCl]{Bu^tX} \quad [Bu^t]^+[Me_3AlX]^- \quad \xrightarrow[-Me_2AlX]{} \quad Me_4C \tag{79}$$

Table 8 Some Physical Properties of Selected Organoaluminate Complexes

Compound	*M.p.* (°C)	*Specific conductivity* (Ω^{-1} cm^{-1} (°C))	*Ref.*
$LiAlMeCl_3$	74		1
$LiAlMe_4$	260 (d)		2
$NaAlEt_3F$	74	0.4×10^{-2} (100)	3
$KAlEt_3F$	58		3
$CsAlEt_4$	112	9.2×10^{-2} (120)	3
$NaAlEt_2H_2$	87		2
$NaAl_2Et_6H$	liq.	5.6×10^{-2} (120)	4
KAl_2Et_6F	129	7.3×10^{-2} (130)	3
$NaAlBu^i_3H$	205		2
$KAlEt_2F(OEt)$	98		5

1. G. J. Sleddon, *Chem. Ind.* (*London*), 1961, 1492.
2. L. I. Zakharkin and V. V. Gavrilenko, *J. Gen. Chem. USSR* (*Engl. Transl.*), 1962, 688.
3. K. Ziegler, R. Köster, H. Lehmkuhl and K. Reinert, *Liebigs Ann. Chem.*, 1960, **629**, 33.
4. K. Ziegler, H. Lehmkuhl and E. Lindner, *Chem. Ber.*, 1959, **92**, 2320.
5. H. Lehmkuhl, *Angew. Chem., Int. Ed. Engl.*, 1964, **3**, 107.

The formation of aluminates has a pronounced effect on the reactivity of C—Al bonds. As a particular application of Wittig's important theory of 'ate' and 'onium' complexes,[100,229] aluminate formation should weaken the carbon—aluminum bond and make the organic group more anionically mobile. Hence, towards electrophiles such aluminates should be more reactive than the neutral RR′R″Al type. Experiment bears out this prediction. The direct carbonation of (*E*)-1-hexenyl(diisobutyl)aluminum (**156**) yields (*E*)-2-heptenoic acid (**158**) in 35% yield (A);[103] if (**156**) is converted beforehand into the aluminate (**157**) by adding methyllithium and then (**157**) is carbonated (B), the yield of acid is 78% (equation 80).[230,231]



(80)

6.3 DYNAMIC EQUILIBRIA

6.3.1 Oligomer–Monomer Interchange

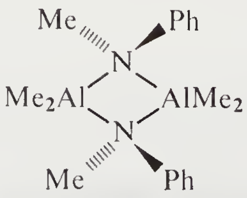
In Sections 6.2.4–6.2.6 various spectroscopic and thermodynamic data are considered as to the types and stability of associated organoaluminum compounds. Since such oligomers, (RR′-R″Al)$_n$, differ from the monomers both in structure and in reactivity, the interconversion of these forms is often important in understanding both spectral data and reaction mechanisms. The dimer–monomer interconversion of trimethylaluminum lends itself readily to NMR spectral analysis, since the room temperature exchange of methyl groups between the bridge and terminal positions (Figure 2) can be slowed down by cooling. Line-shape analysis of the two signals appearing below −40 °C permits an estimate of the rate of exchange.[148-150] The data obtained from such measurements, unfortunately, are subject to serious error: the rates can differ by a factor of ten if measured on different instruments.[150,232] Hence, much controversy has arisen concerning various interpretations of such data.[54,232,233] Consensus, however, seems to obtain on these conclusions: (a) interchange of bridge and terminal methyl groups obeys first order kinetics; and (b) the activation energy of exchange, 65.5 ± 0.8 kJ mol^{-1}, is more consistent with the rupture of both methyl bridges to form monomers (enthalpy of dissociation for $(Me_2Al)_2$ in solution is estimated as 68.5 kJ mol^{-1} [234]) than with the rupture of one bridge only.[148,235] But to account for rate differences in different solvents and in exchanges between trimethylaluminum and trimethylgallium (a monomer), two different interpretations of data have been advanced: (a) dimeric Me_3Al (**159**) dissociates in cyclopentane first to give monomers trapped in a solvent cage (**160**); these can recombine to give (**159**) and thus effect bridge–terminal methyl exchange, or they can diffuse apart (especially in toluene) to give solvent-separated monomers (**161**) which can react with Me_3Ga to give methyl exchange (equation 81);[54,233] (b) alternatively, the same mechanism for methyl exchange in $(Me_3Al)_2$—Me_3Al is accepted, but the same solvent-caged monomers can either recombine or encounter Me_3Ga (equation 82).[150,232] The finding that the rates of bridge–terminal methyl exchange in Me_3Al and of the Me_3Al–Me_3Ga exchange are comparable is in keeping with a common rate-determining step for both processes. Hence, mechanism (b) offers a better accommodation of both processes (with k_1 the slow step), as well as the fact that in contradiction of previous findings k_1 is 20 times larger in toluene than in cyclopentane (the former π-base lowering $\Delta E^{\ddagger}$ of dissociation of (**159**)). The data upon which mechanism (b) is founded are not only internally more consistent than those data for mechanism (a), but also literature values[189] of K_{eq} for (**159**) and (**160**), when combined with k_1, permit an estimate of k_{-1} (*i.e.* $K_{eq} = 10^{-10}$ and $k_1 = 10^{-1}$ s) equal to 10^{-11} s at 50 °C. Such a large value of k_{-1} is inconsistent with mechanism (a), for most Me_3Al units would recombine before leaving the solvent cage. Subsequent studies of bridge–terminal exchange in (**159**) by ^{27}Al and ^{13}C NMR spectroscopy corroborate the exchange rates found with ^1H spectra.[157]

$$\underset{\mathbf{(159)}}{Me_6Al_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathbf{(160)}}{(2Me_3Al)} \rightleftharpoons \underset{\mathbf{(161)}}{2Me_3Al} \xrightarrow[k_2]{Me_3Ga} Me_3Al{\cdot}Me_3Ga \qquad (81)$$

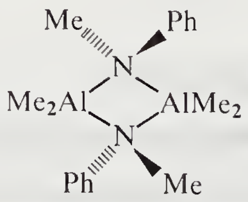
$$\downarrow$$

$$\underset{\mathbf{(159)}}{Me_6Al_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathbf{(160)}}{(2Me_3Al)} \xrightarrow[k_2]{Me_3Ga} Me_3AlMe_3Ga \longrightarrow \text{exchange} \qquad (82)$$

For other oligomers, the dissociation can lead to different intermediates. For example, a ^{13}C NMR study suggests that the intermolecular mechanism, involving exchange between solvent-separated dimers (like (**161**)), is likely to predominate with higher R_3Al dimers and especially in aromatic solvents.[236] With stronger bridges, isomerization by single bridge rupture becomes more important: the *cis–trans* interconversion of (**162a**) and (**162b**) is a case in point. The rate of interconversion (K_{eq} (**162a**)/(**162b**) ≈ 5) is accelerated by bases (THF) which probably cleave one bridge.[237] Likewise, in triarylaluminum dimers (Ar = *m*- and *p*-tolyl) the rate of exchange is independent of concentration (*i.e.* dissociation of the dimer is the slow step) and the activation



(**162a**)



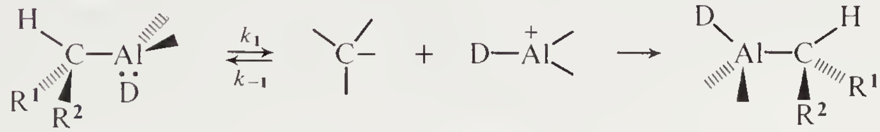
(**162b**)

energies are much smaller than needed for complete dissociation to monomer. These findings support the rupture of only one bridge in the slow step leading to exchange.[238] Single-bridged intermediates are also indicated for exchanges between cyclopropyl- and methyl-aluminum compounds[159] and in μ-methyl-μ-diphenylaminotetramethyldialuminum.[239]

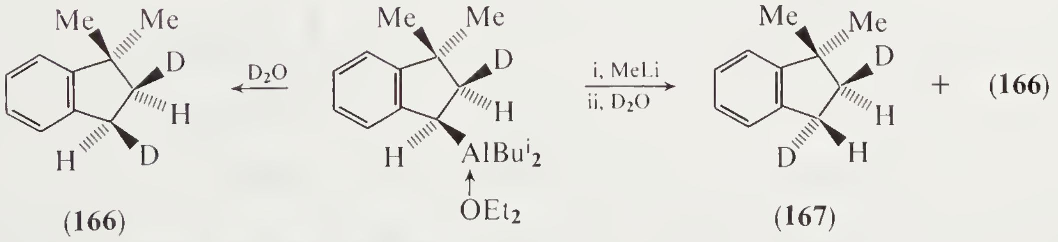
Exchange information on other oligomers presents the following perspective: (a) dimethylaluminum hydride is trimeric at 20 °C, but largely dimeric at 170 °C;[240] (b) the activation energy for ethyl exchange in di-μ-chloro(chloro)triethyldialuminum is 51.7 kJ mol^{-1};[241] and (c) dimethylaluminum phenoxide at 37 °C exists as an equilibrium mixture of dimer and trimer (K, $d^3/t^2 = 0.5$).[242,243]

6.3.2 Configurational Change at sp^3 Carbon–Aluminum Bonds

Another dynamic process of great significance to the synthetic applications of aluminum reagents is the configurational inversion of the RR′R″C—Al bond (*cf.* equations 27, 50 and 51). The ease of inversion varies both with the structure of the alkyl (**163**) and the nature of any donor present (D) (equation 83). By NMR spectroscopy, no evidence for C—Al inversion is found when trineohexylaluminum (**163**) ($R^1 = H$; $R^2 = Me_3CCH_2$) is heated in ethereal ($D = Et_2O$) solution up to 160 °C.[244] Likewise, when tri-2-methylpentylaluminum (**163**) ($R^1 = H$; $R^2 =$ *s*-butyl) is heated in diethyl ether up to 120 °C, no inversion is observed. In pentane–toluene solution, however, the latter compound inverts readily at 25 °C in a first order process ($k_1 = 0.0015\ s^{-1}$, $\Delta H^{\ddagger} = 117.6$ kJ mol^{-1}, $\Delta S^{\ddagger} = 94.4$ J K^{-1} mol^{-1}). Addition of pyridine to this solution enhances the rate, while even 0.1 mol-equivalent of ether retards the inversion. These findings can be interpreted by a donor-induced ionic dissociation (**164**) that would lead to inversion.[59] A sufficiently strong donor would be pyridine or a second molecule of the aluminum alkyl, but not ether. In hydrocarbon media a small amount of R_3Al dimer could be present (even for highly branched R_3Al)[191] and inversion could occur through this ($D = R_3Al$; *cf.* autoionization in equation 29). Corroboration of this view of inversion can be gained from the behavior of etherate (**165**): direct treatment with D_2O yields (**166**) with retention of configuration; but prior treatment with 0.2–1.5 equivalents of methyllithium and standing before D_2O treatment yields a 1 : 1 mixture of (**166**) and (**167**) (equation 84).[245] Clearly, the aluminate complex of (**165**), formed with methyllithium, can readily invert by the dissociative mechanism.



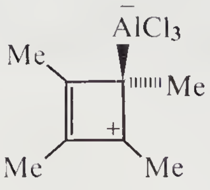
(**163a**) (**164**) (**163b**) (83)



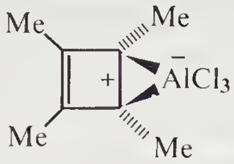
(**166**) (**165**) (**167**) (84)

That firmly associated dimers can undergo inversion is evident from the behavior of tricyclopropylaluminum. At 35 °C a benzene solution of this compound undergoes neither ligand exchange nor inversion. But at 103 °C the NMR spectrum shows that the bridged-terminal cyclopropyl groups are averaged and that inversion has occurred.[133]

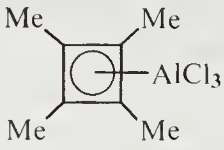
In certain structures a carbon–aluminum σ-bond can exchange sites with apparent retention of configuration. Thus the zwitterionic complex (**168**), derived from the dimerization of 2-butyne with $AlCl_3$, has been shown by variable temperature NMR spectroscopy to undergo shift of its $AlCl_3$ groups around the ring. It is not known whether rearrangement involves a 1,2-bridged five-coordinate aluminate (**168a**) or a π-complex intermediate (**168b**).[246]



(**168**)



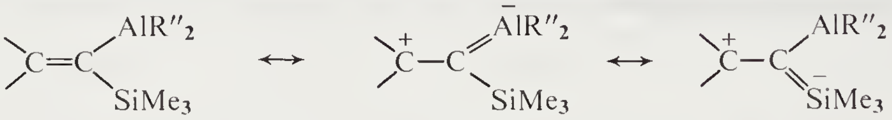
(**168a**)



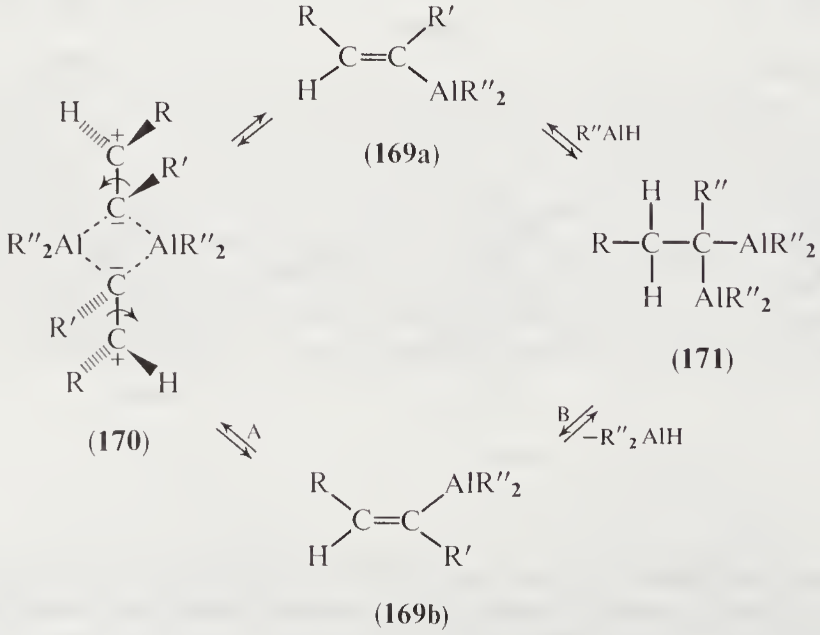
(**168b**)

6.3.3 Configurational Change at sp^2 Carbon–Aluminum Bonds

The relative ease with which vinylic aluminum compounds change their geometrical configuration is remarkable (equation 28). For 1-alkenylaluminum systems, equilibration of the (E) and (Z) forms can apparently be achieved by heating alone (A),[61] or by catalysts, such as R_2AlH(B),[77,103] R_2AlCl[247] (C) or nickel salts[248] (D). The mechanisms of these isomerizations seem to vary with the catalyst and the aluminum compound (Scheme 6). The facility with which 1-trimethylsilyl-1-alkenylaluminum derivatives (**169**) (R = C_6H_5; R′ = MeSi; and R″ = Bu^i) isomerize even at 0 °C[61] (A) seems to stem from auto-association (**170**) which would lower the C=C bond rotational barrier. Electron depletion at the β-carbon of the bridging group could be favored either by donation of π-electrons into the unoccupied $3p$- or $3d$-orbitals of aluminum and $3d$-orbitals of silicon in the monomer (**169a**) and (**169b**), or by the hyperconjugative effect of the C—Al and C—Si σ-bonds in the bridged form (**170**).[249] Owing to the strong tendency of (**169**) to form mixed bridges with dialkylaluminum hydrides,[61,200–202,205] in the presence of hydrides (**169a**) most likely equilibrates with (**169b**) by way of an analogous mixed bridge of the type (**124**), where R′ = Me_3Si and R = C_6H_5. Any other strongly bridging compound like R_2AlZ, where Z = X, OR, Me, should also be able to cause isomerization by this variant of path (A).

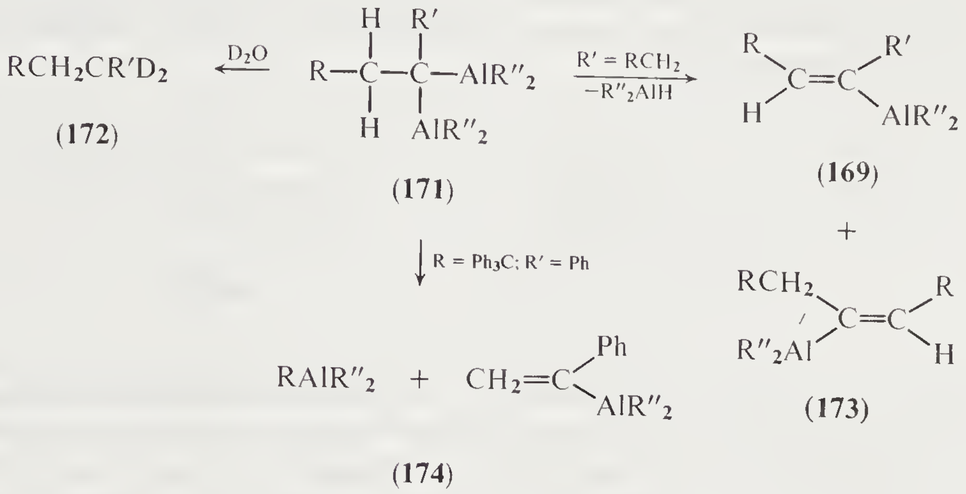


(**169**)



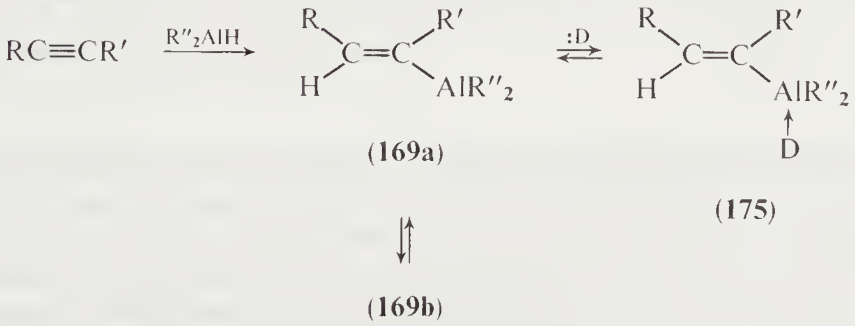
Scheme 6

In other situations there is good evidence that equilibration of (**169a**) and (**169b**) occurs by way of addition–elimination (path B). The isomerizations of (**169a**), where R = and R′ = alkyl or aryl, follow this path. With these systems, dialuminoalkanes (**171**) can be detected by the isolation of dideuteriohydrocarbons (**172**) upon treatment with D_2O, by the migration of C═C bonds (**173**) because of R_2AlH elimination from (**171**) and by the rupture of C—C bonds (**174**) in instances where steric factors hinder the usual mechanism (Scheme 7). The action of nickel salts in these isomerizations probably lies in promoting the hydralumination of (**169a**) and hence in fostering path (B). Nickel intermediates of undefined character are known to promote such additions and to cause C═C bond migration.



Scheme 7

Since the preparation of vinylaluminum compounds (**169**) is often effected by hydralumination of alkynes, great importance lies in the balance between such kinetically controlled *cis* additions and the foregoing thermodynamic equilibrations. High yields of *cis* adducts can usually be obtained from alkyl- and aryl-substituted alkynes by using R''_2AlH in hydrocarbon solution. Even such labile *cis* adducts as those from silyl- and germyl-substituted alkynes (**169**) (R = alkyl or aryl; R′ = R_3Si, R_3Ge, Me_2N) can be made in high stereoselectivity by using R''_2AlH in the presence of ethers or tertiary amines. The resulting Lewis complexes (**175**) have a considerably greater kinetic stability to isomerization (*cf.* the behavior of $RR'R''C$—AlR_2 etherates towards C—Al bond inversion in Section 6.3.2) (equation 85). As might be expected (Section 6.3.2), when an aluminate complex is made from (**169a**) by adding methyllithium (**175**) (D = CH_3^-), such complexes tend to undergo *cis–trans* isomerization upon heating.[250]

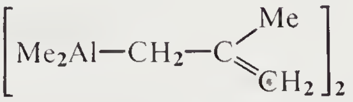


(85)

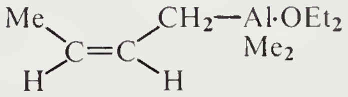
When the hydralumination of alkynes is run under conditions of thermodynamic control, the *trans* adduct (**169b**) is so much more stable that the reaction is a very useful stereoselective route to this isomer. With trimethyl(phenylethynyl)-silanes and -germanes, the ratio of (**169b**) to (**169a**) is 99:1; with diphenylacetylene, the ratio is 84:16. As the relative steric hindrance between R and R′ decreases, then smaller ratios of (**169b**) to (**169a**) will be formed at equilibrium. The hydralumination of trimethyl(1-octynyl)silane by diisobutylaluminum hydride yields a 70:30 ratio of (**169b**) to (**169a**). However, by employing the corresponding triethyl(1-octynyl)silane, a ratio of (**169b**) to (**169a**) of 93:7 can be achieved.[251]

6.3.4 Bonding Sites in Allylic Aluminum Compounds

The relatively weak nature of carbon–aluminum bonds in allylic systems, such as allyl-, benzyl- and cyclopentadienyl-aluminum derivatives, is revealed in various temperature dependent NMR studies. Mention has already been made of the interconversion of bonding sites in allyl(diethyl)-aluminum etherate at 20 °C (equation 24). Diethyl(methallyl)aluminum etherate, on the other hand, displays an unchanged AX_4 pattern between +50 and −40 °C, showing a more facile isomerization. In analogous studies, unsolvated methallyl(dimethyl)aluminum (**176**), which is dimeric in benzene, displays only one signal at 30 °C and such structural isomerization does not disappear until −70 °C. At the other extreme, *cis*-crotyl(diethyl)aluminum etherate (**177**) shows no evidence for equilibrating structures even up to 70 °C. The thermal stability of these allylic derivatives, in the absence of ether, decreases in the order crotyl > allyl > methallyl as their ease of isomerization increases.[56,252]

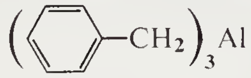


(**176**)

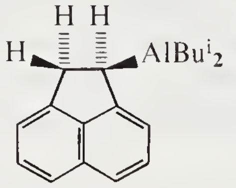


(**177**)

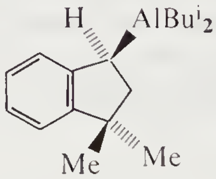
The NMR spectra of tribenzylaluminum (**178**),[81] 1-acenaphthenyl(diisobutyl)aluminum (**179**)[253] and 1,1-dimethyl-3-indanyl(diisobutyl)aluminum (**180**)[253] generally show absorptions to be expected for the non-equilibrating structures given. No great change in the spectrum of (**178**) occurs in aromatic hydrocarbon solution between 150 and −90 °C. With (**179**) the benzylic protons occur as two broad signals (area of 2:1) at 37 °C; at 95 °C, these signals resolve into a doublet and a triplet, respectively, typical of an A_2X pattern. This change indicates equilibrating interconversion of the sp^3 C—Al bond. Also of interest is the occurrence of one of the aromatic protons as an upfield signal (proton signal area at 7.1–7.7 p.p.m.: proton signal area at 6.4–7.1 p.p.m. = 4.3:1), which coalesces to a broad doublet at 6.9 p.p.m. at 95 °C. This signal is most likely due to the C(3)—H. Significantly, (**180**) does not show such a shielded proton, so the signal in (**179**) may stem from some trihapto-bonded aluminum unit, either involving the benzylic carbon-*ortho*-carbon array or arising from bridged dimers.



(**178**)

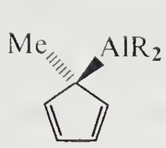


(**179**)

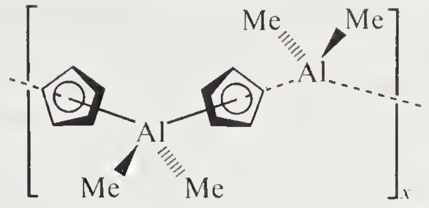


(**180**)

Dialkyl(cyclopentadienyl)aluminum compounds which tend to be dimeric at high concentrations in benzene solution display facile isomerization in NMR studies. The ring protons give a single resonance absorption even down to −90 °C. The spectra of the analogous dialkyl(methylcyclopentadienyl)aluminum compounds also show a singlet for the four ring protons at ambient temperature. At 10 °C, however, this resonance is resolved into two singlets of equal area and these singlets, in turn, are broadened by cooling to −40 °C. Thus, the presence of the methyl group in the ring slows down the isomerization and favors bonding of the aluminum as shown in (**181**).[254,255] The nature of the bonding, however, is apparently most sensitive to the physical state. In the solid state, cyclopentadienyl(dimethyl)aluminum has IR and Raman absorptions consistent with D_{5h} symmetry and therefore with a pentahapto C_5H_5—Al bond (**182**) (*cf.* (**118**)). Although the spectroscopic data are also consistent with a monomeric pentahapto structure, the low volatility, high melting point and the associated character of the cyclopentadienyl derivative in benzene all point to a polymeric bridging structure instead.[256] In the gas phase, the electron diffraction scattering data are best accommodated by a trihapto ring—Al bond (**183**).[257]



(181)



(182)

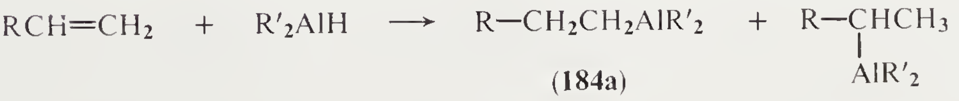
(183)

6.3.5 Isomerization of Alkyl–Aluminum Bonds

The type of sp^3 carbon–aluminum bond most favored by kinetic and thermodynamic factors is a primary carbon–aluminum bond, $RCH_2{-}Al$; secondary ($RR'CH{-}Al$) and tertiary ($RR'R''C{-}Al$) bonds, in turn, are more labile and less stable. Since the positional isomerizations of aluminum alkyls proceed by dissociation into alkene and R_2AlH (equation 23), the relative stability of C—Al bonds can be estimated both by kinetic and thermodynamic studies of alkene–R_2AlH reactions. From a standpoint of reactivity towards diethylaluminum hydride, alkenes follow the relative order shown in Scheme 8.[26] Since 1,2-disubstituted ethylenes (which would yield a secondary C—Al bond with R_2AlH) add the hydride about 1/150 as fast as a terminal alkene, one might expect less than 1% of secondary C—Al bonds (**184b**) in the reaction of equation (86). In actual cases, 3–5% of (**184b**) is found.

$$\begin{array}{lccccccc} H_2C{=}CH_2 & \approx & H_2C{=}CHR & > & H_2C{=}CR_2 & \gg & RCH{=}CHR \\ k_{rel}\ \geq 1 & & 1 & & 0.5 & & 0.01\text{–}0.02 \end{array}$$

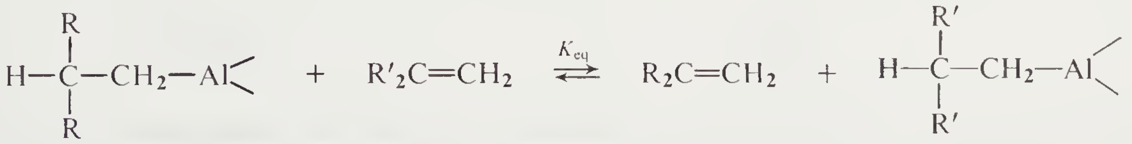
Scheme 8



$$RCH{=}CH_2 + R'_2AlH \longrightarrow R{-}CH_2CH_2AlR'_2 + R{-}\underset{\textstyle AlR'_2}{\underset{|}{C}}HCH_3 \qquad (86)$$

(184a) **(184b)**

Measurement of the equilibrium constant for equation (87) indicates the thermodynamic stability of a given C—Al bond in the presence of an alkene competing for the Al—H bond. The equilibrium lies to the right for alkenes $R'_2C{=}CH_2$, and K_{eq} decreases as shown in Scheme 9.[258] These values reflect a thermodynamic stability of about 50 for a primary C—Al bond over a secondary bond and of 2500 for a primary bond over a tertiary bond. Such a ratio would predict that about 2% of secondary C—Al bonds would exist at equilibrium. This accords reasonably well with what is found upon hydraluminating terminal alkenes and indicates that such reactions do occur under equilibrating conditions.

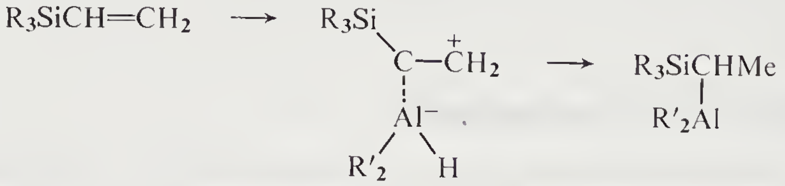


$$H{-}\overset{\textstyle R}{\underset{\textstyle R}{C}}{-}CH_2{-}Al\!\lt + R'_2C{=}CH_2 \overset{K_{eq}}{\rightleftarrows} R_2C{=}CH_2 + H{-}\overset{\textstyle R'}{\underset{\textstyle R'}{C}}{-}CH_2{-}Al\!\lt \qquad (87)$$

$$\begin{array}{lcccc} H_2C{=}CH_2 & > & H_2C{=}CHR & > & H_2C{=}CR_2 \\ K_{eq}\ 1 & & 0.02 & & 0.002 \end{array}$$

Scheme 9

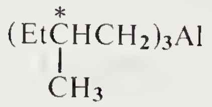
Although the *n*-alkylaluminum isomer (**184a**) is the predominant product with alkyl-substituted alkenes (equation 86) (R = alkyl) and R'_2AlH, aryl or triorganosilyl groups can influence the regioselectivity greatly. Styrene gives a ratio of (**184a**) to (**184b**) of 76:24 (R = Ph),[259] and either triethyl(vinyl)silane or triphenyl(vinyl)silane actually yields the secondary C—Al bonded compound as the principal product ((**184b**) : (**184a**) = 70 : 30, R = R_3Si).[57] Clearly, electronic factors must be the cause of this unusual regiochemistry: in the transition state (**185**), either the $p_\pi \rightarrow d_\pi$ effect or hyperconjugative stabilization of a carbenium ion β- to silicon (Section 6.3.3) can be considered the reason for preferential electrophilic attack of R'_2AlH on the α-carbon (equation 88). However, steric factors which should favor (**184a**) can be made dominant by using one-third an equivalent of triisobutylaluminum (as a source of AlH_3). Under such conditions, tris(triorganosilylethyl)aluminum is formed in which (**184a**) outweighs (**184b**) in a ratio of 82 : 18.[57]



(**185**)

(88)

A rather informative reaction on the course that these isomerizations pursue is the known racemization of optically active tris-2-methylbutylaluminum (**186**) at temperatures above 90 °C. The chirality of the organic group is lost by the reversible loss of 2-methyl-1-butene.[214] In a similar manner, both triisopropylaluminum[55] and tris-2-butylaluminum isomerize slowly at 130 °C into the n-alkylaluminum derivatives. The kinetic data exhibited by the isomerization of triisopropylaluminum and tri-t-butylaluminum are in accord with such an elimination–readdition pathway (Pr^i: $\Delta H^{\ddagger} = 110\ kJ\ mol^{-1}$; $\Delta S^{\ddagger} = 54.6\ J\ K^{-1}\ mol^{-1}$; Bu^t: $\Delta H^{\ddagger} = 125\ kJ\ mol^{-1}$; $\Delta S^{\ddagger} = -21\ J\ K^{-1}\ mol^{-1}$.[260]

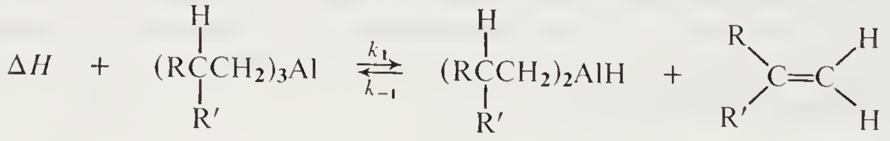


$$(\mathrm{Et}\overset{*}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{HCH_2})_3\mathrm{Al}$$

(**186**)

6.3.6 Dissociation of Aluminum Alkyls into Alkenes and Aluminum Hydride

The synthesis of aluminum alkyls from alkenes and aluminum hydride (or directly from aluminum metal and hydrogen), is, in principle, reversible and all alkylaluminum groups bearing a β-hydrogen undergo thermal alkene elimination (equation 89). The equilibrium dissociation



(187) (187a)

(89)

is markedly dependent upon structure. For comparison, Table 9 lists the degree of dissociation of alkyls formally derived from AlH_3 and three moles of (**187a**) upon being heated at 100 °C in xylene solution.[258] As is mentioned in Section 6.3.5, ethylene and α-alkenes (**187a**) (R′ = H; R = H, alkyl) have a much greater affinity for R_2AlH than unsymmetrically disubstituted alkenes (**187a**) (R,R′ = alkyl). Another measure of this affinity is the exotherm of adding monomeric R_2AlH to the alkene (the reverse of equation (89): ΔH (gas phase, $kJ\ mol^{-1}$) for R_2AlH additions: Et, 123.06; Pr, 111.3; Bu^i, 103.74).[261] For equilibrations in the liquid phase, the elimination of alkene from many n-alkyl- and isoalkyl-aluminum derivatives is endothermic by about $88 \pm 8\ kJ\ mol^{-1}$.[262] However, bulky β-substituents can lower this value markedly: triisobutyl- and tris(2,4,4-trimethylpentyl)-aluminum (**187**) (R = R′ = Me; R = Bu^tCH_2, R′ = Me respectively) undergo decomposition with $\Delta H = 66.4$[263] and 20.2[258] $kJ\ mol^{-1}$. Decomposition in the liquid phase or in concentrated solution probably does not exhibit enthalpies solely of the equilibrium shown in equation (89). If such eliminations were accurately reflected by this equation, then the system should obey Ostwald's dilution law, whereby the degree of association should increase with dilution. The lessened sensitivity to dilution accords with homo- and hetero-complexation of the hydride (*cf.* (**125**)–(**127**)) (equation 90).[258] Cryoscopic measurements confirm that bulky alkyls, such as Bu^i_3Al, are monomeric and that normally trimeric Bu^i_2AlH is monomeric in Bu^i_3Al solution. Therefore, the measured enthalpies for the decomposition of Bu^i_3Al and such bulky alkyls are probably too high, reflecting as they do the enthalpy for eliminating alkene from more stable $R_3Al{\cdot}R_2AlH$ complexes. Calculations suggest that the enthalpy of decomposition for pure liquid Bu^i_3Al should be 53.8 kJ mol^{-1}.[261]

$$5R_3Al \rightleftharpoons (R_3Al)_2{\cdot}R_2AlH + (R_3Al){\cdot}R_2AlH + RR'C{=}CH_2 \qquad (90)$$

Table 9 Degree of Dissociation of Triorganoaluminum Compounds at 100 °C[1]

R_3Al derived from alkene	*Concentration*[a] (mol Al kg^{-1})	*Degree of dissociation*
α-Methylstyrene	0.82	0.01
Isobutylene	5.00[b]	0.12
2-Ethyl-1-hexene	0.87	0.09
2-Butyl-1-octene	0.90	0.13
2-Hexyl-1-decene	0.71	0.11
2-Nonyl-1-tridecene	0.97	0.11
α-Diisobutylene	0.81	0.30
β-Pinene	0.73	0.32
Camphene	0.65	0.46

[a] In xylene. [b] Neat liquid.

1. K. Ziegler, W. R. Kroll, W. Larbig and O. W. Steudel, *Liebigs Ann. Chem.*, 1960, **629**, 53.

The elimination equilibrium can also be approached from a kinetic standpoint.[264–267] The unimolecular elimination of alkene in the gas phase from aluminum alkyls displays the following activation parameters (log A and $E^{\ddagger}$ (kJ mol^{-1})): Bu^i_3Al, 11.2 and 111.7; $BuAlMe_2$, 10.6 and 116.8; and Et_3Al, 10.5 and 126.4. From thermochemical data on such equilibria and the foregoing activation energies, the addition of monomeric Bu^i_2AlH to alkenes in the gas phase is estimated to have values of E according to Scheme 10. The relative rates observed at lower temperatures and conversions show that activation energy and entropy contribute to the $\Delta G^{\ddagger}$ of the tight, four-center transition state (*cf.* (**53**)) in a compensating manner.[267]

	$H_2C{=}CH_2$	$H_2C{=}CHMe$	$H_2C{=}CMeEt$
$E^{\ddagger}$	<5	5.2	6.1
rel. rate (104 °C)	1.32	1.00	2.28
(162 °C)	1.46	1.00	1.25

Scheme 10

The ease with which triisobutylaluminum equilibrates with diisobutylaluminum hydride and isobutene at 110 °C makes this commercially available alkyl an excellent reagent for preparing other tri-*n*-alkylaluminum compounds (**188**). The greater thermodynamic stability of these latter compounds means that the equilibrium will be to the right in equation (91) and the isobutene evolved can be selectively volatilized away or condensed out of a gas stream containing an excess of a more volatile alkene (*e.g.* ethylene) (equation 91).[42]

$$Bu^i_3Al + 3H_2C{=}CHR \xrightleftharpoons{110\ ^{\circ}C} \underset{(\mathbf{188})}{(RCH_2CH_2)_3Al} + 3Me_2C{=}CH_2 \qquad (91)$$

6.3.7 Dissociation of Aluminum Alkyls into Alkenes and a Lower Aluminum Alkyl

In organoaluminum compounds whose carbon atoms β to the C—Al bond bear no hydrogen, heating in the range 100–200 °C can cause alkene elimination and the formation of a new aluminum alkyl. A prime example of such reversible cleavage is tris(2,2-dimethylpropyl)aluminum (**189**),[268,269] which itself is produced by heating trimethylaluminum with a large excess of isobutene (equation 92).[269,270] Even aluminum alkyls having β-hydrogen atoms, such as Bu^i_3Al, can be made to decompose by elimination of Me_3Al if the isobutene is not permitted to escape during pyrolysis (as in equation 89).[271] Other examples of such eliminations are the formation of tritylaluminum compounds from the reaction of dialkylaluminum hydrides with phenyltritylacetylene (Scheme 7)[272] or from the reaction of triphenylaluminum with 3,3,3-triphenylpropene.[75]

$$(Me_3CCH_2)_3Al \xrightleftharpoons{200\ ^\circ C} Me_3Al + 3Me_2C{=}CH_2 \qquad (92)$$

(**189**)

6.3.8 Disproportionation of Unsymmetrical and Mixed Organoaluminum Derivatives

The tendency of organoaluminum compounds to redistribute their groups so as to place as many strong bridging groups as possible in bridging positions has been discussed in Section 6.2.4. Owing to this energetically favorable exchange, trimethylaluminum, when admixed with triisobutylaluminum in a 1:2 formula ratio, will form the methyl-bridged unsymmetrical derivative diisobutyl(methyl)aluminum (**101**) and, when admixed with triphenylaluminum in a 2:1 ratio, will yield the phenyl-bridged dimer of dimethyl(phenyl)aluminum (*cf.* Figure 3). Although such unsymmetrical dimers (or oligomers) are moderately stable in non-polar solvents at lower temperatures, they are in equilibrium with their monomers, especially at higher temperatures and in the presence of donor solvents. In fact, strong donors can completely disrupt any associated forms and yield monomeric, coordination compounds (*cf.* equation 68).

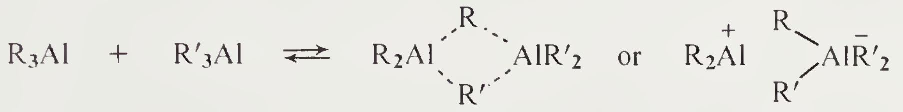
Where such strong bridging preferences do not exist or when bridging has been disfavored by coordination solvents or Lewis bases, unsymmetrical organoaluminum compounds tend to disproportionate into a statistical mixture of possible derivatives (equation 93). Thus, the smaller the enthalpy difference between making and breaking a C—Al bond in such compounds, the more the entropy of random distribution will determine the equilibrium composition of such systems.[273] Tests of such random redistribution have been made with ethyl etherates of diisobutyl(methyl)aluminum, dimethyl(phenyl)aluminum and diethyl(methyl)aluminum, where the equilibrium constants K_{eq} for equation (94) lying to the left are about 6, 8 and 0.5, respectively. Random distribution would give a value of 3.[154,274] Therefore, it is clear that once the unsymmetrical aluminum compound is prevented by solvation (**190**) from association through strong bridges, it loses any special stabilization and thus undergoes redistribution readily.

$$R_3Al + R'_3Al \longrightarrow R_3Al + 3R_2AlR' + 3RAlR'_2 + R'_3Al \qquad (93)$$

$$2R_2AlR'{\cdot}OEt_2 \rightleftharpoons R_3Al{\cdot}OEt_2 + RAlR'_2{\cdot}OEt_2 \qquad (94)$$

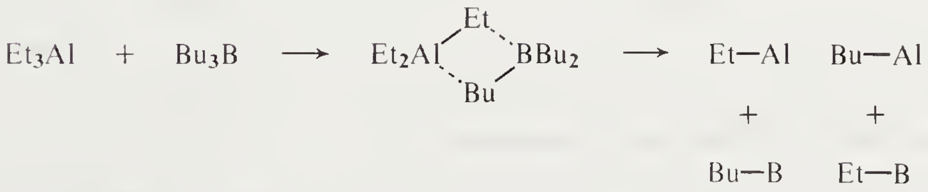
(**190**)

Besides the foregoing thermodynamic factors governing disproportionation and redistribution, kinetic considerations will often prove crucial in preparative and mechanistic studies. There is a compelling body of evidence indicating that such exchange of organic or inorganic groups between aluminum centers occurs by way of bridged dimers (*cf.* Section 6.2.4). Such dimers probably resemble, in the majority of cases, the covalently bonded dimers (**191**) shown to form with many triorganoaluminum compounds, although under some circumstances tight ion pairs (**192**) might be involved (equation 95).[258] A telling series of experiments that offers strong support for an associative mechanism of exchange is the following:[275] (a) pure boron alkyls neither associate with each other nor do they exchange groups readily; (b) aluminum alkyls generally tend to associate to a greater or lesser degree, and they undergo facile group exchange; (c) mixtures of boron and aluminum alkyls undergo ready group exchange; and (d) boron hydrides catalyze group exchange in boron alkyls. Point (c) is especially arresting: although boron alkyls, in contrast with aluminum alkyls, are inert to water, admixing equivalent amounts of triethylaluminum and tributylborane at 20 °C and immediately thereafter hydrolyzing at lower temperature gives 1 : 1 mixtures of ethane and butane. This result shows that admixing of the alkyls must have rapidly yielded equivalent numbers of ethyl–aluminum and butyl–aluminum bonds (equation 96). That only systems containing components able to form bridge dimers (R_3Al and R_2BH) are capable of group exchange speaks decisively for the necessity of intermediates like (**191**) or (**192**). The behavior of certain β-substituted aluminum alkyls, however, might seem to deviate from this pattern. Triisobutylaluminum and tris(2,4,4-trimethylpentyl)aluminum, for example, are essentially unassociated in benzene solution, giving apparent molecular weights of the monomeric form. But there is indisputable evidence that these two alkyls undergo group exchange readily with each other: when the trioctyl derivative is dissolved in pure triisobutylaluminum, the freezing point depression of the latter alkyl gives an apparent molecular weight for tris(2,4,4-trimethylpentyl)-aluminum equal to one-third of the real value.[50] Such an outcome means that by group exchange one mole of $(C_8H_{17})_3Al$ has produced three moles of 'solute' and thus yields the apparent molecular weight (equation 97). From these observations one might conclude that this is a system where group exchange occurs without any evidence for association of the components. But this apparent lack of association in these individual alkyls is true only in very dilute solution. In more concentrated solution, these alkyls do show a definite degree of dimerization: neat triisobutylaluminum is 30% associated at 30 °C, and even at 0.1 mole fraction in hydrocarbons, 5% is still associated.[191] Thus, even with such alkyls, group exchange and association tendencies coexist.



$$R_3Al + R'_3Al \rightleftharpoons R_2Al(\mu\text{-}R)(\mu\text{-}R')AlR'_2 \text{ or } \overset{+}{R_2Al}(R)(R')\overset{-}{AlR'_2} \qquad (95)$$

(**191**) (**192**)



$$Et_3Al + Bu_3B \longrightarrow Et_2Al(\mu\text{-}Et)(\mu\text{-}Bu)BBu_2 \longrightarrow Et{-}Al + Bu{-}B \quad Bu{-}Al + Et{-}B \qquad (96)$$

$$(C_8H_{17})_3Al + 2Bu_3Al \longrightarrow (C_8H_{17})Bu_2Al \qquad (97)$$

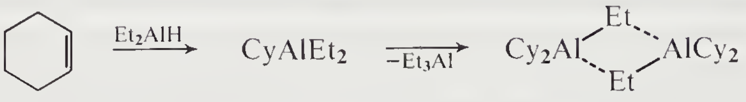
When the unsymmetrical or mixed aluminum derivatives formed in any equilibrium differ markedly in Lewis acidity, then the presence of a strong Lewis base can shift the equilibrium to generate a stronger Lewis acid. In effect, the free energy of Lewis complexation compensates for any stabilization stemming from bridging association. For instance, a 2 : 1 admixture of ethylaluminum dichloride with various donors (D), such as diisopropyl ether, phosphines and tertiary amines, yields a precipitate of complexed aluminum chloride (equation 98).[159,276,277] An important special case of such disproportionation is the conversion of alkylaluminum sesquihalides, which result from the action of aluminum metal on alkyl halides (Section 6.5.5.1), into dialkylaluminum halides. Heating (**193**) with one equivalent of powdered potassium chloride leads to complex (**194**) from which the volatile R_2AlCl can be distilled (equation 99).[276,278,279]

$$2EtAlCl_2 + D \longrightarrow Et_2AlCl + AlCl_3{\cdot}D \qquad (98)$$

$$\underset{(\mathbf{193})}{2R_2AlCl{\cdot}RAlCl_2} + KCl \xrightarrow{\Delta} 3R_2AlCl + \underset{(\mathbf{194})}{KAlCl_4} \qquad (99)$$

Another manner of shifting the equilibrium from unsymmetrical to symmetrical triorganoaluminum compounds is selective volatilization. In the hydralumination of α-alkenes with diethylaluminum hydride[26] the intermediate (**195**) can be largely converted into (**196**) by distilling off the triethylaluminum (equation 100).[280] If, however, the alkene is cyclic or internal, then disproportionation proceeds to the monoethyl product (**197**) so as to leave one good bridging group (equation 101).[26] The sharply reduced tendency of secondary C—Al bonds to participate in bridging probably also contributes to the stability of (**197**) by making further exchange exceedingly difficult.

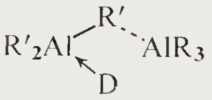
$$\mathrm{RCH{=}CH_2} \xrightarrow{\mathrm{Et_2AlH}} \underset{\mathbf{(195)}}{\mathrm{RCH_2CH_2AlEt_2}} \xrightarrow[-\mathrm{Et_3Al}]{} \underset{\mathbf{(196)}}{\mathrm{(RCH_2CH_2)_3Al}} \qquad (100)$$



(101)

(**197**)

Not only does group exchange require an organic or inorganic group with some bridging tendency, but the process also seems to require at least one three-coordinate aluminum center to accept the bridge (**198**). It follows that the stronger the donor D and the greater the excess of such a base, the slower will be the rate of group exchange (*cf.* Section 6.2.4). Generally, this accords with the findings of various NMR studies, such as the exchange of Me_3Al and $AlCl_3$ in ethers or amines[281] and the exchange between $MeAlCl_2$ and $AlCl_3$ in ethers.[282] For similar reasons, intramolecular *n*-coordination (**199**) will yield unsymmetrical derivatives unusually stable to disproportionation (*cf.* (**131**)–(**132**)).



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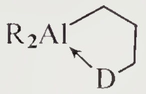
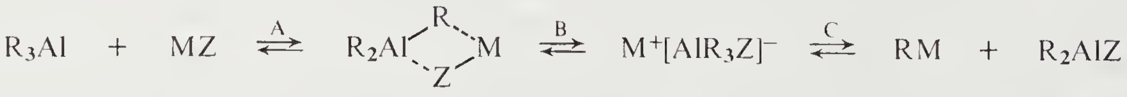


(199)

6.3.9 Interactions with Other Metal Compounds

A number of important equilibria can be set up between organoaluminum derivatives and other metal compounds. In the preceding section, the exchange of groups between organoboron and organoaluminum compounds has been discussed (equation 96). This process of transmetallation or metal–metal exchange (C) represents one extreme of the interactions possible with the compounds of two different metals (Scheme 11). Thus, in step (A) an unsymmetrically bridged association (**200**) of the two components could be formed; or in step (B) an intimate ion pair (**201**) could result from group transfer (Lewis complexation); or in step (C) actual group exchange could ensue. Naturally, products (**202**) could also undergo association as in (**200**). How far a given MZ proceeds in its interaction with R_3Al depends upon the electronegativity of M and the lattice energy of MZ. Generally, for metals much more electropositive than aluminum (Groups IA and IIA, except beryllium), complexation (as in (**200**) or (**201**)) occurs, rather than exchange (**202**). Illustrative complexations include: (a) the formation of lithium tetramethylaluminate from methyllithium and trimethylaluminum in ethereal solution;[283] (b) the formation of sodium trichloro(ethyl) aluminate from heating powdered sodium chloride with ethylaluminum dichloride;[7] and (c) the formation of alkali metal trialkyl(hydrido) aluminates from metal hydrides and trialkylaluminums.[284] The electrical conductivity displayed by such complexes in different media, as well as their other properties, may favor formulation (**200**) or (**201**) in individual cases (*cf.* Section 6.2.6.6).



(**201**) (**202**)

(**200**)

Scheme 11

With salts of most other metals whose electronegativity is either somewhat lower (zirconium, titanium, mercury, thallium, *etc.*) or higher, aluminum alkyls will effect transmetallation to some extent. However, all three groups of R_3Al may not be available, because the resulting R_3AlZ or $RAlZ_2$ may be thermodynamically too stable towards remaining MZ. Thus, diethylzinc is produced in high yield only if a 2:1 ratio of triethylaluminum to zinc chloride is employed (equation 102).[285–287] But in addition to incomplete alkyl transfer, the resulting R_2AlCl and $RAlCl_2$ by-products are strong Lewis acids and therefore may complex with starting material (MZ) or product (RM). Such complexation occurs in the alkylation of gallium(III) chloride, where only about a 50% yield is obtained, as a net result of equations (103a) and (103b). By introducing three equivalents of powdered sodium chloride and warming, the complex $Na[AlEt_2Cl_2]$ is formed and all of the gallium(III) chloride becomes available for forming triethylgallium.[287]

$$2Et_3Al + ZnCl_2 \longrightarrow 2Et_2AlCl + Et_2Zn \qquad (102)$$

$$GaCl_3 + 3Et_3Al \longrightarrow Et_3Ga + 3Et_2AlCl \qquad (103a)$$

$$GaCl_3 + 3Et_2AlCl \longrightarrow Ga[AlEt_2Cl_2]_3 \qquad (103b)$$

The complexing tendencies of alkali metal and tetraethylammonium halides with triethylaluminum show a qualitative trend that is inversely related to the lattice energy of the halide salt (Table 10). Thus, the stability of the complex $M[AlEt_3X]$ increases as the radius of the anion X^- decreases and the radius of the cation M^+ increases.[279,288] Moreover, with a given metal halide (*e.g.* RbX) the stability of the complex with R_3Al tends to decrease with increasing chain length in R: $Et > Bu^i > C_8H^i_{17}$.[279,288,289] With a given alkyl group, the complexing tendency increases in the series $Et_3Al < Et_2AlCl < EtAlCl_2$. Thus, the relatively weak complexing agent LiCl (Table 10) forms a stable complex only with ethylaluminum dichloride but the stronger agent KCl is required to form a stable and isolable complex with triethylaluminum.[288]

Table 10 Complexing Ability of Alkali Metal Halides with Triethylaluminum[1,2]

Cation	*Fluoride*	*Chloride*	*Bromide*	*Iodide*
Lithium	0	0	0	0
Sodium	+	0	0	0
Potassium	+	+	0	0
Rubidium	+	+	+	0
Cesium	+	+	+	0
Tetraethylammonium	+	+	+	+

1. K. Ziegler, R. Köster, H. Lehmkuhl and K. Reinert, *Liebigs Ann. Chem.*, 1960, **629**, 33.
2. H. Lehmkuhl, *Angew. Chem.*, 1963, **75**, 1090.

Another measure of the stability of such aluminate complexes (**201**) is the extent to which Lewis acids (path A) or Lewis bases (path B) can displace their counterparts (Scheme 12). Thus, treatment of sodium ethoxy(triethyl) aluminate with triethylaluminum leads to the displacement in equation (104).[288,290] Accordingly, the Lewis acidity decreases from Et_3Al to Et_2AlOEt. The enthalpy of formation ΔH_f for a number of metal salt complexes of the types $MZ{\cdot}Et_3Al$ and $MZ{\cdot}2Et_3Al$ has now been measured and the observed trends in stability agree with the foregoing qualitative work.[291]

$$R_3Al + M[AlR'_3Z] \xleftarrow[A]{AlR'_3} M[AlR_3Z] \xrightarrow[B]{MY} M[AlR_3Y] + MZ$$

(**201**)

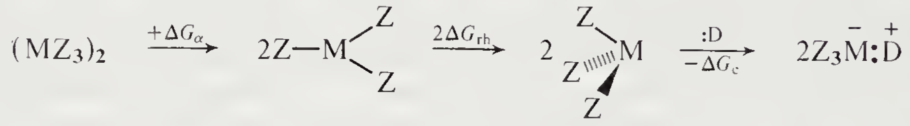
Scheme 12

$$Na[AlEt_3OEt] + Et_3Al \longrightarrow Na[AlEt_4] + Et_2AlOEt \qquad (104)$$

Similar reactions between $M[AlR_3Z]$ and a variety of MY agents have led to the following order of basicity of Y^-:[288] $RO^- > PhO^- > Et^- \simeq H^- > F^- > Cl^- > Br^- > I^-$.

6.3.10 Equilibration with Neutral Lewis Bases

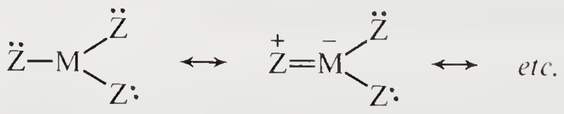
The stability of coordination compounds between neutral Lewis acids and bases has been analyzed in terms of the electronic, steric and reorganization effects.[292] Besides the steric factors which have already been mentioned in Section 6.1.4, the reorganization effect also stems principally from structural changes resulting from coordination. This effect identifies the bond length and angle changes required of the uncoordinated Lewis acids and bases as these components assume the geometry of the final complex. For the dimeric Lewis acid (**203**), clearly one-half the energy of dimerization (ΔG_d) will have to be expended; and for the monomeric form of Group IIIA compounds (**204**), bond rehybridization from a quasi-sp^2 to a quasi-sp^3 (**205**) will have to occur (ΔG_{rh}). The changes in geometry required of most Lewis bases (D), on the other hand, are expected to be relatively slight, since the donor electron pair has already exerted its structure influence on the base (*e.g.* amines are already pyramidal). Any other changes in the base are subsumed under steric factors (F- and B-strain)[293,294] (Scheme 13).



(**203**) (**204**) (**205**) (**206**)

Scheme 13

Contributions to the dimerization tendency of organoaluminum compounds have already been discussed (Sections 6.2.1, 6.2.4 and 6.2.5). The rehybridization energy of (**204**) will encompass electronic and steric (B-strain) contributions. If the B-strain is included in any steric effect in (**206**), then the change from (**204**) to (**205**) can be analyzed in electronic terms alone. The principal energy increase stems from the greater electron pair repulsion in (**205**) over that in (**204**). Another as yet undetermined factor which may increase ΔG_{rh} is any multiple bonding in (**204a**). Such delocalization could also operate, although to lesser effect, in (**205**) and thereby further reduce the Lewis acidity or the actual energy of coordination ΔG_c. The net Gibbs free energy of coordination would then be as shown in equation (105). In this energy analysis, the electronic and steric factors manifest themselves principally in step (**205**) → (**206**), but it follows that very firmly associated Group IIIA derivatives will exhibit a sharply reduced Lewis acidity.



(**204**) (**204a**)

$$-\Delta G_f = \tfrac{1}{2}\delta G_d + \Delta G_{rh} - \Delta G_c \qquad (105)$$

Despite its dimeric character trimethylaluminum is generally the strongest Lewis acid among Group IIIA methyl derivatives, the order for the Group being B < Al > Ga > In > Tl.[295] Similarly, the Lewis acidity of the triphenylmetal derivatives as measured by ΔH_f falls in the series Al > Ga > B > In.[296] Owing to the fact that trimethylborane or triphenylborane is much more sensitive to steric factors, its Lewis acidity relative to the derivatives of gallium, indium and thallium is dependent upon the structure of the Lewis base. Moreover, since only the aluminum alkyl is significantly associated, its complexation with weak Lewis bases may be surpassed by the monomeric alkyls of gallium, where no expenditure of ΔG_d is required. Thus the ranking of Lewis acidities for Group IIIA derivatives will depend upon physical state (gaseous or liquid at a given temperature) and the Lewis base chosen. For example, by measuring changes in the asymmetric C=O stretch of dicarbonyl(cyano)π-cyclopentadienyliron which occur upon coordination with a Lewis acid, the following acidity series has been determined:[297] $BH_3 < BF_3 < BCl_3 \approx BBr_3$; $BCl_3 > GaCl_3 > AlCl_3$; and $Me_3Al > Me_3B \approx Me_3Ga$.

Another method of ranking is the result of correlating Pt—H NMR coupling constants of Lewis acid (A) adducts with cyano(hydrido)bis(triethylphosphine)platinum, $H(Et_3P)_2PtCN{\cdot}A$.[298] The order of Lewis acidity of some pertinent compounds is $AlCl_3 > Ar_3B > R_3B > Ar_3Al > (ArO)_3B > R_3Al > R_2AlOR$. Such studies serve to illustrate how varying contributions from the terms in equation (105) can interchange the apparent Lewis acidity of Group IIIA compounds.

Some estimate of the influence of organic groups on the acceptor strength of aluminum derivatives can be made if the enthalpy of dimerization is known. Taking ΔH_d in R_3Al as 85.7 (Me), 71 (Et) and 75.2 kJ mol^{-1} (Ph),[299] one can compare the heats of formation (ΔH_f) of R_3Al complexes with various ethers, sulfides and amines (Table 11).[299-301] After these values are adjusted for the different ΔH_d values the enthalpies for the reaction of monomeric R_3Al (equation 106) show that ΔH_f for triphenylaluminum is consistently greater than the values for the ethyl and methyl derivatives; the values for the ethyl analogue are only slightly larger than for the methyl. If entropic differences are not too large, then ΔG_f should also rank as Ph ≫ Et > Me. The greater ΔG_f for triphenylaluminum could readily be attributed to the electron-attracting effect of the phenyl group in stabilizing the complex (**206**) (Z = Ph). On the other hand, the decrease in ΔH_f for R_3Al as the chain length of R increases would seem to reflect F- and B-strains upon complexation. The observed ΔH_f for the coordination of R_3Al with isoquinoline in the liquid state varies from 88.6 kJ mol^{-1} for Et_3Al to 75.6 kJ mol^{-1} for $(n\text{-}C_8H_{17})_3Al$.[302] That ΔH_d decreases from 71 kJ mol^{-1} for the ethyl derivative to 61.7 kJ mol^{-1} for the octyl derivative means that the difference in ΔH_f is really 18.1 kJ mol^{-1}. A more evident instance of such steric factors is the complete displacement of ether from tri-*t*-butylaluminum etherate by trimethylamine to form the amine complex (**207**), while no displacement occurs with triethylamine (equation 107).[49]

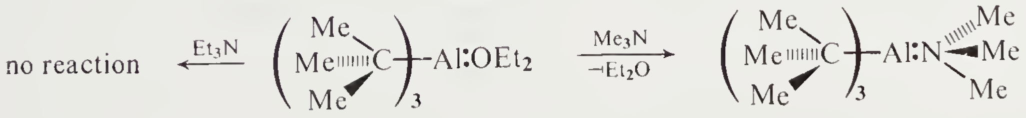
Table 11 Enthalpies of Complex Formation[a] for Selected Triorganoaluminum Compounds[1]

Donor	*Me_3Al*	*Et_3Al*	*Ph_3Al*
Bu_2O	−48.1	−51.8	−52.3
Pr_2S	−27.7	−31.0	−42.1
Et_3N	−71.5	−75.6	−87.5
Pyridine	−72.7	−73.6	−95.4

[a] Values in kJ mol^{-1} for the reaction $1/2\ Al_2R_6 + D \rightarrow R_3Al{\cdot}D$ in benzene solution.

1. Zh. S. Galuashvili, I. P. Romm, E. N. Gur'yanova, N. N. Korneev and K. A. Kocheshkov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1975, **24**, 2598.

$$R_3Al{\cdot}D \rightleftharpoons R_3Al(m) + D + \Delta H_d \qquad (106)$$



(107)

(**207**)

From a standpoint of the Lewis base, extensive studies of Lewis complexation with trimethylaluminum have been carried out in the vapor phase where the enthalpy of dissociation has been determined (equation 106).[48] The following decreasing order of donor strength (ΔH_{donor}) has been determined (values in parentheses in kJ mol^{-1}): $Me_3N > Me_3P > Me_2O$ (>79.8) $> Me_2S$ (79.8) $> Me_2Se$ (67.2) $> Me_2Te$ (<67.2). Where quantitative data are not available, ranking can be decided by competition between donors. Trimethylaluminum, for example, selectively complexes with the amine in mixtures of trimethylamine and trimethylphosphine. Further values of ΔH_f based on monomeric Me_3Al are included in Table 11. Owing to steric and electronic factors, amines are not always stronger donors than ethers. Judged by ΔH_f for the complexation with triethylaluminum in solution, THF (ΔH_f = 58.8 kJ mol^{-1}) and even di-*n*-alkyl ethers (46.2–50.4

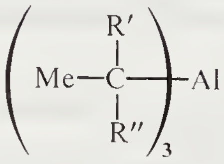
kJ mol^{-1}) are donors of comparable or better strength vis-à-vis such amines as *N*,*N*-dimethylaniline (48.3 kJ mol^{-1}) or 2-methyl-6-ethylpyridine (58.0 kJ mol^{-1}).[301]

6.4 BONDING AND STRUCTURAL VARIETY IN MONOMERIC DERIVATIVES

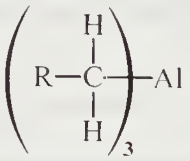
6.4.1 Monomeric Organoaluminum Compounds

The foregoing discussion of physical and spectroscopic properties reveals how these characteristics are largely determined by associated forms of organoaluminum compounds. Since most triorganoaluminum (RR′R″Al) and all mixed (R_nAlZ_{3-n}) derivatives are associated, special experimental techniques or structural circumstances are required to study the properties and bonding in the monomeric form of such compounds. The monomers are the reactive intermediates in many reactions and hence their bonding is important in the understanding of reaction mechanisms.

The association of organoaluminum monomers by bridging groups is very sensitive to steric hindrance, so that monomer formation may often be favored by placing bulky substituents on the α- or β-atom of the potential bridging group. The monomeric character of triisopropylaluminum (**208a**) and tri-*t*-butylaluminum (**208b**) and the largely monomeric character of triisobutylaluminum (**209a**) and tribenzylaluminum (**209b**) exemplify this point. Substitution of bulky groups naturally cannot have such a direct effect on the association of mixed R_2AlZ types where strong bridging by halide, hydride, alkoxide or amide is involved. However, although amides of the type $R_2AlNR'_2$ are usually firmly dimeric, diisobutylaluminum diphenylamide ($Bu^i_2AlNPh_2$) does exist in benzene solution as a mixture of monomer and dimer (degree of association = 1.7).[303]



(**208a**) R′ = H; R″ = Me
(**208b**) R′, R″ = Me



(**209a**) R = Pr^i
(**209b**) R = Ph

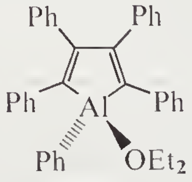
Experimentally, the monomeric form can be favored at equilibrium by working at lower concentrations, lower pressure (Ostwald dilution law), by raising the temperature (since association is exothermic) or by adding a donor to trap the monomer (**210**) (equation 108). In this discussion it will be of interest to consider how the properties of the carbon–aluminum bond vary in going from monomer (**210**) to coordinated monomer (**211**).

$$\Delta H_{\text{dimer}} + (R_3Al)_2 \rightleftharpoons \underset{(\mathbf{210})}{2R_3Al} \overset{:D}{\rightleftharpoons} \underset{(\mathbf{211})}{2R_3Al{:}D} \qquad (108)$$

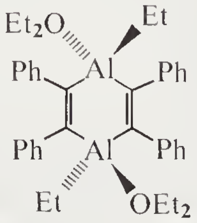
6.4.2 Bond Length and Geometry

What direct evidence there is on the bonding in monomeric trimethylaluminum has been obtained from electron diffraction[146] and Raman spectral data[304] on the alkyl vapor at 215 °C and 30 mmHg pressure. Such measurements are consistent with a trigonal planar array of the methyl–aluminum bonds (D_{3h} symmetry) as sp^2-hybridized aluminum would be expected to have. Noteworthy is the carbon–aluminum bond length of 196 pm. With reference to the bonding differences between (**210**) and (**211**), it is remarkable that a wide variety of trimethylaluminum complexes shows a very similar bond length: $Me_3Al{\cdot}NMe_3$ (196 pm);[143] $2Me_3Al{\cdot}$dioxane (195 pm);[305] $Me_3Al{\cdot}$acetonitrile (200 pm);[306] K[Me_3AlCN] (197 pm);[307] and K[Me_3AlH] (199.8 pm).[308] Even the nonbridging bonds in dimeric trimethylaluminum have similar lengths (196–198 pm). Thus, although the geometry and hybridization of monomeric trimethylaluminum change drastically upon complexation (to sp^3 and distorted tetrahedral), the carbon–aluminum bond length does not.

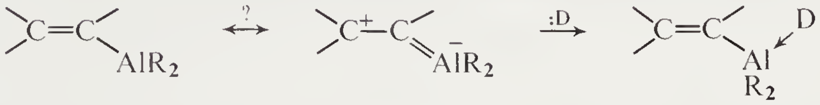
The presence of sp- or sp^2-hybridized carbon–aluminum bonds seems not to change such bond lengths markedly. The lengths of the nonbridging phenyl–aluminum bonds in dimers of triphenylaluminum (Figure 3) and of diphenyl(phenylethynyl)aluminum (Figure 4) are 196 pm and 194 pm, respectively. Enclosure in an unsaturated ring, as in the etherate of pentaphenylaluminole (**212**), also has little effect: the ring carbon–aluminum distance is 196.6 pm[309] and that of the phenyl–aluminum bond is 197.6 pm. Even in *cis* vicinal dialuminoethylene systems, such as the *trans* dietherate of 1,4-diethyl-2,3,5,6-tetraphenyl-1,4-dialumina-2,5-cyclohexadiene (**213**), the carbon–aluminum bonds are 198.4 pm long.[310] What would prove of great value, however, would be sp- or sp^2-carbon–aluminum bond lengths for monomeric, uncoordinated organoaluminum compounds. In such systems the question of whether $C_{p\pi} \rightarrow Al_{p\pi}$ bonding occurs might be answered by examining carbon–aluminum bond lengths in *monomeric* (**214**) and its complex (**215**) (equation 109).



(**212**)



(**213**)



(**214a**) (**214b**) (**215**) (109)

Considerable lengthening of carbon–aluminum bonds does occur, on the other hand, in certain tetramethylaluminate anions: the alkali metal salts show the following C—Al separations: K, 210; Rb, 206; and Cs, 195 pm.[311,312] The trend in lengths is consistent with increasing polarization effects on the distorted tetrahedral Me_4Al anion as the cationic radius decreases. The greater bond distances in the potassium and rubidium salts (and presumably weaker bonds) compared with 196 pm for monomeric trimethylaluminum, provide experimental support for Wittig's solvation–reactivity theory for organometallic compounds (Section 6.2.6.6).

6.4.3 Bond Strength

The average bond dissociation energies of various metal alkyls have been redetermined after assessing the validity of available standard heats of formation (ΔH_f).[261] An acceptable set of ΔH_f° values is required to meet the following criteria: (a) within a class of compounds (alkyls, halides, hydrides, *etc.*), $-\Delta H_f^\circ$ should increase with increasing chain length with the homologous increment in the $-\Delta H_f^\circ$ value being constant starting with R = Et; (b) the heats of formation from class to class (*e.g.* $R_3Al \rightarrow R_2AlCl$) must be consistent; and (c) heats of reaction calculated from such ΔH_f° values must give acceptable agreement with experimentally observed heats. A compilation of such consistent ΔH_f° values for liquid (l) and gaseous (g) monomers of R_3Al and R_2AlH and for dimers of R_2AlCl is given in Table 12.

The average methyl–aluminum bond dissociation energy $\overline{D}(Me—Al)$ is considered to be one-third of the enthalpy change for the reaction shown in equation (110). The ΔH_f° (M, g) of trimethylaluminum is then used with the heat of atomization of aluminum[104] and a value of ΔH_f° for methyl (142.8 ± 4.2 kJ mol^{-1}) to yield a $\overline{D}(Me—Al)$ of 281.4 kJ mol^{-1}. Previously reported $\overline{D}(Me—Al)$ values have ranged from 270.9 ± 8.4 to 277.2 ± 5 kJ mol^{-1}. Experimental ΔH_f° (l) values of -120.54,[313] -151.2[314] and -152.5[315] kJ mol^{-1} have been obtained from combustion or acetolysis of trimethylaluminum and a value of -151.2 kJ mol^{-1} has been judged to meet the three criteria most acceptably.

$$Me_3Al(g) \longrightarrow 3Me(g) + Al(g) \qquad (110)$$

Table 12 Calculated Enthalpies of Formation for Organoaluminum Compounds[1]

Compound	$-\Delta H_f^\circ (M, g)^a$ (kJ mol^{-1})	$-\Delta H_f^\circ (M, l)^b$ (kJ mol^{-1})	$-\Delta H_f^\circ (l)^c$ (kJ mol^{-1})
Me_3Al	87.78	110.46	151.20
Et_3Al	117.18	157.08	192.78
Bu_3Al	179.34	232.68	265.02
$[CH_3(CH_2)_4]_3Al$	241.50	308.28	339.36
$[CH_3(CH_2)_5]_3Al$	303.66	383.88	414.54
$[CH_3(CH_2)_6]_3Al$	365.82	455.28	490.14
$[CH_3(CH_2)_7]_3Al$	427.98	535.08	565.74
	490.14	610.68	640.92
Me_2AlH	26.88	45.36	114.66
Et_2AlH	46.62	77.70	147.00
Pr_2AlH	88.20	128.94	198.24
Bu_2AlH	129.36	180.18	249.48
Me_2AlCl	335.58^d	355.74^d	
Et_2AlCl	357.00	386.82	
Pr_2AlCl	399.42	437.22	
Bu_2AlCl	441.42	487.62	

[a] Values are those for forming the monomer in the gaseous state. [b] Values are those for forming the monomer in the liquid state. [c] Values are those for forming compound in its normal state of association in the liquid state (dimer or trimer). [d] Values apply to the formation of dimeric R_2AlCl.

1. M. B. Smith, *J. Organomet. Chem.*, 1974, **76**, 171.

Use of such internally consistent and experimentally acceptable $-\Delta H_f^\circ$ (l) values provides the following values of $\overline{D}$(Me—M) for Group IIIA derivatives (in kJ mol^{-1}): B (369.6), Al (281.4), Ga (256.2), In (218.4) and Tl (151.2). Similar calculations lead to a value of 290.2 kJ mol^{-1} for $\overline{D}$(H—Al).

Based upon the criteria of monotonic increases in a homologous series, internal consistency and the expected agreement between calculated and experimental ΔH_f° (l), most of the literature values derived from heats of combustion measurements are found unacceptable.[316]

Related to the methyl-aluminum bond energy is the ionization of trimethylaluminum under electron impact either in the mass spectrometer or in the photoelectron spectrometer. Under varying pressures and ionization voltages the most abundant peak by far is that due to the Me_2Al^+ fragment. For example, at 70 eV monoaluminum peaks and their abundances are as follows: Me_3Al^+ (4.9), Me_2Al^+ (100), $MeAl^+$ (6.3), Al^+ (36.5).[158] The ionization potentials of the neutral Me_3Al, Me_2Al and MeAl fragments are estimated to be 9.09, 6.6 and 7.8 eV, respectively. For comparison, the PE spectrum of monomeric trimethylaluminum yields an ionization potential of 9.76 eV for an electron in the highest occupied molecular orbital, which involves primarily the carbon–aluminum bond. Similar PE spectral studies of monomeric and dimeric dimethylaluminum halides conclude that electrons in the bridging aluminum–halogen bonds require a higher ionization potential than those in the Al—X orbitals of the monomer.[317,318]

Analogous mass spectral studies on the triphenylmetal derivatives of Group IIIA have uncovered convincing evidence for the existence of fragments containing two metal atoms (*e.g.* $C_{30}H_{25}M_2$) and at 70 eV gave the prominent peaks listed in Table 13.[319] The similarity of ionization efficiency curves for the derivatives of boron, aluminum and gallium points to the monomer as being responsible for the ionization and decomposition in each case. The estimated ionization potentials for the neutral Ph_3Al, Ph_2Al and Al fragments are 9.0, 10.3 and 1.3 eV, respectively. The cleavage of the first bond in Ph_3Al is said to require 126 kJ mol^{-1}, which value should be compared with a value of about 327.6 kJ mol^{-1} for rupturing the first bond in Me_3Al (obtained from an activation energy value in pyrolytic studies).[320] This discrepancy may mean that the actual fragment is not Ph_2Al, but some isomer that forms through bond reorganization. The relative abundance of the parent peak Ph_3M at 10 eV reflects the decreasing bond strength in the series; B (73), Al (51), Ga (12), In (11), Tl (1).

Table 13 Mass Spectral Behavior[a] of the Triphenyl Derivatives of Group IIIA Metals. Metal-containing Fragments[1]

Ph_3B	*Ph_3Al*	*Ph_3Ga*	*Ph_3In*	*Ph_3Tl*
$C_{18}H_{15}B$	$C_{30}H_{25}Al_2$	$C_{30}H_{25}Ga_2$	$C_{30}H_{23}In$	$C_{18}H_{15}Tl$
$C_{18}H_{15}B^{2+}$	$C_{30}H_{24}Al_2$	$C_{24}H_{20}Ga_2$	$C_{30}H_{22}In$	$C_{18}H_{14}Tl$
$C_{18}H_{14}B$	$C_{24}H_{20}Al_2$	$C_{18}H_{15}Ga$	$C_{24}H_{19}In$	$C_{12}H_{10}Tl$
$C_{18}H_{14}B^{2+}$	$C_{24}H_{19}Al_2$	$C_{18}H_{14}Ga$	$C_{24}H_{18}In$	C_6H_5Tl
$C_{18}H_{13}B$	$C_{18}H_{15}Al_2$	$C_{12}H_{10}Ga$	$C_{18}H_{15}In$	Tl
$C_{18}H_{13}B^{2+}$	$C_{18}H_{14}Al_2$	C_6H_5Ga	$C_{18}H_{14}In$	
$C_{16}H_{13}B$	$C_{18}H_{15}Al$	Ga	$C_{12}H_{10}In$	
$C_{16}H_{13}B^{2+}$	$C_{18}H_{14}Al$		C_6H_5In	
$C_{16}H_{12}B$	$C_{12}H_{10}Al$		In	
$C_{16}H_{12}B^{2+}$	$C_{12}H_9Al$			
$C_{16}H_{11}B$	$C_{12}H_8Al$			
$C_{16}H_{11}B^{2+}$	C_6H_5Al			
$C_{12}H_{10}B$	Al			
$C_{12}H_9B$				
$C_{12}H_8B$				
$C_{10}H_8B$				
$C_{10}H_7B$				
$C_{10}H_6B$				
C_8H_6B				
C_6H_5B				
C_6H_4B				
C_4H_3B				
C_4H_2B				

[a] Spectra taken at 70, 20 and 10 eV.

[1] F. Glockling and J. G. Irwin, *J. Chem. Soc., Dalton Trans.*, 1973, 1424.

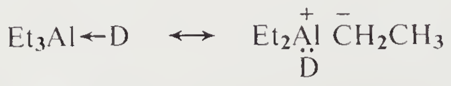
6.4.4 Electronic Spectra

The electronic spectra of the triphenylmetal derivatives of boron, aluminum and gallium are pertinent to the question of π-bonding between carbon and the metal (equation 109). By examining the spectra in dilute solution (10^{-3} M) where even the aluminum compound should exist preponderantly as the monomer the following intense ($\log \epsilon > 4$) long wavelength absorptions are exhibited in methylcyclohexane solution: B, 280–290; Al, 260; and Ga, 250 nm.[321] In diethyl ether solution the intensity and position of the bands of the boron and gallium derivatives are changed very little but the long wavelength band of the aluminum compound is markedly reduced in intensity and acquires vibrational structure characteristic of monosubstituted benzenes like toluene. These observations can be explained by an electronic transition involving an intramolecular transfer of charge from the π-system to the vacant *np* orbital of the metal (**216**). The hypsochromic effect of the ether may be traced to etherate formation ($Ph_3Al{\cdot}OEt_2$), which removes the $3p$ orbital from such p_π–p_π interaction. With boron such etherate formation is lacking and with gallium such complexes are quite weak.

(**216a**) (**216b**)

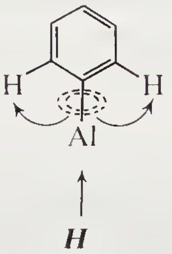
6.4.5 NMR Spectra

The NMR spectra of various organoaluminum systems and their monomeric coordination compounds have been used to assess the relative strength of donors and the electronic influence of the aluminum center. The well-established correlation between proton chemical shifts and electronegativity of Z for derivatives of the type RCH_2Z[322–327] has been extended to encompass both ^1H and ^{13}C spectra of benzyl derivatives including those of tribenzylaluminum. A linearity between Muller's electronegativity values and the CH_2 chemical shift has been uncovered. Likewise, the difference (Δ) between the CH_3 and CH_2 proton chemical shifts of ethylaluminum derivatives[176,328] has been examined (Δ is negative because the CH_3 signal occurs at a higher field than the CH_2 signal). Measurement of Δ for the spectra of triethylaluminum in various donors shows that $|\Delta|$ values increase as the donor character of the solvent increases (*i.e.* $Et_3Sb < Et_2O < Et_3N$). Formation of the symmetrical tetraethylaluminum anion by admixing methyllithium with triethylaluminum ($\Delta = -0.81$), changes Δ to -1.3.[329] In the light of the suggestion that a decrease in Δ (or increase in $-\Delta$) betokens a lowering of the electronegativity of Z in CH_3CH_2Z,[330] coordination tends to favor a more electropositive aluminum (resonance structure (**217**)), greater electron density on the CH_2 group (more shielding) and hence a greater polarization of the carbon–aluminum bond (*cf.* Wittig's 'ate' conception: Section 6.1.5). Similar NMR interpretations of spectra obtained of alkylaluminum complexes with amines or ether have led to the assigning of a varying electronegativity (χ_{Al}) to aluminum in different derivatives R_3Al; Et_3Al (1.37), Et_2AlCl (1.52), $EtAlCl_2$ (1.61), Bu^i_3Al (1.55), Bu^i_2AlCl (1.66), and Bu^iAlCl_2 (1.71).[175] In monomeric tribenzylaluminum not only the CH_2 but also the *ortho* protons are shielded (6.80 p.p.m.) compared with those in toluene (6.99 p.p.m.).[331] On the other hand, the *ortho* protons of triphenylaluminum, either in benzene or in THF, are markedly deshielded (−0.74, −0.49 p.p.m.).[178] Such variation in shielding can be attributed to magnetic anisotropy arising from the carbon–aluminum bond in (**218**) and (**219**). In (**218**) induced magnetic fields strengthen the external field (***H***); in (**219**) such induced fields oppose ***H***.

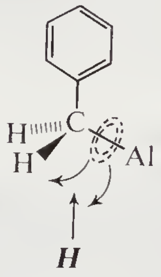


$$Et_3Al \leftarrow D \quad \longleftrightarrow \quad Et_2\underset{\ddot{D}}{\overset{+}{Al}}\ \overset{-}{C}H_2CH_3$$

(**217a**) (**217b**)



(**218**)



(**219**)

6.4.6 IR Spectra

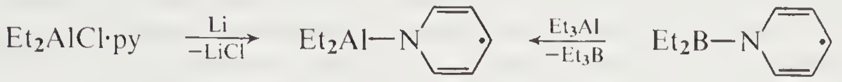
The great value of IR and Raman data in elucidating the structure of associated organoaluminum derivatives and the strength of donor–acceptor complexes, such as $R_3Al{:}N{\equiv}CR'$, has been discussed in Section 6.2.4. There it is mentioned that intermolecular bridging by 1-alkenyl or 1-alkynyl groups in R_2AlR' dimers causes a lowering in the C=C or C≡C stretch over the corresponding carbon–carbon stretch in the complexes $R_2AlR'{\cdot}OR''_2$ or $R_2AlR'{\cdot}NR''_3$. These observations support the view that π-electrons of C=C and C≡C linkages can be donated intermolecularly. To decide whether such π-electron delocalization could be operative intramolecularly (*cf.* equation 109), it would be desirable to examine the IR spectra of *monomeric*, uncomplexed 1-alkenyl- and 1-alkynylaluminum derivatives. Unfortunately, the highly associated character of these compounds has thus far made such measurements unattainable.

6.4.7 NQR Spectra

The change in bond angle and bond strength when monomeric R_3Al undergoes coordination (equation 108) is particularly suitable for study by nuclear quadrupole resonance spectroscopy. By comparing the ^{27}Al NQR coupling constant of monomeric tri-*t*-butylaluminum, whose carbon–aluminum bonds are certainly in a trigonal coplanar array, with those of trimethylaluminum adducts, the strengths of the donor bonds can be ranked. The stronger the coordination, the greater the Me—Al—Me bond angle, and hence the coupling constant should decrease. The decreasing ranking of coupling constants means an increasing strength of the donor D in $Me_3Al{\cdot}D$ as follows;[332] Me_3Sb (32.13) < Me_2S (29.75) < Me_3As (28.45) < Me_3P (23.60) < Me_3N (11.52).

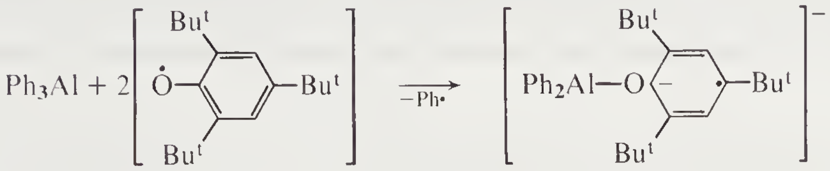
6.4.8 ESR Spectra

Two instances of rather unusual organoaluminum free radicals are those derived from equations (111)[333] and (112).[334,335] In both cases, much of the spin density is on the organic ligand, so it is debatable whether these are really aluminum-centered free radicals. The delocalized nature of the radical **(220)** is shown by its *g* value of 2.003.

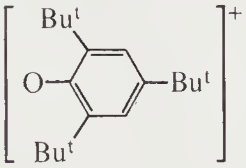


(111)

(220)



(112)



(221)

6.4.9 Dipole Moments

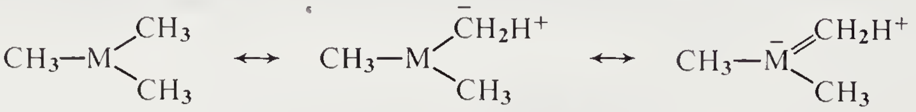
Since monomeric, symmetrical derivatives R_3M of Group IIIA possess a trigonal coplanar bonding array about the metal (D_{3h} symmetry) they would be expected to have no dipole moment (*cf.* equation 17). Even symmetrically bridged dimers of R_3Al would not yield a net moment. Accordingly, dipole measurements in different solvents offer a means of ranking the Lewis acidity of R_3M toward potential donors. Such coordination brings about considerable charge separation and thus a bond moment **(222)** in equation (113). The observed moments of triphenyl- and triethyl-metal derivatives in dioxane show the following gradation (range of 3.7 to 0 D):[336,337] Al > Ga > In > Tl > B. The small but finite moments observed for some of these derivatives (Al, Ga, In, Tl) even in benzene can be ascribed either to the presence of associated forms of R_3M or to the formation of a π-complex with benzene **(222)** (D = C_6H_6) (*cf.* Section 6.2.5).

$$R_3M \quad + \quad :D \quad \rightleftarrows \quad R_3\overset{-}{M}-\overset{+}{D} \qquad (113)$$

(222)

6.4.10 Bonding in the Monomer

The strong dimerizing tendency of trimethylaluminum contrasts with the strictly monomeric character of trimethylborane. The greater stability of $[Me_3Al]_2$ over that of $[Me_3B]_2$ has been variously ascribed to: (a) steric repulsions of the methyl groups in $[Me_3B]_2$;[11,12] (b) greater interaction of the more polar C—Al bonds in $[Me_3Al]_2$,[11,12] compared with that of the less polar C—B bonds in the hypothetical $[Me_3B]_2$; (c) the availability of *d* orbitals on aluminum to strengthen Al—Al bonding in the dimer;[12,141,142] (d) a total of σ- and π-overlap population for the metal–carbon bond in the monomer of <0.8, as calculated by the extended Hückel method with charge iteration;[141b] and (e) selective stabilization of monomeric Me_3B compared with monomeric Me_3Al by hyperconjugation (**223**).[338] Present interpretations of the bonding in dimeric trimethylaluminum accept the first four of these factors as significant, with their relative importance varying from one theoretician to another (*cf.* Section 6.2.2). By consensus, the fifth factor, hyperconjugation, plays no role in determining the tendency of Me_3M to dimerize,[141] but is considered to be a significant contributor to the bonding in the monomer. Hückel calculations with charge iteration estimate that such π-bonding is 7% and 8% of the total M—C bonding for Me_3B and Me_3Al, respectively. The same calculations, with Al(3*d*) orbitals included in the basis set, produce the atomic charge data given in Figure 7. The greater positive charge on Al, compared with B, is thought to be the principal reason for the gradation in Lewis acidity of $Me_3Al > Me_3B$. Previous explanations of the lower acidity of Me_3B have invoked selective steric hindrance or greater hyperconjugation. However, calculations show that there is about the same proportion of hyperconjugation in both Me_3B and Me_3Al. Also steric hindrance is not always an obvious factor, especially if the donor is relatively small. Such is the case with the pyridine complexes of Group IIIA triphenylmetal derivatives, where heats of formation (in parentheses; kJ mol^{-1}) suggest the following ranking of acidity;[296] Al (93.7) > Ga (81.9) > B (75.2) > In (58.4). Thus, charge on the metal atom appears to be a more satisfactory explanation of Lewis acidity.[141b]



(223)

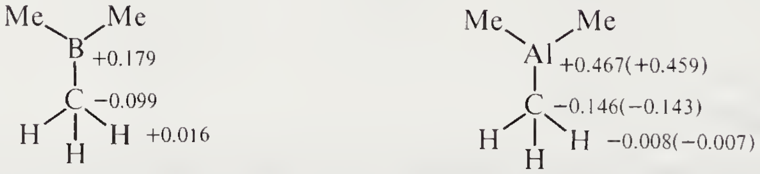


Figure 7 Atomic charge data for monomeric trimethylborane and trimethylaluminum, as derived from extended Hückel calculations with charge iteration. Values in parentheses for Me_3Al are derived by including 3*d*-orbitals of Al in the basis set[141b]

6.4.11 Structures of Unusual Compounds

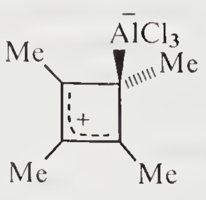
In addition to those discussed thus far, some unusual structures have been found in various organoaluminum compounds. Examples of the following illustrate some noteworthy types of bonding: (a) aluminum–metal bonding (**224**)[339] and (**225**);[340] (b) zwitterionic complex (**226**);[341] (c) heterocyclic aluminate anion (**227**);[342] (d) polyaluminate anion (**228**);[343] and bimetallic bridged complexes (**229**).[344,345] Such types of compounds often play a role in important catalytic processes.

$(Me_3Si)_3Al{\cdot}THF$

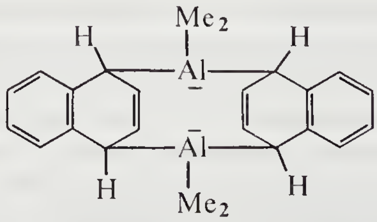
(224)

$[(C_5H_5)_2TiAlEt_2]_2$

(225)



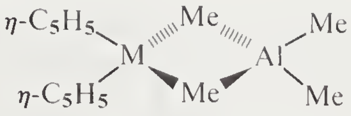
(226)



(227)

$[(Me_3Al)_3SeMe]^-$

(228)



(229) M = Y, Yb

6.5 PREPARATION

6.5.1 General Experimental Considerations

The establishment and maintenance of a moisture- and oxygen-free atmosphere are essential to the success of any preparative work with organoaluminum compounds. An inert gas, such as anhydrous nitrogen or argon, must blanket all transfer, preparation and purification procedures. Any solvent or reagent and all internal surfaces of reaction vessels must be free of any active hydrogen or peroxidic impurities. Further details for carrying out such operations optimally and safely are given in Section 6.8 and in ref. 346.

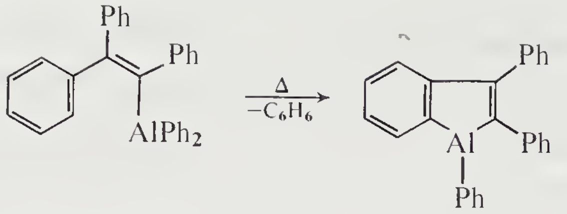
But here attention is drawn to certain intrinsic structural factors connected with preparative work. First of all, the Lewis acidity of organoaluminum compounds will lead to complex formation with solvents such as ethers or amines, with metal salt by-products such as alkali metal halides, or even with an excess of certain starting materials like alkyllithium reagents. Liberation of the desired aluminum compound from these complexes is a difficult or often impossible task. Accordingly, the preparation of an uncomplexed organoaluminum compound will require: (a) the use of non-donor solvents (usually alkanes or aromatic hydrocarbons); (b) the choice of reagents and conditions so as to produce weakly complexing metal salts (*e.g.* lithium halides or alkali metal bromides or iodides (*cf.* Table 10)); and (c) careful attention to stoichiometry and mode of mixing so as to avoid a local excess of RLi in reactions involving the alkylation of aluminum chloride (equation 114).[347]

$$3RLi \quad + \quad AlCl_3 \quad \xrightarrow{\text{heptane}} \quad R_3Al \quad + \quad 3LiCl \qquad (114)$$

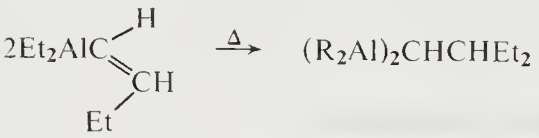
Secondly, with unsymmetrical aluminum products R_2AlR', the tendency for disproportionation must be reckoned with. Such instability is so marked if R and R′ are both alkyl that such compounds cannot be isolated in the pure state. If R′ is a 1-alkenyl or 1-alkynyl group, the uncomplexed R_2AlR' is stabilized through bridging dimerization (*cf.* Section 6.3.7). With these compounds, complexation with ethers or amines often stabilizes the system kinetically against disproportionation but may eventually promote it thermodynamically. The stability of the complex $(C_5H_5)AlMe_2{\cdot}THF$ at −40 °C and its disproportionation at 20 °C illustrate this behavior.[254]

Thirdly, organoaluminum compounds undergo a wide variety of reversible (Section 6.3) and irreversible chemical changes at moderate temperatures. The occurrence of any of these will spoil the desired preparation. Reversible changes, such as allylic, propargylic or benzylic rearrangements, *cis–trans* alkenyl or cycloalkyl isomerization, the conversion of *t*- and *s*-alkyl-aluminum groups into *n*-alkylaluminum groups, the cyclization of ω-alkenylaluminum compounds into cycloalkylaluminum compounds, and the elimination of alkene from R_3Al, can produce impurities or undesired products. Irreversible decomposition can involve C—Al bond homolysis[348] (equation 115), metallative cyclization[53] (equation 116), polymerization by means of intermolecular carbalumination[72] (equation 117) and attack on a complexed donor[49] (equation 118). To minimize the intrusion of these isomerizations and decompositions, unnecessary or prolonged heating should be avoided in any workup or purification. Moreover, in many of these reactions the free R_3Al is more reactive than an ether or amine complex, $R_3Al{\cdot}D$. Thus the isolation of some organoaluminum compounds as a complex is often advantageous. Unfortunately, as equation (118) indicates, such complexes are frequently too stable and attempts to remove the donor lead to profound decomposition.

$$Ph_2Al{-}CPh_3 \quad \xrightarrow{\Delta} \quad [Ph_2Al{\cdot}] \quad + \quad Ph_3C{\cdot} \qquad (115)$$



(116)



$$2Et_2AlC(H){=}CHEt \xrightarrow{\Delta} (R_2Al)_2CHCHEt_2 \qquad (117)$$

$$(Me_3C)_3Al{\cdot}OEt_2 \xrightarrow[-EtH]{\Delta} (Me_3C)_2AlOEt + Me_2C{=}CH_2 \qquad (118)$$

6.5.2 Symmetrical Triorganoaluminum Compounds

6.5.2.1 Displacement between metal alkyls and aluminum metal

A most versatile method for the synthesis of alkyl,[2,9b,214,349–352] alkenyl,[353–355] alkynyl,[356–358] benzyl,[81] cyclopentadienyl[359,360] and aryl[43,196,361–364] derivatives of aluminum is the displacement of mercury from diorganomercury compounds by aluminum.[359,360] Since many organomercury compounds are readily accessible (from mercury salts and Grignard reagents), are stable to moisture and oxygen and do not complex with ethers and amines, they are excellent precursors to unsolvated aluminum derivatives (equation 119). The heterogeneous reaction, which may be promoted by activating the aluminum metal (pre-amalgamation), may require extended heating of the pure reactants or of hydrocarbon solutions. Hence, thermally unstable mercury (dibenzylmercury) or aluminum (trivinylaluminum) compounds will require careful temperature control for successful reaction. In the former case, temperatures over 110 °C lead to dibenzyl and mercury; in the latter case, a reaction temperature of 0 °C and the subsequent addition of ethers or pyridine permits the distillative isolation of $(CH_2{=}CH)_3Al{\cdot}D$. Some other specific applications are given in equations (120)[365] and (121).[356,357] Tris(trimethylsilyl)aluminum and tris(trimethylgermyl)aluminum (as THF adducts)[339,366] and tris(trimethylsilylmethyl)aluminum[367] have likewise been prepared from the corresponding mercury compounds.

$$2Al + 3R_2Hg \longrightarrow 2R_3Al + 3Hg \qquad (119)$$

(120)

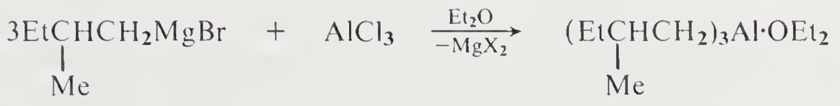
$$3(RC{\equiv}C)_2Hg + 2Al \xrightarrow{Et_2O} 2(RC{\equiv}C)_3Al{\cdot}OEt_2 + 3Hg \qquad (121)$$

6.5.2.2 Metathesis between metal alkyls and aluminum compounds

This method has two principal variations: (a) the treatment of an aluminum salt, usually a halide, with a more reactive organometallic compound such as a derivative of lithium, sodium, potassium or magnesium, or $M[AlR_4]$, whereby thermodynamics strongly favors the products (equation 122)[259,283,368–383] and (b) the interaction of one triorganoaluminum compound (or AlH_3) with an organic derivative of a less reactive metal (boron, mercury) wherein the resulting equilibrium can be shifted by selective removal of the most volatile member (equation 123).[197,275,383–385] In the former method, care must be taken to avoid ether, if the unsolvated R_3Al is required. If ether-free organomagnesium reagents are desired, some of the recent procedures for preparing them in hydrocarbon media should be employed.[386] Again, however, an ether or amine may be advantageous in stabilizing R_3Al to the kinds of isomerizations and decompositions discussed in Section 6.5.1. Successful applications of the second method have been especially numerous for the reaction of boron compounds with triethylaluminum. In the ensuing equilibrium triethylborane is almost always the most volatile member (Et_3B, b.p. 95 °C; $(Et_3Al)_2$, b.p. 186 °C) and can be readily removed. Specific illustrations from the literature can be found in equations (124),[387] (125),[356,388] (126),[275] (127)[133] and (128).[358]

$$3RM + AlX_3 \longrightarrow R_3Al + 3MX \tag{122}$$

$$3R_2M + 2R'_3Al \rightleftarrows 2R_3Al + 3R'_2M\uparrow \tag{123}$$



$$3Et\underset{\displaystyle Me}{C}HCH_2MgBr + AlCl_3 \xrightarrow[-MgX_2]{Et_2O} (Et\underset{\displaystyle Me}{C}HCH_2)_3Al{\cdot}OEt_2 \tag{124}$$

optically active optically active

$$3HC{\equiv}CNa + AlCl_3 \xrightarrow[-NaCl]{Et_2O} (HC{\equiv}C)_3Al{\cdot}OEt_2 \tag{125}$$

$$(1\text{-naphthyl})_3B + Et_3Al \longrightarrow \underset{80\%}{(1\text{-naphthyl})_3Al} + Et_3B \tag{126}$$

(127)

$$3Ph_2Hg + 2AlH_3 \xrightarrow{Me_3N} 2Ph_3Al{\cdot}NMe_3 + 3Hg + H_2 \tag{128}$$

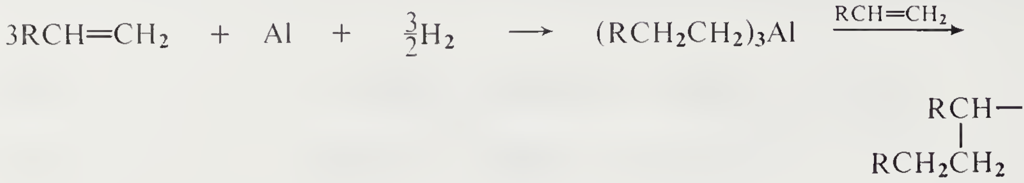
6.5.2.3 Hydralumination of unsaturated hydrocarbons

In this versatile method, trialkyl- or tri-1-alkenyl-aluminum compounds are prepared from alkenes or alkynes and some form of aluminum hydride. According to the source of the AlH_3, the following preparative variants can be distinguished: (a) the generation of aluminum hydride *in situ*, as in the one-step synthesis of aluminum alkyls from the alkene, aluminum metal and hydrogen gas (equation 10);[28,36,389–393] (b) the generation of aluminum hydride from the elements (or NaH and $AlCl_3$) and in the presence of R_3Al, so as to stabilize the hydride as R_2AlH; and the addition of R_2AlH to the alkene in a separate step at lower temperatures (equation 9);[36,394–398] (c) the preparation of aluminum hydride etherate or LAH in a separate step and their subsequent addition to the alkene[26,399,400] (equation 129); and (d) the use of aluminum hydride transfer from one alkene to another, as in the reactions of triisobutylaluminum with α-alkenes (equation 12), whereby the prevailing equilibria can be shifted by various means (large excess of one alkene, or removal of the other).[27,42,258,262]

$$Li[Al(CH_2CH_2R)_4] \xleftarrow{LiAlH_4} RCH{=}CH_2 \xrightarrow{AlH_3{\cdot}OEt_2} (RCH_2CH_2)_3Al{\cdot}OEt_2 \tag{129}$$

Variants (a), (b) and (d) are central to the industrial, large scale synthesis of aluminum alkyls and their successful realization requires the optimizing of many reaction and engineering factors. The extensive pertinent literature on proper industrial practice, as well as Volumes 7 and 8, should be consulted directly.[44,398,401,402] Since variants (a) and (b) involve heterogeneous reactions under pressure where proper activation of the aluminum metal surface is crucial, these procedures are generally inconvenient and unsuitable for the research laboratory. A copious patent literature describes numerous techniques for subdividing the metal (milling, atomizing the molten metal, chemical etching of the surface) and activating it towards hydrogen (addition of Ti, Zr, Hf, Nb, V, La or Sc; avoidance of Fe, Li, Cu, Sn, Pb and Ni).[394,403–405] The one-step synthesis (variant a) is successfully applied to branched α-alkenes, such as isobutylene, which do not undergo carbalumination with the resulting R_3Al under the reaction conditions. This method is suitable for the large scale synthesis of triisobutylaluminum and the corresponding alkyls from 2-methyl-

1-pentene, 2,4,4-trimethyl-1-pentene and limonene. With straight chain α-alkenes, the one-step synthesis fails because of concurrent carbalumination (equation 130). Hence, the two-step synthesis ($R_2AlH \rightarrow R_3Al$) is necessary. Triethyl- and tripropyl-aluminum are made on a large scale in this manner.



$$3RCH{=}CH_2 \quad + \quad Al \quad + \quad \tfrac{3}{2}H_2 \longrightarrow (RCH_2CH_2)_3Al \xrightarrow{RCH=CH_2} \underset{\displaystyle RCH_2CH_2}{RCH}{-}CH_2{-}Al{<} \qquad (130)$$

Variant (c) can be conducted without pressure equipment for reactions of aluminum hydride, but the resulting alkyl will contain some proportion of the etherate.[26,406] If the R_3Al boils at a sufficiently high temperature (R = hexyl, isooctyl), the ether-free alkyl may be isolated. Hydralumination with $LiAlH_4$ may require the use of an autoclave but the process does yield ether-free $LiAlR_4$.[26,407,408] This product can be treated with $AlCl_3$ to yield R_3Al[399] (*cf.* Section 6.5.2.2). Also, $NaAlH_4$ is reported to give 95% of (**230**) at 120–140 °C (equation 131).[409] The tris(phenylethynyl)aluminum tetrahydrofuranate is then obtained by treating (**230**) with $AlCl_3$ in THF.[410]

$$NaAlH_4 \quad + \quad 4PhC{\equiv}CH \xrightarrow[\text{cat.}]{Bu^i{}_2AlH} \underset{\textbf{(230)}}{Na[Al(C{\equiv}CPh)_4]} \qquad (131)$$

As has been mentioned previously (equation 91), the use of triisobutylaluminum in variant (d) is an excellent method for preparing R_3Al compounds from alkenes less volatile than isobutylene.[42]

6.5.2.4 Dehalogenation of organoaluminum sesquihalides

Although organic halides, in general, can react with aluminum metal, a clean formation of the organoaluminum sesquihalides (1 : 1 mixture of (**231**) and (**232**)) takes place only in certain cases (equation 132). The chlorides, bromides and iodides of methyl, ethyl, allyl, 2-butenyl, benzylic, and simple aryl derivatives are reported to form smoothly.[6,40,41,411,412] Butyl- and octyl-aluminum sesquiiodides can be obtained in moderately good yields in the presence of ether; propyl- and butyl-aluminum sesquichloride etherates can be isolated with little decomposition.[413] With other organic halides a variety of dehydrohalogenation, alkene polymerization and protodealumination side reactions interfere. But the methyl-, ethyl- and phenyl-aluminum sesquihalides and their triorganoaluminum compounds are of great importance in fundamental and applied research, and so the method is still most useful. The first step of the preparation which involves the reaction of the organic halide with activated aluminum powder can be unpredictable and dangerous, so the details of tested procedures should be studied carefully beforehand.

$$3RX \quad + \quad 2Al \longrightarrow \underset{\textbf{(231)}}{R_2AlX} \quad + \quad \underset{\textbf{(232)}}{RAlX_2} \qquad (132)$$

In the second step the sesquihalide mixture, either as a neat liquid or in hydrocarbon solution, is heated with portions of metallic sodium or sodium–potassium alloy to form the triorganoaluminum compound.[40,414,415] Since the resulting NaX may complex with (**231**) or (**232**), conversion may be poor. For this reason, better results are obtained by separating (**232**) from (**231**) by complexation with NaCl and dehalogenating only the latter (equation 133). Some success in combining these two steps has been achieved: trialkyl- and triaryl-aluminum derivatives have been prepared by heating the organic halide with a mixture of aluminum and either $AlCl_3$ or magnesium[416–418] (equation 134).

$$3R_2AlCl \quad + \quad 3RAlCl_2 \xrightarrow[-Na[AlRCl_3]]{NaCl} 3R_2AlCl \xrightarrow[-NaCl]{Na} 2R_3Al \quad + \quad Al \qquad (133)$$

$$6PhCl \quad + \quad 2Al \quad + \quad 3Mg \longrightarrow 2Ph_3Al \quad + \quad 3MgCl_2 \qquad (134)$$

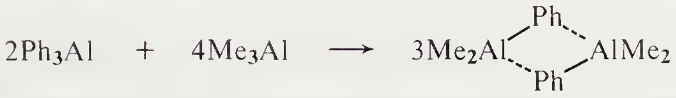
It might be noted that interesting organoaluminum intermediates have been generated by the interaction of aluminum metal vapors and various organic substrates. From the reaction with propylene and subsequent treatment with D_2O various dideuterated propanes and hexanes have been isolated; such products are diagnostic for the intermediacy of C—Al bonds in such reactions (*cf.* Section 6.8.4).[419]

6.5.3 Unsymmetrical Triorganoaluminum Compounds

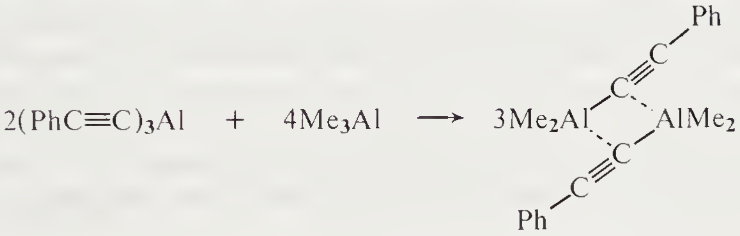
6.5.3.1 Redistribution reactions with symmetrical compounds

Previous discussions have stressed that aluminum alkyl dimers of the type $(R_2AlR')_2$ are only stabilized if R′ is a good bridging group, such as Me, Et, cyclopropyl, 1-alkenyl, 1-alkynyl or Ph. However, such stabilization can be overcome by addition of Lewis bases or by excessive heating, which may then favor disproportionation to the stronger acid, R_3Al, or to the most volatile alkyl. Typical preparations, therefore, involve admixing two equivalents of R_3Al with one of a strongly bridging R'_3Al without heating and in non-polar media. The NMR spectrum can be used to verify the completion of the redistribution. Some additional specific preparations are shown in equations (135),[134] (136)[101,154,420] and (137).[356,373,421]

$$2(\text{cyclo-C}_3\text{H}_5)_3\text{Al} + 4\text{Me}_3\text{Al} \longrightarrow 3\text{Me}_2\text{Al}\begin{smallmatrix}\text{cycloC}_3\text{H}_5\\ \\ \text{cycloC}_3\text{H}_5\end{smallmatrix}\text{AlMe}_2 \qquad (135)$$



$$2\text{Ph}_3\text{Al} + 4\text{Me}_3\text{Al} \longrightarrow 3\text{Me}_2\text{Al}\begin{smallmatrix}\text{Ph}\\ \\ \text{Ph}\end{smallmatrix}\text{AlMe}_2 \qquad (136)$$

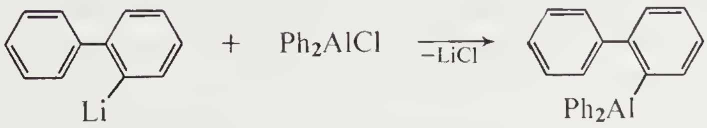


$$2(\text{PhC}{\equiv}\text{C})_3\text{Al} + 4\text{Me}_3\text{Al} \longrightarrow 3\text{Me}_2\text{Al}\begin{smallmatrix}\text{C}{\equiv}\text{CPh}\\ \\ \text{C}{\equiv}\text{CPh}\end{smallmatrix}\text{AlMe}_2 \qquad (137)$$

6.5.3.2 Metathesis between active organometallic compounds and diorganoaluminum halides

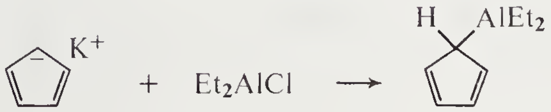
This formation of the unsymmetrical R_2AlR' according to equation (138) proceeds well if R′ in R′M is a good bridging group preferably 1-alkenyl,[422,423] 1-alkynyl,[72,356,388,424] allylic[56] or aryl[381] and M = Li, Na, K or Mg; the group R should be a weaker potential bridging group. As solvents, ethers or hydrocarbons are permissible (equation 138). Some illustrative preparations are given in equations (139),[53] (140)[425] and (141).[254,255,426]

$$R_2AlX + R'M \xrightarrow[-MX]{:D} R_2AlR' \qquad (138)$$



(139)

$$H_2C{=}CHC{\equiv}CNa + Me_2AlCl \xrightarrow[-NaCl]{} Me_2Al{-}C{\equiv}CCH{=}CH_2 \qquad (140)$$

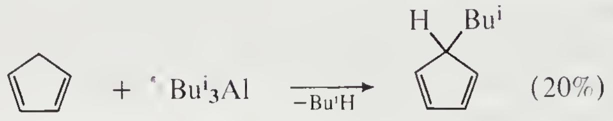


(141)

6.5.3.3 Metallation of carbon acids by aluminum compounds

The replacement of acidic hydrogens in hydrocarbon groups by aluminum is much less common than the analogous metallations with organolithium compounds. With aluminum the reaction is essentially feasible only with terminal alkynes[178,427,428] and, to a limited degree, cyclopentadienes[429,430] (including indenes and fluorenes) (equation 142). Aromatic protons are slowly attacked by triorganoaluminum compounds above 200 °C, but this reaction has little preparative use. However, intramolecular metallation is more facile and is important for the preparation of aluminum heterocycles (see equation 116). The rate of such metallations can often be enhanced by working with complexes of R_3Al (or R_2AlH), such as $R_3Al{\cdot}NR''_3$[431–433] or $M[AlR_4]$.[434–440] The preparations shown in equations (143)–(145) are illustrative.[178,429–431]

$$R'{-}H \quad + \quad R_3Al \longrightarrow R_2AlR' \quad + \quad RH \tag{142}$$



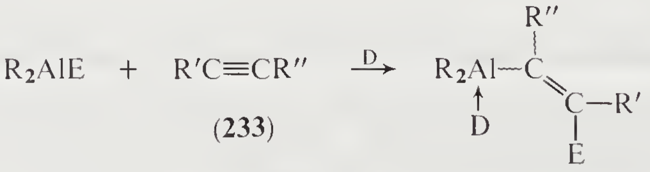
(143)

$$PhC{\equiv}CH \quad + \quad Ph_3Al \xrightarrow[-PhH]{} Ph_2AlC{\equiv}CPh \tag{144}$$

$$BuC{\equiv}CH \quad + \quad Bu^i_2AlH{\cdot}NEt_3 \xrightarrow[-H_2]{} Bu^i_2AlC{\equiv}CBu{\cdot}NEt_3 \tag{145}$$

6.5.3.4 Hydralumination or carbalumination of unsaturated compounds

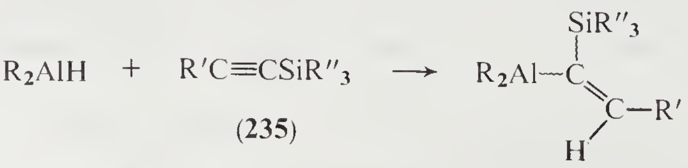
The addition of diorganoaluminum hydrides or triorganoaluminum compounds to alkynes or polyenes often proceeds cleanly enough under moderate conditions to be a useful preparative route to R_2AlR' (equation 146). Owing to facile disproportionation, similar additions to alkenes do not lead cleanly to unsymmetrical alkyls. The presence of a donor (D), such as an ether or tertiary amine, retards these additions markedly (*cf.* Section 6.1.5), but such complexing agents do serve to stabilize the product (**234**) to disproportionation, isomerization (*cis–trans*, allylic, cyclizing) and polymerization. The value of donors in controlling the stereochemistry of addition has been discussed in Section 6.3.3.



(**234**) (146)

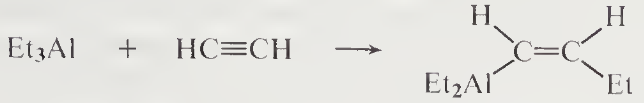
E = R, H

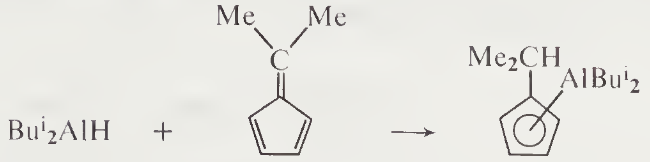
From a preparative standpoint, these reactions have serious limitations. Firstly, terminal alkynes (**233**) (R' = H) undergo competitive metallation (*cf.* equations 144 and 145). This competing process can be suppressed by employing the trialkylsilyl derivative (**235**), which reacts with high regioselectivity to give (**236**).[247] A second difficulty, which is encountered with unsymmetrical



(**236**) (147)

alkynes (**233**) (R′ ≠ R″), is a non-regioselective addition yielding isomeric products (**234**). Only when R′ and R″ have markedly different steric and electronic properties (as in (**235**)) can an acceptable regioselectivity be obtained.[3b,53,60,77,79,441] Instances of these preparations are shown in equations (148),[72] (149)[442] and (150).[245]


(148)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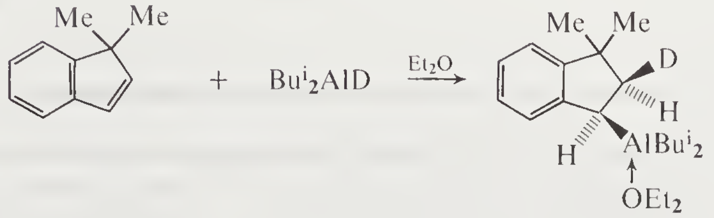
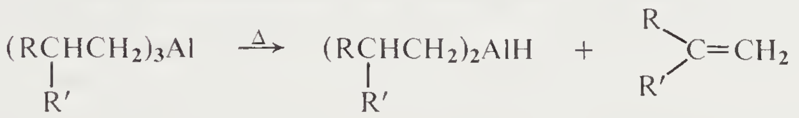

(150)

6.5.4 Organoaluminum Hydrides

6.5.4.1 Alkene elimination from symmetrical triorganoaluminum compounds

Generally, the loss of alkene from an aluminum alkyl is only a feasible route to hydrides if a 2-substituted alkene is generated (equation 151). For such types, the rate is conveniently rapid at 100–150 °C and the alkene has little tendency to undergo an interfering addition of the C—Al bond. The alkyl groups suitable for this synthesis are those that can be tolerated in the one-step preparation of aluminum alkyls (*cf.* Section 6.5.2.3), namely isobutyl, 2,4,4-trimethylpentyl, *etc.*[36,258,271]


(151)

$$(R\underset{R'}{C}HCH_2)_3Al \xrightarrow{\Delta} (R\underset{R'}{C}HCH_2)_2AlH + \overset{R}{\underset{R'}{>}}C{=}CH_2$$

6.5.4.2 Redistribution of triorganoaluminum compounds and aluminum hydride

A method widely applicable to the preparation of organoaluminum dihydrides ($RAlH_2$) and diorganoaluminum hydrides (R_2AlH) is the redistribution reaction (equation 152).[153,443,444] The reaction can be carried out with aluminum hydride generated *in situ*, as in the Ziegler synthesis of triethylaluminum from the metal alkyl, aluminum and hydrogen (equation 9), or from the separate interaction of lithium hydride and aluminum chloride. The reaction proceeds best in non-donor media; ether media seriously lower the yields. Typical examples are given in equations (153)[153] and (154).[205]

$$3RAlH_2 \xleftarrow{2AlH_3} R_3Al \xrightarrow{\frac{1}{2}AlH_3} \tfrac{3}{2}R_2AlH \qquad (152)$$

$$2Ph_3Al + AlH_3 \longrightarrow 3Ph_2AlH \qquad (153)$$


(154)

6.5.4.3 Hydrogenolysis of triorganoaluminum compounds

The selective cleavage of one group from an aluminum alkyl by hydrogen is often a convenient route to di-*n*-alkylaluminum hydrides if pressure equipment is available. Although chromium or titanium salts catalyze the reaction, some commercial aluminum alkyls already have sufficient amounts of such impurities to react. The net reaction is one of hydrogenolysis, but the promoting influence of transition metals indicates that the alkene eliminated from R_3Al is captured by hydrogenation (equation 155).[445–447] Since little pressure drop occurs, the reaction mixture must be analyzed periodically by alcoholysis and the reaction continued until the alcoholysate approaches a 2:1 mixture of alkane and hydrogen.

$$R_3Al \quad + \quad H_2 \quad \xrightarrow[300\ \text{atm}]{150\ ^\circ\text{C}} \quad R_2AlH \quad + \quad RH \tag{155}$$

6.5.4.4 Metathesis between organoaluminum halides and metal hydrides

This reaction is the most generally successful and versatile route to diorganoaluminum hydrides;[448–450] it does not yield the dihydrides cleanly.[449,451] Being heterogeneous, the reaction is greatly promoted by using very finely milled lithium or sodium hydride. The reaction is slower in alkane suspensions than in ether (equation 156). In the latter medium, however, disproportionation can become a serious side reaction (*cf.* equation 20). The method is conveniently applicable to preparing organoaluminum deuterides (equation 157) which are useful in mechanistic studies and in the synthesis of deuterated alkenes by hydralumination reactions (*cf.* equation 254).

$$RAlH_2 \quad + \quad R_2AlH \quad \xleftarrow[n\,=\,1]{MH} \quad R_nAlX_{3-n} \quad \xrightarrow[n\,=\,2]{MH} \quad R_2AlH \quad + \quad MX \tag{156}$$

$$Bu^i{}_2AlCl \quad + \quad LiD \quad \longrightarrow \quad Bu^i{}_2AlD \quad + \quad LiCl \tag{157}$$

6.5.5 Organoaluminum Halides and Pseudohalides

6.5.5.1 Separation from the organoaluminum sesquihalides

For those cases where the organic halide reacts smoothly with aluminum metal to yield the sesquihalide mixture (Section 6.5.2.4), the individual R_2AlX and $RAlX_2$ can often be obtained by distillation, crystallization, selective complexation or shifts in equilibria.[40,277,278,452–455] For example, the sesquihalides obtained from aluminum and either methyl chloride or methyl bromide can be fractionally distilled through a Podbielniak column to yield the more volatile dimethylaluminum halide. The later fractions can be recrystallized from pentane to provide the methylaluminum dihalide. In another procedure, one equivalent of powdered sodium chloride is added to the sesquihalide to complex preferentially with the more acid $RAlX_2$ (*cf.* equation 133) and to permit the free R_2AlX to be separated as a layer or as a vapor. Dimethyl- and diethyl-aluminum chloride have been obtained in this manner.

Instead of just obtaining the amount of R_2AlX originally present in the sesquihalide, one can convert all R groups present into R_2AlX by shifting the equilibrium (equation 158) to favor the formation of AlX_3, the strongest Lewis acid available.[278] In practice, 0.25 equivalent of powdered potassium chloride converts ethylaluminum sesquihalide essentially completely into diethylalu-

$$R_2AlX \quad + \quad 2RAlX_2 \quad \rightleftarrows \quad 2R_2AlX \quad + \quad AlX_3 \tag{158}$$

minum chloride (equation 159) ($R = Et$; $X = Cl$). If, on the other hand, $RAlX_2$ is required, the sesquihalide can be treated with aluminum halide and the dihalide separated by standard procedures (equation 160).[40] As a variation of producing triorganoaluminum compounds directly from aluminum–magnesium alloys and an organic halide (equation 134), such a reaction can also yield diorganoaluminum halides.[40,456–458]

$$2R_2AlX{\cdot}2RAlX_2 + KX \rightarrow KAlX_4 + 3R_2AlX \qquad (159)$$

$$R_3Al_2X_3 + AlX_3 \longrightarrow 3RAlX_2 \qquad (160)$$

6.5.5.2 Redistribution between triorganoaluminum compounds and aluminum chloride

This method is a natural extension of that in equation (160), in that the aluminum alkyl or aryl replaces the sesquihalide. For successful preparation, the stoichiometry and purity of the components must be carefully controlled. Some warming of the reactants is required for proper equilibration but decomposition can be marked at too elevated a temperature (equation 161).[40,459] The driving force for the halogens to enter bridging positions is especially evident in the smooth formation of R_2AlX. A whole series of dialkylaluminum chlorides has been made in this manner. Both diphenylaluminum halides and phenylaluminum dihalides are likewise preparable.[40,362,374,460] In a modified approach for iodides, mixtures of the aluminum alkyl, aluminum and iodine can be employed.[461]

$$3RAlX_2 \xleftarrow{2AlX_3} R_3Al \xrightarrow{\frac{1}{3}AlX_3} \tfrac{3}{2}R_2AlX \qquad (161)$$

6.5.5.3 Selective protodealumination of triorganoaluminum compounds or hydrides

The great sensitivity of these aluminum compounds to protic agents requires that the concentration and amount of reagent, temperature and rate of addition be carefully controlled. Anhydrous acid, diluted in solution with hydrocarbon or as a gas with nitrogen, can be added slowly and with cooling to the aluminum compound. A Lewis base, such as pyridine or ether, moderates the vigor of the reaction, but naturally the product R_2AlZ may then be formed as a donor complex. With hydrides the Al—H bond is preferentially cleaved. The method serves to yield the halides (even the fluoride),[462] but is especially useful for pseudohalides like cyanide or azide[463–466] (equation 162). The useful reagent diethylaluminum cyanide (Section 6.6.3.2) is accessible by this procedure.

$$R_2AlR' + HZ \longrightarrow R_2AlZ + R'H \qquad (162)$$

$$R' = R, H$$

6.5.5.4 Halodealumination of triorganoaluminum compounds or hydrides

Again, for the selective cleavage of one or two bonds to aluminum, experimental conditions must be chosen carefully.[467–469] As with protic sources, the use of Lewis bases (R_2O or R_3N) and lower temperatures may permit a stepwise control in cleaving C—Al bonds. Some sources of the halogen or pseudohalogen may react too vigorously and, which is more hazardous, have induction periods before *exploding* (organic halides like CCl_4). This synthetic approach is most feasible for the preparation of bromides or iodides from elemental halogen, azides from chlorine azide[470–472] and thiocyanates[165] from dithiocyanogen (equation 163). A number of metal salts, such as $ZnCl_2$, $GaCl_3$ and $SnCl_4$, produce R_2AlX by metathesis with R_3Al and can accordingly be viewed as halogenating agents (Section 6.6.4.5). On occasion, this method may be advantageous for preparing R_2AlX because the resulting zinc alkyl can be readily volatilized away.[124,285,473]

$$R_2AlR' + XY \longrightarrow R_2AlX + R'Y \qquad (163)$$

$$R' = H, R$$

6.5.5.5 Metathesis between organoaluminum halides and metal salts

This interaction has been discussed in Section 6.2.6.3. In this case, it is particularly valuable for preparing fluorides,[289] cyanides,[474] azides[475] and other pseudohalides from dialkylaluminum halides (equation 164).

$$Et_2AlCl + NaF \xrightarrow{\Delta} Et_2AlF + NaCl \qquad (164)$$

6.5.6 Organoaluminum Alkoxides, Phenoxides and Oxides

6.5.6.1 Redistribution between triorganoaluminum compounds and aluminum alkoxides

Since many aluminum alkoxides are readily accessible from the reaction of amalgamated aluminum foil with the alcohol, the redistribution reaction of equation (165) is a most convenient and versatile method. By admixing a 2:1 mixture of $Al(OR')_3$ and R_3Al the alkylaluminum dialkoxides can also be made.[40,155] Again, the driving force is that of placing the alkoxy groups in bridging positions of the resulting dimers or trimers (Section 6.2.1). Note that R and R′ can be different groups and that their steric demands may, in some cases, disfavor the desired redistribution.

$$3R'OH \xrightarrow{Al} Al(OR')_3 \xrightarrow[\Delta]{2R_3Al} 3R_2Al(OR') \qquad (165)$$

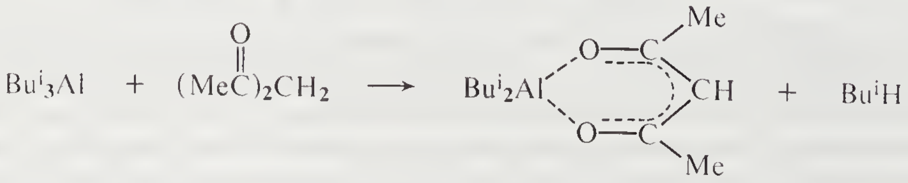
6.5.6.2 Selective protodealumination of triorganoaluminum compounds or hydrides

The controlled addition of water,[476–480] alcohols,[481–485] phenols,[486–488] enols[489–490] or carboxylic acids[491–492] to organometallic compounds of aluminum is a general and broadly applicable method. With R_2AlH the Al—H bond can be alcoholized preferentially. Some specific preparations are given in equations (166)–(168). All these products (except (**237**)) exist as oligomeric or polymeric aggregates and may tend to disproportionation upon heating, especially if the volatile R_3Al can escape.

$$2Et_3Al + H_2O \longrightarrow Et_2Al{-}O{-}AlEt_2 + 2EtH \qquad (166)$$

tetraethyldialuminoxane

$$Me_3Al + PhOH \longrightarrow Me_2AlOPh + MeH \qquad (167)$$



(168)

(237)

6.5.6.3 *Metathesis between organoaluminum halides and metal salts*

Alkali metal salts of the protic agents mentioned in the preceding section can also be employed to make aluminum–oxygen bonds according to equation (169).[484,493] This reaction does not involve the exothermic evolution of a gas and hence is more readily controlled, but it does entail working with heterogeneous reactants and products.

$$R_2AlX + M{-}OZ \longrightarrow R_2Al{-}OZ + MX \qquad (169)$$

6.5.6.4 *Oxidation of triorganoaluminum compounds*

A number of oxygen-containing reagents, such as carbonyl compounds,[494] cyclic ethers[495,496] and epoxides,[497–499] convert aluminum alkyls into alkoxides. The most useful oxygen reagent, however, is molecular oxygen itself.[28,122,500] The vigor with which this oxidation proceeds demands that the same care mentioned for protolysis (Section 6.6.5.3) be exercised here. The reaction is so difficult to perform in a stepwise fashion to yield R_2AlOR or $RAl(OR)_2$ that it is best to produce $Al(OR)_3$ and then use redistribution (equation 165). Such oxygenation is thoroughly unsuitable, however, for producing aluminum vinyloxides or phenoxides, as the corresponding aluminum compounds oxidize in a complex manner (Section 6.6.3.5).

6.5.7 Other Mixed Organoaluminum Compounds

The related derivatives containing aluminum bonded to non-metals such as nitrogen, phosphorus, sulfur and their analogues can be obtained by methods similar to those thus far described. The most applicable method is the protodealumination of aluminum alkyls or hydrides with amines,[48a,167,501,502] thiols[48a,503] or diorganophosphines[504–508] (equation 170). Here again, metal salts of HZ can be used with dialkylaluminum chlorides in an alternative preparative procedure (*cf.* equations 164 and 169). Finally, the reactions of several unsaturated nitrogen compounds, especially those of Schiff bases with alkylaluminum hydrides, proceed cleanly enough to constitute good syntheses (equation 171).[509,510]

$$R_2AlR' + H{-}Z \longrightarrow R_2AlZ + R'H \qquad (170)$$

$$R' = H, R;\ Z = R'_2N, R'S \text{ or } R'_2P$$

$$Et_2AlH + PhCH{=}N{-}Ph \longrightarrow Et_2Al{-}NPhCH_2Ph \qquad (171)$$

6.5.8 Organoaluminum Complexes

6.5.8.1 *Neutral complexes*

The foregoing discussions of the strength of various Lewis bases and the dynamic equilibria of complexation with aluminum alkyls are pertinent to the preparation of such complexes, a simple matter when stable complexes are involved[48a] when it may be effected by admixing the donor with the aluminum compound and purifying, if desired, by distillation or recrystallization. In the case of a labile complex, however, elevated temperatures may cause dissociation or decomposition (*cf.* Section 6.1.5). Hence, their preparation and spectral measurements must be conducted at lower temperatures.[301] Some labile complexes of this type are those of ethers, ketones and primary amines. Furthermore, the tendency of complexation to induce the disproportionation of certain R_2AlR' types should be borne in mind. An extensive compilation of such complexes can be found in ref. 44.

6.5.8.2 Anionic complexes

As with neutral complexes, these complexes result from the simple admixing of R_2AlZ (where Z = R, X, H, *etc.*) with the polar MY (where Y = R′, H, X, *etc.*) according to equation (172). The only practical difficulty arises when the reagent MY is insoluble; this situation will require special milling and stirring techniques. Naturally, complex (**238**) must be stable under such conditions (*cf.* Section 6.2.6.6). Some diverse examples are to be found in equations (173),[511] (174)[230] and (175).[512] Consider also those given in equations (80) and (104) and in structures (**227**) and (**228**).

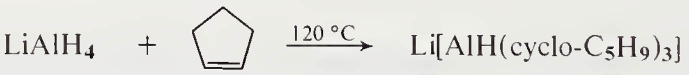
$$R_2AlZ + MY \xrightarrow{\Delta} \underset{(\mathbf{238})}{M[AlR_2YZ]} \qquad (172)$$

$$Et_3Al + NaH \longrightarrow Na[AlEt_3H] \qquad (173)$$

(174)

$$Me_3Al + Me_2Mg \longrightarrow MeMg[AlMe_4] \qquad (175)$$

A second general method is the hydralumination of alkenes with lithium or sodium aluminum hydride. By working at 100–200 °C under pressure the tetraalkylaluminates have been obtained from ethylene, propylene and other 1-alkenes.[26,513,514] Under similar conditions, cyclopentene, cycloheptene and cyclooctene are converted only to lithium tricycloalkylaluminum hydrides, while cyclohexene is unreactive (equation 176).[26]

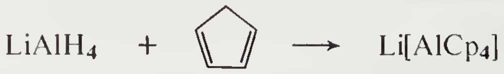


(176)

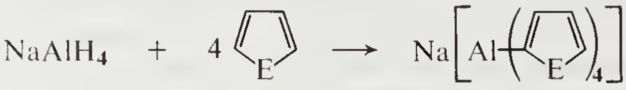
A third approach is the alumination of acidic hydrocarbons by means of either a metal aluminum hydride or metal tetraalkylaluminate (see for example equations 177,[435–439] 178[515–517] and 179[434]). The sodium ethoxide catalyst in equation (178) serves to generate ethylsodium, the actual metallating agent. With more acidic hydrogens $NaAlEt_4$ is not required and even $MAlH_4$ suffices for a smooth reaction (equation 180).

$$LiAlH_4 + 4PhC{\equiv}CH \longrightarrow Li[Al(C{\equiv}CPh)_4] \qquad (177)$$

(178)



(179)

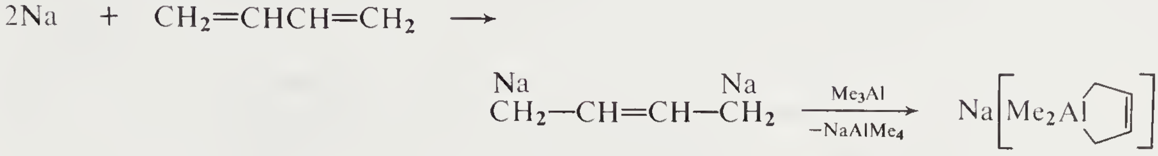


(180)

E = O, S

The fourth method involves the interaction of an alkali metal with some combination of an aluminum compound and often a third component. These preparations can be viewed as variants of the first method given above (equation 172), which differ only in the source of MY. Thus, admixing an alkali metal with R_3Al is a classic metal displacement reaction generating MY (RNa) (equation 181).[518-520] Also, RM can be generated *in situ* from an organic halide and an alkali metal or by forming unsaturated hydrocarbon–metal adducts according to equation (182).[521] A variety of adducts have thus been formed from benzenes, naphthalenes, alkenes and alkynes (*cf.* structure (**227**)).[522]

$$3Na + R_3Al \longrightarrow Al + 3RNa \xrightarrow{3R_3Al} NaAlR_4 \qquad (181)$$



(182)

Finally, there are situations where unsymmetrical aluminates are accessible by redistribution reactions (equation 183).[518,523]

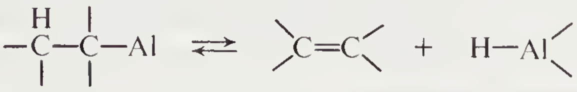
$$NaAlEt_4 + NaAlH_4 \longrightarrow 2NaAlEt_2H_2 \qquad (183)$$

6.6 CHEMICAL REACTIONS

6.6.1 Reactivity and Structure of Organoaluminum Compounds

Many aspects of the reactions of organoaluminum compounds have been treated in the foregoing sections. For ease of reference such pertinent topics are indexed here: (a) structural isomerization (Sections 6.3.2–6.3.5); (b) dynamic equilibria (Section 6.3); (c) reactive intermediates and complexes (Section 6.1.5); (d) reaction mechanisms for the carbalumination and the hydralumination of unsaturated hydrocarbons (Section 6.1.5); (e) rearrangements in organoaluminum reactions (equations 44–51); (f) stereochemistry of various addition reactions to unsaturated organic compounds (Section 6.1.5); (g) thermal decomposition and elimination pathways of organoaluminum compounds (Sections 6.3.6–6.3.7); and (h) diverse preparative procedures, which often involve the reactions of carbon–aluminum bonds (Section 6.5). As a result of these factors the course of organoaluminum reactions can be complicated by the formation of isomeric products, as well as side products. Which reaction course predominates is very dependent on the structure of both the organoaluminum reagent and the substrate.

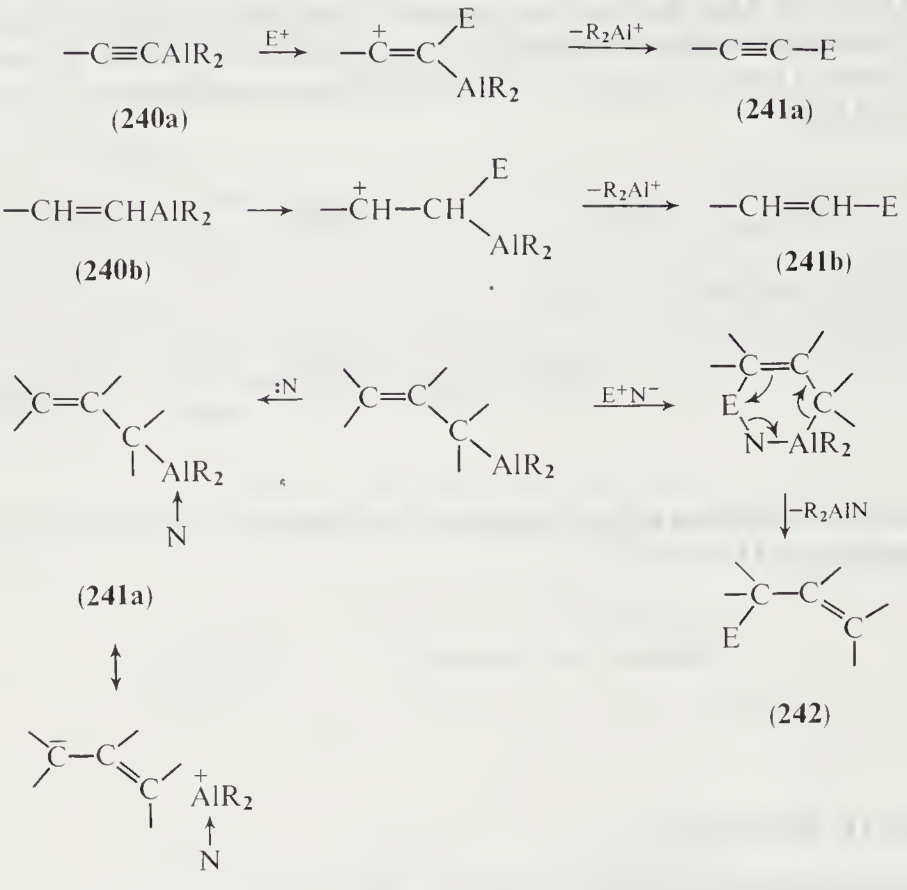
One of the most significant structural features is the presence of an sp^3 C—H bond β to the sp^3 C—Al bond. Owing to the possible thermal or catalyzed elimination of alkene, such an alkyl (**239**) may exhibit competing reactions of both C—Al and H—Al bonds.



(184)

(**239**)

A second structural consideration is the relative reactivity of different C—Al bonds in unsymmetrical R_2AlR' reagents. Since all three C—Al bonds are seldom consumed in many aluminum reactions, it is important to learn which carbon–aluminum bonds are more reactive. From reactivity studies toward proton or carbonyl substrates, it can be concluded that vinyl-aluminum, allyl-aluminum and aryl-aluminum bonds are more reactive than alkyl-aluminum bonds. Likewise, proton, halogen and carbonyl sources cleave alkynyl-aluminum bonds more readily than alkyl-aluminum bonds. Such selectivity suggests that sp^2 or sp C—Al bonds (**240**) are more prone to electrophilic attack (equations 185a and 185b). The greater reactivity of allyl- (and benzyl-) aluminum bonds can be related either to a weaker bond (**241**), or to a rearrangement upon electrophilic attack (**242**) (Scheme 14).



(185a)

(**240a**) (**241a**)

(185b)

(**240b**) (**241b**)

(186)

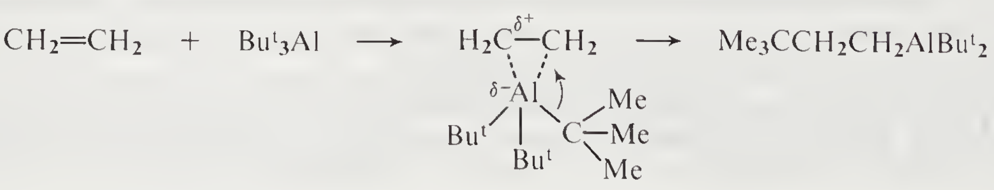
(**241a**)

(**241b**)

(**242**)

Scheme 14

Finally, there is evidence indicating that towards some substrates, *e.g.* ethylene, tri-*t*-butylaluminum is more reactive than triisopropylaluminum and much more reactive than a tri-*n*-alkylaluminum. One reason for this difference is that the tertiary compound is already monomeric, so that the apparent $E^{\ddagger}$ for carbalumination does not include the heat of dissociating the dimeric alkyl. Another factor could be the enhanced nucleophilicity of the *t*-butyl–aluminum bond in the transition state (**243**) because of electron release by the methyl groups (equation 187).



$$\mathrm{CH_2{=}CH_2 + Bu^t{}_3Al \longrightarrow (243) \longrightarrow Me_3CCH_2CH_2AlBu^t{}_2}$$

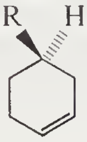
(**243**)

(187)

6.6.2 Selectivity and Substrate Structure

Particular organic substrates may offer two or more competing sites for reactions with the carbon–aluminum or hydrogen–aluminum bonds of the organoaluminum reagent. Furthermore, in addition reactions to unsaturated linkages in the substrates, isomers can result from the regiochemical and stereochemical courses of the reaction. For the present discussion, it is useful to classify the selectivity of organoaluminum reactions in the following manner: (a) locoselectivity, which expresses the discrimination with which an aluminum reagent attacks one of several possible functional groups in the substrate[524] (*e.g.* the attack of Ph_3Al principally on the alkenic hydrogen of PhC≡CH (equation 144), with minor competing addition to the C≡C group and little or no attack on the phenyl hydrogens); (b) regioselectivity, which describes the preferential orientation with which C—Al, H—Al or X—Al bonds might add to unsymmetrically substituted bonds C═E and C≡E[525] (*e.g.*, isomers (**48**) and (**49**) in equation 37); and (c) stereochemistry, which specifies the *syn* and *anti* character of additions to π-bonded substrates (*e.g. cf.* Scheme 6).

Following Izumi,[526] we can further distinguish such selectivity as to enantio- and diastereo-differentiating processes. In the former, prochiral substrates are converted preferentially into one enantiomer by chiral reagents or conditions. In the latter, one enantiomer or a racemic substrate is converted preferentially into one diastereomer. In structure (**244a**) by way of illustration, one could achieve locoselective hydrometallation of the vinyl group by R_2BH or R_2AlH, with little interference from the internal double bonds;[527] moreover, the hydrometallation would be regioselective, leading principally to the isomeric side chain, $—CH_2CH_2MR_2$. In (**244b**), hydrometallation would occur stereoselectively in a *syn* manner.[245] Furthermore, if one were to hydroborate cyclohexene with optically active diisopenocampheylborane, an optically active cyclohexylborane would be formed in an enantio-differentiating process.[528] On the other hand, in (**244c**), hydrometallation may proceed in a *syn* fashion but preferentially *cis* or *trans* with respect to the chiral group. This would constitute a diastereo-differentiating process. In considering factors that might give rise to diastereo-differentiation, two situations naturally come to mind: (1) the steric bulk of R in (**244c**) might favor the approach of the reagent to the cyclohexene ring from the side *trans* to the substituent (selective hindrance); and (2) the Lewis basic character of R in (**244d**) may lead to complexation with the Lewis acidic organometallic reagent R″M, and hence favor intramolecular delivery of the reagent to the C═C bond from the side *cis* to the substituent (selective assistance).



(**244a**) R = $CH{=}CH_2$
(**244b**) R = H
(**244c**) R = alkyl, aryl, heteroatom
(**244d**) R = R′O, O^-, R'_2N, NH^-

6.6.3 Addition reactions

In this section the insertion reactions of multiple bonded substrates with organoaluminum reagents will be surveyed. The additions of carbon–aluminum, hydrogen–aluminum and element–aluminum bonds will be treated sequentially.

6.6.3.1 *Alkenic and alkynic bonds*

(*i*) *Carbalumination*

The addition of triethylaluminum to ethylene is the key reaction in the development of Ziegler chemistry. Despite some earlier reports to the contrary, in the liquid phase this aluminum alkyl shows a rate law (equation 188) for addition to ethylene and other α-alkenes[234,529,530] that is consistent with the necessity of the dimeric alkyl to dissociate to monomeric Et_3Al, which then attacks the alkene in the rate-limiting step (equation 189). The activation energy and Arrhenius

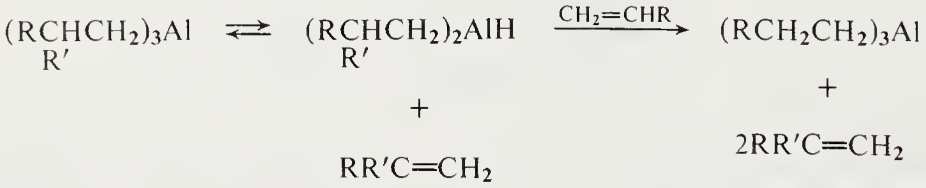
$$\text{rate} = k[\mathrm{Et_6Al_2}]^{1/2}[\text{1-alkene}] \tag{188}$$

$$\mathrm{Et_3Al} + \mathrm{CH_2{=}CHR} \xrightarrow{\text{slow}} \left[\begin{array}{l} \mathrm{CH_2{-}\overset{+}{C}HR} \\ \mathrm{\quad|^{-}} \\ \mathrm{Et_2Al{-}Et} \end{array}\right] \longrightarrow \begin{array}{ll} \mathrm{CH_2{-}} & \mathrm{CHR} \\ | & | \\ \mathrm{AlEt_2} & \mathrm{Et} \end{array} \tag{189}$$

(**245**) (**246**) (**247**)

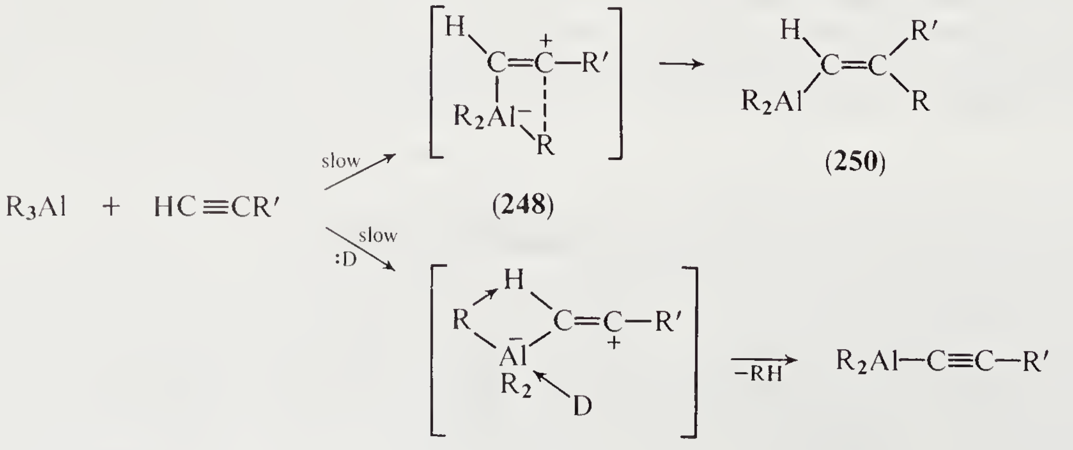
factor for the actual addition of monomeric Et_3Al is 75.6 kJ mol^{-1} and 10^6 l mol^{-1} s^{-1} for the range 110–135 °C.[531] As expected, in the gas phase the reaction of ethylene or propylene with trimethyl- or triethyl-aluminum is first order in each reactant, since the alkyls exist as monomers under these conditions.[532–534] Ethylene is the most reactive alkene, inserting in carbon–aluminum bonds at 110 °C; propylene and other α-alkenes require operating temperatures of 140 °C. This difference in reactivity may arise from steric repulsions of ethyl and R groups in transition state (**246**). However, perdeuteration of ethylene or of triethylaluminum does not affect the rate of addition.[535] The presence of donor groups in the solvent (ethers, amines, *etc.*)[3] or as part of the aluminum alkyl (R_2AlCl, R_2AlOR, $R_2AlNR'_2$) retards the addition or prevents it altogether, showing that three-coordinate R_3Al is the active reagent.[536–539] The lessened reactivity of trimethylaluminum toward ethylene, compared with that of triethylaluminum, apparently reflects the relative difficulty of dissociating the methyl dimer. Since aluminum bonds to ethyl and other *n*-alkyl groups have a similar reactivity toward insertion of ethylene,[27] intermediates like (**247**) (R = H) react with an excess of ethylene in a statistical manner to yield mixtures of long chain aluminum alkyls (equation 6). The resulting distribution of alkyl groups which has been found to accord with that expected from Poisson's equation[540] will show a maximum content of a given R—Al group as the time, temperature or concentration of ethylene is varied.

The most significant competing process with carbalumination is the dissociation of the aluminum alkyl into alkene and aluminum hydrides. The resulting hydride will tend to combine with any alkene present. Such dissociation is favored by higher temperatures, β-branched alkyl–aluminum derivatives (*e.g.* structure (**247**) (R = alkyl)) and the presence of transition metal salts, especially those of nickel.[29b,42,258] For the thermal alkene displacement process (equation 190), the slow step seems to be the dissociation of the alkyl into alkene and R_2AlH, because the rate is insensitive to the concentration and nature of the displacing alkene.[258] Since monomeric aluminum alkyls (Bu^i_3Al) are more reactive than dimeric R_3Al, the monomeric R_3Al must be the active intermediate.[541] The growth reaction (equation 189) can be favored by working at moderate temperatures with an excess of ethylene and minimizing transition metal impurities.



$$\underset{\mathrm{R'}}{(\mathrm{RCHCH_2})_3\mathrm{Al}} \rightleftarrows \underset{\mathrm{R'}}{(\mathrm{RCHCH_2})_2\mathrm{AlH}} + \mathrm{RR'C{=}CH_2} \xrightarrow{\mathrm{CH_2{=}CHR}} (\mathrm{RCH_2CH_2})_3\mathrm{Al} + 2\mathrm{RR'C{=}CH_2} \qquad (190)$$

Like ethylene, acetylene inserts readily into the carbon–aluminum bond of triethylaluminum and triisobutylaluminum.[72] Also, in consonance with the foregoing kinetic comments, the reaction is first order in acetylene and one-half order in triethylaluminum.[69] The monomeric triisobutylaluminum shows a first order dependence, as might be expected (equation 191). The addition is not only retarded by ethers and amines, but such donors favor a competing reaction, metallation (equation 192). The balance between these two processes may depend on whether a π-complex-like



(191)

(**250**)

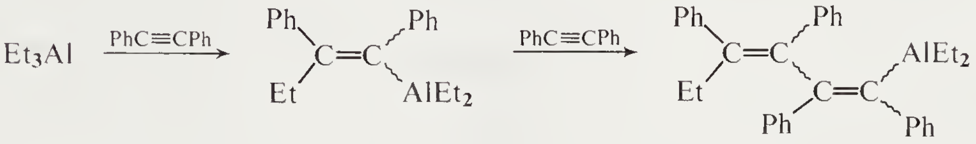
(**248**)

(192)

(**249**)

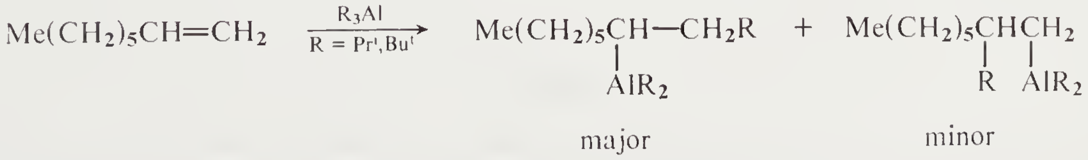
(**248**) or a σ-complex-like (**249**) transition state is preferred. The presence of a donor might prevent configuration (**248**) from being attained, but (**249**) is less demanding sterically (five-coordinate Al) and has an anionically mobile R group (Wittig 'ate' complex). Furthermore, if $R' \neq H$, (**249**) should be favored on steric grounds. Indeed, monosubstituted alkynes undergo preferential metallation in many cases. Finally, it is instructive to point out that acetylene and 1-alkynes undergo principally metallation, rather than addition, with triethylgallium.[542] In this instance, the weaker Lewis acid, Et_3Ga, seems to require more extensive polarization (σ-complexation, (**249**)) in order to achieve reaction. This difference in Et_3Al and Et_3Ga cannot be ascribed to steric factors because the metals have virtually identical covalent radii (Al, 124.8, Ga, 124.5 pm).

The 1-alkenyl(dialkyl)aluminum (**250**), which results from an alkyne insertion, itself undergoes further insertions and does so preferentially at the vinyl–aluminum, rather than the alkyl–aluminum, bond (equation 193).[543] In the case of triphenylaluminum and excess diphenylacetylene, an unusual array of products arises at higher temperatures because the initially formed diphenyl(triphenylethenyl)aluminum undergoes metallative cyclization to 1,2,3-triphenylbenzaluminole (**251**) (Scheme 15; *cf.* equation 116).[544] The hydrocarbons formed upon hydrolysis (**253**)–(**256**) can be rationalized as arising from the putative benzaluminepin intermediate (**252**) by reasonable isomerizations or the generation of phenylaluminum(I).

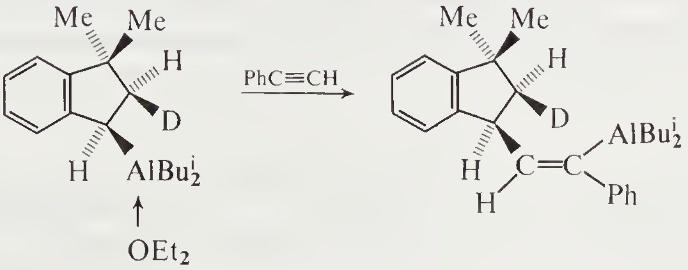


(193)

The locoselectivity of carbalumination has not been studied thoroughly, but generally a C≡C bond is more reactive than a C=C bond in a substrate. Further, a terminal C=C bond is more reactive than a C=C bond in an internal position. The role of polar and steric factors in determining the regiochemistry of carbaluminating internal C=C and C≡C bonds has been considered in Section 6.1.5. For terminal C=C bonds, both factors usually work together to favor attachment of R_2Al to the terminal carbon (*cf.* (**246**)), because R_2Al is the more sterically demanding group and the secondary carbon is better able to sustain any positive charge in the transition state. If R is very bulky, however, the opposite regiochemistry can be favored (equation 194).[545] Finally, by use of appropriate alkenic substrates such as benzonorbornadienes,[74] and alkynes such as *p*-substituted diphenylacetylenes,[3b] the stereochemistry of carbalumination can be shown to occur in a kinetically controlled *syn* manner, in keeping with the tightly-organized trapezial transition state suggested in (**45**). Even the stereochemically defined etherate (**65**) adds to phenylacetylene in a *syn* fashion (equation 195).[93] Since the configuration of both alkyl- and vinyl-aluminum

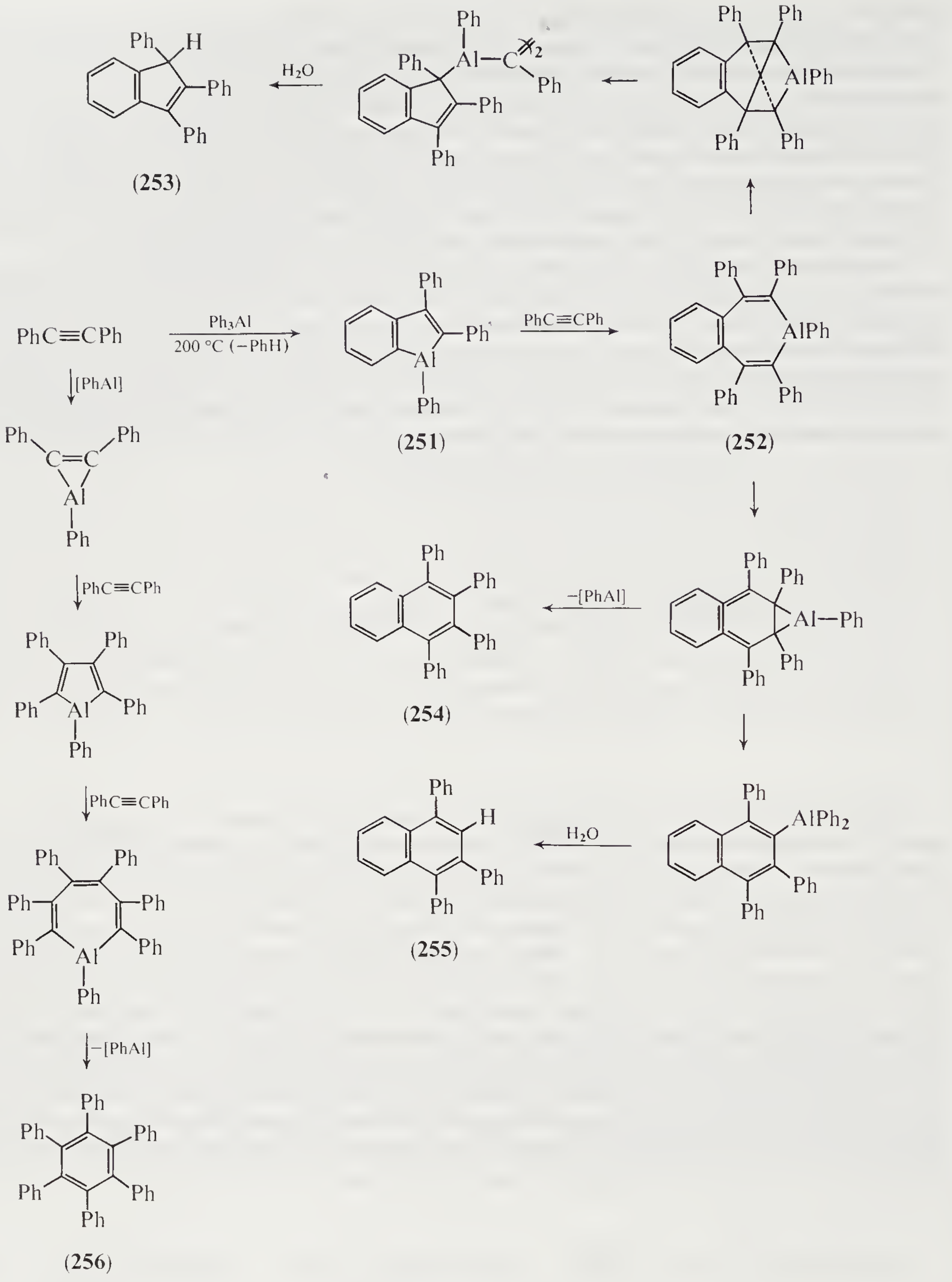


$$Me(CH_2)_5CH{=}CH_2 \xrightarrow[R\,=\,Pr^i,Bu^t]{R_3Al} \underset{\text{major}}{Me(CH_2)_5\underset{AlR_2}{\underset{|}{C}}H{-}CH_2R} + \underset{\text{minor}}{Me(CH_2)_5\underset{R}{\underset{|}{C}}H\underset{AlR_2}{\underset{|}{C}}H_2} \qquad (194)$$



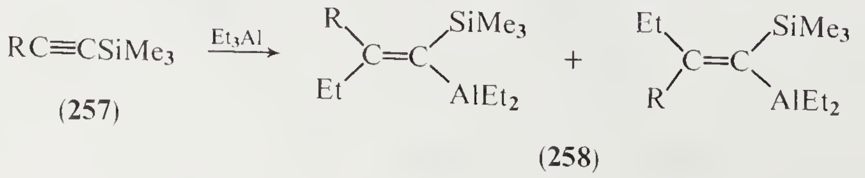
(195)

(**65**)



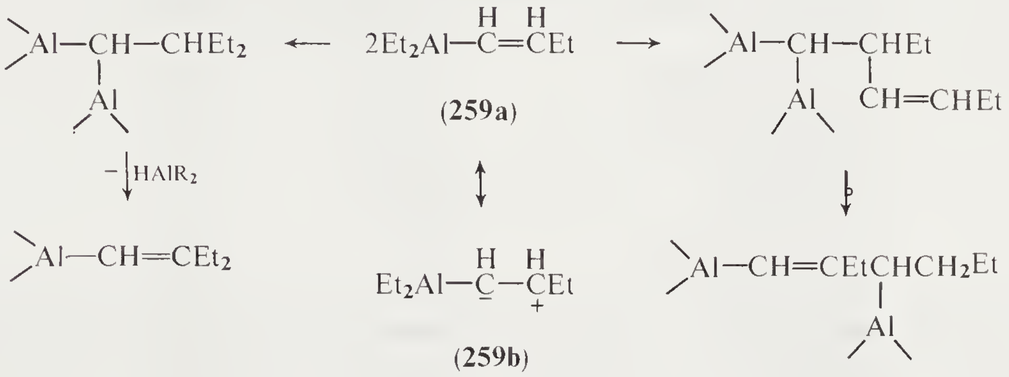
Scheme 15

bonds can be changed by thermal, photochemical or chemical means, however, one may obtain isomeric mixtures of adducts. For example, 1-alkynyl(trimethyl)silanes (**257**) require temperatures of >50 °C for reaction with triethylaluminum. Under these conditions an equilibrated 1 : 1 mixture of (**258**) is formed (equation 196).[546]

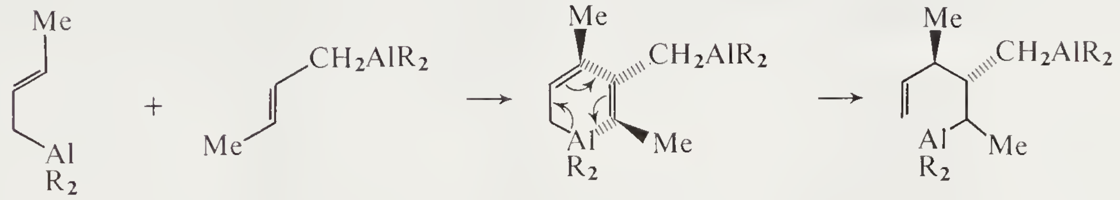


(196)

Unsaturated aluminum compounds, especially of the vinyl or allyl type, can themselves react further with aluminum compounds to yield dialuminum products. Thus, heating (*Z*)-1-butenyl(diethyl)aluminum (**259**) and alcoholyzing the products yields, besides ethane and butane, 3-methylpentane, 2-ethyl-1-butene and 2-ethyl-1-hexene. These principal products can be viewed as arising from autocarbaluminations accompanied by aluminum hydride transfers (Scheme 16).[72] Especially noteworthy is the regioselectivity of carbalumination, which favors the formation of geminal dialuminum intermediates. It seems unlikely that the selectivity stems from steric influences; rather a polarization [(**259b**), p_π–p_π?] may be decisive. When crotyl–aluminum bonds are generated *in situ* from tricrotylborane and triethylaluminum, the crotyl–aluminum system undergoes autocarbalumination to give predominantly *threo*-3,4-dimethyl-1-hexene. This finding supports a cyclic six-membered transition state (**260**) in which the methyl and CH_2AlR_2 groups minimize their repulsions (equation 197).[547]



Scheme 16

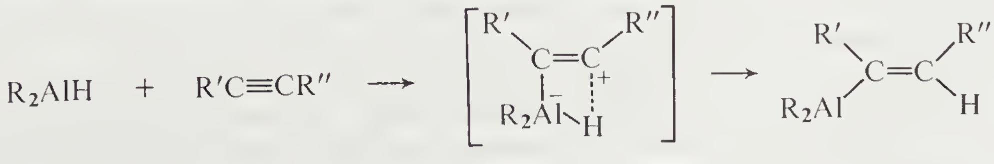


(197)

(260)

(*ii*) *Hydralumination*

The additions of aluminum hydrides to alkenes and alkynes have many similarities in rates, in steric and electronic factors and in experimental conditions to carbalumination reactions. As sources of Al—H bonds, one can employ $AlHZ_2$·solvate, R_2AlH, $LiAlHR_3$ or a β-branched aluminum alkyl (equation 184, *e.g.* $\mathrm{Bu}^i_3\mathrm{Al}$). The addition of diisobutylaluminum hydride to 1-butene at 30–60 °C is first order in alkene and approximately one-half order in hydride.[529] However, because R_2AlH forms mixed complexes with R'_3Al (*cf.* (**125**)–(**127**)), the degree of association of R_2AlH can change as hydralumination proceeds. Hence, the kinetic order in R_2AlH will change as the reaction proceeds. By measuring initial rates ($[R'_3Al] \approx 0$) this difficulty can be avoided. From initial rates, the order dependence on $\mathrm{Bu}^i_2\mathrm{AlH}$ in the hydralumination of alkynes (4-octyne[202] and trimethyl(phenylethynyl)silane)[61] is 0.37–0.38, corresponding to trimeric hydride yielding the monomeric hydride as the reactive intermediate. The direct reaction of the monomeric $\mathrm{Bu}^i_2\mathrm{AlH}$ with ethylene, propylene and 2-methyl-1-butene has been studied by the competitive method through generating low concentrations of the hydride from $\mathrm{Bu}^i_3\mathrm{Al}$ in the gas phase.[267] Only small differences in rates for these alkenes emerge since activation energy and entropic factors work in a compensatory manner. Just such an equalizing of polar and steric effects would be expected from a tight transition state like (**261**). The position of the carbon–carbon unsaturation



(198)

(261)

does markedly change the reactivity on the other hand: internal C=C bonds hydraluminate much more slowly (*cf.* Section 6.3.5). If such C=C bonds are situated in a ring, strain can play a role. The half-life of a cycloalkene towards Et_2AlH (minutes) varies thus: C_4 (40), C_8 (86), C_7 (110), C_5 (200), C_9 (280), C_{11} (1350), C_6 (1880), and C_{12} (2500).[26] The influence of substituents on a C≡C bond can be appreciated by the relative reactivities (initial rates) of alkynes towards Bu^i_2AlH (see Table 14 and Section 6.1.5 for a discussion).

Table 14 Relative Reactivity of Alkynes towards Hydralumination with Diisobutylaluminum Hydride[1]

Alkyne	*Relative reactivity*[a]	*Reactivity ratio*[b]
$PhC\equiv CH$	11.8	10.2
$PhC\equiv CMe$	1.16	
$n\text{-}C_6H_{13}\text{-}C\equiv CH$	115	18.3
$Pr^nC\equiv CPr^n$	6.26	
$n\text{-}C_8H_{17}\text{-}C\equiv CH$	117	16.8
$Bu^nC\equiv CBu^n$	6.92	
$Bu^nC\equiv CBu^n$	6.92	1.11
$Pr^nC\equiv CPr^n$	6.26	
$n\text{-}C_8H_{17}\text{-}C\equiv CH$	117	1.01
$n\text{-}C_6H_{13}\text{-}C\equiv CH$	115	
$Bu^tC\equiv CBu^t$	151	21.8
$Bu^nC\equiv CBu^n$	6.92	
$PhC\equiv CBu^t$	27.8	24.0
$PhC\equiv CMe$	1.16	
$CyC\equiv CMe$	8.22	7.10
$PhC\equiv CMe$	1.16	
$p\text{-}MeC_6H_4C\equiv CC_6H_4Me\text{-}p$	9.84	1.52
$PhC\equiv CPh$	6.47	
$PhC\equiv CPh$	1.00 (k_0)	1.00
$PhC\equiv CMe$	1.16	1.16
$PhC\equiv CH$	11.8	11.8
$PhC\equiv CSEt$	24.6	24.6
$PhC\equiv CBu^t$	27.8	27.8
$PhC\equiv CAlPh_2$	185	185
$PhC\equiv CSiMe_3$	431	431
$PhC\equiv CNMe_2$	19000	19000

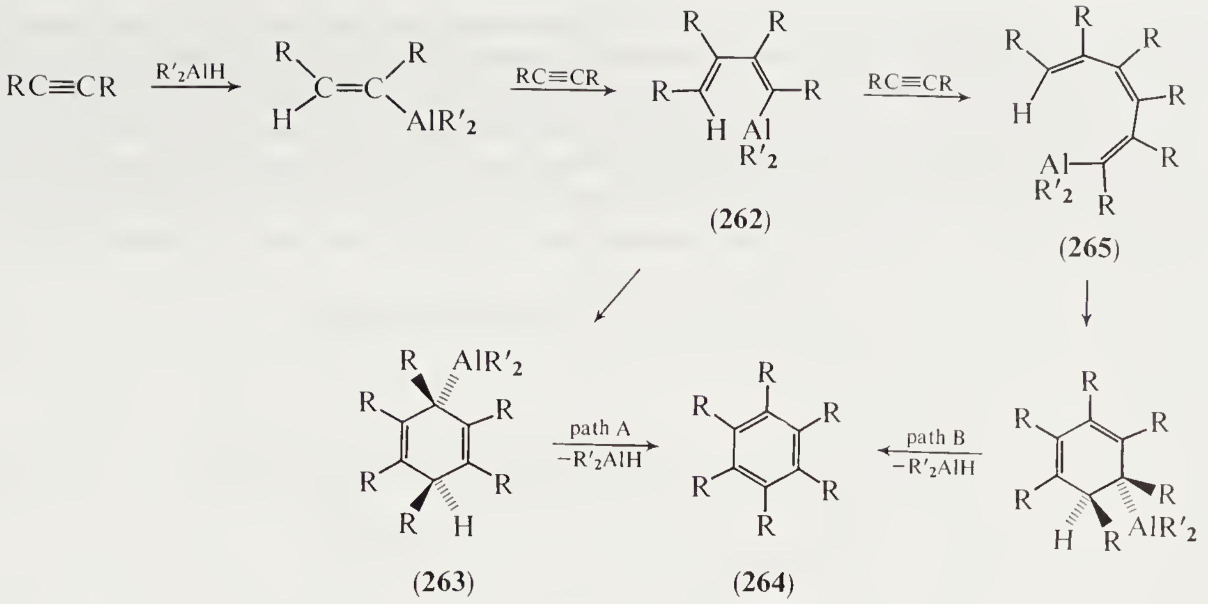
[a] Relative reactivities were determined by the method of initial rates and normalized to 35 °C. [b] For pairs of compounds as indicated; for the last eight entries, relative to PhC≡CPh = 1.

1. J. J. Eisch and S. G. Rhee, *Liebigs Ann. Chem.*, 1975, 565.

In keeping with a three-coordinate R_2AlH monomer as the active agent, ethers and amines retard hydralumination but do not prevent it.[548] Anions, such as AlH_4^- and $AlHR_3^-$ can add to C=C and C≡C bonds, but higher temperatures and glycol ether solvents are usually required (Section 6.5.2.3). A number of transition metal salts, especially those of titanium,[549,550] zirconium[551] and nickel,[248] promote hydralumination reactions.

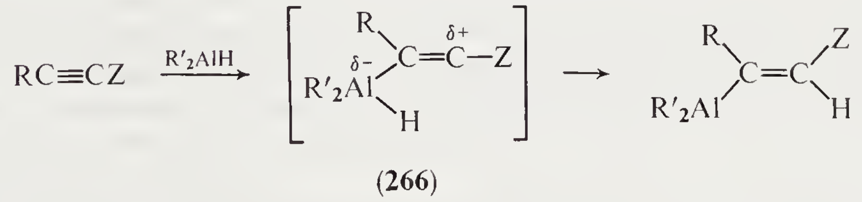
Vinylaluminum compounds resulting from the hydralumination of alkynes are capable of undergoing further insertions of alkynes, in which the vinyl–aluminum bond undergoes preferential reaction.[72] Usually the reaction ceases after the cyclotrimerization of the alkyne to a benzene derivative (**264**), but good yields of the open chain dimer (**262**) can be obtained by heating a 2:1 molar ratio of alkyne to hydride. Although it has been suggested that (**262**) is converted into (**264**) by a Diels–Alder addition (**263**) and R_2AlH elimination (path A), the formation of linear trimer (**265**) and its disrotatory closure (path B) is a more likely route. Two arguments for path B appear cogent: (a) (**262**) is too sterically hindered to assume the *cisoid* conformation necessary for a Diels–Alder reaction; and (b) open chain trimers (**265**), and even tetramers, have been isolated from sterically hindered alkynes like *t*-butyl(phenyl)acetylene[78] (Scheme 17).

As to substrate selectivity, hydralumination occurs with decreasing ease in the order, HC≡CR > RC≡CR > H_2C=CHR > RCH=CHR. Accordingly, the C≡C bond in 3-buten-1-yne is locoselectively attacked.[552] The regioselectivity for unsymmetrical alkynes (which is given in Table 14) is often influenced by the ability of Z to stabilize incipient positive charge

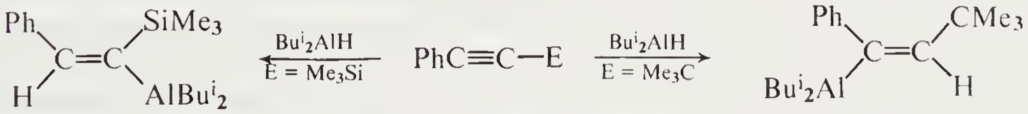


Scheme 17

by an inductive or resonance release of electron density (**266**) (equation 199). Further examples of such regioselectivity are given in equations (147)–(150). In those substrates having particularly bulky groups on the unsaturated linkage, the regioselectivity may be reversed. Consider phenylethynyl derivatives PhC≡CE where E = Bu^t or Me_3Si. Both groups would be considered electron-releasing but the smaller covalent radius of carbon makes *t*-butyl more sterically demanding (equation 200). The electron release of an R_3Si group is seen in the hydralumination of terminal alkenes. Although $RCH{=}CH_2$ gives only about 3–4% of the secondary aluminum adduct (equation 86), $R_3SiCH{=}CH_2$ gives 70% of this isomer (equation 88).[57]

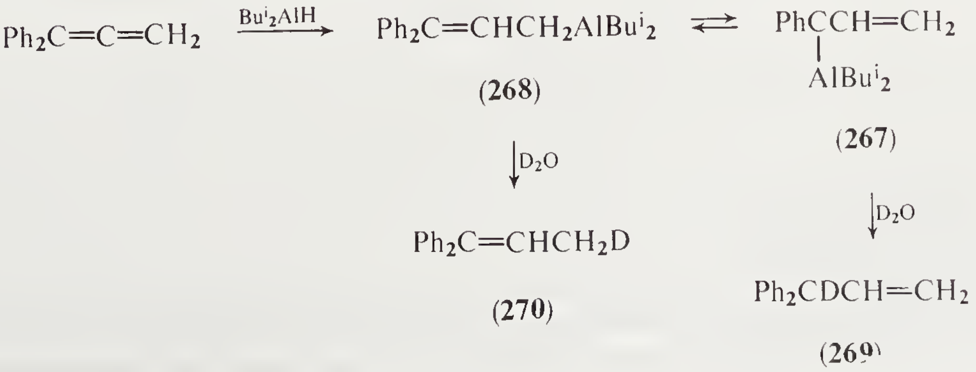


(199)



(200)

The behavior of dienes illustrates some unusual aspects of loco- and regio-selectivity.[57] 1,1-Diphenylallene yields, upon treatment with Bu^i_2AlH and D_2O, a mixture of diphenylpropenes whose deuterons are on C(1) and C(3). The proportion of these isomers depends on the presence of Et_2O ((**267**):(**268**) = 9:1) or Et_3N (6:4). Since 1,1-diphenylethylene undergoes hydralumi-

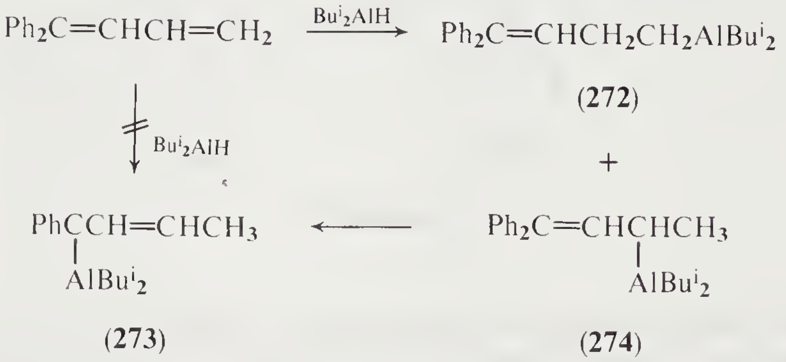


(201)

nation to yield only (**271**) (presumably for steric reasons) (equation 202), it is improbable that (**267**) is formed by direct hydralumination but rather it must result from (**268**) by allylic rearrangement (equation 201). Whether some or all of (**269**) and (**270**) may result from allylic rearrangement during hydrolysis (*i.e.* (**268**) → (**267**)) is uncertain. But, in a similar outcome, 1,1-diphenyl-1,3-butadiene reacts to give a 40:60 mixture of (**272**) and (**273**), for whose presence there is direct NMR spectral evidence. Here again, (**273**) must have arisen from (**274**) rather than from a sterically improbable and unprecedented 1,4-hydralumination (equation 203).

$$Ph_2C{=}CH_2 \xrightarrow{Bu^i_2AlH} Ph_2CHCH_2AlBu^i_2 \qquad (202)$$

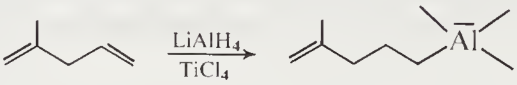
(**271**)



$$\begin{tikzcd} Ph_2C{=}CHCH{=}CH_2 \arrow[r, "Bu^i_2AlH"] \arrow[d, "\not" description, "Bu^i_2AlH"] & Ph_2C{=}CHCH_2CH_2AlBu^i_2 \ (272) \ + \\ \underset{AlBu^i_2}{PhC}CH{=}CHCH_3 & Ph_2C{=}CH\underset{AlBu^i_2}{CH}CH_3 \arrow[l] \end{tikzcd} \qquad (203)$$

(**272**) (**273**) (**274**)

Other dienes,[553,554] alkenes[555] and alkynes[548,556] have been selectively hydraluminated with lithium aluminum hydride in THF, 1,2-dimethoxyethane or glyme solvents in the presence of some titanium(IV) salt, such as $TiCl_4$ or Cp_2TiCl_2 (equation 204). The reaction is very convenient for organic synthesis.

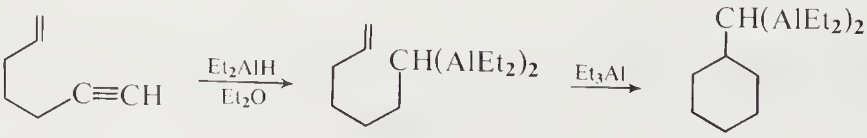


(204)

Finally, *syn* hydralumination of alkenes (equation 150) and of alkynes (equation 146) is the kinetically controlled stereochemistry with uncharged aluminum hydrides. Such adducts tend to isomerize to the more, or equally stable *anti* adducts, especially in the absence of Lewis bases or with transition metals (Sections 6.3.2 and 6.3.3). With lithium aluminum hydride the *anti* adducts are the predominant products, apparently by a direct, kinetically controlled *anti* addition.[556]

Some of the competing reactions encountered with hydralumination are the following: (a) the metallation of terminal alkenes (Section 6.5.3.3) with the evolution of hydrogen, a reaction promoted by the presence of donor solvents like amines; (b) bis hydralumination leading to geminal dialuminoalkanes (equation 205)[72] (here also, the regiochemistry cannot arise from steric factors but from polarization of the vinylaluminum intermediate, *cf.* (**259**)); (c) intra- or inter-molecular carbalumination of resulting alkenylaluminum compounds, which result from hydralumination of alkynes or alkadienes (*cf.* (**137**) and (**138**)) (equation 206).[557]

$$BuC{\equiv}CH \xrightarrow{2Bu^i_2AlH} BuCH_2CH(AlBu^i)_2 \xrightarrow{D_2O} BuCH_2CHD_2 \qquad (205)$$

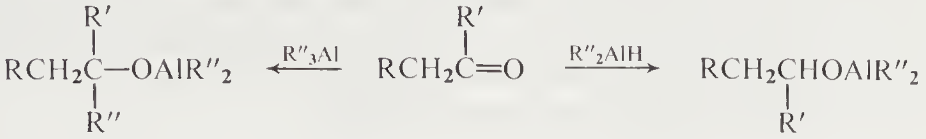


(206)

6.6.3.2 Carbonyl derivatives

(*i*) Aldehydes and ketones

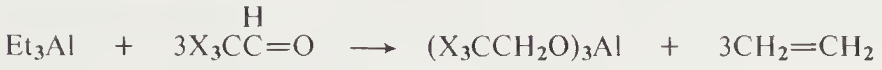
With these substrates and aluminum alkyls, carbalumination and hydralumination[558,559] (*via* equation 184) can be important competing reactions. Often, therefore, both alkylation and reduction of the carbonyl group occur (equation 207). Chloral and bromal represent an extreme instance where only reduction occurs, even with Et_3Al (equation 208) (X = Cl, Br).[560] Furthermore, the starting alkyl or hydride as well as the alkoxides formed, (**275**) or (**276**), can promote a Tishchenko reaction with aldehydes (equation 209)[561] or aluminum enolate formation from carbonyls having acidic α-hydrogen atoms (equation 210).[562–565] In the latter situation, enolate (**277**) may then undergo aldol reactions and further reduction.



$$RCH_2\overset{R'}{\underset{R''}{C}}{-}OAlR''_2 \xleftarrow{R''_3Al} RCH_2\overset{R'}{C}{=}O \xrightarrow{R''_2AlH} RCH_2\underset{R'}{C}HOAlR''_2 \qquad (207)$$

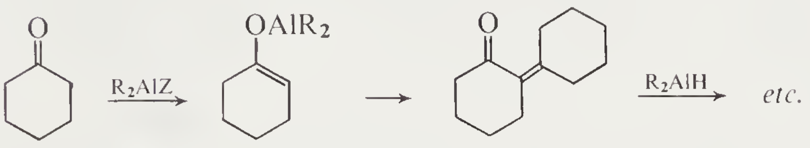
(**275**) (**276**)

$R' = H, R, Ar$



$$Et_3Al \quad + \quad 3X_3C\overset{H}{C}{=}O \longrightarrow (X_3CCH_2O)_3Al \quad + \quad 3CH_2{=}CH_2 \qquad (208)$$

$$2Pr^nHC{=}O \longrightarrow Bu^nO{-}\overset{O}{\overset{\|}{C}}Pr^n \qquad (209)$$

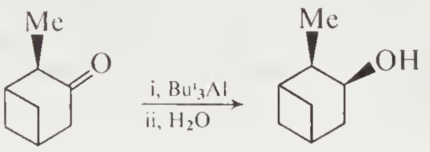


(210)

(**277**)

The carbalumination is generally achieved cleanly only when the aluminum reagent cannot eliminate R_2AlH, as with Me_3Al, Ph_3Al, $(PhCH_2)_3Al$ and $M[AlC{\equiv}CR]_4$, and when the carbonyl substrate has no α-hydrogen atoms. Often, only one C—Al bond of R''_3Al will insert the C=O group, because the alkoxide (**275**) is much less reactive. However, aluminates like $M[AlC{\equiv}CR]_4$[436,566] and $M[AlR_2(C{\equiv}CR)]_2$[567] will react with four and two equivalents, respectively, of the carbonyl compound, with exclusive insertion at the alkynyl–aluminum bond. With other aluminum alkyls the proportion of carbalumination can be enhanced by using tri-*n*-alkylaluminum in excess or in ether, maintaining lower temperatures and restricting reactions to unhindered carbonyl substrates.[562–564,568]

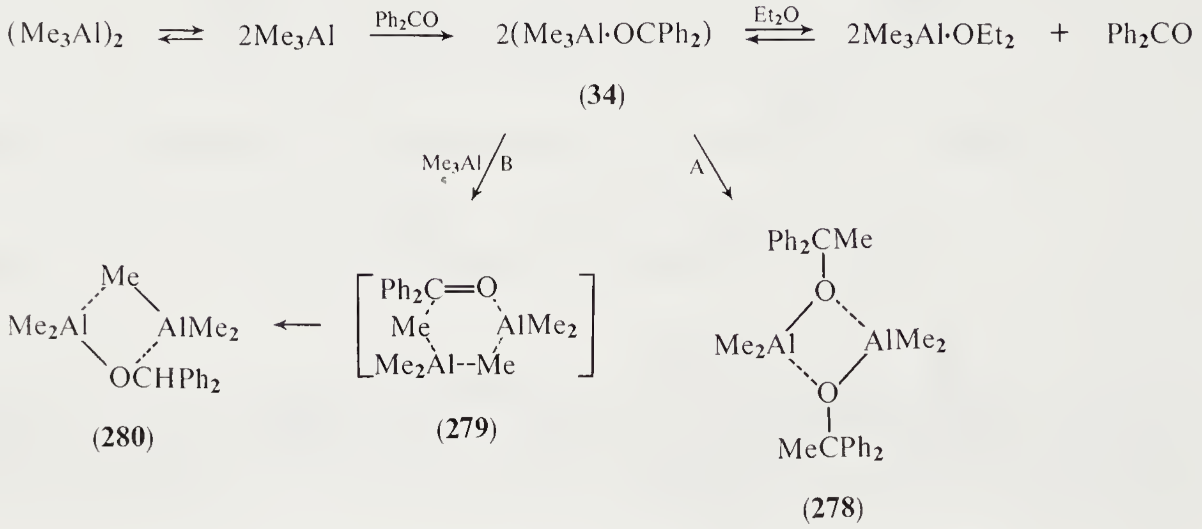
The use of β-branched aluminum alkyls like Bu^i_3Al, with ketones or other hindered carbonyl derivatives especially at higher temperatures with nickel promoters generally favors hydralumination. The hydrocarbon solubility of R''_3Al and R''_2AlH makes such reducing agents valuable alternatives to LAH for converting ketones to secondary alcohols. Often the stereochemistry of addition leads to the less stable product, presumably because the hydride attacks from the less hindered side of the ring (equation 211).[569,570]



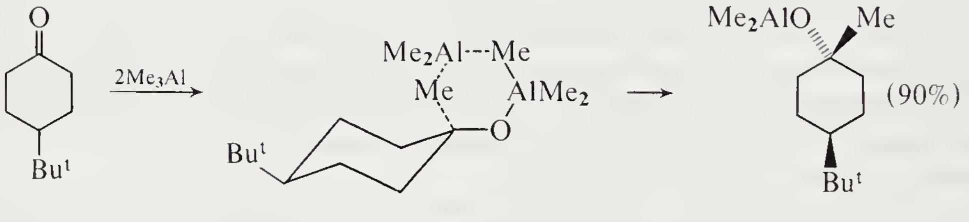
(211)

only product (94% yield)

Owing to the foregoing complexities, kinetic studies of this reaction have principally been conducted with benzophenone and trimethylaluminum. As mentioned before, in benzene these reactants form a 1 : 1 complex (**34**) which slowly rearranges in a first order fashion at 25 °C to yield dimethylaluminum 1,1-diphenylethoxide ($E^{\ddagger} = 80.2$ kJ mol^{-1}, $A = 1.27 \times 10^{10}$ l mol^{-1} s^{-1}, $\Delta H^{\ddagger} = 77.7$ kJ mol^{-1}, $\Delta S^{\ddagger} = 59.2$ J K^{-1} mol^{-1}). In diethyl ether little complexation between ketone and the alkyl occurs since the latter exists as $Me_3Al{\cdot}OEt_2$. Under these conditions the carbalumination is slower, because three-coordinate Me_3Al must be produced from the etherate ($E^{\ddagger} = 95.76$ kJ mol^{-1}, $A = 2.22 \times 10^{11}$ l mol^{-1} s^{-1}, $\Delta H^{\ddagger} = 93.24$ kJ mol^{-1}, $\Delta S^{\ddagger} = -36.12$ J K^{-1} mol^{-1}). With an excess of the Me_3Al in benzene the reaction is quite rapid, being second order in monomeric Me_3Al and first order in ketone ($E^{\ddagger} = 46.62$ kJ mol^{-1}, $A = 6.19 \times 10^8$ l mol^{-1} s^{-1}, $\Delta H^{\ddagger} = 44.1$ kJ mol^{-1}).[90] These data can be given a mechanistic unity by the equations depicted in Scheme 18. Path (A), operative with 1 : 1 reactant ratios in benzene or in ether, leads to dimeric alkoxide **(278)** while path (B) prevailing with excess Me_3Al, proceeds through a six-membered configuration **(279)** and yields the mixed bridge **(280)**. Although **(34)** is suggested to yield **(278)** *via* a four-membered, concerted transition state, stereochemical evidence on carbonyl insertions into chiral carbon–aluminum bonds points to a non-concerted pathway (Section 6.1.5: structures **(81)** and **(82)**, equations 50 and 51). The preferential methylation shown in equation (212) may arise because a six-membered transition state like **(279)** may be lower in energy if the developing alkoxyaluminum group is equatorial **(281)**.[571]



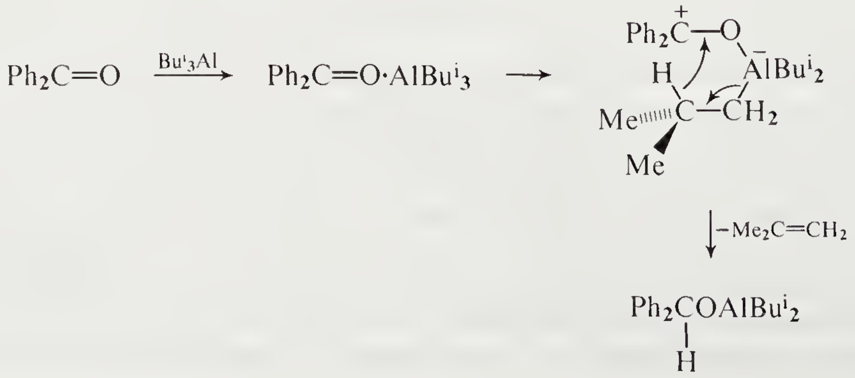
Scheme 18



(212)

(281)

An analogous kinetic study of the reduction of benzophenone by Bu^i_3Al in diethyl ether shows the rate to be first order in each component ($E^{\ddagger} = 68.9$ kJ mol^{-1}, $A = 10^{11}$ l mol^{-1} s^{-1}). A complex analogous to **(34)** is formed and may rearrange to eliminate alkene and transfer hydride (equation 213).[572] The suggested six-membered transition state is useful in understanding stereochemical preferences in reduction, as that given in equation (211). Some other illustrative alkylations and reductions are compiled in Table 15.



(213)

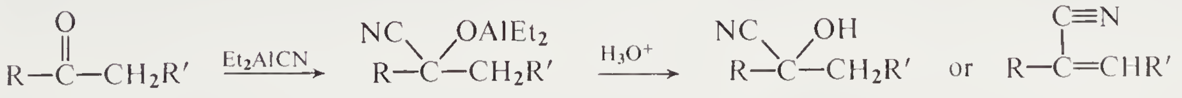
Table 15 Selected Alkylations and Reductions of Carbonyl Compounds by Organoaluminum Reagents

Carbonyl substrate	*Aluminum reagent*	*Product (after hydrolysis)*	*Ref.*
PhCHO	Et_3Al	PhCEt(H)OH (60%)	1
PhCOMe	Me_3Al (2 equiv.)	2-phenyl-2-butanol (100%)	2
PhCHO	$Et_2AlC{\equiv}CPh$	1,3-diphenylpropynol (86%)	3
Succinic anhydride	$EtAlCl_2$	4-oxohexanoic acid (93%)	4
Phthalic anhydride	Et_3Al	Phthalide (46%)	5
$PhCO_2Me$	Et_3Al	1-phenylpropanol and 3-phenyl-3-pentanol (ratio of 2.7 : 1)	5

1. H. Meerwein, G. Hinz, H. Majert and H. Sönke, *J. Prakt. Chem. II*, 1937, **147**, 226.
2. S. Pasynkiewicz and W. Arabas, *Rocz. Chem.*, 1966, **39**, 1393 (*Chem. Abstr.*, 1966, **64**, 17 625).
3. L. I. Zakharkin, V. V. Gavrilenko and L. L. Ivanov, *J. Gen. Chem. USSR* (*Engl. Transl.*), 1967, **37**, 937.
4. H. Reinheckel, K. Haage and D. Jahnke, *Organomet. Chem. Rev.* (*A*), 1969, **4**, 47.
5. Y. Baba, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 1020.

With α,β-unsaturated carbonyl derivatives the question of locoselectivity between the C=O and C=C linkages arises. Especially with aluminum aryls (equations 44 and 45), in the presence of radical promoters (equation 55) and by employing etherates of R_3Al, 1,4-addition to ketones can be made to predominate. Aldehydes, such as cinnamaldehyde, undergo principally 1,2-addition with both Et_3Al and Bu^i_2AlH.[573-579]

An extremely important example of elementalumination (addition of an E—Al bond) is cyanalumination.[580-584] The reagent of choice is diethylaluminum cyanide, which adds readily to aldehydes and ketones at low temperatures (equation 214). Hydrolysis can produce the cyanohydrin or the α,β-unsaturated nitrile. With α,β-unsaturated carbonyl derivatives cyanalumination can be made to proceed mainly in a 1,4-manner to form β-cyano carbonyl products. By the use of $R_2AlNR'_2$[584] and R_2AlSR,[585-587] aminaluminations and thialuminations of carbonyl derivatives can also be achieved.

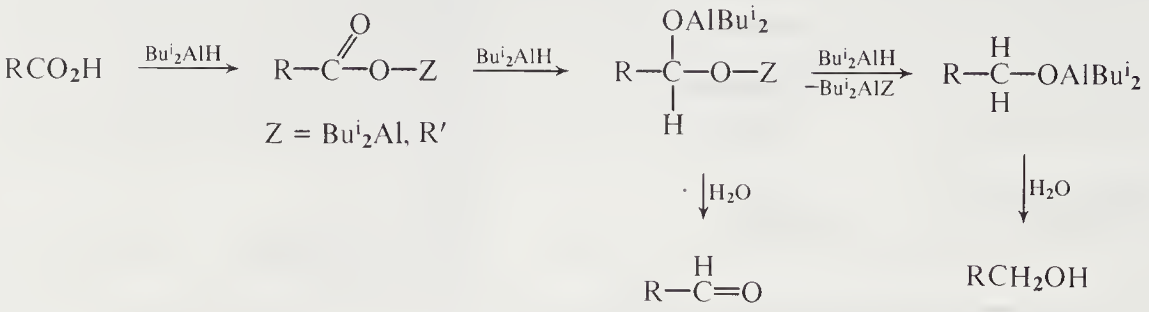


$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2R' \xrightarrow{Et_2AlCN} R{-}C(CN)(OAlEt_2){-}CH_2R' \xrightarrow{H_3O^+} R{-}C(CN)(OH){-}CH_2R' \text{ or } R{-}C(C{\equiv}N){=}CHR' \quad (214)$$

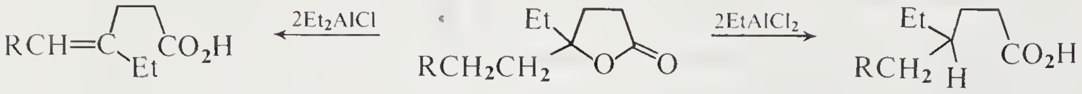
R = H, R

(*ii*) *Acids, esters and lactones*

The interplay of reduction and alkylation recurs with these and other carbonyl derivatives as well. Agents like Et_3Al, Me_3Al or Ph_3Al favor carbalumination, while Bu^i_3Al inevitably effects hydralumination. Esters[588,589] and lactones[590] respond to two equivalents of triethylaluminum in the same manner as to Grignard reagents: high yields of the diethyl(alkyl)methanols result upon hydrolysis. Aside from the initial substitution of the carboxyl hydrogen atom, these three derivatives react similarly: reduction can be controlled to yield aldehydes[128,591-593] or primary alcohols (equation 215).[558,559,594] Analogously, simple lactones give good yields of ω-hydroxyaldehydes or α,ω-diols with one or two equivalents, respectively, of Bu^i_3Al or Bu^i_2AlH. Some γ-lactones bearing tertiary alkoxy groups can undergo cleavage with alkylaluminum halides to yield, upon hydrolysis, carboxylic acids (equation 216).[595] Some α,β-unsaturated γ-lactones are reduced to furans by Bu^i_2AlH.[596,597]



(215)



(216)

(*iii*) *Acid anhydrides and halides*

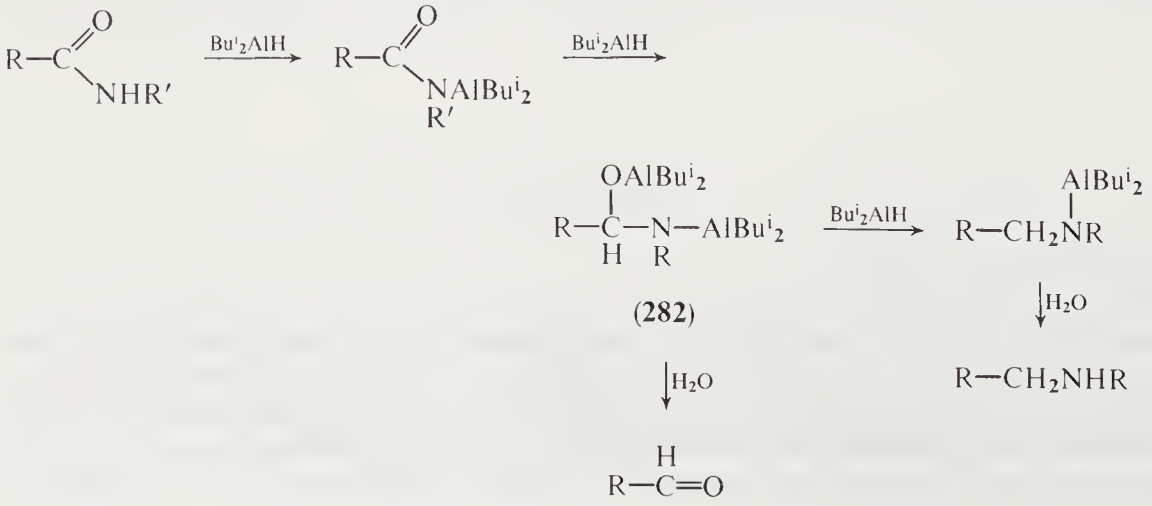
The most useful organoaluminum reaction with these compounds is their reaction with alkylaluminum chlorides to yield ketonic derivatives (equation 217).[598–600] The lower alkylating capability of $R'AlCl_2$ ($NaAlRCl_3$ or $R'_3Al_2Cl_3$) avoids attack on the resulting ketone. With cyclic compounds, such as succinic, glutaric and phthalic anhydrides, two equivalents of $RAlCl_2$ give high yields of keto acids.[601,602] Noteworthy is the locoselectivity shown with α,β-unsaturated derivatives, where high yields of ketones are also obtained (equation 218).[603] Of course, these carbonyl derivatives can be reduced to primary alcohols by Bu^i_2AlH.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Z \;+\; R'AlCl_2 \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-R' \;+\; AlCl_2Z \qquad (217)$$

(218)

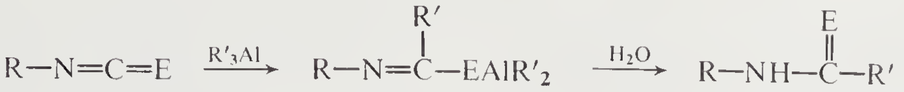
(*iv*) *Amides and lactams*

The pattern of reaction resembles that of carboxylic acids, where substitution of any NH proton is followed by stepwise reduction (equation 219).[558,604,605] By controlling the amount of hydride, intermediate (**282**) can be favored in some cases and good yields of aldehydes obtained.[604,605]



(219)

Although amides do not undergo clean carbalumination, they are themselves readily prepared by the carbalumination of isocyanates (equation 220).[606-609]

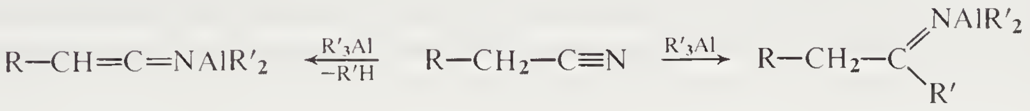


$$\mathrm{R{-}N{=}C{=}E} \xrightarrow{\mathrm{R'_3Al}} \mathrm{R{-}N{=}\overset{\overset{\displaystyle R'}{|}}{C}{-}EAlR'_2} \xrightarrow{\mathrm{H_2O}} \mathrm{R{-}NH{-}\overset{\overset{\displaystyle E}{\|}}{C}{-}R'} \qquad (220)$$

E = O, S; R′ = at least one R group and two X

6.6.3.3 *Azomethine and nitrile derivatives*

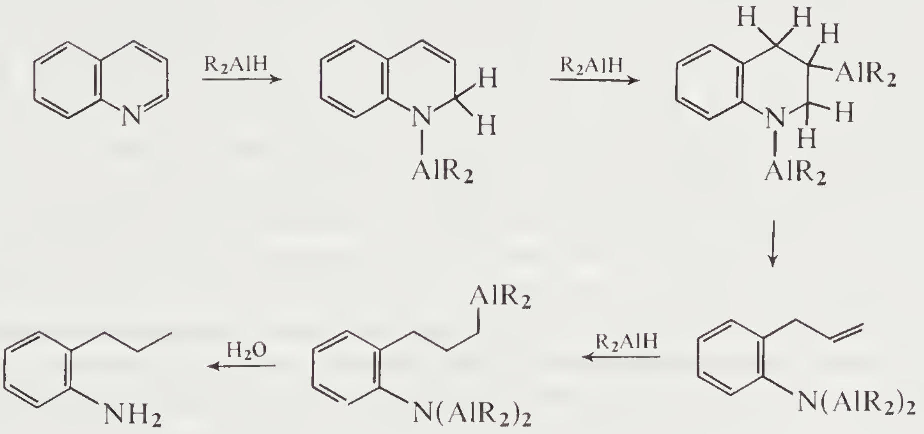
The basicity of these derivatives leads to preliminary complexation with aluminum reagents (*cf.* (**116**)). This complexation, together with the lower reactivity of their unsaturated carbon–nitrogen bond, leads to substitution of their α-hydrogen atoms as a side reaction (equation 221).[610] However, with some nitriles carbalumination leads to satisfactory yields of ketones by the hydrolysis of intermediate (**283**).[606,611,612] This addition is significantly promoted by the presence of nickel salts.[613] Another competing process is hydralumination, possibly proceeding like the reaction shown in equation (213). Such a reduction becomes the principal course with $\mathrm{Bu^i_2AlH}$, where again stepwise reduction followed by hydrolysis can lead to aldehydes[611,612,614] or amines[558,615] (*cf.* equation 219). Azomethine compounds generally undergo carbalumination so slowly that hydralumination is the predominant outcome. A pertinent example of sequential reactions is the behavior of aza-aromatic compounds.[303,616] Thus, quinoline undergoes the 1,2-addition to the C═N bond as do all azomethines, and then further additions and cleavage at higher temperatures (Scheme 19).



$$\mathrm{R{-}CH{=}C{=}NAlR'_2} \xleftarrow[\mathrm{-R'H}]{\mathrm{R'_3Al}} \mathrm{R{-}CH_2{-}C{\equiv}N} \xrightarrow{\mathrm{R'_3Al}} \mathrm{R{-}CH_2{-}C}\begin{matrix}\mathrm{{}^{\nearrow}NAlR'_2} \\ \mathrm{{}_{\searrow}R'}\end{matrix} \qquad (221)$$

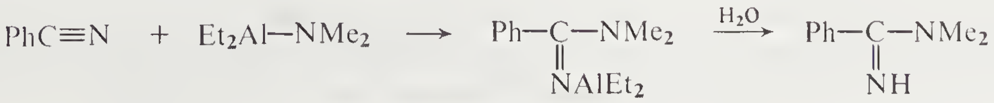
(**283**)

$$\mathrm{RC{\equiv}N} \xrightarrow{\mathrm{Bu^i_2AlH}} \mathrm{R{-}\overset{H}{C}{=}NAlBu^i_2} \xrightarrow{\mathrm{Bu^i_2AlH}} \mathrm{RCH_2N(AlBu^i)_2} \qquad (222)$$



Scheme 19

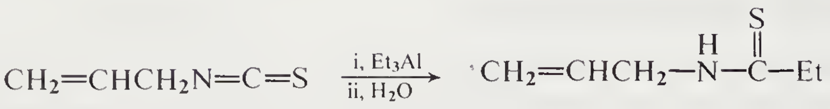
Nitriles can also undergo a number of useful elementaluminations with such reagents as $\mathrm{R_2AlNR_2}$,[617-619] $\mathrm{R_2AlSR}$[618] and similar compounds, *e.g.* equation (223). Several of these reactions can lead to nitrogen heterocycles.



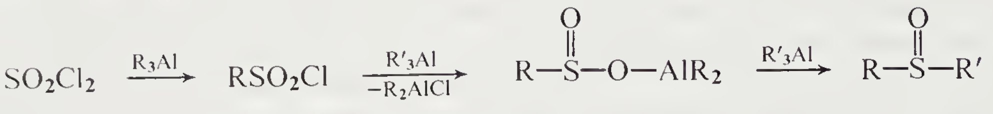
$$\mathrm{PhC{\equiv}N} + \mathrm{Et_2Al{-}NMe_2} \longrightarrow \mathrm{Ph{-}\underset{\underset{\displaystyle NAlEt_2}{\|}}{C}{-}NMe_2} \xrightarrow{\mathrm{H_2O}} \mathrm{Ph{-}\underset{\underset{\displaystyle NH}{\|}}{C}{-}NMe_2} \qquad (223)$$

6.6.3.4 Thiocarbonyl and sulfonyl derivatives

Many of these reactions resemble closely those of their carbonyl counterparts. Thus, isothiocyanates carbaluminate to yield thioamides[606-609] (equation 224); sulfuryl chloride gives alkylsulfonyl chlorides,[620] which in turn yield sulfinic acids[621] or sulfoxides[621,622] (equation 225). Conversion to the sulfoxide (**285**) is especially feasible when arylsulfonyl halides (**284**) are employed.



$$CH_2{=}CHCH_2N{=}C{=}S \xrightarrow[\text{ii, }H_2O]{\text{i, }Et_3Al} CH_2{=}CHCH_2{-}\overset{H}{N}{-}\overset{\overset{S}{\|}}{C}{-}Et \qquad (224)$$



$$SO_2Cl_2 \xrightarrow{R_3Al} RSO_2Cl \xrightarrow[-R_2AlCl]{R'_3Al} R{-}\overset{\overset{O}{\|}}{S}{-}O{-}AlR_2 \xrightarrow{R'_3Al} R{-}\overset{\overset{O}{\|}}{S}{-}R' \qquad (225)$$

(**284**) (**285**)

6.6.3.5 Small molecule addends

Of prime importance among these reagents is molecular oxygen, which converts alkyl–aluminum bonds into aluminum alkoxides efficiently (*cf.* Section 6.1.5, equation 57).[28,122,500] Unsaturated carbon–aluminum bonds, however, do not respond cleanly but give extensive carbon–carbon coupling.[623,624] Thus, triphenylaluminum yields only 30% phenol and much biphenyl.[106,625] These oxidations appear to involve free radical chains which do not arise from any long-lived complex, $R_3Al{\cdot}O_2$. In the oxidation of Ph_3Al the presence of phenyl radicals has been demonstrated by solvent attack in both ^{14}C-labeled benzene and in ether.[626] Possibly *via* a parallel mechanism, sulfur (S_8) can give good yields of thiols (equation 226).[627]

$$Et_3Al + S \longrightarrow Et_2AlSEt \xrightarrow{H_2O} EtSH \qquad (226)$$

The acid anhydrides CO_2, SO_2 and SO_3, can all be inserted into one carbon–aluminum bond of R_3Al to give acceptable yields of the organic acids, if provision is taken to protect intermediate (**286**) from further attack (equation 227). Cooling, the addition of amines or the use of less active agents ($RAlX_2$) have been employed to increase yields. The resulting carboxylic,[216] sulfinic[216,628] and sulfonic acids[629,630] can be formed from aluminum alkyls in 70–100% yield, based on consumption of one C—Al bond. With SO_3 and SO_2, two or even three of the C—Al bonds can be made to react. Aluminate salt formation ($M^+AlR_4^-$) again permits only one C—Al bond to react with carbon dioxide if R is alkyl. When R is 1-alkynyl, all four bonds can be carbonated.[631] Finally, in unsymmetrical aluminates $MAlR_2R'_2$ or $MAlR_3R'$ where R is alkyl and R′ is 1-alkynyl or 1-alkenyl, the R′—Al bonds react preferentially with carbon dioxide.[230,231,567] As shown in equations (54) and (80), such insertions with 1-alkenylaluminates occur with retention of configuration. Furthermore, even though 2-alkenyl and benzylic aluminum compounds undergo an allylic rearrangement upon carbonation (*cf.* (**74**)–(**76**)), the reaction of tribenzylaluminum with sulfur dioxide gives normal insertion. The benzylsulfinic acid isolated supports the reaction of at least two benzyl–aluminum bonds.[632]

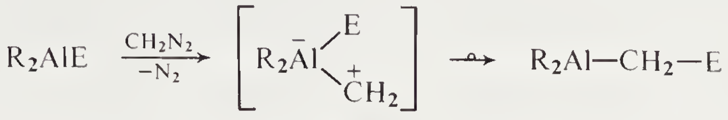
$$R_3Al + E{=}G \longrightarrow R_2Al{-}G{-}ER \xrightarrow{H_3O^+} R{-}E{-}GH \qquad (227)$$

(**286**)

$E = CO, SO, SO_2$
$G = O$

With CS_2,[603] COS[633] and even with CO_2,[216] intermediate (**286**) (E = C; G = O, S) can react further, so as to trialkylate E. Thus, passing these addends into Et_3Al yields, upon hydrolysis, triethylmethanol (from CO_2) and triethylmethanethiol (from CS_2 or COS).

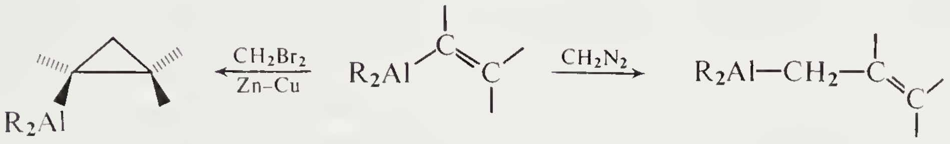
The insertion of methylene into aluminum–element bonds has been achieved by the use of diazomethane.[218,634–636] The reactions can be viewed as resulting from rearrangements of an ylide (**287**) (equation 228). The migratory aptitudes of group E from aluminum to carbon seem to rank thus: H, X > OR > 1-alkenyl > alkyl. The behavior of 1-alkenylaluminum systems is particularly interesting: with diazomethane they give insertion to form allylaluminum compounds (**289**);[637] with another methylene reagent, $CH_2Br_2/(Zn—Cu)$, cyclopropanation occurs to give (**288**) (equation 229).[638]



(228)

(**287**)

E = R, H, X, OR



(229)

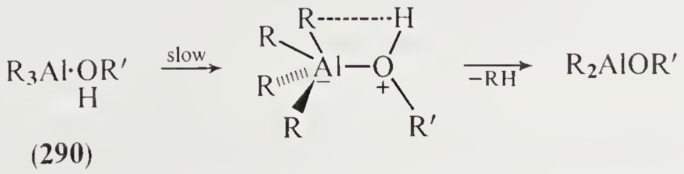
(**288**) (**289**)

6.6.4 Substitution Reactions

Of great interest for reaction mechanisms and synthetic applications is whether the substitution of aluminum by a group occurs with any change of configuration. Since organoaluminum compounds themselves enter into a wide variety of dynamic processes (Section 6.3), rearrangements during substitution can be anticipated. With this awareness, it may be all the more remarkable to learn that a considerable number of substitutions take place with retention of configuration.

6.6.4.1 Protodealumination

The sensitivity of organoaluminum compounds to all types of Brønsted acid is a principal reason for the circumspection and techniques required for experimentation. Not only acids of the type EH (E = RO, RS, R_2N, R_2P, X, *etc.*) but even hydrocarbons of the alkynes or cyclopentadienyl type can cleave C—Al bonds. The reactivity toward cleavage seems roughly to parallel the acidity of EH and the nucleophilicity of the carbon in C—Al bonds (C≡C—Al > C=C—Al > R_3C—Al). Pertinent to the mechanisms are the overall protium–tritium isotope effects for the alcoholysis of tri-*n*-octylaluminum: values of k_H/k_T of 2.87 for MeOH and 7.82 for Bu^iOH at 0 °C support considerable stretching of the O—H bond in the transition state.[639] The bulk of the latter alcohol may destabilize intermediate (**290**) and require more O—H stretching. Support for a similar four-center trapezial transition state (**291**) is found in the retention of configuration displayed in the hydrolysis of alkenylaluminum (Scheme 6) or indanylaluminum compounds (equation 84). Accordingly, treatment of these types of compound with D_2O constitutes a reliable way of preparing specifically deuterated compounds.[129] Perhaps the aluminum systems most prone to hydrolytic rearrangement are the allylic, benzylic and propargylic, with which the proportion of rearrangement is sensitive both to structure and experimental conditions. The acenaphthenylaluminum system shown in equation (26) gives a 60:40 mixture of unrearranged to rearranged hydrocarbons with Bu^tOH; a 95:5 mixture results from use of a water–pyridine reagent.[58]



(230)

(**290**) (**291**)

6.6.4.2 Halodealumination

The course of the reaction with halogen presents many similarities to the preceding:[350,467] from the behavior of alkenyl- and cyclopropyl-aluminum derivatives, halogenative cleavage occurs with retention of configuration. Compounds (**250**) and (**288**) give high yields of the bromo- or iodo-alkenes[231] or cyclopropanes[638] with the appropriate halogen at −50 °C. Again, the selectivity for cleaving the more electronegative C—Al bond should be noted. Also, dialkyl(alkynyl)aluminum undergoes selective cleavage of the C≡C—Al bond with one equivalent of halogen,[640] and aluminates of the type $MAl(C{\equiv}C{-}R)_4$ can be completely cleaved with four equivalents.[641] With the pseudohalogens XCN, the mode of reaction depends on the halogen (equation 231).[642,643]

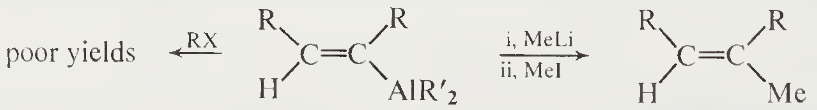
$$R_2AlCN \; + \; RBr \xleftarrow{BrCN} R_3Al \xrightarrow{ClCN} R_2AlCl \; + \; R{-}C{\equiv}N \qquad (231)$$

6.6.4.3 Carbodealumination

The substitution of aluminum by carbon can be effected by the use of organic halides, ethers or cyanogen. Although the halogen–alkyl exchange reaction (equation 232) should be an attractive way of making carbon–carbon bonds, it is often overwhelmed by dominant side reactions, such as hydride reduction of R″X to R″H, dehydrohalogenation of R″X and competitive coupling to yield R—R″ as well. A reminder of the violent reaction between some polyhalides and aluminum alkyls is in order here. Generally, only when R and R′ have different electronegativities (*i.e.* R = alkyl and R′ = 1- or 2-alkenyl) and R″ is allylic, propargylic or simple *n*-alkyl do such reactions give useful yields of R′—R″. Furthermore, formation of the aluminate is often necessary to promote reaction. Some examples are given in equations (233),[644] (234)[250,251] and (235).[645]

$$R_2AlR' \; + \; R''X \longrightarrow R'{-}R'' \; + \; R_2AlX \qquad (232)$$

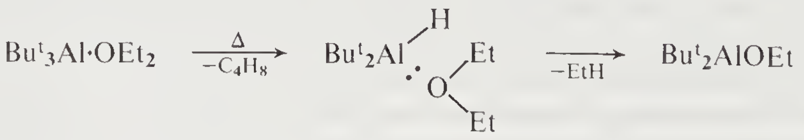
$$(BuC{\equiv}C)_3Al \; + \; Me_3CCl \longrightarrow BuC{\equiv}CBu^t \; + \; (BuC{\equiv}C)_2AlCl \qquad (233)$$



(234)

$$Me_3Al \; + \; Ph_3CCl \longrightarrow Ph_3CCMe_3 \; + \; Me_2AlCl \qquad (235)$$

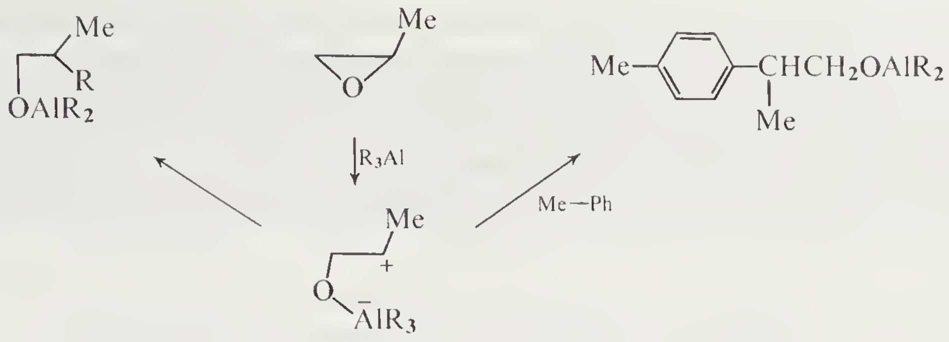
That ordinary ethers are cleaved by organoaluminum halides is not surprising, since aluminum halides themselves cleave ethers. Cleavage of ethers by aluminum alkyls, on the other hand, usually requires higher temperatures where it appears that R_2AlH is the active agent (equation 236).[49] In a similar way, orthoesters, acetals and ketals are reduced to ethers by Bu^i_2AlH.[646]



(236)

Carbodealumination, however, is observed with more reactive ethers, such as orthoesters and epoxides. Allyl- or propargyl-aluminum bromides convert ethyl orthoformate into the corresponding diethyl acetals,[647] and aluminum alkyls readily cleave the epoxide ring. With ethylene oxide itself, all three bonds of triethylaluminum can react to yield aluminum tributoxide.[648,649] The behavior of propylene epoxide supports the generation of carbenium ion intermediates (**292**), both in the cleavage to generate the more stable carbocation (secondary)[650] and the Friedel–Crafts alkylation observed in aromatic solvents[651] (Scheme 20). The generation of such cations can also cause hydride shifts, proton loss and cationic polymerizations with certain epoxides.[652–654] Through such side reactions, rearrangements to carbonyl and allylic alcohol derivatives can occur. These reactions are often encountered with R_2AlX and R_2AlH reagents which can not only directly cleave epoxides to alcohols but can hydraluminate the foregoing rearrangement products.

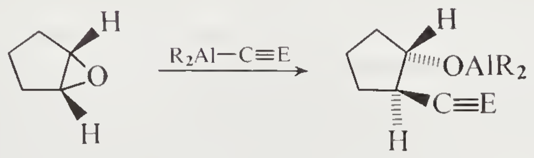
Cyanogen, $(CN)_2$, reacts very selectively with the vinyl–aluminum bond in 1-alkenyl(dialkyl)aluminum compounds (*cf.* equation 231) to give excellent yields of the 1-alkenyl nitrile. The stereochemistry of the original C—Al bond is retained in the nitrile product.[655]



(292)

Scheme 20

Alkylation of epoxides appears to occur with inversion of configuration at the ruptured C—O bond, as has been demonstrated with the isomeric epoxides of (*E*)- and (*Z*)-2-butene and with epoxycycloalkanes by the use of the isoelectronic reagents $R_2AlC{\equiv}E$ (E = CR′, N) (equation 237).[656,657]

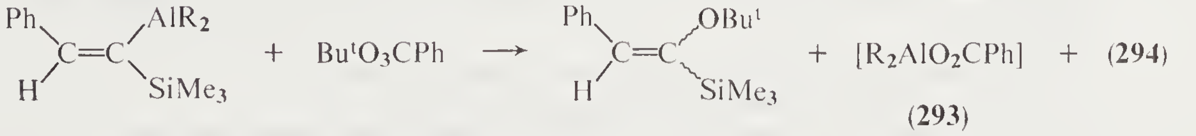


(237)

6.6.4.4 Oxydealumination

The substitution of aluminum by oxygen can be achieved by the action of various peroxide derivatives, such as di-*t*-butyl peroxide,[658] benzoyl peroxide[107,659] and *t*-butyl perbenzoate[660] (*cf.* equation 58). The main reaction of the peroxide (equation 238) is accompanied by side products typical of a free ethyl radical intermediate, namely ethane, ethylene and *n*-butane. Similarly, aluminum alkyls and aryls are oxidized by the benzoyl peroxide to form benzoate esters and the benzoate R_2AlO_2CPh (**293**). Oxidation of the alkenylaluminum compound (**294**) with *t*-butyl perbenzoate gives about 45% of *cis* and *trans* ether (**295**), with recovery of about one-half of (**294**) (as alkene, after hydrolysis) (equation 239). Apparently here, and in reactions of benzoyl peroxide, the benzoate (**293**) complexes with the starting organometallic compound and deactivates it towards oxidation.[660]

$$(Bu^tO)_2 \quad + \quad Et_3Al \quad \longrightarrow \quad Et_2AlOBu^t \quad + \quad Bu^tOEt \qquad (238)$$



(294) **(295)** **(293)** (239)

6.6.4.5 Metallodealumination

The preparation of carbon–metal or –metalloid bonds from organoaluminum compounds and the appropriate metal salt is widely applicable to most elements except those of Groups IA and IIA (equation 240). The feasibility of this substitution depends upon several factors: (a) the capability of R_3Al to exchange one, two or three of its organic groups with MZ_n (*i.e.* the reactivity of R_2AlZ and $RAlZ_2$ with R_mMZ_{n-m}); (b) the thermal stability of the metal alkyl produced;

$$MZ_n \xrightarrow[-R_2AlZ]{R_3Al} \underset{\textbf{(296)}}{RMZ_{n-1}} \xrightarrow{(n-1)R_3Al} \underset{\textbf{(297)}}{R_nM} \qquad (240)$$

and (c) the isolation of the metal alkyl from the Lewis acidic R_nAlZ_{3-n} by-products. The driving force for this exchange is principally the great strength of the resulting Al–Z bond; the same consideration explains the failure of aluminum alkyls to alkylate the highly stable salts of the alkali and alkaline earth metals (but complexes are formed: *cf.* Section 6.2.6.6.). Beryllium is an understandable exception, in that its salts are more covalent. However, by the use of less stable salts such as alkoxides, aluminum alkyls can yield aluminates with these metals (equation 241).[290]

$$\mathrm{KOEt} \quad + \quad 2\mathrm{Et_3Al} \longrightarrow \mathrm{K[AlEt_4]} \quad + \quad \mathrm{Et_2AlOEt} \qquad (241)$$

The method has been successful for the preparation of compounds of beryllium, zinc, cadmium, mercury, boron, gallium, indium, silicon, germanium, tin, lead, phosphorus, arsenic, antimony, bismuth and many transition metals. With the transition metals the lability of their carbon–metal bonds often constitutes a serious limitation to isolation of the products. Successful preparation then requires the presence of stabilizing ligands on the metal, such as cyclopentadienyl, bipyridyl and phosphines.

The metal salt employed, MZ_n, may be a halide, carboxylate, acetylacetonate, alkoxide, dialkylamide, oxide, sulfide or even another hydrocarbon group (*cf.* the exchange between organoboron and organoaluminum compounds: Section 6.5.2.2). With tin or lead, the metal(II) salts have been employed to yield equivalent amounts of R_4M and metal. In order to achieve a good utilization of the reagents, it is often necessary to add a Lewis base to complex with the aluminum product R_mAlZ_{n-m}. Especially when Z is halogen, such products can complex with MZ_n and prevent alkylation, or with R_mMZ_{n-m} and hinder further alkylation (*e.g.* preparation of gallium or tin alkyls). By adding powdered potassium chloride, an ether or a tertiary amine, R_mAlZ_{n-m} will complex preferentially with these or liberate MZ_n or R_mMZ_{n-m}. Illustrations of specific preparations are given in Table 16.

Table 16 Preparation of Other Organometallic Compounds from Organoaluminum Reagents

Metal salt	*Aluminum reagent*	*Product* (%)	*Ref.*
$SnCl_4$	Et_3Al (+KCl)	Et_4Sn (80)	1
Et_3SnCl	Et_2AlH	Et_3SnH (89)	2
$GeCl_4$	Me_3Al (+NaCl)	Me_4Ge (73)	3
$PbCl_2$	$Et_3Al{\cdot}OEt_2$	Et_4Pb (70)	4
$ZnCl_2$	Bu^i_3Al	Bu^i_2Zn (95)	5
$GaCl_3$	Et_3Al (+KCl)	Et_3Ga (84)	6
$HgCl_2$	$NaAlEtCl_3$	EtHgCl (91)	7

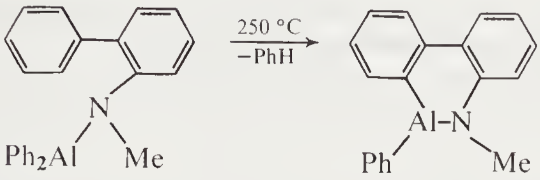
1. H. Jenker and H. W. Schmidt, *Ger. Pat. Appl.* 1 048 275 (1955) (*Chem. Abstr.*, 1960, **54**, 19 486).
2. W. P. Neumann and H. Niermann, *Liebigs Ann. Chem.*, 1962, **653**, 164.
3. F. Glockling and J. R. C. Light, *J. Chem. Soc.* (*A*), 1967, 623.
4. S. M. Blitzer and T. H. Pearson, *US Pat.* 2 859 228 (1959) (*Chem. Abstr.*, 1959, **53**, 9150).
5. K. Ziegler, *US Pat.* 3 124 604 (1956) (*Chem. Abstr.*, 1964, **60**, 15 909).
6. J. J. Eisch, *J. Am. Chem. Soc.*, 1962, **84**, 3830.
7. S. Pasynkiewicz, *Przem. Chem.*, 1960, **39**, 225 (*Chem. Abstr.*, 1961, **55**, 3417).

Quite analogously, alkylaluminum hydrides react with the same metal salts or organometallic salts to yield hydrides (equation 242). The preferential exchange of hydride over R′ does not always obtain: borate esters undergo alkylation with R'_2AlH. The method has however been applied, for example, to the synthesis of R_2GaH, R_nSiH_{4-n}, R_nSnH_{4-n} (n = 1–4), $(Ph_3P)_3Co(N_2)H$ and $(Ph_3P)_3RhH$.[661]

$$R_mMZ_{n-m} \quad + \quad (n - m)R'_2AlH \longrightarrow R_mMH_{n-m} \quad + \quad (n - m)R'_2AlZ \qquad (242)$$

6.6.5 Elimination Reactions

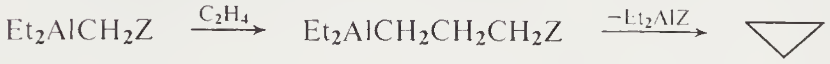
The principal elimination characteristic of organoaluminum compounds, namely aluminum hydride and alkene formation, has been discussed in Sections 6.3.5 and 6.3.6. Other eliminations are peculiar to special structural types. Since trimethylaluminum cannot form alkene, the formation principally of methane at temperatures of 300–500 °C suggests the occurrence of an autometallation. The solid residues from such pyrolyses approach the composition of aluminum carbide, for treatment with D_2O yields CD_4 in addition to CHD_3 and CH_2D_2.[271] A similar autometallation occurs when triphenylaluminum is heated above 200 °C: benzene is evolved and treatment of the residue with D_2O yields *m*- and *p*-dideuteriobenzenes and some trideuteriobenzenes (mainly the 1,3,5-isomer).[362,662,663] In the elimination of benzene from various phenylaluminum derivatives such metallation can occur intramolecularly to yield aluminum heterocycles (*cf.* equations 73, 116 and 243).[664]



(243)

Appropriate substitution can favor the homolysis of a C—Al bond, as exemplified by the decomposition of certain tritylaluminum compounds at 140 °C (equation 115).[348]

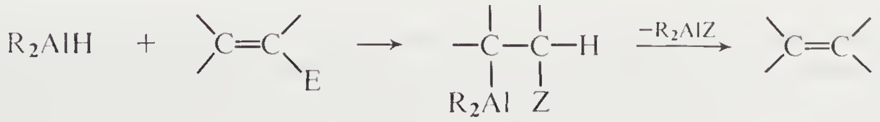
In addition, a number of heteroatom-substituted compounds can undergo *apparent* α-, α,β- or α,γ-eliminations of the elements of R_2AlZ. The *apparent* α-elimination when halomethylaluminum compounds cyclopropanate alkenes is actually a combination of carbalumination and α,γ-elimination ($Z = X$) (equation 244).[218,634] Intermediates like (**298**) can also be generated by the hydralumination of allyl ethers ($Z = OR$) and similarly producing cyclopropane.[220] By employing α,ω-alkenyl halides with R_2AlH some success has been achieved in preparing the C_4 and C_5 cycloalkanes.[665]



(**298**)

(244)

Even though the intermediate (**299**) has not been intercepted, it is probable that the cleavage of enamines[666] and vinyl ethers[219] by R_2AlH involves hydralumination and a rapid α,β-elimination (equation 245).



(**299**)

$E = OR', NR'_2$

(245)

6.6.6 Electrolytic Decomposition

The marked enhancement of electrical conductivity observed when organoaluminum compounds are treated with neutral or anionic Lewis bases has been discussed in Sections 6.1.4 and 6.2.6.6. Such Lewis complexes, especially $MX{\cdot}2Et_3Al$, are suitable electrolytes for the electroplating or refining of aluminum metal. Passage of electrical current through a cell having such an electrolyte and an anode of unpurified aluminum leads to the decomposition of highly pure aluminum metal (99.9999%) on the cathode.[667] This method may be adapted for the separation of pure gallium and indium metal from aluminum residues.[668] By employing anodes of less reactive metals with various aluminate complexes, the electrode processes of equations (246) and (247) take place. Metal alkyls of lead, magnesium, zinc, cadmium, mercury, tin, antimony and bismuth can be obtained in this manner.[669]

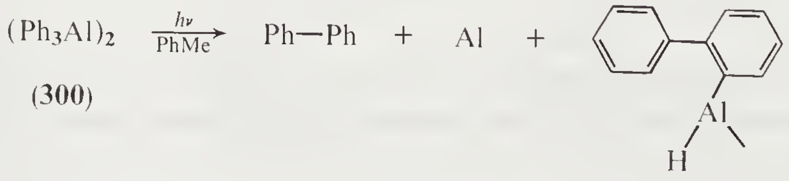
$$\text{Anode: M} + \text{AlR}_4^- \longrightarrow \text{R}_n\text{M} + \text{R}_3\text{Al} + e^- \qquad (246)$$

$$\text{Cathode: Na}^+(\text{K}^+) + e^- \longrightarrow \text{Na(K)} \qquad (247)$$

The electrolysis of ethylaluminate complexes with an inert anode apparently generates the ethyl radical, for ethane, ethylene and butane are evolved.[511]

6.6.7 Photolysis

Aluminum alkyls can undergo photolysis in the presence of sensitizers. Thus, triethylaluminum reacts with diphenylacetylene to give 1,4-diethyl-2,3,5,6-tetraphenyl-1,4-dialuminacyclohexadiene (equation 61).[115,116] That these reactions probably involve homolysis of carbon–aluminum bonds is supported by the formation of products typical of ethyl radicals (C_2H_6, C_2H_4 and n-C_4H_{10}). Also, the scission of the trityl compound shown in equation (115) can be achieved photochemically. However, the interesting photorearrangement of aluminum aryls (equation 60) does not seem to involve much attack of phenyl radicals on the toluene solvent.[113,114] When triphenylaluminum is photolyzed in toluene and treated with D_2O, biphenyl (45%), aluminum metal and hydrogen are formed. The hydrogen is >98% HD and the biphenyl is 20% undeuterated and 80% deuterated at the 2-position. These findings are consistent with equation (248). The toluene solvent does not participate significantly: the observed ratio of biphenyl : bibenzyl (a likely sign of radical H-atom abstraction) is 99 : 1. Also, the Al—H is not derived from solvent attack, for when toluene-d_8 is used, the hydrogen gas obtained upon work-up with D_2O is still >98% HD.

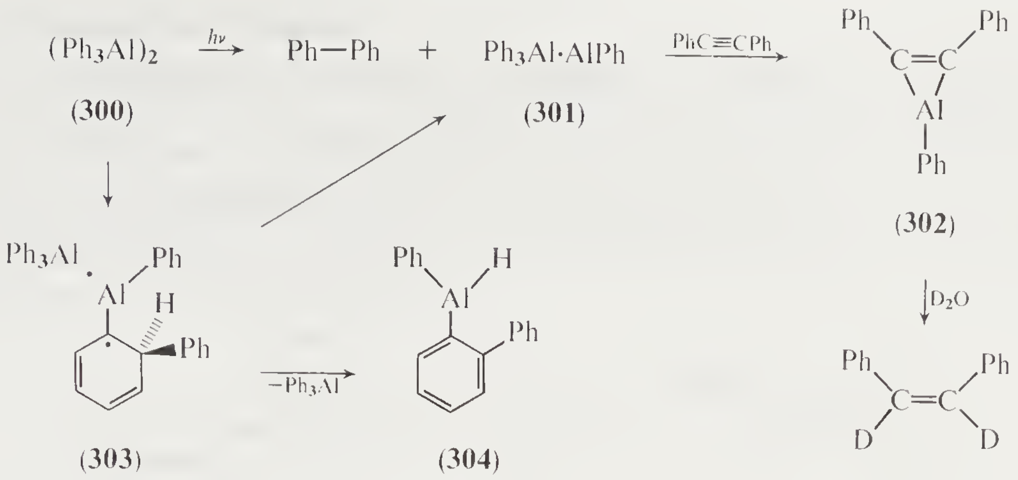


(300)

(248)

That the photoreaction involves the dimer (**300**) is made probable by the observed photo-inertness of the etherate $Ph_3Al{\cdot}OEt_2$. Moreover, when (**300**) is irradiated in the presence of diphenylacetylene, no aluminum is deposited nor is hydrogen evolved upon hydrolysis. Work-up with D_2O gives α-deuterio-*cis*-stilbene and α-deuterio-triphenylethylene, products expected to arise from addition of Al—H and Ph—Al bonds to the alkyne, but about 50% of the *cis*-stilbene is now dideuterated. These results can be reconciled by Scheme 21. Phenyl migration to the *ortho* position would give (**303**), which could rearrange to (**304**) or eliminate biphenyl to form (**301**). Addition of this phenylaluminum(I) to the alkyne (carbene-like reaction: *cf.* equation 61) would lead to (**302**). Such a precursor may dimerize to a dialuminacyclohexadiene. The postulated phenyl migration to the *ortho* position is supported by the photobehavior of tri-*m*-tolyl- and tri-*p*-tolylaluminum. The *meta* isomer yields, upon hydrolysis, a 50 : 50 mixture of 2,3′- and 3,4′-bitolyls; and the *para* isomer gives only 3,4′-bitolyl. This explanation does not require the generation of free phenyl radicals and thus accounts for the lack of significant attack on the solvent.

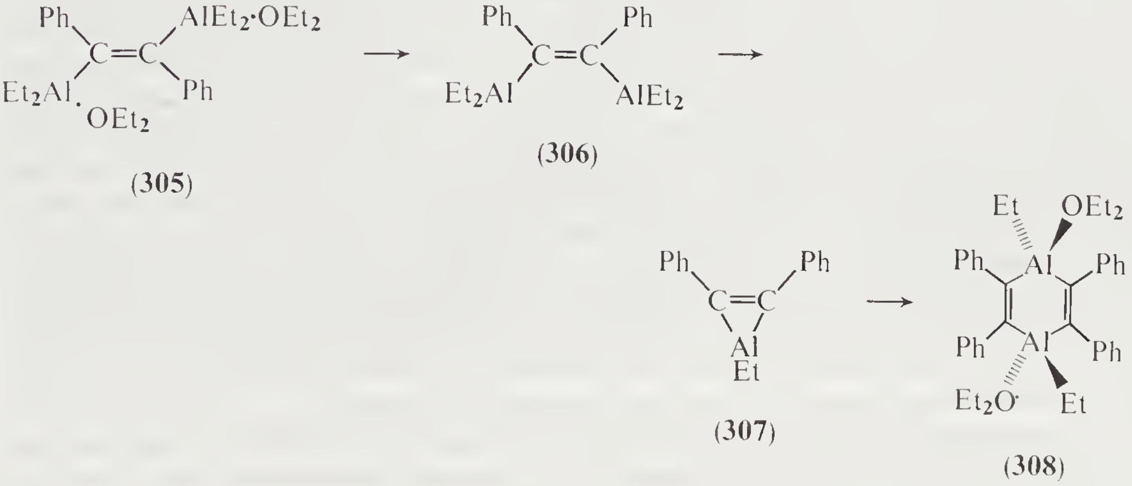
The photobehavior of monomeric triphenylgallium and triphenylindium in toluene solution is consistent with this pathway. The gallium compound undergoes photolysis very inefficiently



Scheme 21

under the conditions successful with aluminum aryls. Only 4% of biphenyl is formed and it is accompanied by 2% of bibenzyl and 2% of the methylbiphenyls, products signaling free radical attack on the solvent. The photolysis of triphenylindium gives a 44% yield of biphenyl, but here again comparable amounts of bibenzyl (33%) and the methylbiphenyls (16%) point to intermolecular free radical attack.[670]

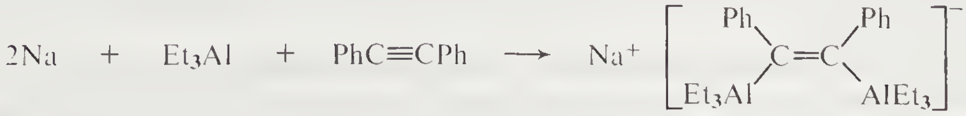
Irradiation of (*E*)-1,2-bis(diethylalumino)-1,2-diphenylethene diethyl etherate (**305**) leads to the elimination of $Et_3Al{\cdot}OEt_2$ and the formation of (**308**), presumably by way of (**306**) and (**307**) (equation 249).[115,116] A similar dialuminacyclohexadiene results from the photodimerization of a (*Z*)-1,4-bis(diethylalumino)butatriene.[671]



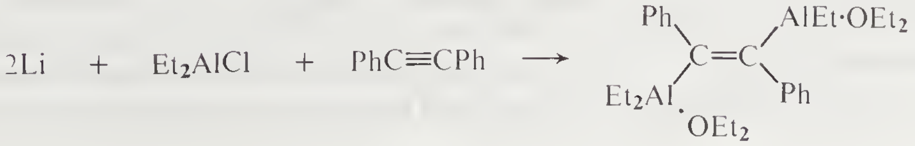
(249)

6.6.8 Reactions with Active Metals

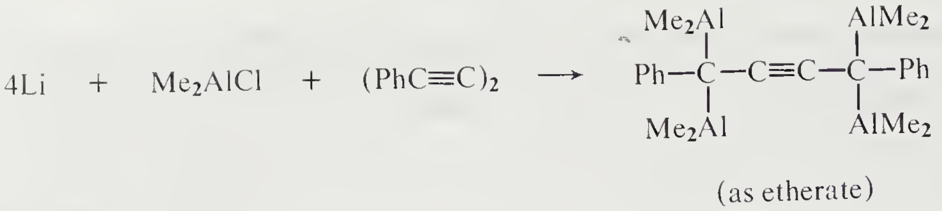
As indicated in equation (181), alkali metals convert aluminum alkyls and aryls into the alkali metal tetraorganoaluminates with displacement of aluminum metal. However, some aluminum compounds form metal adducts instead. Unusual organoaluminum compounds can result if an extended conjugated system is present (equations 250–253).[672–675]



$$2Na + Et_3Al + PhC{\equiv}CPh \longrightarrow Na^+[(Et_3Al)PhC{=}CPh(AlEt_3)]^- \qquad (250)$$

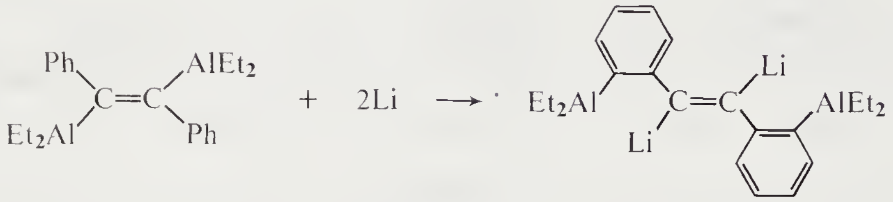


$$2Li + Et_2AlCl + PhC{\equiv}CPh \longrightarrow (Et_2Al{\cdot}OEt_2)PhC{=}CPh(AlEt{\cdot}OEt_2) \qquad (251)$$



$$4\mathrm{Li} + \mathrm{Me_2AlCl} + (\mathrm{PhC{\equiv}C})_2 \longrightarrow \mathrm{Ph{-}}\overset{\mathrm{Me_2Al}}{\underset{\mathrm{Me_2Al}}{\mathrm{C}}}\mathrm{{-}C{\equiv}C{-}}\overset{\mathrm{AlMe_2}}{\underset{\mathrm{AlMe_2}}{\mathrm{C}}}\mathrm{{-}Ph} \quad (252)$$

(as etherate)



(253)

6.7 SYNTHETIC APPLICATIONS

6.7.1 Reagents and Methodology

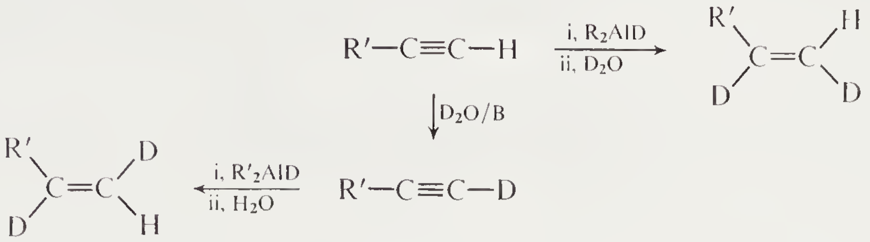
Commercially available organoaluminum reagents encompass the following types: (a) R_3Al, where R = Me, Et, Pr^n, Bu^n, Bu^i, *n*-hexyl, 2-methylpentyl and *n*-octyl; (b) R_2AlH, where R = Et and Bu^i; (c) $R_3Al_2Cl_3$, where R = Me, Et and Bu^i; (d) R_2AlCl, where R = Me, Et, Pr^n, Bu^n, Bu^i; (e) R_2AlX, where R = Et and X = Br, I; (f) $RAlCl_2$, where R = Me, Et and Bu^i; and (g) R_2AlOR', where R = Et and Bu^i and R′ = Me, Et, Pr^i and *i*-pentyl.[130] These reagents are stable in alkane hydrocarbon solution if kept under an anhydrous, inert atmosphere. Besides alkanes, other suitable reaction solvents for R_3Al and R_2AlH compounds are aromatic hydrocarbons, non-cyclic aliphatic and aromatic ethers and saturated tertiary amines. Ethers and amines will form complexes with the aluminum reagents and such complexes will have a reduced reactivity toward many substrates. In some cases, this moderated reactivity is advantageous (hydralumination), in other cases it is unacceptable (carbalumination). Although admixing aluminum alkyls with some polyhalogenated solvents, such as $CHCl_3$ or CCl_4, can give *violent reactions*, methylene chloride is reported to react slowly or not at all with Et_3Al, Et_2AlH and Bu$^i_2$AlH at 25 °C.[600] Accordingly, it has been recommended as a useful solvent for reductions and alkylations at or below room temperature. Use of such solvents as THF above 70 °C, DMF, carbon disulfide, 2,2′-dimethoxydiethyl ether and phenetole can lead to vigorous reaction with these aluminum reagents. Finally, all alkylaluminum halides form strong complexes with all ether solvents and some of these will decompose upon warming to yield alkyl halides (Section 6.6.4.3).

An important limitation on the synthetic value of aluminum alkyls and hydrides is that often only one C—Al or Al—H bond of the reagent will react with the substrate A═B. The reactivity of the remaining C—Al bonds in the adduct R_2Al—A—B—R is then too low for further insertions. Sometimes the use of higher temperatures, catalysts or coreactants will overcome this limitation. Thus, triethylaluminum reacts with CO_2 under pressure at 220 °C with CO_2 insertion into two C—Al bonds.[216] Also, by employing a nickel salt catalyst, Bu$^i_3$Al or Bu$^i_2$AlH behave as a source of three Al—H bonds for reductions at a lowered temperature. Finally, the aluminum reagent's reactivity can be enhanced by making an aluminate complex with an alkali metal alkyl or hydride ($LiAlR_4$ and $NaAlR_2H_2$).

In the discussions of chemical reactions of C—Al and Al—H bonds, many instances are cited where the course of the reaction depends upon kinetic and thermodynamic factors. These are in turn very sensitive to the temperature, time, solvent and catalysts employed. Where selectivity of reaction is important, it is well to make a systematic study of such experimental variables. Especially noteworthy is the profound influence that traces of transition metals can exert on organoaluminum reactions. After all, the impressive growth of organoaluminum chemistry in the last 30 years owes much to some adventitious nickel present in an aluminum alkyl reaction (*cf.* equation 7).

6.7.2 Carbon–Hydrogen Bonds

Any reaction producing a C—Al bond is tantamount to C—H bond formation, because of the ease and universality with which C—Al bonds undergo hydrolysis. Since hydrolysis of alkyl- and 1-alkenyl-aluminum bonds can be made to occur without rearrangement, the use of D_2O or MeOD constitutes a method for preparing specifically labeled deuterated hydrocarbons (*cf.* equation 84). By combining hydralumination with R_2AlD and hydrolysis, stereoisomers can be prepared (equation 254).[129] Furthermore, geminal deuterated alkanes can be produced by bishydraluminations (equation 255; *cf.* equation 205).[72,441]



(254)

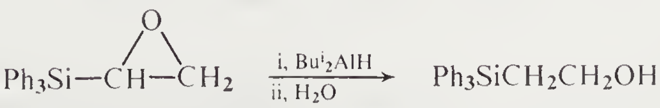
$$\underset{Z = H}{RCH_2CD_2H} \xleftarrow[\text{ii, } D_2O]{\text{i, } 2R'_2AlH} R'C{\equiv}CZ \xrightarrow[\text{ii, } D_2O]{\text{i, } 2R'_2AlH} \underset{Z = D}{RCH_2CD_3} \qquad (255)$$

As previous discussion has brought out, hydralumination of alkynes can often be conducted to produce a preponderance of either the *syn* or *anti* adduct (Section 6.3.3). In these instances, then, this reduction method provides an excellent route to both the *cis* and *trans* alkene. The syntheses of (*Z*)- and (*E*)-1-alkenyl(trialkyl)silanes exemplify this possibility.[247] With organic substrates containing competing carbon–carbon unsaturation, hydralumination (and hence reduction) can be effected preferentially at C≡C over C═C bonds (*cf.* equation 206), at $CH{=}CH_2$ over $CMe{=}CH_2$ bonds (equation 204) and at $CH{=}CH_2$ over $RCH{=}CHR$ bonds (Scheme 5). Generally, the polar C═O, C═N and C≡N bonds undergo hydralumination in preference to C≡C and C═C bonds. Even where C═C and C═O are conjugated, as in α,β-unsaturated aldehydes and ketones, such selectivity obtains to give high yields of the allylic alcohol (equation 256).[558] The reductions of esters and nitriles can be stopped at the aldehyde (equations 215 and 222) and hence the use of R_2AlD provides a route to deuterated aldehydes. Similarly, complete reduction of amides or nitriles with R_2AlH yields primary or secondary amines of the type $R'CD_2NHR''$ (equations 219 and 222), just as complete reduction of $R'CO_2R''$ (R'' = H, OR, Cl) yields RCD_2OH. The stereochemical control possible when hydraluminating cyclic ketones to secondary alkoxides has been mentioned (*cf.* equation 211).

$$3PhCH{=}CH\overset{H}{C}{=}O \xrightarrow{Bu^i_3Al} (PhCH{=}CHCH_2O)_3Al \qquad (256)$$

The formation of C—H (or C—D) bonds by substitution reactions with alkali metal aluminum hydrides has been achieved with a variety of organic halides, ethers and amines. More pertinent to the present topic are substitutions effected by organoaluminum hydrides. With halides, reduction to the hydrocarbon seems to be especially favored when the C—X bond is allylic or secondary or tertiary alkyl. The reduction of allyl,[220] benzyl, tropylium,[676] and isopropyl[677] halides typifies this behavior. Also with other linkages only the more reactive types, namely cyclic or allylic ethers, ortho esters, acetals and ketals, undergo C—O bond scission and C—H bond formation with R_2AlH. Some illustrative reductions are to be found in equations (257)–(259).[646,678] The stepwise reductions of ortho esters to acetals or to ethers shown in equation (259) are useful.

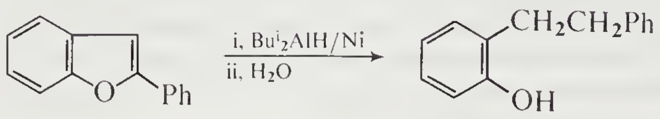
$$PhCH_2OEt \xrightarrow[140\ ^\circ C]{Bu^i_2AlH} PhCH_3 + Bu^i_2AlOEt \qquad (257)$$



(258)

$$PrCO(OEt)_3 \xrightarrow[30\ ^\circ C]{Bu^i_2AlH} PrCH(OEt)_2 \xrightarrow[80\ ^\circ C]{Bu^i_2AlH} PrCH_2OEt \qquad (259)$$

The cleavage of aromatic C—O, C—X, C—N and C—S bonds by R_2AlH requires vigorous conditions and, usually, transition metal catalysts. Some instances of such cleavages are shown in equations (260)–(262).[679–681]



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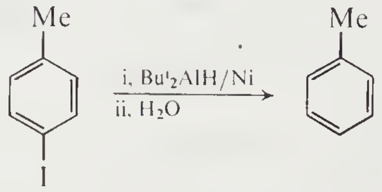
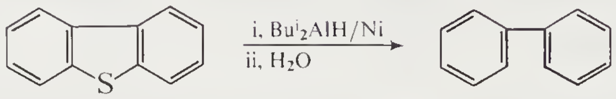


(261)

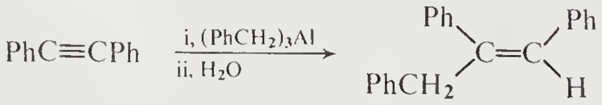


(262)

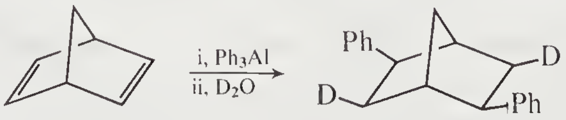
6.7.3 Carbon–Carbon Bonds

Although C—C bonds can be formed by carbaluminating C≡C, C=C, C≡E and C=E bonds and carbodealuminating C—O and C—X bonds, the carbalumination of alkenes and alkynes is the most general and valuable method. Organomagnesium and organolithium reagents have a limited capability of adding to C=C and C≡C bonds. On the other hand, they are generally preferred for the carbometallation of C≡E and C=E bonds, since the reactions proceed more cleanly and with the utilization of all available C—M bonds. Carbalumination of carbonyl groups, however, may in certain cases provide a superior stereoselectivity in C—C bond formation (*cf. infra*). Carbon–carbon bond formation by carbodemetallation (*cf.* Section 6.6.4.3) has limited scope for all organometallic reagents and side reactions are prominent. Possibly one special synthetic advantage of carbodealumination would be the formation of quaternary carbon atoms by the alkylation of *t*-alkyl halides (*cf.* equations 78, 79, 233 and 235).

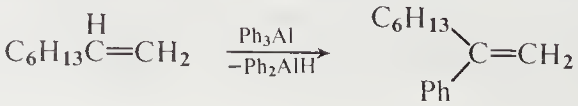
The ability of R_3Al reagents to add to unconjugated C=C and C≡C bonds in a *syn* manner is of great value for the stereoselective formation of carbon skeletons. Furthermore, the configuration at the original carbon–aluminum bond (sp^3 or sp^2 C—Al) can be retained upon such additions (*e.g.* equation 195). Further examples include those shown in equations (263),[81] (264)[75] and (265).[73]



(263)

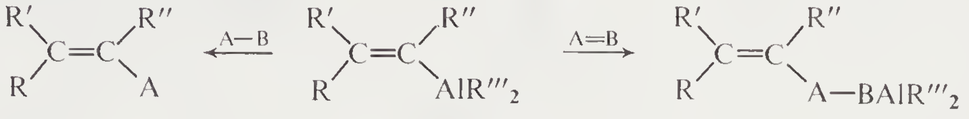


(264)



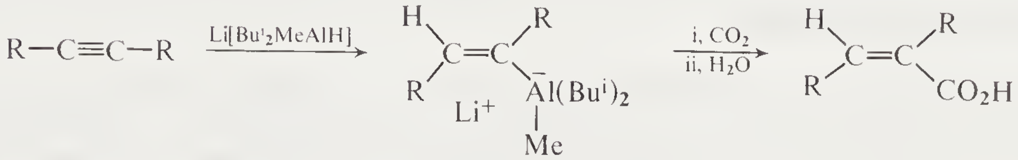
(265)

The organoaluminum intermediates resulting from such carbaluminations or hydraluminations of alkynes can be further employed to make C—C bonds. A wide variety of addition and substitution processes at vinylic C—Al bonds leads stereoselectively to new C—C bonds (equation 266). Reagent A═B may be CO_2,[103] H_2CO,[230] $RHCO$[231] or $ClCOOR$[682] and reagent A—B may be $(CN)_2$,[655] $\overline{CH_2CH_2O}$[683] or RX.[684,685] In this case, the preferred reaction of just the vinyl-aluminum bond is an advantage; R‴ groups can be sacrificed. In some reactions, substrate (**309**) may require activation by aluminate formation with methyllithium to achieve C—C bond formation in good yield (equation 234). An alternative approach to such more reactive aluminates is a modification of that given in equation (267), namely the direct *anti* hydralumination of the alkyne with lithium diisobutyl(methyl)aluminum hydride.[230]



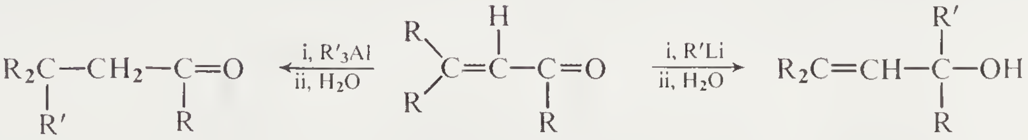
(**309**)

(266)



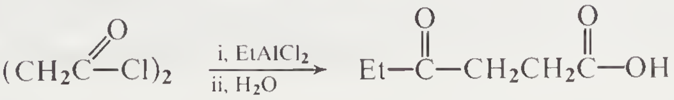
(267)

With α,β-unsaturated carbonyl substrates, the alternative use of either the organolithium or the organoaluminum reagent permits a complementary locoselectivity between 1,2- and 1,4-additions. 1,2-Addition can be fostered by the use of R′Li and 1,4-addition by R'_3Al (equation 268). Possibly 1,4-addition is favored because of a cyclic reaction complex (equations 44 and 45). To impede further 1,2-addition with R'_3Al it is recommended that R'_3Al be used as its etherate or that free radical (R_2O_2) or copper or nickel salt promotion be tried (equations 55 and 56). It might be noted that much recent research has been devoted to carbometallations and hydrometallations effected by a combination of an organoaluminum reagent and either a stoichiometric or catalytic amount of a transition metal compound. Since the transition metal is undoubtedly the active center in most of these reactions, a detailed discussion of this aspect falls naturally under the purview of other chapters in this work (but *cf.* Section 6.7.8). References to some current themes in this research are pertinent here, however: (a) alkylations of alkynes with Me_3Al and $(\eta\text{-}C_5H_5)_2ZrCl_2$;[686] (b) alkylations of alkynes with R_3Al and $(\eta\text{-}C_5H_5)_2TiCl_2$;[546,687] (c) nickel-catalyzed reductions of alkynes by Bu^i_2AlH,[688] and (d) alkylation of alkynols by R_2AlCl and $(\eta\text{-}C_5H_5)_2TiCl_2$.[689]



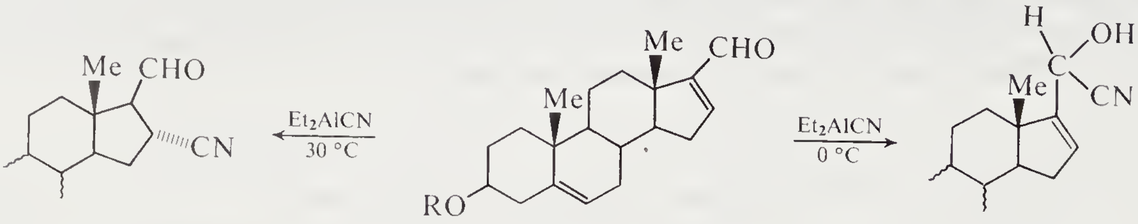
(268)

In the conversion of acid halides and anhydrides into ketonic products (equations 217 and 218), the reduced reactivity of aluminum reagents offers an advantage over the corresponding magnesium and lithium reagents. Moreover, since $RAlCl_2$ can be employed, there is no waste of C—Al bonds. High yields (70–90%) under moderate conditions (−30 to 0 °C) strongly recommend the method over the use of organozinc or organocadmium compounds (equation 269).[590]



$$(CH_2\overset{O}{\overset{\|}{C}}—Cl)_2 \xrightarrow[\text{ii, }H_2O]{\text{i, EtAlCl}_2} Et—\overset{O}{\overset{\|}{C}}—CH_2CH_2\overset{O}{\overset{\|}{C}}—OH \qquad (269)$$

Two closely related and particularly valuable unsymmetrical aluminum reagents are the dialkyl(1-alkynyl)aluminum and the dialkyl(cyano)aluminum compounds. Towards aldehydes, ketones, α,β-unsaturated carbonyls and epoxides they display remarkably parallel behavior. As noted in Section 6.6.4.3 (equation 237), they both cleave epoxides with inversion of C—O bond configuration. With carbonyl substrates, the *sp* C—Al bond reacts selectively[567] and with α,β-unsaturated systems 1,4-addition can be made the principal outcome.[690] These reagents differ, however, in that cyanoalumination of the C═O group is reversible, while carbalumination is not. For example, the kinetically controlled product obtained from (**310**) is (**311**), the more stable product is (**312**) (equation 270).[583] In steroid and prostaglandin syntheses, both reagents have found wide application because of loco- and stereo-selectivities shown in C—C bond formation.

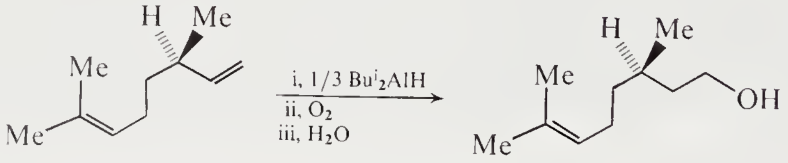


(**312**) (**310**) (**311**) (270)

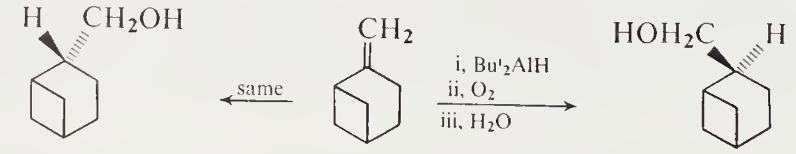
6.7.4 Carbon–Oxygen Bonds

Since no cheaper or more convenient oxidant than air is available, the efficient air oxidation of aluminum alkyls to alkoxides is of great industrial appeal. All three C—Al bonds are utilized and subsequent treatment with water provides an alcohol in 70–90% yield and a highly pure form of alumina (*cf.* Volume 7, Chapter 46 for a detailed discussion). Commercially, this oxidation and hydrolysis have been applied to the mixture of higher aluminum *n*-alkyls obtained by the multiple insertions of ethylene units into the C—Al bonds of triethylaluminum (the Ziegler 'Aufbau' or 'growth' reaction; *cf.* equation 6), in order to produce even-numbered *n*-alkanols. The composition of the resulting alkanols is determined by the prevailing Poisson distribution in the growth reaction (Section 6.6.3.1).

On a laboratory scale, such oxidation can be combined with the hydralumination of alkenes by Et_2AlH and Bu^i_2AlH to form a convenient, anti-Markownikov method of hydrating alkenes, often also in a stereoselective manner. The conversions shown in equations (271)[691] and (272)[692] are illustrative.



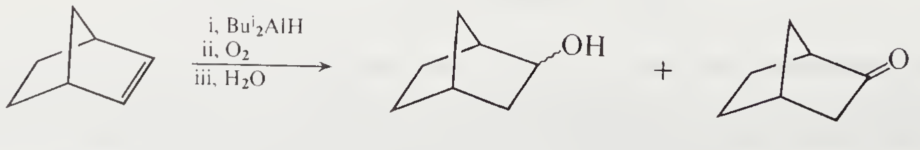
(271)



thermodynamic kinetic

(272)

Unfortunately, there exists no efficient method for oxidizing 1-alkynyl–, 1-alkenyl– or aryl–aluminum bonds to aluminum alkoxides. Carbon–carbon coupling and other complexities predominate in such oxidations. Even with certain sp^3 C—Al bonds, the free radical nature of the oxidation gives non-selective and non-stereoselective products (equation 273).[71] Also, in the oxidation of long chain aluminum alkyls, about 10% of aldehydes, esters and glycols are formed, the last product probably by intramolecular reactions of intermediate $RO_2\cdot$ radicals.[122,693]



exo: 55%
endo: 12%
18%

(273)

Simultaneous formation of C—C and C—O bonds can be achieved in a non-oxidative manner by inserting formaldehyde, other carboxyl derivatives or ethylene oxide into C—Al bonds (*cf.* equations 212, 237 and 266 and Scheme 18).

6.7.5 Carbon–Sulfur Bonds

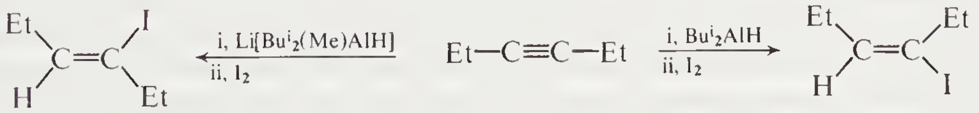
In contrast with oxygen, elemental sulfur inserts effectively into only one C—Al bond of Et_3Al or Bu^i_3Al affording compounds R_2AlSR in 83–86% yield.[627] Although these hydrolyze smoothly to yield thiols, utilization of the C—Al bonds is inefficient. Further treatment with sulfur leads to the formation of RSR and RSSR. Alternatively, these sulfides or disulfides can be obtained from aluminum alkyls and SCl_2 or S_2Cl_2, respectively.[627] The reactions of either gaseous sulfur dioxide or sulfur trioxide as a pyridine or ether complex are more advantageous, since all three C—Al bonds react (equation 274). Yields of 70–90% can be obtained when R = *n*-alkyl and the aluminum sulfinates (**313**) are convertible directly into RSO_2Cl, RSO_3H or RSH. Thus, sulfur dioxide insertion is a more efficient route than sulfur insertion for the preparation of thiols. Other routes to sulfinic acids and sulfonyl chlorides are given in equation (225).

$$(RSO_3)_3Al \xleftarrow{3SO_3} R_3Al \xrightarrow{3SO_2} \underset{\mathbf{(313)}}{(RSO_2)_3Al} \qquad (274)$$

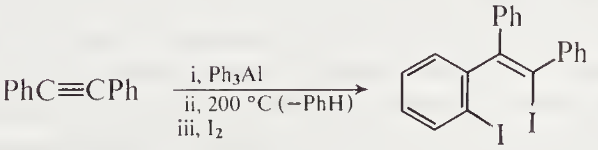
6.7.6 Carbon–Halogen Bonds

Three equivalents of chlorine, bromine or iodine can cleave the C—Al bonds in aluminum alkyls.[26,467–469] But to avoid violent side reactions brought on by attack of the resulting aluminum halides on the haloalkanes, the halodealuminations are best conducted at lower temperatures in the presence of ether or pyridine (equation 275). In this manner yields of 50–90% of the halides can be isolated. As noted in Section 6.6.4.2, 1-alkynyl, 1-alkenyl and cyclopropyl groups bonded to aluminum can be selectively cleaved by halogen in the presence of alkylaluminum groups. Accordingly, isomeric haloalkenes can readily be prepared *via* the appropriate *syn* or *anti* hydralumination adduct (equation 276).[231] Also, by way of aluminum intermediates, such as aluminoles (equation 115), vinyl iodides can be obtained stereoselectively (equation 277).[53]

$$R_3Al + 3X_2 + D \longrightarrow 3RX + AlX_3{\cdot}D \qquad (275)$$



(276)

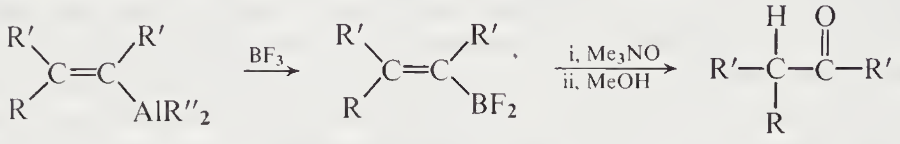


(277)

6.7.7 Carbon–Metal Bonds

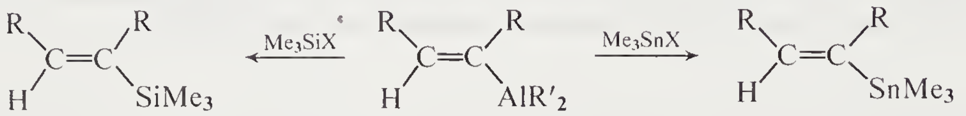
In Sections 6.6.4.5 and 6.6.6 are described the preparations of other metal alkyls from aluminum alkyls by metathesis and electrolysis, respectively. Before treating an aluminum reagent with a halogenating, oxidizing or similar substrate, it may be advantageous to convert the carbon–

aluminum group to a different carbon–metal linkage. The new metal reagent may react more cleanly with the substrate. For example, it has been mentioned that vinylaluminum compounds do not oxidize smoothly with oxygen. But vinylboranes can be oxidized cleanly with trimethylamine oxide.[694] Thus, it might be useful to convert (**314**) into (**315**) and then apply this oxidant as in equation (278). Similarly, there may be occasions when it is useful to prepare the air stable, but synthetically versatile vinyl-silanes[695] and -tin[696] derivatives from the aluminum analogue (equation 279). The silicon compound can be transformed into various alkene and carbonyl derivatives;[697] the tin compound can be converted into the vinylic lithium reagent by exchange with alkyllithium.[698]



(**314**) (**315**)

(278)



(279)

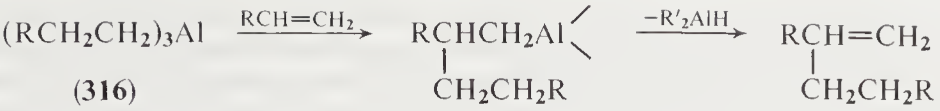
Another way in which aluminum alkyls can effect the formation of carbon–metal bonds is by the alkylative reduction of transition metal salts in the presence of carbon ligands (equation 280). If M is chromium, molybdenum, tungsten or manganese and L is carbon monoxide under high pressure, good yields of the metal carbonyls result.[389,699,700] From admixture of iron(III) acetylacetonate and Et_3Al in the presence of diphos, the complex $(Ph_2PCH_2CH_2PPh_2)_2Fe\cdot CH_2{=}CH_2$ is produced.[701] Likewise, reduction of nickel acetylacetonate with Et_3Al in the presence of 1,5-cyclooctadiene (cod) yields $(cod)_2Ni$.[702] Numerous examples of these transformations are encountered in transition metal chemistry and industrial catalysis (*cf. infra*).

$$MZ_n \xrightarrow{nR_3Al} R_nM \xrightarrow[-nR]{:L} ML_m \qquad (280)$$

6.7.8 Oligomerizations of Alkenes and Alkynes

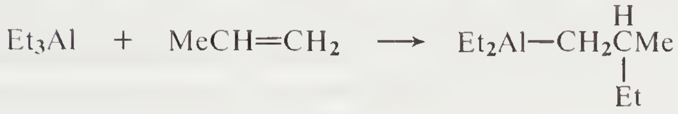
The uncatalyzed stepwise insertion of an alkene or alkyne into a carbon–aluminum bond (the Ziegler growth reaction) is only capable of leading to long carbon chains with the simplest alkene, ethylene.

Alkynes tend to undergo, at most, the insertion of two to four molecules into a C—Al bond, thereby producing dienes, trienes, benzene derivatives, *etc.* (equation 193 and Schemes 15 and 17). Likewise, propylene and other α-alkenes tend to dimerize when heated with the corresponding alkyl, because elimination of Al—H bonds from dimer (**317**) is much faster than the addition of (**316**) to a second alkene (equation 281). The eliminated R'_2AlH can add to the alkene to reform (**316**), so the alkenic dimerization is catalytic in R'_2AlH. In practice, R'_2AlH can be Bu^i_2AlH, since ready alkene displacement will form (**316**) *in situ*. Thus high yields (90%) of (**318**) can be obtained by employing an alkene excess with small amounts of Bu^i_2AlH: propylene gives 2-methyl-1-pentene; 1-butene, 2-ethyl-1-hexene; 1-octene, 2-hexyl-1-decene; and cyclopentene, 1-cyclopentyl-1-cyclopentene.[27] The technically important dimerization of ethylene to 1-butene requires that the elimination of R'_2AlH from (**317**) ($R = H$) be faster than further insertion of ethylene. This outcome can be favored by working at low ethylene pressure, at higher temperatures and with a nickel catalysis (equation 7).[29b] The terminal alkenes containing 11, 12, 14, 15 and 18 carbon atoms dimerize with somewhat lower yields (55–70%). It has even been proved feasible to conduct a mixed dimerization between ethylene and propylene by use of triethylaluminum in a two-step process (equations 282 and 283).[27,703] The first step is carried out with only partial conversion to (**319**); then, before many propyl-aluminum groups arise from (**319**) transferring Et_2AlH to propylene, step two reconverts any aluminum compound to Et_3Al. In this way, 90% yields of 2-methyl-1-butene can be attained.



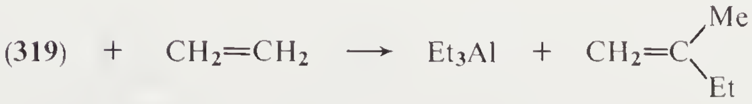
$$\mathrm{(RCH_2CH_2)_3Al} \xrightarrow{\mathrm{RCH{=}CH_2}} \underset{\mathrm{CH_2CH_2R}}{\mathrm{RCHCH_2Al}{<}} \xrightarrow{-\mathrm{R'_2AlH}} \underset{\mathrm{CH_2CH_2R}}{\mathrm{RC{=}CH_2}} \qquad (281)$$

(316) **(317)** **(318)**



$$\mathrm{Et_3Al} + \mathrm{MeCH{=}CH_2} \longrightarrow \mathrm{Et_2Al{-}CH_2}\overset{\mathrm{H}}{\underset{\mathrm{Et}}{\mathrm{C}}}\mathrm{Me} \qquad (282)$$

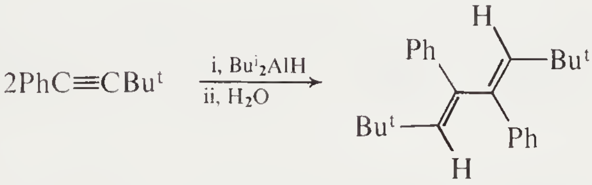
(319)



$$\mathbf{(319)} + \mathrm{CH_2{=}CH_2} \longrightarrow \mathrm{Et_3Al} + \mathrm{CH_2{=}C}\begin{smallmatrix}\mathrm{Me}\\ \mathrm{Et}\end{smallmatrix} \qquad (283)$$

Naturally, higher α-alkenes from C_6 to C_{20} can be obtained by combining the same two steps in equations (282) and (283), growth and displacement, but this will be discussed in Volume 7.

The dimerization of alkynes by R'_2AlH is stoichiometric because the intermediate (**262**, Scheme 17) does not easily lose hydride. This reaction is a useful route to stereochemically defined dienes in some cases. Although unsymmetrical alkynes can produce regioisomeric dienes, sometimes steric or polar factors will favor one isomer (equation 284).[78] The same considerations apply to the catalytic trimerization of alkynes by R_2AlH. This reaction proceeds well at higher temperatures to give good yields of hexasubstituted benzenes. With unsymmetrical alkynes $RC{\equiv}CR'$ there may be a preference for the 1,2,4-isomer over the 1,3,5-isomer because of the intermediate dienylaluminum (**262**) (equation 285).[77] Generally, dimerization and trimerization do not work well with terminal alkynes because side reactions intervene (equations 144 and 205).



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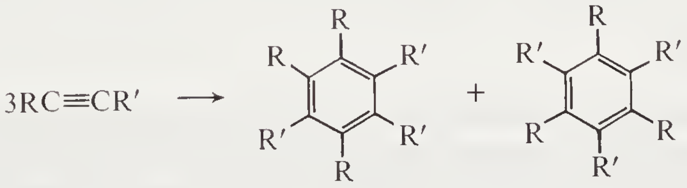


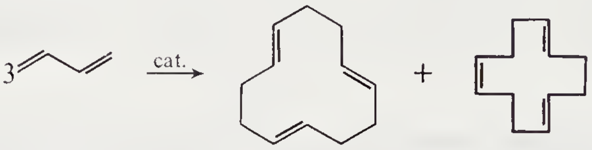
(285)

In addition to these aluminum-promoted oligomerizations, there are many such reactions where aluminum alkyls are used to generate the actual transition metal oligomerizing catalysts. The role of the aluminum compound may simply be that of a reducing agent for the transition metal (equation 280). In some situations, the original aluminum alkyl or the aluminum halide produced also acts as a cocatalyst with a low-valent transition metal. The details of these reactions lie outside the scope of the present treatment but mention should be made of some principal types. These reactions are extraordinarily important for generating linear and cyclic carbon skeletons, which are of value to industry and to organic synthesis. Some significant examples include (a) the dimerization of propylene by a combination of π-allylnickel halide and $RAlX_2$ or AlX_3, modified by phosphines so as to give varying ratios of hexenes, methylpentenes and dimethylbutenes (equation 286);[127] (b) the cyclotrimerization of butadiene by $(cod)_2Ni$ (generated from $Ni(acac)_2$

$$\mathrm{2MeCH{=}CH_2} \xrightarrow[\text{with}]{\text{cat.}} \text{hexenes} + \text{methylpentenes} + \text{dimethylbutenes} \qquad (286)$$

	hexenes	methylpentenes	dimethylbutenes
Ph_3P	22	74	4
Cy_3P	3	38	59
Bu^t_2PEt	1	22	77

and Et_3Al in the presence of cod (equation 280) or by titanium- or chromium-containing catalysts, to yield (*E*,*E*,*E*)- and (*E*,*E*,*Z*)-1,5,9-cyclododecatrienes (equation 287);[702,703] (c) the cyclodimerization of butadiene by phosphine-modified $(cod)_2Ni$ to yield varying proportions of four-, six- and eight-membered rings (equation 288);[704,705] (d) the cyclotrimerization of alkynes (even RC≡CH; *cf.* equation 285) by salts of titanium, chromium and other metals combined with aluminum alkyls to yield substituted benzenes;[706] (e) the codimerization or cotrimerization of ethylene or acetylene with butadiene, mediated by nickel catalysts derived from $NiX_2(R_3P)_2$ and R_2AlCl or by $(cod)_2Ni$ (equation 289);[707–710] and (f) the alkene metathesis catalysts, generated from WCl_6 and EtOH (1 : 1) with $EtAlCl_2$ or from molybdenum salts and alkylaluminum halides (equation 290).[711–713]



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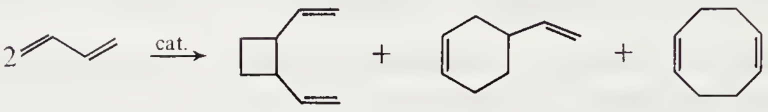

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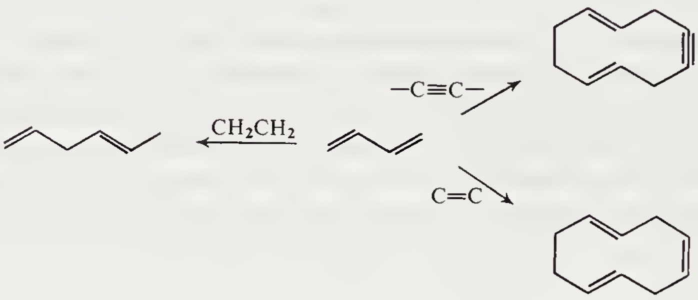

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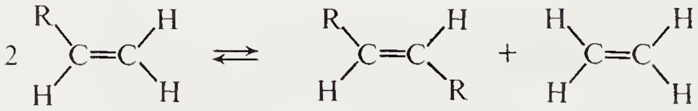
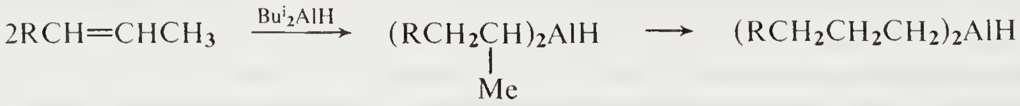


(290)

6.7.9 Isomerization

Because *n*-alkyl–aluminum bonds are more stable than *s*-alkyl–aluminum bonds, heating internal straight chain alkenes with one-third equivalent of Bu^i_3Al should yield aluminum *n*-alkyls by isobutylene displacement and a series of Al—H eliminations and readdition (equation 291).[558] Uncatalyzed, temperatures of 200 °C are required for isomerization and dimerization of the α-alkene can be a significant side reaction (equation 281). The use of titanium(IV) or zirconium(IV) salts lowers the isomerization temperature by about 100 °C.[551] Conversely, some nickel salts used to catalyze the alkene displacement (equation 7) can cause migration of the C=C bond to an internal position.


(291)

$$2RCH{=}CHCH_3 \xrightarrow{Bu^i_2AlH} (RCH_2\underset{\displaystyle Me}{\underset{|}{C}}H)_2AlH \longrightarrow (RCH_2CH_2CH_2)_2AlH \qquad (291)$$

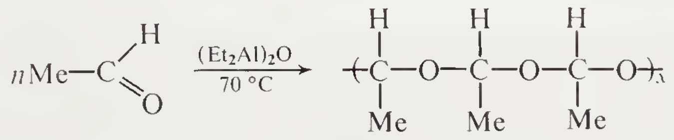
6.7.10 Polymerization

As important as combinations of transition metal salts and aluminum alkyls are in oligomerizations, it is in the polymerization of unsaturated compounds that such catalysts have attained their greatest prominence. The transformations of ethylene into high-density polyethylene (MW

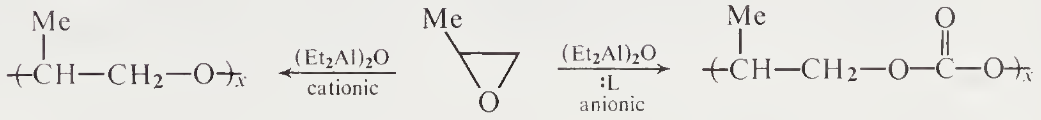
≈3 000 000), of propylene and other α-alkenes into stereoregular polymers and of 1,3-dienes into a variety of 1,2-, *cis*-1,4- and *trans*-1,4-polyenes have revolutionized polymer technology. The significance and scope of these so-called Ziegler–Natta catalysts merit a separate, detailed discussion, which can be found in Volumes 7 and 8.

Besides their use as cocatalysts in alkene polymerization, aluminum alkyls and their derivatives have found applications as the principal catalysts for the polymerization of cyclic ethers, carbonyl derivatives and heteroatom-substituted vinyl monomers. In contrast with Ziegler–Natta catalysts whose active site seems to reside on the transition metal, the polymerization of polar monomers by aluminum alkyls appears to stem from two properties of R_3Al: (a) its Lewis acidity; and (b) the ability of R_3Al to generate free radicals upon contact with oxygen or polyhalides like CCl_4. Accordingly, the resulting polymerizations tend to exhibit cationic or free radical chain mechanisms.[654,711]

The cationic mechanism seems to obtain for the polymerization of epoxides, oxetanes, THF, aldehydes and vinyl ethers, where aluminum alkyls pretreated with a little water or alkylaluminum halides are more active than aluminum alkyls alone. The water serves to generate dialuminoxanes, $R_2AlOAlR_2$ (equation 166) which are stronger Lewis acids. By the polarity of the intermediates, a head-to-tail linking of the monomer units is obtained. Where a chiral or prochiral center is present in the monomer (*e.g.* propylene oxide or acetaldehyde), stereoregular polymerization becomes possible. Indeed, acetaldehyde can be polymerized at −70 °C by tetraethyldialuminoxane to yield an isotactic polymer (equation 292).[711] Undoubtedly, the aluminum catalyst exerts stereocontrol on the course of reaction through a coordination complex. Depending upon how the aluminum catalyst has been modified, an intermediate complex may steer a polymerization towards a cationic or an anionic pathway, as has been found with propylene oxide. The copolymerization of carbon dioxide with either propylene oxide or oxetane is effected by a catalyst obtained by admixing Et_3Al, H_2O and $(MeCO)_2CH_2$ in a 2:1:1 ratio. This so-called Vandenburg catalyst appears to operate through an anionic coordination mechanism. The anionic character of the copolymerization is particularly shown by the enhanced CO_2-content of the polymer when ethers, amines or phosphines are added (equation 293).[712,713]



(292)



(293)

The catalytic properties of aluminum alkyls when admixed with traces of oxygen[714] or with CCl_4[715] can be ascribed to the generation of free radicals. As has been mentioned, the radical-promoted 1,4-carbalumination of α,β-unsaturated ketones has demonstrated how oxygen or peroxides can promote chain reactions with these reagents (*cf.* equation 55). Such a radical mechanism is probable for the polymerization of acrylic esters or nitriles, vinylic esters or halides and styrene. On the other hand, admixing alkylaluminum halides with easily ionizable organic halides (*e.g.* Bu^{t}Cl) can generate carbenium ions (equations 78 and 79) which can unleash the cationic polymerization of styrene and other dienes.

6.8 EXPERIMENTAL TECHNIQUE AND ANALYSIS

6.8.1 Manipulation

With the general precautions against accidental hydrolysis and oxidation in mind (Section 6.1.7), a chemist unfamiliar with aluminum reagents should consult available industrial brochures and monographs for specific handling procedures. A thorough discussion and illustration of many appropriate techniques can be found in refs. 346 and 716. The requisite inert atmosphere of nitrogen or argon will entail the purchase of the high purity, oil-pumped gas and its purification just before use. Removal of residual oxygen and moisture is achieved by passing the gas through a column of heated, copper turnings or preferably through a bed of freshly reduced copper on a porous support (BASF Katalysator). Thereupon, the gas is thoroughly dried by passing through a column of dispersed phosphorus pentoxide. Alternatively, higher-boiling aluminum alkyls such as diethylaluminum chloride or the acetylene adduct of triethylaluminum can be used both to deoxygenate and dehydrate the inert gas simultaneously. Naturally one must be certain that any resulting hydrocarbon (RH) will not interfere in the emerging inert gas. If this is so, then the purified gas can be passed through a cold trap (−80 to −100 °C) to remove any organic vapors. But whatever method of purification is employed, success depends upon the following: (a) maintaining a sufficiently slow gas flow rate for efficient removal of impurities; (b) regenerating purification columns in a timely manner; and (c) using air-tight connections and non-porous flexible tubing for all apparatus.

Since not only aluminum compounds but most reagents used have to be protected from air and moisture, all transfer of purified starting materials must be made under an inert atmosphere. The most convenient and general technique for liquids in the laboratory is the use of gas-tight syringes in conjunction with vessels provided with septa or inert-gas connections. The transfer of solids will demand some type of inert atmosphere chamber: this may be as elaborate as a glove-box with an antechamber or as simple as a small glass apparatus or a collapsible plastic bag.

The most common reaction and storage vessels for aluminum compounds are all variants of the classic Schlenk tube: a two- or three-necked vessel, one of whose necks is provided with an inert gas inlet (three-way stopcock). The other neck(s) serve to bear a condenser, stirrer, addition funnel or a stopper (septum). All ground glass joints must be greased well with vaseline. Silicone grease may be used for reaction vessels but not for storage vessels, since it is attacked by aluminum alkyl vapors.

Not only the reagents but also the solvent and the apparatus must be freed of oxygen and water before use. The assembled glass apparatus should be heated to about 100 °C, evacuated and refilled with inert gas several times. The solvents should be dried with an appropriate reagent (*no alkali metals for halocarbons*) and distilled under an inert atmosphere.

6.8.2 Physical Measurements

Reliable measurements of physical properties and spectral data require exacting techniques and special apparatus. Suitable procedures have been published for obtaining melting and boiling points, densities, refractive indices, spectra, dipole moments, electrical conductivities, molecular association (apparent molecular weights) and enthalpies of reaction and of solution for organoaluminum compounds. Obviously the resulting data are accurate only if the measurements are made in a scrupulously purified and inert medium. Since aluminum compounds themselves are such excellent scavengers of protons and oxidants, all vessels and surfaces involved in the measurement should be rinsed beforehand with some of the aluminum compound.[716]

6.8.3 Chemical Analysis

Samples of liquids are best taken up into thin walled glass ampules having drawn-out capillary tips. Procedures and apparatus for filling such inverted ampules by alternating evacuation and gas pressure have been described. Likewise, descriptions are available for the transfer of solid samples to ground glass stoppered ampules by an auger-like plunger or by resort to a dry box.[716]

Such weighed samples are cautiously treated with ether (in the case of titrimetric analyses, the liquid-filled glass ampules can be crushed under a layer of ether) and then hydrolyzed. The aluminum content can be determined by forming the AlF_6^{3-} complex by adding potassium fluoride and determining the generated hydroxide ion by titration with acid.[717] Alternatively, titration of the hydrolyzed aluminum sample with EDTA or cyclohexanediamine tetraacetic acid is a superb method for the determination of aluminum in the presence of other alkali and alkaline earth metal cations.[718] Other inorganic constituents, such as halides, ammonia and sulfides, may be determined in similarly hydrolyzed samples by conventional methods.

Less volatile organic products may be determined by extracting them from the aforementioned hydrolysate with a hydrocarbon solvent, drying the organic extract, adding a known amount of an internal standard to a known volume of extract and then determining the amount of each constituent by gas chromatography. For gaseous protolysis products, such as hydrogen, methane, ethane and propane from R_3Al and R_2AlH, a special apparatus for treating aluminum alkyl samples with a higher alcohol (hexanol or 2-ethylhexanol) and collecting the evolved gas in a mercury-filled buret has been devised.[715] The composition of the gas is then determined by mass spectrometry.

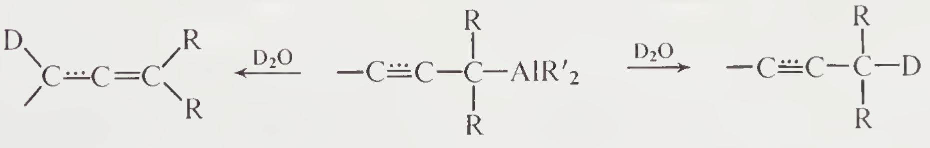
Especially pertinent to the use of organoaluminum compounds in preparative and catalytic processes is not only the purity but also the proportions of different contaminants in a sample. The analyses of greatest importance are the amounts of R_3Al, R_2AlOR, R_2AlH and R_2AlCl. The last component can readily be estimated by Volhard titration of a hydrolysis sample. Since only R_3Al and R_2AlH compounds generally complex or react with amines, the content of these two compounds can be measured by their selective reaction with ammonia or their complexation with pyridine.[719] The content of R_2AlOR is best measured by hydrolysis of a sample and titration of the liberated alcohol (if primary or secondary) with a cerium(IV) or chromium(VI) oxidant.[720,721] Finally, determination of the relative amounts of R_3Al and R_2AlH is such an important analysis that a wide variety of discriminating methods have been developed. One of the most useful and convenient is the titration of aluminum alkyls with isoquinoline and the spectrophotometric determination of the absorbance at 460 nm.[722]

6.8.4 Characterization of Organoaluminum Intermediates

In exploring unknown reactions it is important to monitor any changes in the site or stereochemistry of a carbon–aluminum bond. The most broadly applicable method for detecting such a bond is deuterolysis. The smooth and complete scission of all types of carbon–aluminum bonds by D_2O or ROD gives excellent yields of the deuterium-labeled organic products. By means of the quantitative methods given in the previous section and by use of mass, IR and NMR data the amount and position of deuterium incorporation can often be determined. This method has limitations, however, with certain types of C—Al bonds. With higher alkyl-aluminum bonds, deuterolysis yields a deuterated alkane in which the position of the C—D bond may be difficult to discern by ^1H NMR or IR spectroscopy. In this case it may be preferable to oxidize the C—Al bonds and to identify the resulting alcohols instead. The yields in such oxidations can be made to approach 90% (equation 294).

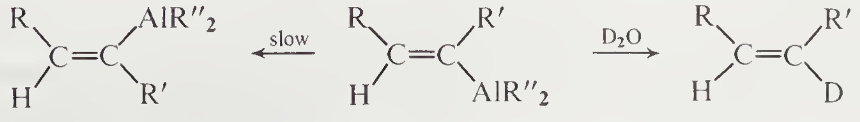
Where the C—Al bond is allylic, benzylic or propargylic, the deuterolysis may occur both at the site of the original C—Al bond and at the γ-position with rearrangement (equation 295). In this situation the proportions of products (**321**) and (**322**) do not reflect the types or amounts of the original C—Al bond. To clear up this ambiguity in labeling, the structure of the original compound (**320**) must be examined directly by spectral means (*cf.* Section 6.3.4).

$$2ROH \quad + \quad R'OH \quad \xleftarrow[\text{ii, } H_2O]{\text{i, } O_2} \quad R_2AlR' \quad \xrightarrow{D_2O} \quad 2RD \quad + \quad R'D \qquad (294)$$


(295)

(322) (320) (321)

Finally, the configuration of C—Al bonds can be changed by thermal and chemical means (*cf.* Sections 6.3.2 and 6.3.3). Both vinylaluminum and alkylaluminum compounds can be deuterolyzed with D_2O to yield deuterated products with retention of configuration at the new C—D bond (*cf.* equations 84 and 296). To hinder any isomerization before or during deuterolysis ((**323**) → (**324**)), the vinylaluminum compound must not be heated unduly and it can be stabilized by complexing with ethers and tertiary amines. Further, the isomerizability of certain types, *e.g.* (**323**) (R = Ph, R′ = Me_3Si and R″ = Bu^i), requires the hydrolysis to be done at low temperatures.[61]


(296)

(324) (323)

Other chemical reactions sometimes useful in preparing derivatives of C—Al bonds are those with halogens (especially for providing organic iodides), carbon dioxide (for vinylic and alkynic aluminum compounds) and sulfur dioxide (for consuming all three C—Al bonds). Again, with vinylaluminum bonds (**323**), many of these reactions proceed with retention of configuration.

6.9 SUMMATION AND PROSPECT

In just 25 years organoaluminum chemistry has emerged as a relatively mature field: new syntheses have been developed, much of its basic chemistry has been explored and many of the prevailing structural types have been delineated. The motivating force for such fundamental studies has been the widespread industrial importance of these organometallic compounds in stoichiometric and catalytic processes. With so much accomplished, what does the future hold?

Organoaluminum reagents still have much unrealized potential in stoichiometric applications. Being the cheapest and most available of the active metals, aluminum is an excellent starting material for preparing reducing and alkylating agents, which could in many uses supersede lithium, sodium or magnesium reagents. Especially towards carbon–carbon unsaturation, the aluminum reagents are often more suitable for forming carbon–carbon and carbon–hydrogen bonds than their Group IA and IIA counterparts. Thus, in any future hydrocarbon technology, be it based on petroleum or coal, organoaluminum chemistry is bound to hold a prominent position. But also in the general art of organic synthesis, whether in fundamental research or in the production of fine chemicals, aluminum reagents will undoubtedly prove of special value. That many carbalumination and hydralumination reactions can be made to occur with regio- and stereo-selectivity has great implications for the stereospecific construction of hydrocarbon skeletons. Furthermore, many reactions at carbon–aluminum bonds with oxidants, halogens, protons and carbonyl substrates have been found to occur with retention of configuration. Such selectivity permits useful functional groups to be introduced into the carbon skeleton in a controlled manner.

A possible limitation in using organoaluminum compounds is that often only one carbon–aluminum bond of R_3Al reacts readily with some substrates, such as carbonyl compounds. However, it should be observed that this limited conversion is not always disadvantageous. With unsymmetrical types R_2AlR', such as 1-alkenyl- or 1-alkynyl-(dialkyl)aluminum, it is often convenient to have just the unsaturated carbon–aluminum bond react with the carbonyl substrate. The two alkyl–aluminum bonds are often expendable; their subsequent hydrolysis leads to an easily separable hydrocarbon RH. But there are a considerable number of other useful cleavage reagents that consume two or more carbon–aluminum bonds of R_3Al, such as the halogens and the sulfur oxides. Where no R group in R_3Al is expendable, recourse to such halo- or thio-dealumination reactions may be synthetically useful. Finally, with some carbonyl substrates, such as acyl halides and acid anhydrides, even organoaluminum dihalides bring about ketone formation in high yield (equation 217), so that no R group is wasted.

Despite the attainments in understanding organoaluminum chemistry itself, it is in the interactions of aluminum alkyls and transition metal compounds that much remains to be learned. The copious empirical findings on Ziegler–Natta stereoregular catalysis have served to guide many industrial concerns towards patentable polymerization processes, but they have added little and indeed have often confused our understanding of the underlying reaction mechanisms. Reawakened fundamental research on how organometallic aluminum compounds react with and activate transition metals promises to be an important and rapidly developing area in the next 20 years. Novel stoichiometric procedures for forming carbon–carbon bonds, the controlled oligomerization or polymerization of hydrocarbons and the efficient conversion of carbon monoxide and hydrogen into useful fuels and chemicals, all these and related aspects will probably be important goals for organoaluminum chemical research for the remainder of this century.

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7

Gallium and Indium

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7.1 INTRODUCTION

Gallium and indium continue to remain the least explored elements of Group IIIB, a statement which is as true in the organometallic field as it has been of inorganic and coordination chemistry. Possible reasons for this include the relative scarcity and expense of the elements and the absence of extensive industrial applications, although the latter argument is somewhat diminished by the significance of organometallic compounds in the production of semiconductors. An equally important reason may be that as long as the chemistry of both lighter and heavier elements presents challenging problems, some will find little challenge in exploring the idiosyncracies of gallium and indium.

A number of surveys of the chemistry of the elements have appeared, and the coordination chemistry has been reviewed for gallium,[1] and more recently indium.[2] In the most common oxidation state (III), both elements show well established coordination numbers of three, four, five or six, depending on the element, the ligand, and in the case of certain anionic complexes, the balancing cation. We shall return to the matter of coordination number throughout this chapter, since the stereochemistry of the organometallic complexes, as with the inorganic, is most conveniently discussed in such terms. The Lewis acidity of MX_3 and R_3M molecules is another equally important feature to which frequent reference will be made.

The inorganic chemistry of the lower oxidation states of these two elements has received scant attention, and it is therefore no surprise to find that information on the organometallic chemistry of gallium and indium in the I or II states is very limited, although recent developments hold out some promise that this situation will improve.

7.2 LOW OXIDATION STATE COMPOUNDS

Although the dominant chemistry of gallium and indium, unlike thallium, centres on the III oxidation state, there is now significant information on the preparation and properties of compounds of the I and II states. This inorganic and coordination chemistry need not concern us here except in the sense of a comparison with the small number of studies of organometallic compounds of these low oxidation states.

Little is known of the inorganic chemistry of gallium(I), but recent work[3] has shown that the treatment of $Ga(CH_2SiMe_3)_3$ with MH (M = Na, K) leads to $MGa(CH_2SiMe_3)_2$, believed to be formed by the reductive elimination of CH_4 from $MGa(CH_2SiMe_3)_3H$. These sharp-melting crystalline colourless materials are the first σ-bonded organogallium(I) compounds, and the size of the CH_2SiMe_3 group no doubt contributes to the stability. Molecular weight determinations show that $KGa(CH_2SiMe_3)_2$ is dimeric in benzene, whereas the Na analogue is trimeric, with the association ascribed to Ga—M—Ga bridge bonding; the spectral properties are consistent with this formulation. Adducts (1 : 1) with DME (Na, K, Li), THF (Na) and Me_3N (Na) were characterized by ^1H NMR spectroscopy. Extensions of these studies have led to the preparation of similar indium(I) anionic complexes,[4] and of mixed ligand complexes such as $M[MeGa(CH_2SiMe_3)]$. This work has opened up a new field of organo-gallium and -indium chemistry, since the only previously known indium(I) compounds differ markedly from the $[MCH_2SiMe_3]_2^-$ species in terms of the bonding involved (see below).

The II states of gallium and indium have been stabilized as both neutral and anionic halide complexes, but attempts to synthesize the corresponding M_2R_4 or $M_2R_6^-$ analogues have met with little success. Attempted substitution reactions with MeLi or PhLi on $In_2X_6^{2-}$ anions resulted in decomposition to, *inter alia*, indium metal.[5] Earlier reports[6] of the preparation of $Na_2Ga_2Me_6$ by the reaction of Me_3Ga with sodium in liquid ammonia have not been confirmed, and analogous reactions in other media (*e.g.* K–Me_3Ga–DME) were equally unsuccessful.[7] This topic clearly invites further work, and it may be that the use of bulky ligands will prove as useful here as it has done in the case of M(I) species.

7.3 CYCLOPENTADIENYL COMPOUNDS

7.3.1 Introduction

Compounds in which either gallium or indium is bonded to a cyclopentadienyl group form a convenient transition from low oxidation state compounds to those in which the elements are in the more common M(III) state. Cyclopentadienylindium(I) and the MeCp analogue are the only compounds of M(I), but a number of interesting M(III) compounds are conveniently considered as derivatives of CpGa and CpIn from both an organizational and a structural viewpoint.

7.3.2 Cyclopentadienylindium: Preparation and Properties

The first synthesis of CpIn was reported by Fischer and Hofmann[8] who treated $InCl_3$ with a fourfold excess of NaCp; after 3–4 h, the reaction mixture was heated to 150 °C under vacuum, when needles of CpIn sublimed. The reaction is unusual in that an indium(I) species is obtained from an indium(III) starting material. Fischer and Hofmann also isolated small (≈0.2%) amounts of Cp_3In, and later workers[9] concluded that the probable reaction sequence was as shown in equations (1) and (2), since the yield of Cp_3In is increased when LiCp replaces NaCp, and it was argued that this reflected the use of a less efficient reducing agent. The thermal decomposition of Cp_3In to CpIn *in vacuo* above 150 °C was confirmed in this latter investigation. Essentially analogous methods yielded MeCpIn *via* $(MeCp)_3In$, but attempts to prepare an indium(I) indenyl compound were unsuccessful, presumably because of the higher thermal stability of the indium(III) species (see Section 7.3.4), and no derivatives of fluorene were obtained. A more recent publication[10] reports the preparation of CpIn by the condensation of the metal vapour on to a matrix of C_5H_6 at 77 K. In view of the usefulness of CpIn as a starting point in the synthesis of other compounds (see below), it is unfortunate that the compound is not as readily accessible as the thallium(I) species.

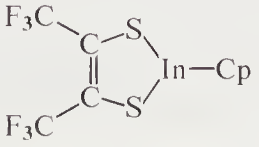
$$InCl_3 + 3MCp \longrightarrow Cp_3In + 3MCl \qquad (1)$$

$$Cp_3In + Cp^- \longrightarrow CpIn + \tfrac{3}{2}Cp_2 \qquad (2)$$

Cyclopentadienylindium(I) is unusually stable in the solid state, being sensitive to attack by air but unaffected by water,[8] while the MeCpIn compound is much more sensitive to air.[9] Mass spectrometric studies suggest that thermal decomposition of CpIn and MeCpIn proceeds *via* equation (3).

$$CpIn + O_2 \longrightarrow [(CpIn)_2O] \longrightarrow In_2O_3 + (CpOH)_2 \qquad (3)$$

One of the most interesting features of the structure of CpIn (see Section 7.3.3) is the presence of a pair of electrons, the much discussed lone pair of the M(I) compounds of Group III, and in keeping with this a series of 1:1 adducts with BX_3 (X = F, Cl, Br, Me) has been prepared.[11] Another reaction[12] typical of indium(I) compounds is the insertion reaction with 1,2-bis(trifluoromethyl)dithiete, cleaving the S—S bond to form (**1**), which is polymeric in the solid state, but which gives monomeric adducts with bipy and phen. A further, and perhaps simpler, oxidation is with molecular iodine to produce $CpInI_2$, from which the neutral adduct Cp_2InI and $CpInI_3^-$ can be obtained.[13] An interesting feature of all these indium(III)-cyclopentadienyl species is that spectral evidence shows that the Cp ring is in the monohapto σ-bonded mode, in contrast to the structure of CpIn itself.



(**1**)

A second series of useful reactions makes use of the fact that CpIn is the only readily available stable and soluble indium(I) compound, so that reaction with suitable acids can be used to give C_5H_6 and the appropriate InX compound. Reactions of this type have been used to synthesize neutral InX complexes (X = oxinate, acac, *etc.*)[14] and tetraalkylammonium salts of InX_2^- anions (X = Cl, Br, I).[15]

7.3.3 Structural and Spectroscopic Results

The X-ray structure of crystalline CpIn[16] shows a homopolymeric chain, with each indium atom sandwiched between two C_5H_5 rings, lying on the C_5 axis of the ring, and at a distance of 3.19(10) Å from the centre. Vapour phase electron diffraction studies[17] show that the monomer is indeed a half-sandwich structure with precise C_{5v} symmetry (In—C 2.62(5) Å, C—C 1.427(7) Å). The indium is much closer to the ring than in the solid state, with the distance to the ring centre now only 1.59 Å.

A number of attempts have been made to develop experimental criteria which would provide a simple test of the mode of metal–ring bonding in CpIn and other similar main group compounds. The comprehensive review by Fritz[18] provided a basis for discussion of the IR spectra in terms of ionic or covalent compounds. ^{1}H NMR spectra show that, as expected, in solution the protons are all identical, but the chemical shifts cannot be used diagnostically.[9] More recently, two groups[19,20] have reported vapour phase photoelectron spectra for CpIn and other compounds, but here again the results do not allow a clear distinction to be made between σ- and π-bonded complexes.

Given this lack of any spectral touchstone, attempts have been made to resolve the matter of the bonding by theoretical methods. An early calculation[21] which suggested that CpIn was the ionic species Cp^-In^+ has been shown to be incorrect, and subsequent work[17] showed that a satisfactory description involves the interaction of ring carbon p_π-orbitals with a hybrid sp-orbital on indium and with indium p_{xy} orbitals. These and later CNDO[22] calculations show that a covalent description is appropriate; a feature of these results in both cases is the lone pair on indium, pointing away from the Cp ring. Such models are in satisfactory agreement as far as they go with the known chemical and physical behaviour of this very interesting substance.

7.3.4 Dialkylcyclopentadienyl Compounds

A small number of R_2MCp compounds have been prepared either from R_2MCl (R = Me, Et; M = Ga, In) and Na(K)Cp,[23] or from Me_3In (but not Me_3Ga) and CpH.[24] A related reaction of interest is that in which CpH reacts with $(Me_2InNMe_2)_2$ to give both Me_2InCp and the adduct $Me_2InCp{\cdot}NHMe_2$, with the latter corresponding to the formal addition of CpH across the In—N bond. The indium compounds are inert to air, and insoluble in non-polar solvents.[24] There is some evidence of intermolecular association in the solid state, and to a lesser extent in solution. Thus Me_2InCp is said to be polymeric in the solid state,[24] while both gallium compounds show degrees of association in the range 1.3–1.7 in benzene or cyclohexane.[23,25] It seems probable that this association is related to that identified in crystalline Cp_3In (see Section 7.3.5 below). ^{1}H NMR spectra show alkyl resonances close to TMS, and a singlet (at room temperature) for the Cp ring at δ = 6.2–6.4 p.p.m. in various solvents.[23,24] The ^{13}C NMR spectra of these and other cyclopentadienyl compounds have been reported, but neither the resonance frequencies (δ = 107.5–112.7 p.p.m. depending on R and M) nor the coupling constants can be used for structural assignment.[26]

The particular structural problem obviously relates to the mode of bonding of the Cp ring, and the most informative result is that the vibrational spectra of R_2GaCp (R = Me, Et) and Et_2InCp are similar to those of R_2AlCp.[25] The electron diffraction structure of Me_2AlCp[27] shows that in this molecule the Cp ring is neither η^1 nor η^5, and it seems likely that either η^2 or η^3 conformations, which have a low energy barrier to conversion, may be involved. Lacking other evidence, it seems reasonable to assume that a similar situation holds for R_2GaCp and R_2InCp.

7.3.5 Tris(cyclopentadienyl)indium and Related Compounds

As noted above, Cp_3In, $(MeCp)_3In$ and $(indenyl)_3In{\cdot}OEt_2$ can be easily prepared by the reaction of $InCl_3$ with the appropriate organolithium reagent.[9] The NMR spectrum of Cp_3In is a sharp singlet even at −90 °C, so that the molecule has the expected fluxional behaviour, as has the indenyl complex; $(MeCp)_3In$ is insufficiently stable for detailed investigations, although it was concluded that the metal atom and Me group are attached to the same ring carbon atom. The vibrational spectrum of Cp_3In is similar to but more complex than that required by the presence of σ-bonded diene ligands, and a later X-ray crystallographic study[28] explained this result. Each indium atom is in a slightly distorted tetrahedral environment, bonded to two formally monodentate σ-bonded diene rings, and to one bridging ring in which there is greater delocalization than in the diene case. As in other R_3In compounds (see Section 7.4.2), the electron deficiency of the Cp_3In system leads to an unusual type of bridging.

Another way in which Cp_3In and its analogues behave as other R_3In compounds is in the formation of adducts with neutral donors (bipy, phen, Ph_3P, OEt_2) and of R_4M^- anionic complexes[9] (*cf.* Sections 7.4 and 7.10).

7.4 TRIALKYL AND TRIARYL COMPOUNDS

7.4.1 Preparation

The preparative methods used in the synthesis of R_3M compounds are in the main the standard techniques of organometallic chemistry. Table 1 lists the compounds which have been prepared by the following general methods.

(a) Grignard reagents react with the trihalides of gallium and indium, and this route has found special favour in the case of phenyl, substituted phenyl and other aryl compounds, but is less satisfactory than transmetallation in the case of Ga/propyl and Ga/vinyl reactions.[29] One significant difficulty lies in the necessity of working in Et_2O or other oxygenated solvents (*e.g.* dioxane) which results in the formation of the appropriate R_3M adduct; removal of the base is not always easy, since thermal decomposition of R_3M may occur.

An interesting variant of the use of RMgBr involves the reaction of In/Mg alloys or mixtures with RBr in Et_2O (R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s),[30] and a similar route yields Me_3Ga from Ga/Mg alloy and MeI.[31] High yields are reported in these reactions.

(b) Reaction of the metal with R_2Hg appears to have been used more frequently than the Grignard reaction, especially for R = alkyl. The main advantages of the reaction, here as elsewhere, are the absence of solvent, which makes for easy separation of the MR_3 product, and the fact that the reaction generally goes to completion; the main disadvantages are that the reaction is often slow and requires relatively high temperature (*e.g.* 150 °C for several days). This can be overcome by the use of highly activated indium metal (prepared by treating $InCl_3$ with potassium) which reacts completely with Me_2Hg at 100 °C in 3 h; Ph_3In can be prepared equally efficiently by this technique.[32]

One interesting special case is the reaction of gallium or indium with $Hg[(CH_2)_4CH{=}CH_2]$ since the product, after long reaction times (3 weeks, ~100 °C) is $M(CH_2\text{-cyclo-}C_5H_9)_3$. The rearrangement of the alkene to yield the cyclopentylmethyl ligand has been the subject of a detailed NMR study.[33]

(c) Reaction of MX_3 with organo-lithium (or -sodium) compounds is a useful route to a number of trialkyl-gallium and -indium compounds. The main disadvantage is the presence of a solvent which may coordinate to the final product, and a second consideration is the potential reducing power of some organosodium compounds.[9] Vinylsodium was found to be unsatisfactory in the preparation of $Me_2Ga(vinyl)$ from Me_2GaCl.[29]

(d) Ligand redistribution reactions between MX_3 (M = Ga, In, X = halogen) and alkyl compounds of other metals have frequently been used in the preparation of R_3M compounds (R = Me, Et, Bu^i). The alkyls of zinc, mercury and aluminium have all been used in such preparations, as has Me_2GaCl.

Over and beyond these methods, a number of techniques have been used in only one or two cases. Such reactions include the following examples.

(e) The electrochemical attack of $NaF{\cdot}2AlEt_3$ on an indium anode yields Et_3In.[34]

(f) The reaction of Me_3M (M = Ga, In) with tolane (50 °C, 12 h) gives $[Me_2MC{\equiv}CPh]_2$.[35]

(g) Indium metal reacts with C_6F_5I (160 °C, 6 h) to give $In(C_6F_5)_3$ in yields of ~30%.[36,37]

(h) This latter product is also formed when $(C_6F_5)_2TlBr$ reacts with the metal (160 °C, 1 d), but a similar reaction with gallium metal (190 °C, 4 d) gave only brown tar.[38]

(i) The reaction of Bu^i_3Ga with 1-decene yields $Ga(C_{10}H_{23})_3$.[39] The mechanism of the related formation of Et_3Ga from Bu^i_3Ga and C_2H_4 has been studied at 416–500 K; the slow rate-determining step is $Bu^i_3Ga \rightarrow HBu^i_2Ga + BuH$, followed by hydrometallation of ethylene. Repetition of these reactions leads to Et_3Ga.[40]

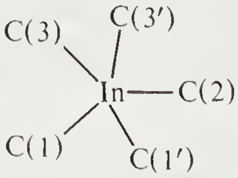
Table 1 Reported R_3M and $R_2R'M$ Compounds of Gallium and Indium

	Gallium	*Indium*
R = alkyl	Me	Me
	Et	Et
	Pr^n, Pr^i	Pr^n, Pr^i
	Bu^n, Bu^i, Bu^s	Bu^n, Bu^i, Bu^s
	CH_2-cyclo-C_5H_{10}	CH_2-cyclo-C_5H_{10}
	CH_2SiMe_3	CH_2SiMe_3
	vinyl	C_9H_{19}
	isopropenyl	vinyl
	cis-, *trans*-propenyl	
	Bz	
R = aryl	Ph	Ph
	2-Me-, 3-Me-, 4-MeC_6H_4	2-Me-, 3-Me-, 4-MeC_6H_4
	4-$Bu^tC_6H_4$	4-EtC_6H_4
	4-MeOC_6H_4	4-$Bu^tC_6H_4$
	3-F-, 4-FC_6H_4	4-MeOC_6H_4
	2-Cl-, 3-Cl-, 4-ClC_6H_4	3-F-, 4-FC_6H_4
	3-Br-, 4-BrC_6H_4	4-ClC_6H_4
	2,4,6-$Me_3C_6H_2$	4-BrC_6H_4
	Nap	Cp
	2-thienyl	MeCp
	C_6F_5	indenyl
R_2, R'	Me_2, MeC≡C—	Me_2, MeC≡C—
	Me_2, PhC≡C—	Me_2, PhC≡C—
	Me_2, Cp	Me_2, Cp
	Et_2, Cp	Et_2, Cp

In general, the synthesis of tri-alkyl and -aryl compounds of gallium and indium does not present any difficulties, and has certainly not hindered the development of the organometallic chemistry of these elements.

7.4.2 Structural Information

Vapour phase electron diffraction studies have established that both Me_3Ga[41] and Me_3In[42,43] exist as monomeric planar trigonal species (see Table 2 for distances). The crystal structure of Me_3Ga has yet to be determined, but that of Me_3In[44,45] has long been a matter of interest. The overall structural unit is a tetramer, consisting of planar trigonal Me_3In units in which each indium is apparently bonded to two carbon atoms of two neighboring Me_3In molecules, giving indium an effective coordination number of five (**2**). The mode of bonding of these latter two long-distance carbon atoms C(1′) and C(3′) has been discussed,[44] as has the question of whether such a weak interaction constitutes a bond at all,[45] but in view of the evidence on Me_2In—C≡CPh and Ph_3M structures, a model involving electron donation into the metal does appear justifiable.



(**2**)

Triphenyl-gallium and -indium both show evidence of unusual intermolecular interaction in the solid state.[46,47] In each case the metal atom is bonded to the three phenyl groups in a trigonal planar MC_3 kernel, and in each case the metal is also situated above and below a carbon atom of the phenyl rings in neighbouring molecules. The difference is that with gallium the carbon atoms in question are those in the *meta* position whereas indium is sited below the *ortho* carbon (**3, 4**), although in both cases the distances involved are relatively large (Ga—C 3.42, In—C 3.07 Å). A similar lattice interaction is identified in $Me_2InC{\equiv}CPh$,[48] where the stereochemistry (**5**) strongly suggests donation from ligand π-orbitals into metal acceptor orbitals.

Table 2 Important Lengths and Angles in R_3M and Related Compounds

Molecule	*Kernel*		*r(M—C)* (Å)	*C—M—C angles* (°)	*Ref.*
$Me_3Ga(g)$	GaC_3		1.967(2)	118.6	1
$Me_3In(g)$	InC_3		2.16(4)	(120)	2
			2.093(6)	(120)	3
$Me_3In(s)$	$InC_3C'_2$	C	2.24(6)	122.2(1.8)	4, 5
			2.25(6)	120.5(1.8)	
			2.16(4)	117.3(1.3)	
		C′	3.11	C′—In—C′	
			3.59	163.5	
$Me_2In—C\equiv CPh$	InC_2C'	Me	2.147(12)	129.9(4)	6
			2.222(14)		
		$C\equiv C$	2.193(14)		
		$\begin{array}{l}\text{C}\\ \vert\vert\vert\text{—In}\\ \text{C}\end{array}$	2.899		
Ph_3Ga	$GaC_3C'_2$	C	1.946(7)	120.6(2)	7
			1.968(5)	118.9(4)	
		C′	3.42		
Ph_3In	$InC_3C'_2$	C	2.111(14)	121.6(3)	7
			2.155(14)	116.8(6)	
		C′	3.07		
$K[GaMe_4]$	GaC_4		2.31(3)	125.9(10)	8
				81.9(10)	
$Rb[GaMe_4]$	GaC_4		2.20(2)	127.7(4)	8
				101.2(4)	
$Li[InMe_4]$	InC_4		2.223(4)	109.47	9
			2.195(4)		
$K[InMe_4]$	InC_4		2.239(3)	105.7(2)	10
				117.2(2)	
$Cs[InMe_4]$	InC_4		2.26(2)	105.6(1.4)	10
				117.6(1.5)	
$M[InPh_4]$	InC_4		2.230(3)	110.2(3)	10
				108.1(3)	
$CpIn(g)$	C_5In		2.62(5)	—	11
$CpIn(s)$	C_5InC_5		3.19(10) from ring centre	—	12
Cp_3In	$In(C_t)_2(C_{br})_2$	C_t	2.237(9)	$C_t—C_{br}$ 92.1(3)	13
			2.243(9)	$C_t—C_t$ 110.2(4)	
		C_{br}	2.374(7)	(and others)	
			2.466(8)		
Me_3GaNMe_3	C_3GaN		1.998(4)	116.7	14
		Ga—N	2.20(3)		
Me_3GaPMe_3	C_3GaP		1.997(8)	117.9	14
		Ga—P	2.52(2)		

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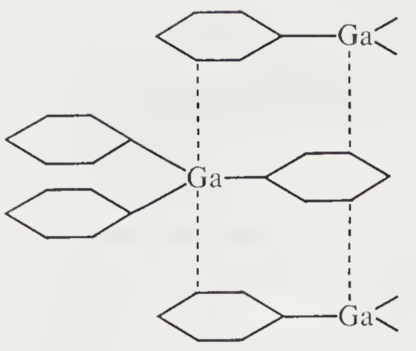
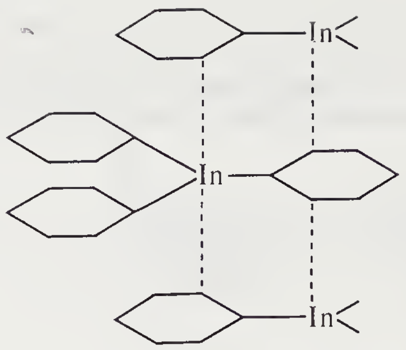


(3)



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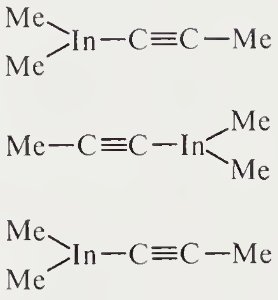

(5)

The question of the degree of association of R_3M compounds in solution, or in the gas or solid phases, has been of some dispute. There is little or no evidence of oligomers in the gas phase.[29,49,50] The early determinations of molecular weight in solution were taken to indicate the presence of dimers, *etc.*, and in particular the conclusion that Me_3In was tetrameric in solution[51] persisted for some time; it now seems likely that the problems associated with the high reactivity of these substances to air and moisture were not always successfully overcome in such work (*e.g.* ref. 52). The following compounds have been shown to be monomeric in the solvents given in parentheses: Me_3Ga (C_6H_6, cyclo-C_5H_{10}),[53] Et_3Ga (C_6H_6, cyclo-C_5H_{10}),[53] Pr^n_3Ga (C_6H_6),[54] $Ga(CH_2SiMe_3)_3$ (hydrocarbons),[55] Ph_3Ga (Et_2O, C_6H_6),[56] Me_3In (C_6H_6, toluene, CH_2Cl_2, cyclo-C_5H_{10}),[49,57] Et_3In (C_6H_6),[58] Pr^n_3In (C_6H_6),[54,58] $In(CH_2SiMe_3)_3$ (C_6H_6),[59] Ph_3In (Et_2O),[56] $In(C_6F_3)_3$ (C_6H_6),[36] $In(Nap)_3$ (C_6H_6).[58] Association in solution into dimers has been reported for $Me_2GaC{\equiv}CPh$ and $Me_2InC{\equiv}CPh$ in C_6H_6[35] and for $Ga(vinyl)_3$ in cyclohexane,[29] and it seems reasonable to assume that in each case the dimerization depends on interactions similar to those in crystalline $Me_2InC{\equiv}CMe$. Dimerization of the alkynic compounds does not occur in THF,[35] due no doubt to the formation of solvate monomers. Quantitative treatments of the bonding in these dimers and higher species are lacking, as are detailed analyses of the structures of R_3Ga and R_3In species. Nuclear quadrupole resonance[60,61] and charge transfer spectra[62] have been taken to show that the ring-metal interaction in substituted phenyl compounds is small, and ^{13}C NMR results[61,62] are in keeping with this conclusion. Further work on these problems would be welcome.

7.4.3 Vibrational Spectroscopy

The most detailed studies of the vibrational spectra have been of the trialkyls, and of Me_3M in particular. Two concordant analyses[63,64] of Me_3Ga identified Ga—Me stretching modes at 521 (ν_{sym}) and 570 cm^{-1} (ν_{as}); other significant vibrations are the GaC_3 deformation at 163 cm^{-1}, and the $GaCH_3$ rocking modes at 612, 727 and 769 cm^{-1}. The corresponding values[64,65] for Me_3In are 467 (ν_{sym}(In—Me)), 495 (ν_{as}(In—Me)), 132 (InC_3 deformation), 635, 687, 725 (In—Me rock) cm^{-1}. The derived stretching force constants are 2.41 (Me_3Ga) and 1.93 (Me_3In), in agreement with the independent values[66] of 2.22 and 1.92 N cm^{-1}.

The results for other trialkyl compounds are less satisfying. A diagrammatic presentation[66] of the stretching modes of R_3Ga and R_3In (R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s) suggests that the ranges are 535–544 cm^{-1} for Ga and 465–467 cm^{-1} for In for all except R = Me or Bu^i, but unfortunately only one ν(M—C) vibration is identified. For Et_3Ga, a limited IR study[67] gave a concordant value of 538 cm^{-1} for ν(M—C), with the Ga—Me rock at 640 cm^{-1}. Later work[68] (IR and Raman) produced stretching frequencies for R_3Ga at 485–537 (R = Et), 520–610 (Pr^n), 485–525 (Pr^i), 520–625 (Bu^n) and 560–680 cm^{-1} (Bu^i). The results confirm the planarity of the MC_3 kernel for Me, Et and Pr^i; the range of values for the butyl compounds is explained in terms of various *trans–gauche* conformers. The stretching force constants are *ca.* 2.0 N cm^{-1} for Ga and 1.6 N cm^{-1} for In for all these R_3M compounds, except that for R = Bu^i the values are 2.6 and 2.4 N cm^{-1}. The limited frequency range, and that of the resultant constants, is surprising, and it would be interesting to see whether the bond strengths are similarly constrained.

A large number of the preparative papers discussed elsewhere in this chapter refer to the results of vibrational spectroscopy for identification and structural assignment. No attempt has been made to summarize these many sets of results, but the reported ν(M—C) frequencies for a wide variety of R_2MX compounds fall into the following ranges (R_2M, ν_{sym}, ν_{as}): Me_2Ga, 540 ± 20, 600 ± 20; Et_2Ga, 510 ± 10, 550 ± 25; Me_2In, 480 ± 20, 510 ± 25; Et_2In, 460 ± 20, 510 ± 20 cm^{-1}. There are insufficient results to justify stating analogous values for other alkyl or aryl compounds.

7.4.4 NMR Studies

As with vibrational spectroscopy, a large number of the preparative papers on organo-gallium and -indium compounds report ^1H NMR results as part of the characterization of the product. There seems little point in trying to assess all these results, especially since the variety of organic solvents must introduce unknown small changes in chemical shift, but one immediate conclusion is that alkyl group protons in R_3M and substituted derivatives are shielded to much the same extent as are those in TMS. In general the ranges of δ values, independent of solvent, are (p.p.m. from TMS) Me—Ga (0 ± 0.5), Et—Ga (0.5 ± 0.3, 1.1 ± 0.1), Me—In (0.2 ± 1.0) and Ph—In (6.5–7.5). Detailed NMR studies have been reported *inter alia* for complexes with R = C≡CPh,[35] vinyl[69] and propenyl,[70] and of the reaction[33] in which Hg(1-hex-5-enyl)$_2$ reacts with gallium or indium metal to give M(cyclopentylmethyl)$_3$.

In addition to the use of NMR for diagnostic purposes, there have been a number of investigations, notably by Oliver and co-workers, of the solution behaviour of R_3M compounds and their adducts. In particular, studies of the exchange process

$$Me_3GaL + Me_3Ga \rightleftharpoons Me_3Ga + Me_3GaL$$

are readily carried out. Thus for L = NMe_3 at 0 °C in cyclopentane, two resonance lines are observed, one for each component, and by conventional methods it is possible to obtain $\Delta H^{\ddagger}$. The detailed findings of such experiments are listed in Table 3. The mechanisms of such exchange processes have been established. In some cases (*e.g.* 1, 4, 7 and 8 in Table 3), dissociation of the 1 : 1 adduct is identified as the rate-controlling process, and in such cases there are correlations between the activation energy and the dissociation enthalpy. In other reaction systems (*e.g.* 5 and 6 in Table 3), electrophilic displacement is the slow step following the formation of a bimolecular bridged transition state.

7.4.5 Thermal Decomposition

The thermal decomposition of R_3M (R = alkyl) compounds in the gas phase is a matter of both intrinsic and applied interest. The pyrolysis of Me_3Ga in toluene vapour (410–510 °C, 6.1–31.1 mmHg) was found[71] to result in the formation of CH_4 and the deposition of a black solid $(MeGa)_n$ *via* the two-step decomposition shown in equations (4) and (5). The corresponding rate equations are (6) and (7), and the activation energies (in kJ mol^{-1}) are believed to correspond to D(Me_2Ga—Me) and D(MeGa—Me) (see Section 7.4.6 for further discussion of these values). Later work[72,73] confirmed that the thermal decomposition involved the cleavage of Ga—Me bonds and the elimination of Me radicals. In keeping with findings, Me_3Ga was shown[74] to methylate a number of hydrides (SiH_4, $MeSiH_3$, Si_2H_6, GeH_4 and B_2H_6, but not PH_3 and AsH_3); the products from (say) SiH_4 include H_2, CH_4, $MeSiH_3$, Me_2SiH_2 and Me_3SiH. The reaction of Me_3Ga with AsH_3 at 203–259 °C produces GaAs, with decomposition of the 1 : 1 adduct *via* the intermediates Me_2GaAsH_2 and MeGaAsH, eliminating CH_4 at each stage[75,76] (*cf.* Section 7.5.3). The thermal decomposition of Bu^i_3Ga proceeds *via* the elimination of butane (equation 8) and similar successive steps.[40]

Table 3 Exchange Reactions Involving R_3Ga and Related Compounds

	System	*Solvent*	$\Delta H^{\ddagger}$ (kJ mol^{-1})	*Comments*	*Ref.*
1	Me_3GaNMe_3/Me_3Ga	cyclo-C_5H_{10}	93.2		1
2	Me_3GaPMe_3/Me_3Ga	cyclo-C_5H_{10}	—	Intermediate in rate between NMe_3 and OMe_2 systems	1
		CH_2Cl_2	70.6 ± 2.1		2
3	Me_3GaOMe_2/Me_3Ga	cyclo-C_5H_{10}, Freon 11	—	Too fast to observe, even at −100 °C	1, 3
4	Me_3GaNMe_2H/Me_3Ga	Freon 11	80.3	Slow exchange (NMR scale) 0 °C (?)	3
5	$Me_3GaNMeH_2/Me_3Ga$	Freon 11	42.0	Slow exchange (NMR scale) −9 °C	3
6	Me_3GaNH_3/Me_3Ga	Freon 11	35.5	Slow exchange (NMR scale) −40 °C	3
7	Me_3InNMe_3/Me_3In	CH_2Cl_2	82.3 ± 4.2		4
8	Me_3InNMe_2H/Me_3In	CH_2Cl_2	64.4 ± 2.5		4
9	$Me_3InNMeH_2/Me_3In$	CH_2Cl_2	48.5 ± 0.4		4
10	Me_2Cd/Me_3Ga	CH_2Cl_2, Me-cyclo-C_6H_{11}	32.6 ± 3.4	Bimolecular bridged transition state	5
11	Me_2Cd/Me_3In	CH_2Cl_2, Me-cyclo-C_6H_{11}	35.1 ± 0.2	Bimolecular bridged transition state	5
12	$Me_2AlMe(NPh_2)AlMe_2/Me_3Ga$	toluene	84.0 ± 3.5	Al—Me_{br} rate determining step	6

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$$\mathrm{Me_3Ga} \longrightarrow \mathrm{Me_2Ga} + \mathrm{Me} \tag{4}$$

$$\mathrm{Me_2Ga} \longrightarrow \mathrm{MeGa} + \mathrm{Me} \tag{5}$$

$$\log_{10}k_1 = 15.54 - 248.7 \times 10^3/2.303RT\ \mathrm{s^{-1}} \tag{6}$$

$$\log_{10}k_2 = 7.94 - 148 \times 10^3/2.303RT\ \mathrm{s^{-1}} \tag{7}$$

$$\mathrm{Bu^i_3Ga} \longrightarrow \mathrm{Bu^i_2GaH} + \mathrm{BuH} \tag{8}$$

With Me_3In, three separate steps are identified in the toluene flow experiment[77] (550–781 K, 6–33.5 mmHg) (equations 9, 10 and 11) leading to the rate equations (12) and (13) from which one obtains values of 197.3 kJ mol^{-1} for $D(Me_2In—Me)$ and 170.1 kJ mol^{-1} for $D(In—Me)$. Results have also been reported for Me_3In, $Me_3In{\cdot}OEt_2$ and Et_3In.[78] The oxidation of Et_3In occurs only slowly in the gas phase even at 100 °C, as compared with the spontaneous ignition of the liquid in air or oxygen at room temperature.[79] The mechanisms proposed are shown in Scheme 1. The products identified from the gas phase reaction include C_2H_6, C_2H_4, EtOH, Et_2O, MeCHO and solid peroxides.

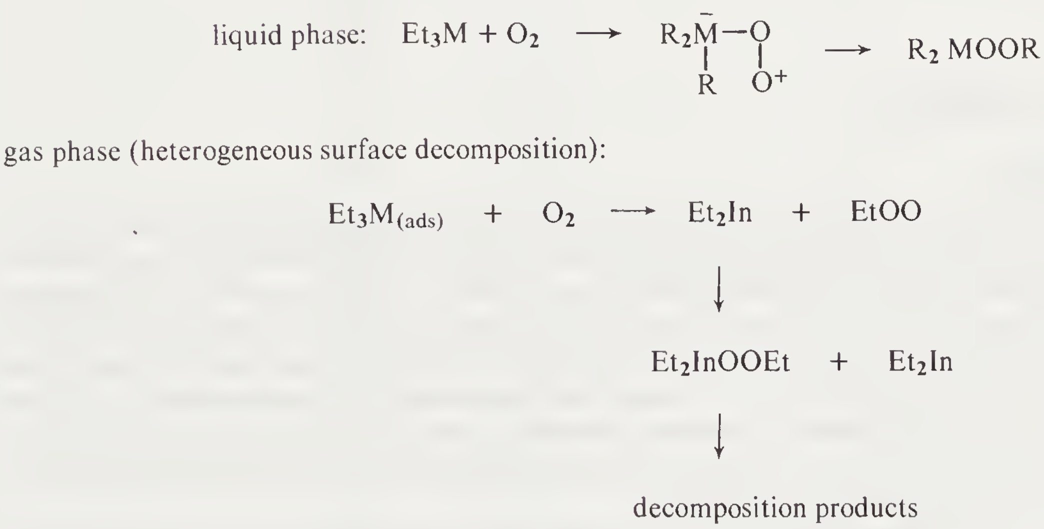
$$\mathrm{Me_3In} \longrightarrow \mathrm{Me_2In} + \mathrm{Me} \tag{9}$$

$$\mathrm{Me_2In} \longrightarrow \mathrm{MeIn} + \mathrm{Me} \tag{10}$$

$$\mathrm{MeIn} \longrightarrow \mathrm{In} + \mathrm{Me} \tag{11}$$

$$\log_{10}k_1 = 15.72 - 197.3 \times 10^3/2.303RT\ \mathrm{s^{-1}} \tag{12}$$

$$\log_{10}k_3 = 10.91 - 161.8 \times 10^3/2.303RT\ \mathrm{s^{-1}} \tag{13}$$



Scheme 1

7.4.6 Thermochemical Results

Measurements of ΔH_f° have been reported for only a very small number of compounds, and bond energy information is correspondingly sparse. The recommended values[80] for Me_3Ga, based on ΔH_r for equations (14)[81] and (15)[82] are ΔH_f° ($Me_3Ga(l)$) = −79.8 ± 6.3 kJ mol^{-1}, ΔH_f° ($Me_3Ga(g)$) = −46.8 ± 6.7 kJ mol^{-1}, assuming a value[83] of ΔH_{vap} (Me_3Ga) = 32.6 kJ mol^{-1}. For Me_3In, ΔH_r for equation (16) gives the values[80,84] ΔH_f° ($Me_3In(c)$) = 122.0 ± 5.9 kJ mol^{-1}, ΔH_f°($Me_3In(g)$) = 170.5 ± 6.3 kJ mol^{-1}, assuming[57] ΔH_{vap} (Me_3In) = 48.5 kJ mol^{-1}. The only other values are (R_3M, ΔH_f°): $Et_3Ga(l)$, −117 ± 4; $Et_3Ga(g)$, −75; $Bu^n_3Ga(l)$, −280 ± 4; $Bu^n_3Ga(g)$, −222; $Bu^i_3Ga(l)$, −289 ± 4; $Bu^i_3Ga(g)$, −234 (all in kJ mol^{-1}) determined by static bond calorimetry,[85] but the reliability of these results has been questioned.[86]

$$Me_3Ga_{(l)} + 6O_{2(g)} \longrightarrow \tfrac{1}{2}Ga_2O_{3(c)} + 3CO_{2(g)} + 4\tfrac{1}{2}H_2O_{(l)} \quad (14)$$

$$Me_3Ga_{(l)} + 3I_{2(soln)} \longrightarrow GaI_{3(soln)} + 3MeI_{(soln)} \quad (15)$$

$$Me_3In_{(c)} + 3Br_{2(soln)} \longrightarrow InBr_{3(soln)} + 3MeBr_{(g)} \quad (16)$$

Bond energies can be derived for the overall decomposition $R_3M(g) \rightarrow M(g) + 3R(g)$, or for the individual steps $R_3M(g) \rightarrow R_2M(g) + R(g)$, *etc.* The numerical values for $\bar{D}$ *etc.* depend on ΔH_f° (Me) (137.9), ΔH_f° (Ga)(g) (275.9) and ΔH_f° (In)(g) (243.3 kJ mol^{-1}).[87] Taking these in conjunction with the thermochemical measurements[80,81,82,84] and the thermal decomposition results[71,77] one finds the following bond energy values (Me_3M, $\bar{D}$, D_1, D_2, D_3): Me_3Ga, 245, 249, 148, 339; Me_3In, 162, 197, 119, 170 kJ mol^{-1}. The value for $\bar{D}(Ga—Me_3)$ is in agreement with the results of mass spectrometric appearance potentials,[50] from which one finds $\bar{D}(Ga—Me_3) = 232 \pm 8$ kJ mol^{-1}.

One interesting point in these results is the thermodynamic stability of $(M—Me)_g$ which is of course the methyl derivative of M^I, a surprising conclusion in view of the failure to prepare any such simple derivatives of gallium(I) and indium(I). There is a clear need for more information on this whole matter of the thermochemical properties of R_3M compounds.

7.5 NEUTRAL ADDUCTS

7.5.1 Introduction

As noted earlier, much of the characteristic chemistry of Group III trihalides relates to the electron pair acceptor property of the metal atom, which results in the formation of a large number of adducts with neutral donors.[2] These may be of the type MX_3L, MX_3L_2 or MX_3L_3, depending *inter alia* on the properties of M, X and L, and it is therefore not surprising that there has been a similar interest in the preparative and structural study of adducts between neutral ligands and the tri-alkyls or -aryls of these elements. Having made the analogy, it is appropriate to note that the range of such work is far below that on the trihalide complexes. This may partly reflect the difficulties associated with the prior preparation of the R_3M species. Some of the lacunae in our knowledge of these compounds are noted below.

The preparation of the adducts calls for little comment, since for the most part mixing equimolar quantities of reagents in some suitable solvent will suffice. Compounds of the triorgano-gallium or -indium species have been reported with more than 30 different neutral ligands (see Table 4), with donation *via* N, P, As, Sb, O, S, Se and Te. The only reported attempt to form a bond through Bi, using Me_3Bi and Me_3Ga, was unsuccessful.[88] It is striking that the preparative work has been so restricted to the adducts of Me_3Ga or Me_3In with monodentate ligands, and there has been no systematic study of other R_3M compounds to match the work of Coates on these trimethyl systems.[88,89] Equally interesting is that little has been done to investigate the adducts of Ph_3In or other triaryls, apart from studies of $(C_6F_5)_3In$[37,38,90] and the very extensive work with 1,4-dioxane and various R_3M and R_2R^1M compounds (see Table 4). There has been no systematic investigation of complexes with bidentate ligands; it is not clear for example whether 1,4-dioxane is mono- or bi-dentate in the various triaryl compounds listed in Table 4.

In general, structural information from diffraction methods is surprisingly lacking. Electron diffraction[91] studies of $Me_3Ga{\cdot}NMe_3$ and $Me_3Ga{\cdot}PMe_3$ show that the expected structural changes consequent on adduct formation result in essentially distorted tetrahedral stereochemistry at gallium (see Table 2). Further work is required in this area.

Table 4 Neutral Adducts of R_3Ga and R_3In

Ligand (*L*)	*Complex*	*Ref.*
NH_3	Me_3GaL	1, 2, 3, 4
	Me_3InL	5
	not formed at −35 °C	
	Et_3GaL	6
	Pr^n_3GaL	7
	Pr^i_3GaL	7
	$(vinyl)_3GaL$	7
NH_2Me	Me_3GaL	3, 4
	Et_3GaL	4
$NHMe_2$	Me_3GaL	3, 4
	Et_3GaL	4
	Me_3InL	5
NMe_3	Me_3GaL	3, 4, 8
	Et_3GaL	4
	Pr^n_3GaL	7
	Pr^i_3GaL	7
	$(vinyl)_3GaL$	7
	Me_3InL	5
	$(Me_3SiCH_2)_3GaL$	9
NEt_3	Me_3GaL	10
$NHPh_2$	Me_3GaL	11
	Me_3InL	11
by	$(C_6F_5)_3InL$	12, 13
bipy	$[(C_6F_5)_3In]_2L$	12, 13
	Cp_3In	14
TMEDA	$(C_6F_5)_3InL$	13
phen	Cp_3In	14
MeCN	Me_3GaL	15, 16
PhCN	Me_3GaL	16
	Et_3GaL	16
Bu^tCN	Et_3Ga	16
PH_3	Me_3InL	17
$PHMe_2$	Me_3GaL	18
	Me_3InL	18
PMe_3	Me_3GaL	3, 8
	Et_3GaL	4
	Me_3InL	5
$PHEt_2$	Me_3GaL	18
	Me_3InL	18
$PHPh_2$	Me_3GaL	11
PPh_3	$(C_6F_5)_3InL$	13, 19
	Cp_3In	14
$AsMe_3$	Me_3GaL	3
	Me_3InL	5
$AsMe_2H$	Me_3GaL	18
	Me_3InL	18
$AsPh_2H$	Me_3GaL	11
	Me_3InL	11
$AsEt_3$	Me_3GaL	20
$SbMe_3$	Me_3GaL	3
$SbEt_3$	Me_3InL	21
OMe_2	Me_3GaL	3, 4
	Et_3GaL	4
OEt_2	Me_3GaL	1, 2, 22, 23
	Et_3GaL	24
	Me_3InL	5
	no adduct identified	6
	$(Me_3In)_2L$	25
	$(C_6F_5)_3Ga$	26
	$(indenyl)_3In$	14
DMSO	$(C_6F_5)_3InL_2$	13
Ph_3PO	$(C_6F_5)_3InL$	13
Ph_3AsO	$(C_6F_5)_3InL$	13
THF	$(vinyl)_3InL$	27
	$(C_6F_5)_3InL_2$	13
	$(Me_3SiCH_2)_3InL$	28
acetone	Me_3GaL	15
SO_2	Ph_3InL	29
1,4-dioxane	Ph_3GaL	30, 31, 32

Table 4 (*continued*)

Ligand (*L*)	*Complex*	*Ref.*
1,4-dioxane	R_3GaL (R = Ph, O, M, *p*-MeC_6H_4, *p*-BrC_6H_4, Nap, Bz, 2-thienyl)	31
	RR'_2GaL R = 2-thienyl, R′ = Ph; R = Ph, R′ = 2-thienyl	33
	$(RR'_2Ga)_2L$ R = Ph, R′ = 1-naphthyl; R = 1-naphthyl, R′ = Ph	33
	Ph_3InL	34, 35
	R_3InL R = *o*-, *m*-, *p*-MeC_6H_4, 1-thienyl, *p*-BrC_6H_4	34, 35
	$(C_6F_5)_3InL$	12, 36
SMe_2	Me_3GaL	3, 4
	Et_3GaL	4
	Me_3InL	5
$SeMe_2$	Me_3GaL	3
$TeMe_2$	Me_3GaL	3

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7.5.2 Chemical Properties

Investigations of the chemical properties of the adducts have generally focused on the thermal stability. One important facet is the elimination of alkane or arene between acid and base, discussed below; a second is the dissociation of complex into its components. The ease or otherwise of this dissociation is of some importance in terms of synthesizing free R_3M, since reaction in a basic organic solvent yields the appropriate adduct from which the solvent must subsequently be removed. The decomposition temperatures which have been reported for the aryl–dioxane complexes, for example, are in the range 50–150 °C, which makes for convenience in handling both adduct and parent triaryl.

The dissociation enthalpy for the process shown in equation (17) has been measured by vapour pressure methods[88,89] and by calorimetry;[92] NMR methods have also been used to establish the relative order of base strengths $MeNH_2 > NH_3 > NHMe_2 > NMe_3 > PMe_3 > OMe_2 > SMe_2$ for Et_3Ga.[93] Coates[88] established a concordant order in terms of donor atoms for adducts with Me_3Ga (Scheme 2) and a similar (partial) order, $S \geqslant Te > Se$, has been reported[94] for the dimethyl chalcogenides; ΔH_{mix} is negative in each case. The numerical values of ΔH_{diss} in Table 5 emphasize, as in the preparative work, the focus on Me_3M compounds, and the absence of information for triaryls of gallium or indium. The interpretation of the thermochemical values has not been at a very detailed level, partly because of the lack of a quantitative base on which to found comparative arguments. As in so many other areas of organo-gallium and -indium chemistry, one can only conclude that further work is required.

$$R_3ML \longrightarrow R_3M + L \qquad (17)$$

$$N > P \gg As > Sb > Bi$$

$$O > S > Se = Te$$

Scheme 2

Table 5 Dissociation Energies for Neutral Adducts of R_3M

Acid	*Base*	ΔH_{diss} (kJ mol^{-1})	*Ref.*
Me_3Ga	NMe_3	72	1
		71	1
		88	2
	PMe_3	76	3
	$AsMe_3$	42	3
	OMe_2	38	3
	SMe_2	≈33	3
	$SeMe_2$	42	3
	$TeMe_2$	≈33	3
Et_3Ga	SMe_2	25	1
(vinyl)$_3$Ga	NMe_3	88	1
Me_3In	NMe_3	83 ± 2	4
	PMe_3	71.5 ± 3	4

1. L. G. Stevens, B. Park and J. P. Oliver, *J. Inorg. Nucl. Chem.*, 1964, **26**, 97.
2. G. E. Coates and N. D. Huck, *J. Chem. Soc.*, 1952, 4501.
3. G. E. Coates, *J. Chem. Soc.*, 1951, 2003.
4. G. E. Coates and R. A. Whitcombe, *J. Chem. Soc.*, 1956, 3351.

7.5.3 Alkane Elimination from Neutral Adducts

The elimination of CH_4 or other hydrocarbon between the acid and base components of a suitable adduct is a most important feature of the chemistry of boron and aluminium. Similar reactions with gallium and indium are well established, and a range of interesting compounds has been prepared by such routes. We shall return later (Section 7.9) to similar reactions in which the formation of a stable adduct is precluded by the immediate elimination of RH.

The 1 : 1 adducts of Me_3Ga with NH_3, NH_2Me and $NHMe_2$ all decompose on heating, eliminating CH_4, and in the ammonia case more intense heating leads to further reaction[88] (Scheme 3). Extensive measurements of the physical properties, including vapour pressure and ΔH_{sub}, were carried out; the dimeric formulation derives from the vapour pressure, later confirmed for $(Me_2GaNHMe_2)_2$ by molecular weight measurements in benzene.[95] The indium analogue[89] prepared similarly (equation 18) is a crystalline solid which becomes a glass at 70–80 °C, and melts at 174–175 °C; the comparable values for $(Me_2GaNMe_2)_2$ are 55–80 °C and 157–161 °C, respectively. Analogous elimination reactions have been shown[96] to lead to Et_2InNEt_2. The adduct $Me_3In{\cdot}PH_3$ decomposes on heating to the polymer $(MeInPH)_n$, eliminating both CH_4 and H_2, with no evidence for the existence of Me_2InPH_2.[97]

$$2Me_3Ga{\cdot}NH_3 \xrightarrow{70\text{–}90\ °C} (Me_2GaNH_2)_2 \longrightarrow (MeGaNH)_x$$

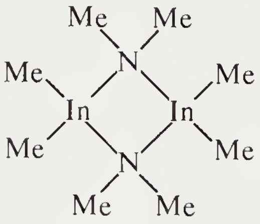
$$2Me_3Ga{\cdot}NH_2Me \xrightarrow{120\text{–}130\ °C} (Me_2GaNHMe)_2 \quad \text{(stable to >180 °C)}$$

$$2Me_3Ga{\cdot}NHMe_2 \xrightarrow{115\text{–}130\ °C} (Me_2GaNMe_2)_2 \quad \text{(stable to >180 °C)}$$

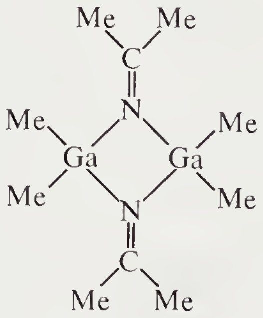
Scheme 3

$$Me_3In{\cdot}NHMe_2 \xrightarrow{140\text{–}160\ °C} (Me_2InNMe_2)_2 \qquad (18)$$

The crystal structure[98] of $(Me_2InNMe_2)_2$ confirmed the dimeric nature of the compound (**6**), and permitted analysis and assignment of the vibrational spectrum. The structures of the related species $[Me_2C{=}NMMe_2]_2$, prepared from the reaction between $Me_2C{=}MCl$ and Me_3M (M = Ga[99] or In[100]) are also based on a four-membered (M_2N_2) ring[100,101] (**7**). The results (Table 6) show significant changes in ring distances and angles due to substituents on nitrogen, but the kernel stereochemistry is not affected. There are strong structural similarities between these M_2N_2 ring systems and a number of other compounds discussed in Section 7.9.



(**6**)



(**7**)

Adducts with Me_2PH, Et_2PH and Me_2AsH also undergo decomposition at temperatures which vary markedly with both ligand and metal.[102] The resultant compounds Me_2MER_2 (M = Ga, In; E = P, As) are polymeric glasses in the solid state, but trimeric in benzene; NMR studies show rapid inversion of the six-membered ring at 25 °C, and a slower motion at −90 °C. The ligands $PhPH_2$, $MeAsH_2$ and $PhAsH_2$ give rise to involatile polymers such as $(MeMAsMe)_2$ by eliminating $2CH_4$ (*cf.* Me_3PPh_3 discussed above), although with $Me_3Ga{\cdot}AsMeH_2$ only $1.43CH_4$ is released, even at 200 °C. The phenyl compounds $Me_3Ga{\cdot}EPh_2H$ (E = N, P, As) decompose at temperatures between 120 °C (E = N) and 30 °C (E = As) forming $(Me_2GaEPh_2)_2$, and similar reactions occur with Me_3In, albeit at higher temperatures.[103] The thermal decomposition of $Me_3In{\cdot}SbEt_3$ eventually produces InSb, with $Me_2InSbEt_2$ identified as a possible intermediate.[104]

Table 6 Important Bond Distances and Angles in R_2MX Compounds ($X \neq Cl, Br, I$)

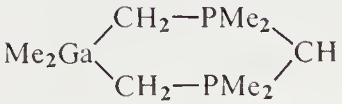
Compound		$r(M—C)$ (Å)	$C—M—C$ (°)	Other distances and angles		Ref.
$Me_2GaH_2BH_2$		1.938	119	Ga—B	2.152	1
$(Me_2InNMe_2)_2$		2.168(19)	131.3(4)	In—N	2.225(13)	2
					2.247(13)	
				N—In—N	85.7(4)	
				In—N—In	94.3(3)	
$(Me_2GaN{=}CMe_2)_2$		1.968(8)	124.5	Ga—N	2.000(3)	3
					1.978(3)	
				N—Ga—N	82.1	
				Ga—N—Ga	97.9	
$(Me_2InN{=}CMe_2)_2$		2.119(10)	126.7(4)	In—N	2.194(4)	4
		2.164(12)		N—In—N	79.5(2)	
				In—N—In	100.5(2)	
	Me	1.971(6)	113.7(3)	—	—	5
	CH_2	2.068(5)	105.5(2)			
		2.048(5)				
$(Me_2GaDMA)_2$		1.991(5)	114.7	Ga—N	1.981(4)	6
		2.005(4)			1.977(4)	
				N—Ga—N	100.0(2)	
$(Me_2Ga$ oxamidine$)_2$		2.006(13)	122.5(6)	Ga—N	1.984(9)	7
		2.002(13)			1.976(10)	
				N—Ga—N	84.0(4)	
$(Me_2In$ oxamidine$)_2$		2.182(6)	131.8	In—N	2.182(5)	7
		2.173(6)			2.183(5)	
				N—In—N	76.0(2)	
$[Me_2Ga(Me_2pz)]_2$		1.955(9)	125.1(6)	Ga—N	1.988(5)	8
		1.969(10)			1.998(5)	
				N—Ga—N	102.9(2)	
$Me_2Ga(OH)(Me_2pz)GaMe_2{\cdot}2Me_2pzH$		1.946(7)	122.5(6)	Ga—O	1.936(4)	8
		1.959(8)			1.932(4)	
		1.940(8)				
		1.945(8)		Ga—N	1.993(4)	
					1.985(4)	
				Ga—O—Ga	118.0(2)	
$C_2H_4(Me_2GaNCC_6H_4O)_2$		1.948(6)	124.6(4)	Ga—O	1.869(2)	9
		1.950(5)		Ga—N	2.026(3)	
				N—Ga—O	94.0(1)	
$Me_2GaOC_2H_4NH_2$		1.974(9)	123.3(4)	Ga—O	1.916(5)	10
		1.962(8)		Ga—N	2.056(6)	
				N—Ga—O	87.1(2)	
$[Me_2GaOC_2H_4NMe]_2$		1.963(6)	126.7(4)	Ga—O	1.913(3)	11
		1.948(7)		Ga—N	2.078(3)	
				O—Ga—O	74.6(1)	
				N—Ga—O	75.6(1)	

Table 6 *(continued)*

Compound	*r(M—C)* (Å)	*C—M—C* (°)	*Other distances and angles*		*Ref.*
$[Me_2Ga(C_7H_5O_2)]_2$	1.939(5)	136.3(3)	Ga—O	1.927(3)	12
	1.938(6)			2.462(3)	
				2.120(3)	
$MeGa(OAc)_2$	1.942(4)	—	Ga—O	1.899(3)	13
				1.912(3)	
				1.928(3)	
	1.950(4)	—	Ga—O	1.873(3)	
				1.942(3)	
				2.219(3)	
				2.086(3)	
$Me_2Ga(ox)$	1.934(22)	136.3	Ga—O	2.051(7)	14
	1.948(24)			2.124(9)	
			O—Ga—O	78.5	
Me_2Ga(prolinate)	1.936(5)	126.9(3)	Ga—N	2.027(3)	15
	1.952(5)		Ga—O	2.036(3)	
				2.695(3)	
			O—Ga—N	80.5(1)	
Me_2InOAc	2.08(1)	152.2	In—O	2.371(5)	16
	2.11(1)			2.600(5)	
Et_2InOAc	2.22(3)	125.7	In—O	2.44(2)	17, 18
	2.29(3)			2.67(2)	
$Et_2InS(Ac)$	2.14		In—O	2.47	19
				2.56	
			In—S	2.63	

1. A. J. Downs and P. D. P. Thomas, *J. Chem. Soc., Dalton Trans.*, 1978, 809.
2. K. Mertz, W. Schwartz, B. Eberwein, J. Weidlein, H. Hess and H. D. Hausen, *Z. Anorg. Allg. Chem.*, 1977, **429**, 99.
3. F. Zettler and H. Hess, *Chem. Ber.*, 1977, **110**, 3943.
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5. H. Schmidbaur, O. Gasser, C. Krueger and J. C. Sekutowski, *Chem. Ber.*, 1977, **110**, 3517.
6. H. D. Hausen, F. Gerstner and W. Schwartz, *J. Organomet. Chem.*, 1978, **145**, 277.
7. F. Gerstner, W. Schwartz, H. D. Hausen and J. Weidlein, *J. Organomet. Chem.*, 1979, **175**, 33.
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Other studies of the thermal decomposition of adducts involved those formed between Me_3Ga and Et_3Ga and MeCH, PhCN or Bu^tCN.[105] There are some interesting contrasts in behaviour, so that the acetonitrile adduct of Me_3Ga loses CH_4 on heating to give $(Me_2GaNC_2H_2)_n$, whereas $Me_3Ga{\cdot}PhCN$ yields 2,4,6-$Ph_3C_3N_3$. The Et_3Ga adduct of PhCN melts (25–27 °C) and then at 160 °C loses C_2H_4 to form $(PhC{=}NGaEt_2)_2$, dimeric in benzene, and with a structure presumably similar to (**7**). It appears that the stability of the four-membered M_2E_2 ring is of considerable significance in these decomposition processes.

7.6 ORGANOMETALLIC HALIDES

7.6.1 General Preparative Methods

The synthetic routes to the organometallic halides and dihalides of gallium and indium include most of the common methods of organometallic chemistry, and what follows is a summary of those most frequently used, with illustrative examples. Some more specialized methods are discussed in Sections 7.6.2 and 7.6.3.

(a) Reaction of MX_3 with an organolithium reagent in appropriate molar ratios: Bu_nGaCl_{3-n} ($n = 1, 2$);[106] $RGaCl_2$ (R = Et, Pr^n, Bu^n, Bu^i, Bu^s, Bu^t);[107] $Ga(CH_2SiMe_3)_nX_{3-n}$ (X = Cl, Br; $n = 1, 2$);[55] Me_2InCl, Me_2InI.[108]

(b) Redistribution reactions between MX_3 and R_3M: $Me_2GaCl{\cdot}OEt_2$;[103] Et_2GaCl;[109] Ph_nGaCl_{3-n} ($n = 1, 2$);[110] Ph_nGaX_{3-n} ($n = 1, 2$; X = Cl, Br, I);[111] Ph_nGaCl_{3-n} and substituted phenyl derivatives;[112] $MeInCl_2$;[113] Ph_nInX_{3-n} (X = Cl, Br, I);[114] $(C_6F_5)_2InBr{\cdot}Et_2O$;[115] $In(CH_2SiMe_3)_nCl_{3-n}$;[59] Cp_2InI.[13]

(c) Reaction of R_3M with HX: Me_nGaCl_{3-n} ($n = 1, 2$);[116,117] Ph_2GaCl;[110] Me_2InBr;[108] $MeInCl_2$;[113] $In(CH_2SiMe_3)_nCl_{3-n}$.[59] This method yields only trace quantities of Me_2InF from Me_3In and KHF_2 in Et_2O.[108]

(d) Grignard reagent with MX_3: Ph_2InBr, $(Nap)_2InBr$;[58] $(C_6F_5)_nInCl_{3-n}$;[37] $(C_6F_5)_2InBr$.[115]

Other processes which have been used in singular instances include the following examples.

(e) The reaction of Me_4Si, $(Me_2SiO)_4$, $(Me_3Si)_2O$ or Me_4Ge with $GaCl_3$ produces $[MeGaCl_2]_2$; Me_4Sn under similar conditions yields the 1:1 adduct $Me_3SnCl{\cdot}MeGaCl_2$ which on heating yields only the starting materials.[117,118]

(f) Organofluorides are formed from the reaction of R_3M and $BF_3{\cdot}OEt_2$.[108,119,120]

(g) The addition of $HGaX_2$ (X = Cl, Br) across a C=C double bond has been shown to yield $RGaX_2$ compounds (R = Et, Pr^n, C_7H_{15}, cyclo-C_6H_{11}; X = Cl, Br).[121,122]

(h) Halogenated methanes react with Et_3In to give Et_2InX (X = Cl, Br, I).[123,124]

(i) Halogens react with Ph_3Ga[111] or Ph_3In[125] yielding Ph_nMX_{3-n} compounds; iodine oxidizes CpIn to $CpInI_2$.[13]

7.6.2 Preparations involving Metals

Indium metal reacts, albeit rather slowly, with various organic bromides and iodides to give a mixture of $RInX_2$ and R_2InX_2 and R_2InX, analyzing as $R_3In_2X_3$ (R = Me, Et, Pr^n; X = Br, I). The reactions, carried out *in vacuo*, typically require 1–3 d for iodides and 3–5 d for bromides.[126,127] No mechanism was suggested for these reactions: the presence of both R_2InX and $RInX_2$ species implies solution redistribution reactions following the formation of a single primary product. The rate of such reactions is much enhanced by the use of activated indium metal, prepared by the reaction of $InCl_3$ with potassium. This mixture is refluxed under nitrogen for 4–6 h to give a black reactive powder, which itself reacts with RI (R = Me, Et) to give R_2InI in almost quantitative yield after 2 h at 80 °C.[128] Similar reactions with PhBr, PhI and tolyl iodide, either neat or in xylene, gave the corresponding R_2InI compounds in >90% yield (2 h, 150 °C), and by way of comparison one may note that commercial In powder reacts with PhI at 150 °C to give only a 30% yield of Ph_2In after 25 h.[129]

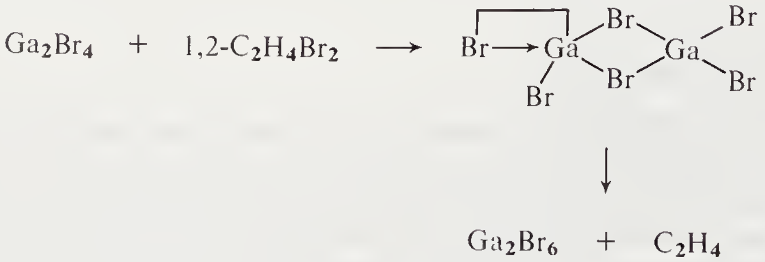
The availability of activated indium metal has led to the preparation of the compound $BrIn(CH_2CO_2Et)_2$, which is the indium analogue of the Reformatsky reagent.[130] The preparation of β-hydroxy esters is readily accomplished in a one-step one-pot, almost quantitative synthesis by refluxing a mixture of activated In, $BrCH_2CO_2Et$ and cyclohexanone (2 h, 55 °C), whereas non-activated indium powder gives much poorer yields. The structure of $BrIn(CH_2CO_2Et)_2$ might be interesting, since there are a number of different modes of inter- and intra-molecular association by which indium may increase its coordination number beyond three.

Finally we note that the electrochemical synthesis[131] of organoindium halides, stabilized as neutral adducts, also involves the use of indium metal as a starting material in cells of the type $Pt_{(-)}|RX + MeCN + bipy|In_{(+)}$. The proposed mechanism involves the formation of halide ions by cathodic reduction of RX, followed by anodic formation of InX, which by reaction with RX gives $RInX_2$ (*cf.* Section 7.6.3). Subsequent solution rearrangement reactions give rise to R_2MX or RMX_2 adducts, depending *inter alia* on R and X.

7.6.3 Oxidative Insertion Reactions

The reaction of a low oxidation state metal complex with an organic halide to yield a product in which the metal has inserted into a C—X bond is well known in transition metal chemistry. The application of such procedures for main group metals is less well known, but nevertheless constitutes an important part of the chemistry of the M(I) compounds of Group III. Of special relevance is the use of such reactions to synthesize organometallic halides of gallium and indium, using both M(I) and M(II) halides as starting materials.

The first report[132] concerned the reaction of Ga_2Cl_4, which dissolves in MeI and on removal of excess solvent yields a compound formulated as $Me(I)GaCl_2GaCl_2$. Later investigations[133] showed that Ga_2Br_4 reacted rapidly with both MeBr and EtBr at room temperature to give RGa_2Br_5, again formulated as neutral dimer species $R(Br)GaBr_2GaBr_2$. Other organic halides ($R = Pr^n, Pr^s, Bu^n, Bu^t$, Bz) rapidly produced red oils which were taken to be decomposition products from the reaction of $RGaBr_5$ with excess RX. With 1,2-$C_2H_4Br_2$, 1,3-$C_3H_6Br_2$ and 1,5-$C_5H_{10}Br_2$, the decomposition was shown to go by the sequence shown in Scheme 4. These reactions are general for all gallium(II) halides with MeX or EtX.[134] Reactions were carried out at −20 °C in order to minimize halogen exchange; under such conditions MeI reacts with all three dihalides to give $MeGa_2X_4I$, but in other systems the rate of halogen exchange is relatively rapid, so that with Ga_2I_4 and MeX (X = Cl, Br) for example, the product is $MeGa_2X_5$.



Scheme 4

The analogous reactions with indium(II) halide have not been reported but there is ample evidence that indium(I) bromide and iodide can be oxidized by organic halides to $RInX_2$ compounds. The reaction between InBr and MeBr is slow at room temperature (~1 week) but the yields are almost quantitative.[135] With InI and MeI, the time required for complete reaction has been reported to be 24 h,[136,137] or 1 h.[138] Other iodides which also react with InI are EtI, Pr^nI and Bu^nI, and the corresponding bromides react with InBr.[139] Dioxane adducts of $RInX_2$ can be prepared from the reactions of RX and InX in that solvent (R = Bz, allyl; X = Br, I).[140]

There seems to be little doubt that the oxidation occurs *via* other subhalides, but there is some disagreement as to the details involved. In the reaction between MeI and InI, InI_2 was identified as an intermediate,[138] as were compounds related to In_2I_6 such as $Me(I)InI_2InI_2$, $Me(I)InI_2InMe_2$, *etc.*, and some importance was ascribed to the solution redistribution reaction (equation 19). In the InBr/RBr reaction, a variety of sub-bromides were identified,[139] and the overall mechanism is summarized in equations (20)–(23). The features common to the InI/RI discussion above are the formation of In_2X_4 and the formation of both R_2InX and $RInX_2$. The elucidation of the mechanism of such a sequence of reactions, involving as they do both heterogeneous and homogeneous processes, is clearly a major problem, and further work on these reactions is needed.

$$2MeInI_2 \rightleftharpoons Me_2InI + InI_3 \tag{19}$$

$$8InBr + 2RBr \longrightarrow In_7Br_9 + RInBr_2 \tag{20}$$

$$In_7Br_9 + R_2InBr + 6RBr \longrightarrow 8RInBr_2 \tag{21}$$

$$In_7Br_9 + 2RBr \longrightarrow In_5Br_7 + RInBr_2 \tag{22}$$

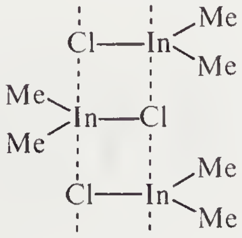
$$In_7Br_9 + 3RBr \longrightarrow RInBr_2 + In_2Br_4 \tag{23}$$

Gallium monohalides are poorly characterized species, but there is one report of the preparation of $RGaI_2$ compounds ($R = Me, Et, Pr^n, Bu^n$) by oxidative insertion.[141] The reaction of $Ga + \frac{1}{2}I_2$ (250 °C, 24 h, *in vacuo*) gives a mixture of Ga, Ga_2I_3 and Ga_2I_4 which over 1–2 weeks reacts with RI to give a solution from which $RGaI_2$ can be recovered. A simpler route involves a reaction mixture of $Ga + \frac{1}{2}I_2$ + excess RI, but the process is still sufficiently slow as to require reaction times of 1–2 weeks at room temperature.

7.6.4 Structure and Properties

The importance of the electron pair acceptor properties of gallium and indium compounds is clearly illustrated by the chemistry of the trihalides,[1,2] and it is therefore not surprising that similar behaviour dominates the structural chemistry of the organometallic halides. There is no evidence of monomeric species in the solid state, and the X-ray and other structural evidence clearly point to the formation of dimers and higher species.

The detailed information from X-ray studies is summarized in Table 7. Such investigations show that dimers exist in the solid state for $MeInCl_2$,[142] while for Me_2InCl the structure consists of stacked alternating molecules which give indium an apparent coordination number of five (**8**).[143] In the Me_2InBr lattice,[144] indium achieves tetragonal bipyramidal stereochemistry, InC_2Br_4, with bromine (but not carbon) atoms shared by neighbouring metal atoms.



(**8**)

Table 7 Important Bond Lengths and Angles in Organometallic Halides of Gallium and Indium and Related Compounds

Compound	*Kernel*	*r(M—C)* (Å)	*C—M—C angle* (°)	*r(M—X)* (Å)		*Other angles* (°)		*Ref.*
Me_2InCl	$C_2InCl(Cl')_2$ approx. trigonal bipyramid	2.179(7)	167.3	Cl Cl′	2.673(9) 2.945(6)	Cl—In—Cl′ In—Cl—In′	86.6 93.4	1
$[MeInCl]_2$ $\equiv Me(Cl)InCl_2In(Cl)Me$	$ClInCl_t(Cl_{br})_2$	2.059(9)	—	Cl_t Cl_{br}	2.384(1) 2.400(1)	Cl_{br}—In—Cl_{br} In—Cl_{br}—In′ Cl_t—In—C	85.3 92.6 129.4	2
Me_2InBr	C_2InBr_4 approx. tetragonal bipyramid	2.116(6) 2.226(7)	all angles ≈90°		3.105			3
$In[C_6H_4(CH_2NMe_2)]_2Cl$	C_2InN_2Cl approx. trigonal bipyramid	2.144(3) 2.154(3)	153.3	Cl N	2.465(1) 2.442(3) 2.482(2)	Cl—In—N C—In—N	89.6 (av) 77.0(1)	4
$MeGaCl_3^-$	$CGaCl_3$ (C_{3v})	1.934(8)			2.211(3) 2.224(3) 2.232(3)			5
$Me_2GaCl_2^-$	C_2GaCl_2	1.975(13) 1.985(13)	99.7(1)		2.276(4) 2.277(4)	C—Ga—Cl	106.8(4)	5
$MeInCl_3^-$	$ClnCl_3$ (C_{3v})	2.183(16)			2.409(3) 2.394(3) 2.397(4)	—		6
$Me_2InBr_2^-$	$C_2InBr_2^-$	2.112(18) 2.212(13)			2.644(3) 2.635(2)			7

1. H. D. Hausen, K. Mertz, E. Veigel and J. Weidlein, *Z. Anorg. Allg. Chem.*, 1974, **410**, 156.
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Spectroscopic investigations (IR, Raman, nuclear quadrupole resonance, mass spectrometry) have also led to the conclusion that associated species are the general rule in the solid state and in solution. The vibrational spectra of $[RGaCl_2]_2$ (R = Me, Et) and $[Et_2GaCl]_2$ show that these compounds are all halogen-bridged dimers,[119,145] like the parent Ga_2Cl_6.[1] Similar conclusions were reached in work on $[Bu^t_2GaX]_2$ (X = Cl, Br),[146] and confirmed by independent molecular weight determinations (in benzene) for $[Bu^nGaCl_2]_2$ and $[Bu^n_2GaCl]_2$.[106] The size of the organic group is not significant here, since dimers exist in benzene for $GaLCl_2$, $GaLBr_2$ and GaL_2Br (L = CH_2SiMe_3),[55] and for the corresponding indium compounds.[59]

Nuclear quadrupole resonance spectroscopy studies (NQR) of Me_2InX (X = F, Cl, Br, I) (^{115}In, halogen resonances) show that Me_2InF is probably similar in structure to Me_2InOAc (see Section 7.9.7), a homopolymer in which the Me_2In groups are non-linear; Me_2InBr and Me_2InI, in contrast, involve linear ClInC units,[147] a conclusion subsequently confirmed for the bromide by X-ray work (see above). The NQR work also confirmed the ionic dimer structure $[Me_2In][InI_4]$ for $MeInI_2$ (*cf.* ref. 138), and showed that $MeInBr_2$ and $EtInI_2$ are both halogen-bridged dimers; IR spectroscopy led to the same type of structure for $MeInBr_2$,[135] $EtInI_2$ and Bu^nInI_2.[138] Further NQR investigations[148] revealed a correlation between the asymmetry parameter[149] and the C—In—C angle in a series of Me_2InX compounds including X = F, Cl, Br and I, taking the difference between ν_s and ν_{as} for ν(In—C) as a measure of this angle. In general then, the accumulated evidence shows that dimerization is the most common type of association in these halides, although higher association (*e.g.* Me_2InBr) is also possible, as is the formation of ionic dimers when the anion is especially stable.

For aryl compounds, a range of methods has been used to show that Ph_nGaX_{3-n} (X = Cl, Br, I; n = 1, 2; all combinations) are again dimers in the solid state,[111] as they are in solution in benzene.[110] Diphenylindium halides, and the dihalides, are polymeric in the solid; $PhInI_2$ may be the ionic dimer $[Ph_2In][InI_4]$.[114] One surprising exception is $(Nap)_2InBr$, which is reported to be monomeric in benzene.[58]

There is little to report on the chemical properties of these organometallic halides. Equation (24) suggests that the halides might find some use as alkylating agents.[150] Another interesting field of enquiry might be the biological activity of these compounds, since the corresponding organometallic compounds of neighbouring elements certainly show a variety of such effects. The only thermochemical information[151] relates to ΔH°_f for $MeGaCl_2$ (-45.1 kJ mol^{-1}) and Me_2GaCl (-52.3 kJ mol^{-1}), and further work in this area could be useful.

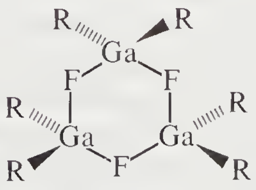
$$R_2InCl \quad + \quad SbCl_5 \quad \longrightarrow \quad InCl_3 \quad + \quad R_2SbCl_3 \qquad (24)$$

$$(R = Me, Et)$$

7.6.5 Organometallic Fluorides

The organometallic fluorides of gallium and indium are sufficiently different in structure from the other halides as to warrant separation from the general discussion given above.

Only two organogallium fluorides have been reported, namely Me_2GaF and Et_2GaF.[109,121,122] The compounds are soluble in a range of organic solvents, and cryoscopic measurements showed that $[Me_2GaF]_3$ and $[Et_2GaF]_3$ are the solute species in benzene. The vibrational spectra of the solids show that this association persists in the solid state, with the six-membered ring structure (**9**). When $(Me_2GaF)_3$ is held at 5–15 °C for 2–3 weeks, the product is the tetramer,[122] now with a Ga_4F_4 ring; slight changes in IR and NMR spectra were reported.



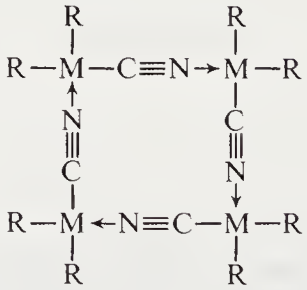
(9)

The indium compounds Me_2InF[108] and Et_2InF[125] have been prepared by the action of $BF_3{\cdot}OEt_2$ or Et_3SnF on the appropriate trialkyl compound. Although the In—Me vibrations of Me_2InF do not differ significantly in frequency from those of other dimethylindium halides, the fluoride has a higher melting point and lower solubility in organic solvents, suggesting a higher degree of association for the latter. This is confirmed by the NQR studies[147] which imply that indium is five-coordinate in the lattice. A systematic study of the structures of such R_2MF compounds would doubtless prove most interesting. Neither adducts of these diorganofluorides, nor organodifluorides, have been reported.

7.6.6 Organometallic Pseudohalides

In addition to the halides, a number of neutral organometallic pseudohalides have been prepared and studied.

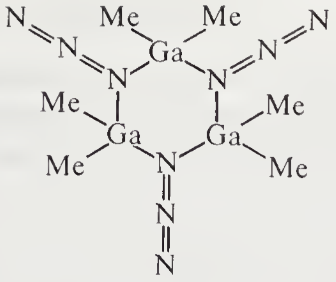
The reaction of HCN with Me_3M in either benzene (M = Ga) or diethyl ether (M = In) yields the tetramer $[Me_2GaCN]_4$,[152] and the same species was also obtained by treating Me_3M with Me_3GeCN.[153] No crystal structure results are available, but molecular weight determinations in benzene identify the tetramer: IR and mass spectrometric data are also reported. The compounds are formulated as cyano-bridged systems (**10**), and this type of association is also invoked for other pseudohalides in which the ambidentate nature of the ligand favours intermolecular association. The gallium compound absorbs four moles of Me_3N, suggesting dissociation of the $Ga_4(CN)_4$ ring to yield $Me_2Ga(CN){\cdot}NMe_3$,[152] and other adducts could presumably also be prepared. Slow hydrolysis in air releases HCN, leaving Me_2GaOH.



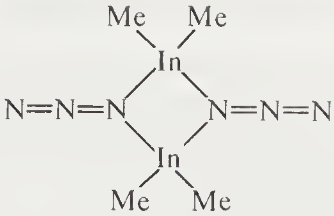
(**10**)

The compounds $[Et_2MSCN]_3$, prepared by the treatment of Et_3M (M = Ga, In) with $(SCN)_2$ in benzene, are viscous hygroscopic oils which can be distilled *in vacuo*.[154] The species in benzene solution is a trimer.

Organometallic azides have been prepared by one of three different routes, namely (a) $R_3M + ClN_3$ (in benzene);[155,156,157] (b) $R_3M + HN_3$ (Et_2O/benzene);[157] (c) $R_3M + Me_3SiN_3$ (with heating).[158] The compounds prepared by these routes are Me_2GaN_3 (a, b, c), Me_2InI_3 (c) and Et_2MN_3 (a). The compounds have differing but useful solubilities in organic solvents; the trimer $[Et_2GaN_3]_3$ is present in benzene, while the dimer $[Et_2InN_3]_2$ is identified in nitrobenzene.[156] The IR and Raman spectra of the solids are compatible with the ring systems (**11**) and (**12**).[155,156] The temperature dependent ^{15}N NMR spectrum of $(Me_2GaN_3)_3$ has been interpreted in terms of azide exchange.[157]



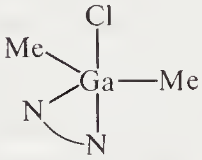
(11)



(12)

7.6.7 Addition Compounds

One of the earliest studies of organogallium chemistry[118] led to a compound formulated as $Me_2GaCl{\cdot}NH_3$ (from HCl on $Me_3GaCl{\cdot}NH_3$). Later work[159] by a more convenient route ($Me_2GaCl + NH_3$ in hexane) showed that the correct formulation is $[Me_2Ga(NH_3)_2]Cl$, in which the gallium is presumably four-coordinate. The related $[Me_2Gaen]Cl$ is readily prepared, and the cation survives the metathetical reaction with Ag_2SO_4 to give $[Me_2Gaen]_2SO_4$, and subsequent reconversion to the chloride. Further studies of these and other presumed cationic complexes might be worthwhile, especially in view of the X-ray crystallographic study of $Me_2Ga(phen)Cl$ obtained from equimolar quantities of Me_2GaOH + HCl + phen. This five-coordinate monomer has distorted trigonal bipyramidal stereochemistry (**13**), but a lack of experimental results prevents any discussion of the factors which determine the coordination number and stereochemistry in such compounds. Other adducts of gallium compounds include an interesting series of 1:1 and 2:1 adducts of 1,4-dioxane with $PhGaCl_2$ and Ph_2GaCl.[112]



(13)

An extensive series of adducts of Me_2InCl, Me_2InI and $MeInCl_2$ has been prepared by direct reaction in appropriate organic solvents.[108,113] IR and conductivity measurements were used in elucidating the probable structures, but again some definitive X-ray work is clearly needed. The compounds prepared include $MeInCl{\cdot}L$ (L = py, Ph_3PO, Ph_3AsO, phen, bipy, en), $Me_2InI{\cdot}L$ (L = py, Ph_3P, Ph_3PO, bipy, en) and $MeInCl_2{\cdot}L$ (L = bipy, terpy, 2py). The compounds are believed to be four-, five- or six-coordinate monomers in the solid state, although the significant conductivity implies rearrangement reactions in solution. Complexes with NH_3 (1:1, 1:2, 1:3) were also identified from tensimetric studies.[113] With Me_2InCl and Ph_2P, the product is a 2:1 adduct, which raises a number of interesting structural possibilities, since the IR spectrum and high conductivity (in MeOH) suggest some significant difference from the other adducts. Two adducts of $CpInI_2$, with bipy and phen, prepared by direct reaction in Et_2O,[13] may involve five-coordination at indium, whereas $Cp_3In{\cdot}PPh_3$ is presumably tetrahedral. Adducts of Me_3SbS and R_nInCl_{3-n} (R = Me, Et; n = 1, 2) are also known.[161]

Two routes to organoindium halide adducts involving unusual reaction pathways were noted above (Section 7.6.3). Reaction of InX and RX in 1,4-dioxane yields the monodioxane adduct as the product (X = Br, I; R = Bz, allyl),[140] and an extensive series of 2,2′-bipyridine adducts was obtained by the electrochemical oxidation of indium in a non-aqueous cell.[131] As the oxidation of the sacrificial anode proceeds, the adduct either precipitates or may be recovered from the solution by addition of Et_2O; the compounds produced in this way were the bipy adducts of Me_2InI, $MeInI_2$, Et_2InI, $EtInBr_2$, $BzInX_2$ (X = Cl, Br, I), $PhInX_2$ (X = Cl, Br, I) and $C_6F_5InBr_2$.

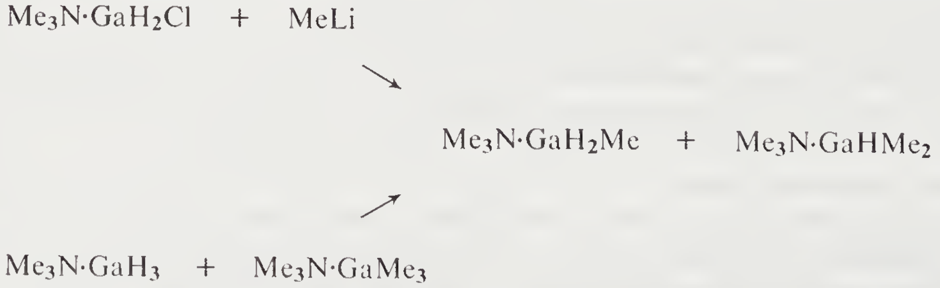
7.7 ORGANOGALLIUM HYDRIDES

The chemistry of gallium hydrides has been a matter of interest for some years, and understandably so in view of the extensive hydrido chemistry of boron and aluminium. This interest has carried over into the organometallic chemistry, with both neutral and anionic compounds now known (see Section 7.8.5).

The earliest attempts at preparing organogallium hydrides involved the passage of a silent electric discharge through a gaseous mixture of Me_3Ga and hydrogen.[162,163] The identification of $(Me_2GaH)_2$ was claimed, along with decomposition to Ga_2H_6 and adducts of Me_3Ga in the presence of tertiary amines, but later workers reported that the products of the Me_3Ga/H_2 reaction were only poorly characterized, with no evidence for the presence of any liquid corresponding to $(Me_2GaH)_2$.[164] The first unambiguous preparation of an organogallium hydride involved the reaction shown in equation (25). The yields are low (25–30%), with Et_3Ga and GaH_3 amongst the other species formed.[109] Another synthetic route investigated without success involved the reaction of Et_2AlH with Et_3Ga, which yielded *inter alia* H_2 and gallium metal, possibly *via* Et_2GaH decomposition. The reaction of H_2 with Et_3Ga at high temperatures and pressures (85–140 °C, 90–100 atm) is very slow, with little evidence of Et_2GaH formation. The compound Et_2GaH is highly pyrophoric, and reacts vigorously with water; addition across a double bond gives rise to mixed alkyl compounds such as $Et_2Ga(C_{10}H_{21})$ (*cf.* ref. 122). The species Bu^i_2GaH is identified as an intermediate in the thermal decomposition of Bu^i_3Ga.[40]

$$Et_2GaCl \;+\; KCl \;+\; AlEt_2H \longrightarrow Et_2GaH \;+\; K[AlEt_2Cl_2] \qquad (25)$$

Despite the difficulties of synthesizing R_2GaH compounds, the preparation of Me_3N adducts of both $MeGaH_2$ and Me_2GaH is simply achieved. Neither the reaction of Me_2Hg with $Me_3N{\cdot}GaH_3$, nor that of excess LiH with $Me_3N{\cdot}MeGaCl_2$, yields the desired adducts, but two other reactions are efficient (namely Scheme 5), with the products depending on the mole ratio of the reactants.[165] The Me_3N adducts are slightly associated liquids, with extended melting over the range 0–20 °C, and are less stable than the analogous boron and aluminum compounds, being similar to $Me_3N{\cdot}GaH_3$ in this respect. The NMR spectra show that each compound undergoes rapid redistribution and exchange in solution to give all the species from Me_3NGaH_3 to Me_3NGaMe_3, and various reaction mechanisms for this exchange were suggested.



Scheme 5

The general conclusion then must be that while the Me_3N adducts are relatively easily prepared and studied, the uncomplexed organogallium hydrides are unstable and incompletely characterized. No indium analogues have been reported, paralleling the absence of known inorganic indium–hydrido compounds.

7.8 ANIONIC COMPLEXES

7.8.1 Introduction

One way in which inorganic MX_3 complexes demonstrate their Lewis acid character is by forming anionic complexes MX_{3+n}^{n-}, in which the value of n depends on the nature of X^-, and to some extent on the properties of the balancing anion.[2] Given that organo-gallium and -indium compounds are also electron pair acceptors, it is not surprising that a number of salts of the corresponding anionic complexes have been prepared and studied. These complexes may either involve four identical organic groups as ligands (*i.e.* MR_4^-) or a mixture of organic and halogeno (or pseudohalogeno) ligands $[MR_nX_{4-n}]^-$. There appear to have been no reports of mixed complexes of the type $[MR_nR'_{4-n}]^-$ or $[MR_n(X,Y)_{4-n}]^-$.

7.8.2 Tetra-alkyl and -aryl Complexes

Potassium or rubidium salts of the $GaMe_4^-$ anion can be prepared by the treatment of Me_3Ga with the metal (mole ratio 5:6) in THF.[166,167] The salts are isostructural with the aluminium analogues, and were shown by X-ray crystallography to contain $GaMe_4^-$ anions (see Table 2 for structural details). The compounds are very hygroscopic, but not pyrophoric. The indium analogues $MInMe_4$ (M = Li, Na, K, Rb, Cs) were again prepared by treating Me_3In with the appropriate metal, or in the case of lithium by the direct reaction of LiMe with $InMe_3$.[168] The properties are similar to those of the gallium complexes. Structural details have been reported for the Li and Na salts,[168] and later for the K and Cs analogues.[169] Salts with Me_4P^+, Me_4As^+ and Me_4Sb^+ cations have also been prepared,[170] and the vibrational spectra analyzed; ν(M—C) modes are identified in the region of 490 (Ga) and 450 (In) cm^{-1}. A detailed analysis yielded force constants for these anions and their isoelectronic neighbours; the values of f_r in the series $InMe_4^-$, $SnMe_4$ and $SbMe_4^+$ are 1.304, 2.096 and 2.643 N cm^{-1}, respectively, demonstrating a very pronounced effect of formal charge on the stretching force constant, and therefore presumably upon the bond strength.

The reaction of an alkali metal with Ph_3In again gives the anionic complexes $MInPh_4$ (M = Li, Na, K, Rb, Cs).[171] The structure involves $InPh_4^-$ anions in which the InC_4 kernel is essentially tetrahedral; ν(In—C) is reported to be in the region of 440 cm^{-1}. The $[In(indenyl)_4]^-$ anion, as the lithium salt, has been prepared by the more conventional route of reacting MeLi with indene and $InCl_3$ in benzene; similar reactions in ether gave $Li[In(indenyl)_4]{\cdot}OEt_2$.[9] The ν(In—C) vibrations were identified as being in the 340–370 cm^{-1} region, substantially lower than in the $InPh_4^-$ anion, and some further work on the reality of these assignments seems required.

Anionic complexes with ethylenic ligands have been prepared by using $MGaH_4$ (M = Na, K) and the appropriate 1-alkyne as starting materials, so that with $HC{\equiv}C(CH_2)_4R$ (R = H, Me, Et) the products are $M[Ga(CH{=}C(CH_2)_4R]_4$ although ligand exchange to $M[Ga(C{\equiv}C(CH_2)_4R]_4$ may also occur; the ratio of products is said to depend on the reaction conditions.[172] With $HC{\equiv}CPh$, the product from $NaGaH_4$ is $Na[Ga(C(CH_2)Ph)_4]$. A general observation is that $NaGaH_4$ is less reactive in these respects than the corresponding aluminium compound.

There seems to have been little or no investigation of the chemical properties of GaR_4^- or InR_4^- anions, and even such matters as redistribution reactions in solution have not yet been studied in detail.

7.8.3 Anionic Organometallic Halide Complexes

Anionic complexes in which gallium or indium is bonded to both alkyl and halide ligands can be prepared by the conventional reaction of R_3M with R'_4NX, which has been used to obtain Me_4N^+ salts of R_3GaF^- (R = Me, Et) and Me_3GaBr^-.[173] The method involves condensing an equimolar quantity of R_3M on to the tetraalkylammonium salt *in vacuo*. If two molar equivalents of R_3M are used, the products are of the form $R'_4N[(R_3Ga)_2X]$ (R = Me, Et; X = F, Cl, Br; not Et/F), in which the anion has the structure $[R_3GaXGaR_3]^-$. The IR spectra of these anions have been analyzed.[173] Another approach uses Me_2GaOH as starting material; reaction with HCl in Et_2O, or with $SOCl_2$, yields salts of $MeGaCl_3^-$.[160]

A group of interesting papers discusses the use of Me_3AsX_2 and Me_3SbX_2 as halogenating agents for Me_3M (M = Ga, In). A typical reaction is shown in equation (26)[174] and a series of $Me_{4-n}MX_n^-$ anions (M = Ga, In; X = Br, I; n = 1, 2, 3) can be obtained by using Me_3M or Me_2MX as starting material with Me_3AsX_2, Me_4AsX or the corresponding antimony halides.[150,175] The existence of the anionic complexes was demonstrated by vibrational spectroscopy, and later X-ray studies[176–178] gave detailed structural information (See Table 7). In addition to assignments of the vibrational spectra, the ^1H NMR spectra for all 12 compounds[175] show some nice correlations, as exemplified by the results in Scheme 6. These ^1H NMR frequencies also correlate with the mean ν(M—C) frequency, and $\Delta\nu$(In—C) correlates with the C—In—C angle derived from X-ray results.[178] Similar discussions of the results for neutral Me_2MX compounds are noted in Section 7.6.4. All in all, these anionic complexes have been subjected to a very thorough structural examination, with satisfying agreement between X-ray, vibrational and ^1H NMR results.

$$\mathrm{Me_3AsBr_2 \;+\; Me_3In \;\longrightarrow\; [Me_4As][Me_2InBr_2]} \tag{26}$$

		Me_3MX^-	$Me_2MX_2^-$	$MeMX_3^-$
Ga	Br	24	2	−28
	I	45	20	−17
In	Br	26	11	−30
	I	41	20	−18

^1H NMR data (δ, p.p.m.) for anionic halide complexes

Scheme 6

The only aryl complex reported to date is $CpInI_3^-$, formed by the simple addition of Pr^n_4NI to $CpInI_2$,[13] but no doubt other anions could be synthesized by similar methods. A general route to $RInX_3^-$ (R = Me, Et, Ph, Bz; X = Cl, Br, I) is *via* the electrochemical oxidation of the metal in non-aqueous solutions of RX in MeCN containing R'_4NX; the yields are typically 80–90%, based on metal dissolved.[131] No doubt the method could also be applied to gallium, and to combinations of R and X other than those actually used.

One interesting group of anionic complexes is the bridged species $[R_3GaXGaR_3]^-$ obtained by treating R_4NX with 2 mol of condensed R_3Ga (R = Me, Et; X = F, Cl, Br; not Et/Br).[171] These are the analogues of the inorganic $X_3GaXGaX_3^-$ anions.[179] Another series are the anions $[X(MMe)_4]^{2-}$, formed by condensing excess Me_3M (M = Ga, In) on to K_2X or Cs_2X (X = O, S, Se; not In/O).[180] The structure proposed on the basis of the vibrational spectra is a tetrahedral arrangement of Ga or In atoms around a central X^{2-}, with methyl groups occupying the remaining cubic corners, and the remaining terminal positions of the four-coordinate metal. It could be interesting to establish how many other such non-metallic elements could serve to bridge organogallium or -indium groups in this way.

7.8.4 Anionic Organometallic Pseudohalide Complexes

As with the neutral compounds, anionic species containing both alkyl and pseudohalide ligands are known, and again the ambidentate properties of the ligand give rise to some interesting structural possibilities. The neutral complex $[Me_2GaN_3]_3$ reacts with molten Me_4NN_3 to give $Me_4N[Me_2M(N_3)_2]$, which in the presence of excess Me_3Ga affords $[Me_2Ga(N_3)_2(GaMe_3)_2]^-$.[181] Cyano, thiocyanato and cyanato compounds of the form $Me_4N[R_3GaX]$ (R = Me, Et) have been synthesized by the direct addition of R_3Ga and Me_4NX, but again other compounds can be formed, depending on the mole ratio of the reagents.[182] With Me_4NCN (or Me_4NN_3)[181] and Me_3Ga, the primary product is $Me_4N[(Me_3Ga)_2CN]$, whose anion is presumably analogous in structure to $[Me_3GaXGaMe_3]^-$ or an oligomer of such species. With Me_4NNCO and Me_4NNCS, the only products are $Me_4N[Me_3GaNCO]$ or $[Me_3GaSCN]^-$, while the cyano analogue can be obtained by heating $Me_4N[(Me_3Ga)_2CN]$ at 120 °C *in vacuo*.[182] With $K_2Hg(CN)_4$ and Me_3Ga as starting materials, the product is $K[Me_2Ga(CN)_2]$.[183]

It seems probable that these and related methods could be used to synthesize the whole range of $[R_nMX_{4-n}]^-$ pseudohalides, bridging the gap between inorganic and organometallic complexes.

7.8.5 Anionic Organometallic Hydrido Complexes

Gavrilenko and co-workers have conducted a series of preparative and other studies of $[R_nMX_{4-n}]^-$ anions. The gallium compounds are apparently more readily prepared than the indium analogues, in keeping with the known inorganic chemistry of these elements. The simplest preparation is *via* $Me_3Ga + LiH \rightarrow Li[Me_3GaH]$,[184] but another interesting route involves the reaction of Ga/Mg mixed powder with Et_2O or Bu_2O; after the initial vigorous reaction, MeI, and then LiH, are added to give $Li[Me_3GaH]$ *via* the initially formed Me_3Ga. The sodium salt was also reported, but not that of potassium, for which the product is said to be GaH_3. Later syntheses involved redistribution reactions between $NaGaR_4$ and $NaGaH_4$, $NaGaR_4$ and $NaGaR'_4$, $NaGaEt_4$ and Me_3Ga, and $NaGaH_4$ and Et_2Mg, leading to $Na[R_nGaH_{4-n}]$ ($R \neq R' = Me, Et$).[167] This paper also noted that while direct reaction of Et_3Ga with NaH or KH gives $M[Et_3GaH]$, the product with LiH is $LiH{\cdot}2Et_3Ga$; it is possible that the latter anion is a bridged species $[R_3GaHGaR_3]^-$ and further investigations would seem warranted.

As noted above, the organoindium hydrido anions are less stable than the gallium compounds. The reaction of Me_3In with MH (M = Li, Na, K) gives an unstable species MMe_3InH which decomposes to $MInMe_4$, MH and indium metal.[185] A later report refers to the reaction of MH (M = Li, Na, K) with R_3In or R_2InCl, and the products MR_3InH (R = Me, Et) are reported, as is $NaEt_2InH_2$, but again decomposition to $MInMe_4$ is important.[186] Such compounds should prove useful as a starting point for further syntheses by utilizing the reactivity of the M—H bond.

7.9 REACTIONS OF R_3M WITH ACIDS

7.9.1 Introduction

One of the most important reactions of organometallic chemistry is the elimination of alkane or arene between $\geqslant$M—R and HX which provides a convenient preparative route to a large number of organometallic derivatives. Gallium and indium compounds are no exception to this, and in the following sections we review the many examples involving R_3Ga and R_3In. The preparation of organometallic halides (see Section 7.6.1) and the elimination of alkane from adducts (see Section 7.5.3) provide other instances of the generality of these reactions. The latter processes suggest that the most attractive mechanism involves the formation of an unstable adduct from which alkane elimination then occurs.

A most convenient arrangement is in terms of the final product (*i.e.* M—O, M—O_2, M—ON, *etc.*), although we shall begin with a discussion of the parent R_2M^+ cation, and the compounds formed by hydrolysis of R_3M are also singled out for separate treatment.

One important point to note at the outset is that for gallium and indium the only product from the reaction of R_3M and excess HX is generally R_2MX. Even the use of forcing conditions rarely leads to the loss of more than one R group so that we are concerned essentially with the synthesis and structural study of R_2MX compounds, where X represents a wide range of organic bases. Structural results are collected in Table 6.

7.9.2 R_2M^+ Cations

In addition to their importance as the parent unit of R_2MX compounds, R_2M^+ cations are of interest in their own right, since they represent the lowest coordination number for M(III) derivatives. The stability of the R_2M^+ cation in any medium must depend *inter alia* on the properties of the balancing anion, and especially its nucleophilicity, and on the properties of the group R. In practice the results are confined to R = Me or Et, perhaps because of the ease of preparation of the parent compounds, but the use of ligands such as CH_2SiMe_3 might lead to significant stabilization.

Dissolution of Me_2GaOH in the appropriate aqueous acid yields solutions of Me_2GaClO_4 or Me_2GaNO_3 in which the cation is uncomplexed by the anion, but is apparently coordinated by two H_2O molecules. The Raman spectrum (ν_{sym} ~555, ν_{as} 618 cm^{-1}) implies a bent C_{2v} structure,[187] probably similar to $Me_2Ga(NH_3)_2$, *etc.*[159] Later work[188,189] with R_2MSO_4 confirmed the results for Me_2Ga^+, and gave corresponding values for Et_2Ga^+. The chemical shifts in the ^1H NMR spectrum of Me_2Ga^+ are close to those for TMS.[187,188] The aqueous phase hydrolysis of $[MeGa(OH_2)_2]^+$ has been studied, and the formation constant for $[Me_2GaOH]_2$ derived.[190]

The vibrational spectra for Me_2In^+ (from aqueous solutions of Me_2InClO_4 at 0 °C) were first interpreted in terms of a linear C—In—C kernel,[191] but later studies on the hydrolysis of Me_2InOAc[192] and $Me_2In(MeSO_3)$[189] showed that C_{2v} symmetry is the correct assignment. Comparisons with the known coordination chemistry of indium(III) suggest that the species in solution is probably *cis*-$[InMe_2(H_2O)_4]^+$, and also that other complexes of the type $[InR_2L_n]^+$ should be accessible (n = 2, 3, 4, depending on the neutral donor L).

A number of workers have claimed the identification of Me_2In^+ in the solid state, and in all cases the anion is known to be weakly- or non-coordinating. The compound $MeInI_2$ is formulated as $Me_2In^+\cdot InI_4^-$ on the basis of vibrational spectroscopy,[138] plus the fact that the compound is a 1 : 1 electrolyte in nitromethane. Similar conductivity and NMR evidence leads to the structure $Me_2In^+[B_{10}H_{12}InMe_2]^-$ for one of the compounds obtained from the reaction of Me_3In and $B_{10}H_{14}$.[193] Other compounds formulated as ionic species include Me_2InReO_4[148] and $Me_2InSbCl_6$,[150] as is Ph_2InInI_4 (= $PhInI_2$).[114]

The gas phase represents the ultimate in non-coordinating media, and R_2M^+ has been identified as the predominant ion in the mass spectra of a number of organo-gallium and -indium compounds.[50,194,195] This stability is presumably explained by the fact that R_2Ga^+ and R_2In are isoelectronic with the corresponding (stable) neutral zinc and cadmium compounds.

7.9.3 Hydroxides, Alkoxides, *etc.*

7.9.3.1 Organometallic hydroxides and related compounds

The decomposition of many organo-gallium and -indium compounds by water is often an extremely exothermal reaction, but under controlled conditions, it is possible to obtain some of the intermediates in the complete hydrolysis to alkane and metal hydroxide. These R_2MOH compounds are of some interest then in the context of hydrolysis reactions and also in that they represent the prototype of a series of R_2MOR' species.

The controlled hydrolysis of $Me_3Ga\cdot OEt_2$ by small quantities of water produces the compound Me_2GaOH which is a crystalline sublimable solid, soluble in a number of organic solvents.[196] On heating (*e.g.* 150 °C, 6 h) the substance loses CH_4 to give $[(Me_2GaO)_n]$. A slightly conflicting report[197] identified $[(Me_2Ga)_2O]_n$ as the hydrolysis product, and the formation of a 1 : 1 adduct with Me_3N was reported, but it may well be that this latter work involved different experimental conditions from those used by Kenny and Laubengayer.[196] The Me_2GaOH compound is polymeric in benzene solution, and the solid state structure[199] is of a tetramer, based on a puckered Ga_4O_4 ring. The substance dissolves in aqueous perchloric or nitric acids with no cleavage of the Ga—C bonds, and can be precipitated from aqueous $HClO_4$ solution with NaOD to give Me_2GaOD.[187] The tetramer is not present in significant concentrations in aqueous solution.[190] Hydrolysis of Et_3Ga yields $(Et_2GaOH)_n$, which on heating becomes $(Et_2GaO)_n$.[109]

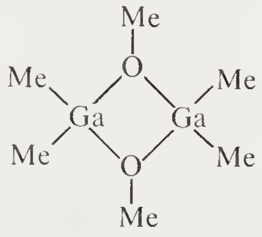
The corresponding Me_2InOH compound has not apparently been prepared. The compound $(Me_2In)_2O$ was identified[51] as one product in the hydrolysis of Me_3In, while other workers report that the material is MeInO.[113] An early study of Ph_3In reported that the oxidation product of that molecule is $(Ph_2In)O$, although the latter was not completely characterized.[200]

A molecule which may be structurally related to these organometallic oxides is EtInS, which is obtained in >90% yield from the reaction of Et_3In with $(Me_2SnS)_3$ (equation 27) or a similar process with Ph_2SnS.[124] The high melting point (>250 °C), and the insolubility in common organic solvents may be the result of polymerization, as with the oxides.

$$Et_3In \quad + \quad (Me_2SnS)_3 \quad \xrightarrow{C_6H_6} \quad EtInS \quad + \quad Me_2Et_2Sn \tag{27}$$

7.9.3.2 Organometallic alkoxides and aryloxides

A series of compounds related to Me_2GaOH is derived by alkane elimination between Me_3Ga and ROH, and some indium derivatives are known. The reactions between Me_3Ga and MeOH, MeSH and MeSeH yield the crystalline solids $[Me_2GaOMe]_2$, *etc.*,[201] which are dimeric in the vapour phase and formulated as oxo-bridged molecules (**14**) with structures similar to those in Ga_2N_2 species (*e.g.* (7)). The bridging can be disrupted by Me_3N which forms 1 : 1 adducts with the —SMe and —SeM compounds, but not with the alkoxide. This compound can also be obtained by the reaction of MeOH with the peroxy derivative $Me_2GaOOMe$,[202] which itself can be regarded as an interesting derivative of Me_2GaOH. Two analogous compounds are Bu^t_2GaOMe and $Bu^t_2GaOBu^t$,[146] and it would be interesting to establish the degree of association of the latter in view of the presence of the bulky Bu^t group.



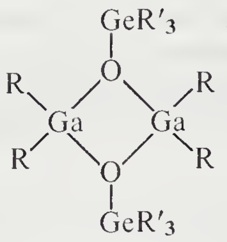
(**14**)

The indium analogue Me_2InOMe was prepared by the reaction of Me_3M with MeOH, and is a glassy colourless material which cannot be crystallized, suggesting some extensive polymerization in the solid state,[89] and Bu^tOH similarly gives rise to the dimers $[Me_2MOBu^t]_2$ (M = Ga, In). An interesting route to a related compound is the reaction[108] of Me_3In with $(CF_3)_2CO$, which yields $Me_2InOC(CF_3)_2Me$, again emphasizing the easy cleavage of the first In—C bond. The reaction of Ph_3In with PhCHO produces Ph_2CO, and the indium product is suggested to be Ph_2InOBz, but this material was not characterized.[200]

Aryloxides can be prepared by the treatment of Me_3Ga with the appropriate phenol to give the dimeric species $[Me_2GaOC_6H_4R]_2$ (R = H, Bu^t).[201] Similar thio and seleno compounds are also obtained, and all of these compounds form 1 : 1 adducts with Me_3N, indicating cleavage of the oxo bridging. Thiol derivatives of Ph_3Ga and Ph_3In have also been synthesized, with both Ph_2MSR and $PhM(SR)_2$ species reported (M = Ga, In; R = $C_{12}H_{25}$).[203,204]

7.9.3.3 Silyloxy and germyloxy derivatives

The silicon and germanium compounds $R_2MOER'_3$ (E = Si, Ge) expand the group of R_2MOH derivatives. The silyl compounds can be prepared in the standard way from $Me_3M + R_3SiOH$ (M = Ga, In; R = Me, Ph) and in each case the products are the dimers $[Me_2MOSiR_3]_2$, which are solids or high melting liquids.[205] The germanium compounds can be synthesized from $R_3M + Ph_3GeOH$, or $R_2MCl + LiOGeMe_3$, and the products include $[Me_2MOGeMe_3]_2$, $[Me_2GaOGePh_3]_2$ and $[Ph_2GaOGeR_3]_2$ (R = Me, Ph).[203,206] The structures are of the type (**15**), similar to (**14**), with a planar $GeOGa_2OGe$ moiety, and questions as to the type of bonding which gives rise to such planarity have inevitably been discussed in terms of π-bonding.

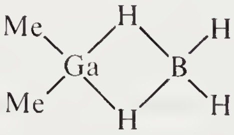


(15)

Further products which correspond to the elimination of two methyl groups have been prepared by reacting $MeMCl_2$ (M = Al, Ga) with Me_3SiONa to give $[MeM(OSiMe_3)_2]_2$ and a presumably anionic derivative is $K[Me_2M(OSiMe_3)_2]$ (M = Al, Ga, In).[207] No structural information is available on these species.

7.9.4 Metal–Boron Bonds

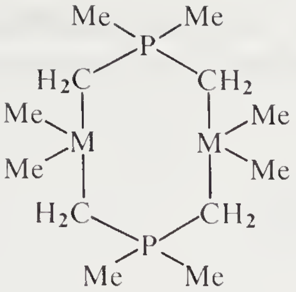
The reaction of Me_3Ga and B_2H_6 leads to the thermally fragile compound Me_2GaBH_4; an alternative route is *via* $Me_2GaCl + LiBH_4$.[208] Gas phase electron diffraction[209] shows a monomeric structure (**16**) in the gas phase. The molecule is decomposed by HCl, and forms adducts (NMe_3, NH_3) of unknown structure. Decaborane and Me_3In react at room temperature to give the salt $[Me_2In][B_{10}H_{12}InMe_2]$ which is a 1:1 electrolyte in solution.[193] The structure of the $B_{10}H_{12}InMe_2^-$ anion is a matter of speculation. The gallium species $[(\mu\text{-}Me_2Ga)C_2B_4H_7]$ is obtained from Me_2GaCl and $Na[2,3\text{-}C_2B_4H_7]$ and corresponds structurally to the bridge insertion of Me_2Ga into a B—B bond.[210] It seems probable that an extensive chemistry remains to be explored in the interaction of boron hydrides with R_3Ga and R_3In compounds.



(16)

7.9.5 Metal–Carbon Bonds

The absence of suitable hydrogen atoms attached to carbon normally prevents the synthesis of R_2MR^1 molecules by alkane elimination, but nevertheless a small number of such reactions have been demonstrated. One of these, the formation of $CpInMe_2$ from Me_3In and CpH, has been noted earlier[24] (see Section 7.3.4). The remaining examples relate to the work of Schmidbaur and his colleagues on the reactions between $Me_3P{=}CH_2$ and related compounds and Me_3Ga or Me_3In. Both compounds form highly reactive but thermally stable adducts $Me_3P^+CH_2\bar{M}R_3$ (M = Ga, In, R = Me; M = Ga, R = Et) which are monomers in benzene,[211] but the product of reacting $Me_3P{=}CH_2$ with Me_2MX (M = Ga, In; X = Cl, Br) (2:1 mole ratio) is the cyclic ylide (**17**).[212] The bisphosphorane $Me_3P{=}C{=}PMe_3$ reacts with $Me_3Ga{\cdot}OEt_2$ to give the compound (**18**)[213] whose structure has been confirmed by X-ray diffraction studies.[214] A related GaC_2P_2N ring system, in which N replaces CH above, is obtained from the reaction of Me_3Ga and $Me_3P{=}N{-}P(Me_2){=}CH_2$[215] (see also Section 7.9.6).



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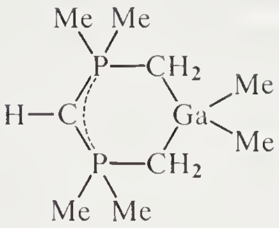
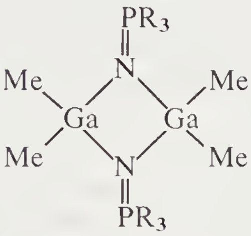


(18)

7.9.6 Metal–Nitrogen Bonds

One group of R_2MN_2 bonded molecules can be prepared by reactions parallel to those just discussed. Both Me_3Ga and Me_3In form thermally stable 1 : 1 adducts with $R_3P{=}N{-}SiMe_3$ (R = Me, Et, Ph), with donation from the nitrogen atom,[216] and $R_3P{=}N{-}GeMe_3$ behaves similarly,[217] but the corresponding adduct of $R_3P{=}N{-}SnMe_3$ loses Me_4Sn readily to give $[R_3PNGaMe_2]_2$ (R = Me, Et) which is formulated as (**19**) with the familar Ga_2N_2 ring system.[217] Again, the bisphosphoranes are more reactive, so that compounds $Me_2Si(N{=}PR_3)_2$ may form 1 : 1 adducts (Me_3Ga, Me_3In), 1 : 2 adducts (Me_3In), or undergo rearrangement and ring closure to (**20**).[218] Finally, the compound $Me_3SiN{=}P(Ph_2)_2NHSiMe_3$ reacts with Me_3M (M = Ga, In) by methane elimination, again yielding a cyclic product (**21**).[219]



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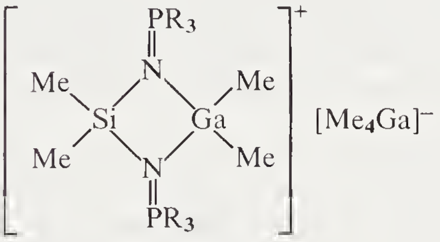

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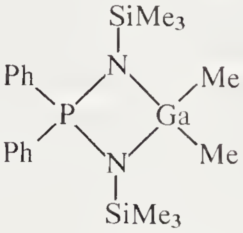
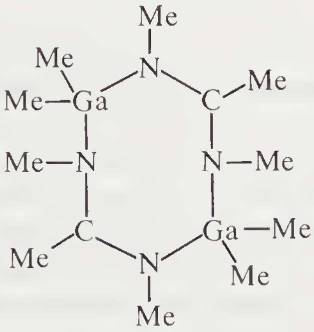


(21)

The reactions of other perhaps simpler N—H acids have also been investigated. Both *N*-methyl-[220] and *N*,*N*-dimethyl-acetamide[221] react to give $R_2MN(Me)Ac$ and $R_2MN(Me)_2Ac$ (M = Ga, In; R = Me, Et), and the crystal structure[222] of the Me_2Ga derivative confirms the predicted eight-membered puckered $(GaNCN)_2$ ring (**22**). *N*,*N'*-Dimethyloxamidine similarly yields (**23**) (M = Ga, In) which has been shown to be an essentially planar bicyclic system.[223]



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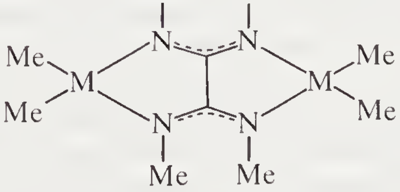
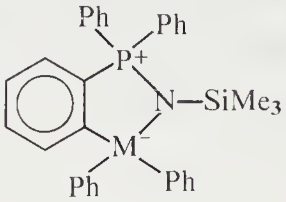


(23)

An interesting series of compounds derives from pyrazole (Hpz) which reacts with Me_3Ga or Et_3Ga under mild conditions to yield $[R_2Gapz]_2$.[224] The dimeric formulation was confirmed by an X-ray study of $[Me_2Ga(Me_2pz)]_2$, in which the Ga_2N_4 ring was identified.[225] An interesting derivative is the hydrolysis product $Me_2Ga(OH^-)(Me_2pz)GaMe_2{\cdot}2Me_2pzH$ in which the ring is now N_2Ga_2O. Anionic derivatives of the neutral dimer are obtained *via* the sodium salt of formula $Na[Me_2Ga(pz)_2]$, and an interesting series of transition metal derivatives has also been prepared.[226]

The 1 : 1 adducts of Ph_3Ga with $Ph_3P{=}NSiMe_3$ lose 1 mol C_6H_6 at 230 °C to give the cyclic compound (**24**) containing N—M—C units *via* orthometallation of a phenyl ring.[227,228]

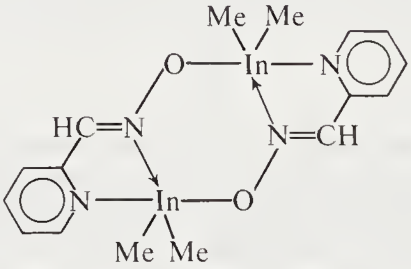


(**24**)

7.9.7 Metal–Nitrogen, –Oxygen Bonds

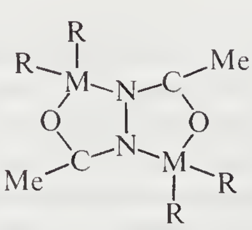
There are a significant number of organic acids which have other basic functional groups in the molecule, and of course such compounds are potential bidentate ligands. Of particular concern in the present section are those in which the reaction of R_3M with —OH or —NH leads to the formation of $R_2\underline{MO^\frown N}$ structures.

Oximes constitute an important class of OH acids, and typically the reaction of Me_2CNOH with Me_3M (M = Ga, In) yields the dimer $[Me_2C{=}NOMMe_2]_2$.[229] A similar reaction involves Me_3Ga or Me_3In with pyridine-2-carbaldehyde oxime (=HL),[230] and a subsequent X-ray investigation of the $[Me_2InL]_2$ compound confirmed the structure (**25**).[231] In contrast, the reaction between Et_3Ga and 8-hydroxyquinoline gave the monomeric product $Et_2GaONC_9H_6$.[232] Two products were obtained from *N*,*N*-ethylenebis(salicylideneimine) ($=H_2L$), namely Me_2GaLH monomer, and the digallium compound $L(GaMe_2)_2$, in which the GaC_2NO kernel has distorted tetrahedral stereochemistry.[233]



(**25**)

An interesting situation is found in the products of the reaction of Me_3Ga with $H_2NC_2H_4OH$[234] and $Me_2NC_2H_4OH$,[235] in that the first yields the monomer $Me_2\overline{GaOC_2H_4N}H_2$, whereas the latter produces a dimer based on a Ga_2O_2 central ring and a $\overline{GaOC_2N}$ outer ring. Structural determinations have also been reported on transition metal derivatives including $Ni\{Me_2Ga(OC_2H_4NH_2)(pz)\}_2$[236] and $[Me_2Ga(OC_2H_4NH_2)(pyz)]_2Cu_2(pz)_2$.[237] More conventional products were obtained from Me_3In and 2-substituted pyrroles (R = CHO, COMe),[238] and from *N*,*N*-diacetylhydrazine,[239] where the product is the bicyclic species (**26**). Studies of derivatives of H(R)NCOCON(R)H (R = H, Me) demonstrated the existence of isomerism arising from the different ring formations which may occur.[240–242]

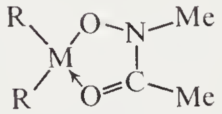


(**26**)

7.9.8 Metal–oxygen bonds

In addition to the compounds formed with carboxylate ligands (see Section 7.9.8.1), derivatives of a number of other OH acids are known. Dimethyl-gallium and -indium acetylacetonates are readily prepared,[89,201] and these or related trifluoromethyl[243] compounds have been the subject of NMR studies of ligand exchange kinetics,[243,244] albeit with different conclusions as to the mechanism involved. A related monomeric product is obtained from the reaction of Me_3Ga with Ac_2NH,[245] and has understandably similar spectroscopic properties to $Me_2Ga(acac)$.

A series of sulphinates, $Me_2MO_2SMe_2$, has been reported,[246] as have the analogous derivatives of O_2PF_2, O_2PCl_2, O_2PH_2, O_2PMe_2 and $O(S)PMe_2$[247–251] (M = Ga, In). Dimeric structures are found except for $Me_2InO(S)PMe_2$, where the molecularity (in benzene solution) is 1.66. The dimer formation is explained in terms of eight-membered $M_2O_4P_2$ rings, on the evidence from vibrational and ^{31}P NMR spectroscopy,[248–251] and this is confirmed by X-ray work.[252] Hydroxyamato derivatives are monomeric (**27**) (R = Me, Et; M = Ga, In),[253] while the reaction of Me_3Ga with salicylaldehyde gives a dimeric product in which the gallium is five-coordinate, with a C_2GaO_3 kernel.[254] Compounds obtained from the reaction of R_3In (R = Me, Et) with alkyl nitro compounds may also involve M—O bonding, although some X-ray structural evidence on these interesting $R_2InO_2NCH_2$ compounds would be welcome.[255,256]



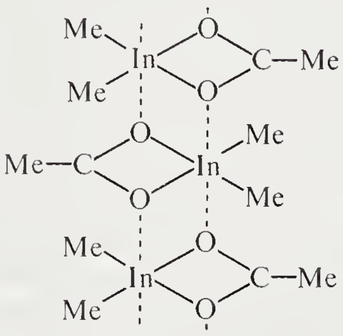
(**27**)

It now appears that the products of the reaction of SO_2 with Me_3In are in fact not simple adducts but sulphinates, either $In(O_2SMe)_3$ or the dimeric $Me_2In(O_2SMe)_2InMe_2$.[257,258] Similar conclusions were reached for R_3M/SO_3 systems[189] where the products are formulated as (*e.g.*) $Me_2Ga(O_3SMe)$, which on dissolution in water is reported to give $Me_2Ga^+_{(aq)}$ ions.

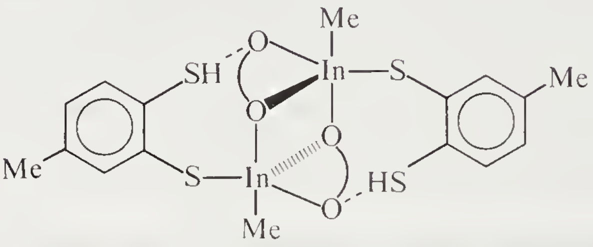
7.9.8.1 Organometallic carboxylates

Trimethylgallium reacts with acetic acid in benzene eliminating methane and forming $Me_2Ga(OAc)$. Molecular weight determinations show that the substance is dimeric in solution,[201] but in view of later work on related organo-gallium and -indium acetates, it would not be surprising if the solid material were polymeric. The reaction of $Me_3Ga{\cdot}OEt_2$ with excess acetic acid gives $MeGa(OAc)_2$, which is again associated in benzene ($n \approx 2$–3.3), but an X-ray structural determination revealed a homopolymeric lattice in which gallium is found in two different sites. In one of these, the metal is in distorted trigonal bipyramidal GaO_4C stereochemistry, while the other is a distorted tetrahedral GaO_3C site. In each case, bridging by acetato groups is responsible for the polymeric nature.[260] The only other acetate derivative reported is Bu^t_2GaOAc, whose vibrational spectrum has been briefly discussed.[146]

The carboxylate derivatives of trialkylindium are all of the type $R_2InO_2CR^1$, with no evidence for displacement of two alkyl groups, although it is clear that under sufficiently forcing conditions complete elimination of $3CH_4$ can lead to the formation of $In(O_2CR)_3$ (R = H, Me, Et, Pr^n, Bu^s, Bu^t).[261] The product of the reaction of Me_3In and HOAc in ether is $Me_2In(OAc)$,[113] whose chemical properties (solubility, mass spectrum) suggested that the solid state structure is a homopolymer. This was confirmed by a subsequent X-ray crystal structure determination[262] which revealed the presence of six-coordinate indium, with the InC_2O_4 kernel being formed by two carboxylate oxygens of the 'bonded' acetato group and two greater distances from the acetato ligands of two neighbouring Me_2InOAc units (**28**). The polymeric nature of solid Me_2InOAc has some interesting consequences in terms of further elimination reactions involving the methyl groups and dibasic acids, since 2, 1 or $\frac{2}{3}$ mol CH_4 may be eliminated per Me_2InOAc depending on the acid involved and upon the reaction conditions. For example with the acid toluene-3,4-dithiol (H_2TDT),[263,264] the reaction sequence can be written as in Scheme 7; the proposed structure for the dimer is (**29**), and it is suggested that the unreacted acidic hydrogen atom of HTDT is hydrogen bonded to an acetato oxygen atom. When the reaction is carried out in ethanol, $[MeInOAc(HTDT)]_2$ is precipitated, but in DMSO the reaction proceeds smoothly with elimination of $2CH_4$ to give In(OAc)(TDT). Equally dimer (**27**) decomposes on being dissolved in DMSO, eliminating $2CH_4$ per dimer, and it is presumed that the monomer MeIn(OAc)(HTDT)(DMSO) is formed by breakdown of the bridging acetato linkages in this basic solvent. The ability of this substance to react in monomeric or dimeric form is also revealed by its coordination chemistry, where adducts may be of the type $Me_2In(OAc)L$ (L = DMSO, py), $[Me_2InOAc]_2L$ (L = bipy, phen) or $Me_2In(OAc)L$ (L = en, diphos).[265] The first of these types is presumed to be five-coordinate and monomeric (*e.g.* InC_2O_2N) and the last six-coordinate (*e.g.* $InC_2O_2N_2$), while the bipy and phen derivatives are identified as dimeric Me_2InOAc units in which each indium atom is coordinated to one basic nitrogen of the bidentate ligand. It would be interesting to see to what extent other bridged organometallic polymers display similar behaviour.



(28)



(29)

$$Me_2InOAc \xrightarrow[-CH_4]{H_2TDT} \underset{(\mathbf{29})}{\text{dimer}} \longrightarrow \begin{matrix}\text{solvated}\\ \text{monomer}\end{matrix} \xrightarrow[-CH_4]{} In(OAc)TDT$$

Scheme 7

Diethylindium acetate is also a bridged polymer[192,265] with a solid state structure very similar to that of the dimethyl analogue, in that indium achieves six-coordination *via* bridging carboxylate groups. In the related thiocarboxylate compound $Et_2InO(S)CMe$, indium is five-coordinate (InC_2O_2S), with only the oxygen atom of the thiocarboxylate involved in bridging.[266] The electron pair acceptor property of indium and gallium obviously plays a most important role in the chemistry of these compounds, both in determining the solid state structure and in generating the formation of a variety of adducts. The behaviour of Me_2InOAc in this regard was discussed above, and $Me_2GaO(S)Me$ similarly forms a 1 : 1 adduct with pyridine.[267] Another polymeric carboxylate derivative is that formed from Me_3Ga and proline;[268] gallium is here five-coordinate (GaC_2O_2N).

The synthesis of the dialkyl thiocarboxylates can be achieved by two routes. The more obvious is by alkane elimination between R_3M (or $R_3M{\cdot}OEt_2$) and MeCOSH (M = Ga, In; R = Me, Et); alternatively R_3M reacts with gaseous COS which by insertion yields $R_2MO(S)CR$.[269] Parallel reactions of R_3M (M = Ga, In; R = Me, Et) have been used to obtain R_2MO_2CR compounds.[270] Oxalic acid derivatives $[(R_2M)_2O_4C_2]$ (R = Me, Et; M = Ga, In) are also readily prepared.[271] The structure of the Me_2Ga compound is based upon an almost planar $GaO_2C_2O_2Ga$ unit.[272]

Triaryl compounds also undergo elimination reactions, and by appropriate choice of conditions the compounds $PhM(O_2CR)_2$ and Ph_2MO_2CR can be obtained (M = Ga, In; R = Me, Et).

Monochloracetic acid has also been successfully used in such work. The products are colourless infusible solids, and information on their structure could make for an interesting comparison with the alkyl compounds.[273,274]

7.9.9 Metal–Sulphur Bonds

Dithiophosphinic acids were the subject of studies paralleling those noted above (Section 7.9.8.1); one notable difference is that $Me_2GaS_2PMe_2$ is monomeric in benzene. The same situation prevails with $Me_2InS_2CNMe_2$, and $RIn(S_2C{=}NMe_2)_2$ (R = Me, Et),[275] but the reaction between toluene-3,4-dithiol (H_2TDT) and Me_3In gives polymeric MeIn(TDT), from which adducts with ligands such as py, DMSO, bipy, *etc.* can be formed; these may be monomeric or dimeric, apparently depending on the steric properties of the ligand.[276]

7.10 COMPLEXES WITH TRANSITION METAL CARBONYLS

The preparation of compounds in which a main group element is bonded to one or more transition metal carbonyl, or organometallic carbonyl, groups has been well developed for both gallium and indium (*cf.* Chapter 41). Most of these compounds are of the type ML_3 or $X_{3-n}ML_n^{n-}$ (L = transition metal anion, X = halogen), but a small number of compounds are known with alkyl or aryl groups in place of halogen. Thus the reaction between Me_3Ga and $CpW(CO)_3H$ gives $Ga[W(CO)_3Cp]_3$ or $Me_2Ga[W(CO)_3Cp]$ depending on the reaction conditions, and $MeGa[W(CO)_3Cp]_2$ is also identified as an intermediate from studies of the rate of reaction. Other compounds made by this route include $Et_2Ga[W(CO)_3Cp]$ and $Me_2Ga[W(CO)_2(Ph_3P)Cp]$.[277] Similar reactions have been reported between Me_3Ga and $M(CO)_3CpH$ (M = Mo, W), and again both GaL_3 and Me_2GaL compounds were reported. The crystal structure of $Me_2Ga[W(CO)_3Cp]$ shows that the Me_2Ga moiety is bonded to tungsten, with almost trigonal geometry at gallium in the $WGaC_2$ kernel. Exchange and redistribution reactions in solution were identified by NMR methods; in these compounds, as in those discussed earlier, the ^1H resonances of the methyl groups bonded to gallium are close to those in TMS.[278]

No comparable organoindium compounds have been prepared, despite an extensive investigation of Me_3In with transition metal carbonyl hydride complexes (M = Mo, W, Re, Fe, Co). In each case the products were InL_3, rather than $Me_{3-n}InL_n$.[279]

A second series of compounds involves the addition of transition metal carbonyl anions, which are Lewis bases, to Ph_3Ga or Ph_3In.[280,281] The reactions occur readily in solution, and the resultant anionic complexes include $Ph_3MCo(CO)_4^-$ (M = Ga, In), $Ph_3InMn(CO)_5^-$, $Ph_3InW(CO)_3Cp^-$ and $Ph_3MFe(CO)_2Cp^-$ (M = Ga, In). Measurements of the formation constants for the equilibrium (28) (m^- = transition metal carbonyl anion) lead to the conclusion that a delicate balance of factors must be invoked to explain the results. The order of base strengths is found to be $Fe(CO)_2Cp^- \gg W(CO)_3Cp^- > Mn(CO)_5^- > Co(CO)_4^-$; with $Mn(CO)_5^-$, $Ph_3In > Ph_3Ga$, but for other anions $Ph_3Ga \geqslant Ph_3In$. An especial interest attaches to $Ph_3Ga/W(CO)_3Cp^-$, since equal concentrations of the Ga—W—CO and Ga—OC—W linkage isomers are present in CH_2Cl_2 solution. The latter isomer is structurally similar to the adducts studied earlier by Shriver *et al.* in terms of the basic properties of the oxygen atoms of carbonyl ligands.[282]

$$Ph_3M \quad + \quad m^- \quad \rightleftharpoons \quad Ph_3Mm^- \tag{28}$$

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8

Thallium

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8.1 INTRODUCTION

Thallium can take the oxidation state of both +1 and +3 when it forms organometallic derivatives that are sufficiently stable to isolate. Among the thallium(III) compounds, diorganothallium(III) derivatives have been known since almost the earliest classical organometallic chemistry (19th century).[1] Studies on tri- and mono-organothallium(III) derivatives, however, began as late as about 1930.[2,3] The isolation of the first organothallium(I) compound, namely C_5H_5Tl, was reported some five years after the discovery of the then new type of chemical bonding in ferrocene.[4]

Since about 1960 there has been a steady progress of modern organothallium chemistry with emphasis on the aspects of bonding, coordination, structure and spectroscopy.[5] A rapid expansion of organic syntheses with the aid of thallium compounds in recent years[6] has particularly stimulated studies of reactivity and mechanism of organothallium compounds.

8.2 THALLIUM(III) COMPOUNDS

For the organic derivatives of thallium(III) it seems more conventional to classify the compounds according to the number of organic groups bound to the metal *via* carbon, for each class exhibits quite distinct stability and reactivity trends. Triorganothallium compounds are very liable to thermal decomposition, air oxidation and hydrolysis. The ease with which monoorganothallium compounds undergo reductive decomposition is obviously one of the bases for some key steps involved in thallium-mediated synthetic reactions (see Chapter 47). On the other hand, the dialkyls and diaryls are by far more stable and less reactive than the other two classes of compound.

8.2.1 Triorganothallium Compounds

8.2.1.1 Preparation and properties

The triorganothallium compounds, R_3Tl (R = Me, Et, Bu^i, Ph), are usually prepared by the reaction between the corresponding diorganothallium halides and the organolithium or the Grignard reagents in diethyl ether or THF.[5] An alternative and more convenient method of preparing Me_3Tl is the reaction between thallium(I) iodide and methyllithium in the presence of methyl iodide (equation 1).[5] This reaction may proceed *via* the formation of methylthallium(I), which either disproportionates (equation 2) or reacts with methyl iodide (equation 3). The thallium formed in equation (2) may react with methyl iodide to regenerate methylthallium(I) (equation 4). Triferrocenylthallium can also be prepared by a reaction similar to equation (1).[7]

$$2MeLi + MeI + TlI \longrightarrow Me_3Tl + 2LiI \tag{1}$$

$$3MeTl \longrightarrow Me_3Tl + 2Tl \tag{2}$$

$$MeTl + MeI \longrightarrow Me_2TlI \tag{3}$$

$$2Tl + MeI \longrightarrow MeTl + TlI \tag{4}$$

The tris(pentafluorophenyl)[8] and tris(polychlorophenyl)[9] derivatives are prepared from $TlCl_3$ and the lithium or the Grignard reagents in one step. The polyfluorophenyl derivatives, R_3Tl (R = 2,3,4,5-, 2,3,4,6- or 2,3,5,6-C_6HF_4 or 2,4,6-$C_6H_2F_3$), can be obtained, although not isolated as such but as dioxane or bipy adducts, from the corresponding diorganothallium compounds either through reductive symmetrization (equation 5),[10] decarboxylation[11] or desulfination[12] (equation 6).

$$3R_2TlBr + 2Cu \longrightarrow 2R_3Tl + TlBr + 2CuBr \tag{5}$$

$$R_2TlO_2YR \longrightarrow R_3Tl + YO_2 \tag{6}$$

$$Y = C, S$$

Dimethyl(ethynyl)thallium compounds are prepared from RC≡CH (R = H, Me, Ph) and Me_2TlNH_2[13] or Me_3Tl.[14] Dimethyl(cyclopentadienyl)thallium can similarly be obtained from cyclopentadiene and Me_3Tl.[14]

Representative triorganothallium compounds and their physical properties are shown in Table 1.

Trimethyl- and triethyl-thallium decompose, sometimes explosively, when heated above 90 °C in the former and 125 °C in the latter case; they are also light sensitive. When heated above its melting point, Ph_3Tl decomposes into thallium with the formation of some biphenyl.[15] The dissociation energy for the first Tl—C bond of Me_3Tl has been estimated as 152 kJ mol^{-1} from a kinetic study of pyrolysis in a toluene gas carrier flow system.[16] This is smaller than the corresponding values for Me_3Ga (249 kJ mol^{-1}) and Me_3In (197 kJ mol^{-1}).

Table 1 Triorganothallium Compounds

Compound	*M.p.* (°C) *or b.p.* (°C/mmHg)	*Ref.*
Me_3Tl	38.5	1
Et_3Tl	43/1	2
Bu^i_3Tl	74–76/1.6	3
Ph_3Tl	188–189	3
$[(C_5H_5)Fe(C_5H_4)]_3Tl$		4
$(C_6F_5)_3Tl$	139–141	5
$(C_6Cl_5)_3Tl$	280	6
$(2,3,5,6\text{-}Cl_4C_6H)_3Tl$	209	6
$Me_2(C_5H_5)Tl$		7
$Me_2(MeC{\equiv}C)Tl$		8
$Me_2(PhC{\equiv}C)Tl$		8
$Me_2TlC{\equiv}CTlMe_2$		8

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8.2.1.2 Coordination chemistry

Trimethylthallium is a crystalline solid at room temperature which contains a polymeric three-dimensional framework constructed of Tl—Me· · ·Tl bridges (Figure 1).[17] The compound is formally isostructural with Me_3In. The coordination for thallium is a distorted trigonal bipyramid with the three short bonds equatorial (2.22, 2.30 and 2.34 Å) and the two long bridge bonds apical (3.16 and 3.31 Å). The polymer dissociates into monomers in benzene solution and in the vapor phase.

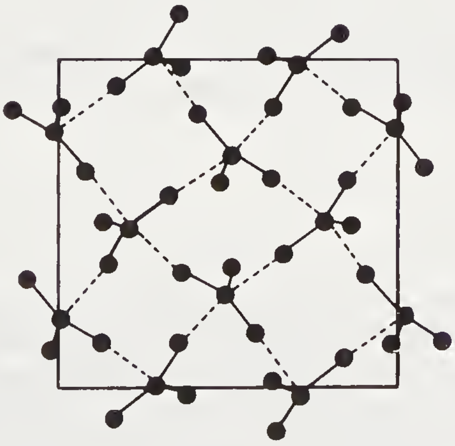
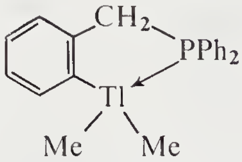


Figure 1 The structure of Me_3Tl in projection down the *z*-axis; full lines represent 'short' Tl—C bonds and broken lines 'long' Tl—C bonds (From *J. Chem. Soc.* (*A*), 1970, 28).

Some solid complexes of the formula R_3TlL or R_3TlL_2 can be isolated, although most of these complexes dissociate rather readily into their components at higher temperatures. Typical examples are shown in Table 2. The triorganothallium compounds are apparently much weaker acceptors than the corresponding indium and gallium analogues.

Table 2 Coordination Compounds of Triorganothallium

Compound	*M.p.* (°C)	*Ref.*
$\mathrm{Me_3TlPMe_3}$	27–28	1
$\mathrm{Ph_3TlNMe_3}$		2
$\mathrm{(C_6F_5)_3Tlbipy}$	202–203	3
$\mathrm{(C_6Cl_5)_3Tl(py)_2}$	285	4
	76–80	5
$\mathrm{Me_3\overset{-}{Tl}CH_2\overset{+}{P}Me_3}$	53–54	6
$\mathrm{Li[Me_4Tl]}$		7
$\mathrm{[Bu^n_4N][(C_6F_5)_4Tl]}$	127 dec.	8
$\mathrm{[Bu^n_4N][(C_6F_5)_2(C_6Cl_5)_2Tl]}$	142 dec.	8
$\mathrm{K[(MeC{\equiv}C)_4Tl]}$		9

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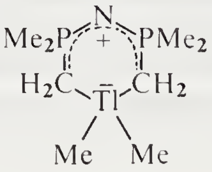
Other compounds containing a four-coordinate thallium atom are ate complexes of the type $[R_4Tl]^-$. Typical examples are also shown in Table 2. All of those in the table except $[Me_4Tl]^-$ can be obtained by simply adding the corresponding carbanion to Me_3Tl, $(C_6F_5)_2TlBr$ or $TlCl_3$. Even a six-coordinate complex, $[Bu^n_4N]_3[(C_6F_5)_6Tl]$, can be isolated in a similar way.[18] The preparation of $[Me_4Tl]^-$ is shown below. The reaction of Me_3Tl with the double ylide $Me_3P{=}N{-}PMe_2{=}CH_2$ affords an interesting ate complex (**1**).[19] The reaction between $[Me_4Tl]^-$ and $Me_3SnSnMe_3$ gives the mixed ate complexes $[Me_n(Me_3Sn)_{4-n}Tl]^-$ (n = 1, 2, 3).[20]



(**1**)

The other type of ate complexes, $[R_3TlX]^-$, can be obtained by adding halide ions to the triorgano compounds. Typical examples include $[Me_3TlCN]^-$, $[Me_3TlFTlMe_3]^-$[21] and $[(C_6F_5)_3TlCl]^-$.[18]

8.2.1.3 Reactions

Trimethyl- and triphenyl-thallium react with mercury according to equation (7).[5] On the other hand, both gallium and indium metals are known to react with Me_2Hg, giving Me_3M (M = Ga, In) and mercury metal. The reaction of Me_3Tl with lithium has been used for the preparation of the tetramethylthallate as shown in equation (8).[20] The analogous reaction of Me_3Tl with potassium, however, has been reported to give a thallium(II) compound, $K_2[Me_3TlTlMe_3]$.[22] The polarographic reduction of Ph_3Tl in DMF at −30 °C is assumed to produce the anion $[Ph_4Tl]^-$ as the primary product.[23]

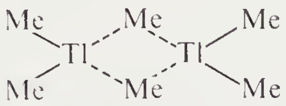
$$2R_3Tl + 3Hg \longrightarrow 3R_2Hg + 2Tl \qquad (7)$$

R = Me, Ph

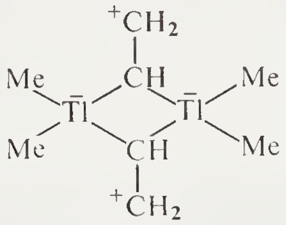
$$4Me_3Tl + 3Li \longrightarrow 3Li[Me_4Tl] + Tl \qquad (8)$$

Intermolecular exchange of methyl groups occurs in solutions of Me_3Tl, as is evident from the disappearance of Tl–H spin-spin couplings in the proton NMR spectra.[24] A dimeric transition state (**2**) may be assumed for this reaction. The methyl exchange rates observed in dimethyl ether or trimethylamine solution are slower than in benzene. This can be attributed to a weak complex formation between Me_3Tl and those donor solvents.

A rapid exchange of alkyl groups also occurs in mixtures of Me_3Tl and Et_3Tl, generating the mixed compounds Me_2EtTl and $MeEt_2Tl$.[25] Vinyl groups of $Me_n(CH_2{=}CH)_{3-n}Tl$ ($n = 1, 2$) undergo a much more rapid exchange, presumably owing to a greater stabilization of the dimeric transition state by the bridging vinyl groups as shown in (**3**). The cyclopentadienyl ligand in $Me_2(C_5H_5)Tl$, possibly bound to thallium in an η^1 fashion, also undergoes a rapid intermolecular exchange, but no redistribution reaction of the compound is evident.[14]



(**2**)



(**3**)

Another redistribution reaction of synthetic interest is that between Me_3Tl and $Tl\{W(CO)_3Cp\}_3$ to give $Me_2Tl\{W(CO)_3Cp\}$ (equation 9).[26]

$$2Me_3Tl \quad + \quad Tl\{W(CO)_3Cp\}_3 \quad \longrightarrow \quad 3Me_2Tl\{W(CO)_3Cp\} \tag{9}$$

Exchange of organic groups occurs also with other organometallic compounds, the typical example being shown in equation (10).[5] Trimethylthallium reacts with $Hg(SiMe_3)_2$ to give a tris(silyl)thallium compound as shown in equation (11).[5]

$$Ph_3Tl \quad + \quad 3Bu^nLi \quad \longrightarrow \quad Bu^n{}_3Tl \quad + \quad 3PhLi \tag{10}$$

$$2Me_3Tl \quad + \quad 3Hg\{SiMe_3\}_2 \quad \longrightarrow \quad 2Tl\{SiMe_3\}_3 \quad + \quad 3Me_2Hg \tag{11}$$

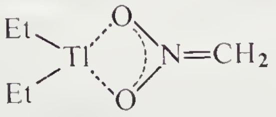
One of the three organic groups of triorganothallium is cleaved with great ease by the action of various electrophiles, including acids and halogens, as typically shown in equations (12)–(14).[5] Protolysis of R_3Tl with water or alcohols does not proceed further than the R_2TlY stage (Y = OH, OR). The reaction of Me_3Tl with cyclopentadiene and phenylacetylene to give the interesting mixed compounds has already been described. Similarly, the reaction between Me_3Tl and diazomethane[27] or that between Et_3Tl and nitromethane[28] gives the largely ionic compounds $(Me_2Tl)_2CN_2$ or $Et_2Tl(CH_2NO_2)$, respectively. The latter has been indicated by vibrational spectroscopy to contain Tl—O rather than Tl—C bonding, as shown in (**4**). The reaction of R_3Tl (R = Me, Et) with $MH(CO)_3Cp$ (M = Mo, W),[26] $B_{10}H_{14}$[29] or Et_3MH (M = Si, Ge)[5] affords the thallium–metal bonded compounds $Me_2Tl\{M(CO)_3Cp\}$, $[Me_2Tl][Me_2Tl(B_{10}H_{12})]$ (**5**) or $Tl(MEt_3)_3$.

$$Me_3Tl \quad + \quad HCl \quad \longrightarrow \quad Me_2TlCl \quad + \quad CH_4 \tag{12}$$

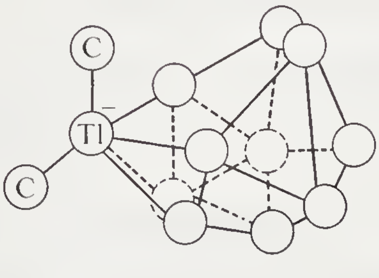
$$R_3Tl \quad + \quad ClN_3 \quad \longrightarrow \quad R_2TlN_3 \quad + \quad RCl \tag{13}$$

$$R = Me, Et$$

$$Ph_3Tl \quad + \quad Se(SeCN)_2 \quad \longrightarrow \quad Ph_2TlSeCN \quad + \quad PhSeCN \quad + \quad Se \tag{14}$$



(**4**)



(**5**)

Insertion of SO_2 and SO_3 into the one Tl—C bond of Me_3Tl occurs as shown in equation (15).[30,31] The reaction of Et_3Tl with oxygen in octane initially affords $Et_2TlOOEt$, which subsequently decomposes into Et_2TlOH when heated at 50 °C.[32] Similarly, $(Ph_2Tl)_2O$, phenol and biphenyl have been found in the products of a slow oxidation of Ph_3Tl with dry oxygen.[5] The carbene $:CCl_2$ inserts into the Tl—C bond of Et_3Tl to yield the unstable intermediate (**6**), which undergoes chlorine abstraction as shown in equation (16).[33]

$$\mathrm{Me_3Tl} \quad + \quad \mathrm{SO}_n \quad \longrightarrow \quad \mathrm{Me_2TlO}_n\mathrm{SMe} \qquad (15)$$

$$n = 2, 3$$

$$\mathrm{Et_3Tl} \quad + \quad \mathrm{:CCL_2} \quad \longrightarrow \quad \underset{(\mathbf{6})}{\mathrm{Et_2TlCCl_2Et}} \quad \longrightarrow \quad \mathrm{Et_2TlCl} \quad + \quad \mathrm{CHCl{=}CHMe} \qquad (16)$$

8.2.2 Diorganothallium Compounds

8.2.2.1 Preparation and properties

Various organometallic compounds are available for the preparation of relatively inert diorganothallium derivatives. The reaction of Grignard reagents with $TlCl_3$ (equation 17) is the most usual way of preparing diorganothallium halides, although yields are sometimes poor owing to the oxidation of the Grignard reagents by $TlCl_3$.[5] Some di-*n*-alkylthallium bromides, R_2TlBr (R = normal alkyl with carbon number 1 to 10), can also be prepared in a moderate yield by a one-step reaction between RMgBr and TlBr in a 1:2 mole ratio. However, in an analogous reaction of aryl or secondary alkyl Grignard reagents, there have been obtained only coupled products in moderate yield.

$$\mathrm{2RMgX} \quad + \quad \mathrm{TlCl_3} \quad \longrightarrow \quad \mathrm{R_2TlX} \quad + \quad \mathrm{MgXCl} \qquad (17)$$

Diaryl- and divinyl-thallium derivatives can conveniently be obtained in aqueous solution by the reaction of the corresponding organoboronic acids with TlX_3 (equation 18; X = halogen, carboxylate).[5] Aryl and vinyl derivatives of mercury, tin, lead and bismuth also react with TlX_3 to give the same organothallium products. On the other hand, the analogous reaction of the *alkyl* derivatives of these metals with $TlCl_3$ is much less satisfactory due to the formation of TlCl as the main product. The use of $Tl(OAc)_3$, instead of $TlCl_3$, in the reaction with methyl- and ethyl-tin compounds leads to the formation of good yields of dimethyl- and diethyl-thallium compounds.[5]

$$\mathrm{2RB(OH)_2} \quad + \quad \mathrm{TlX_3} \quad \xrightarrow{\mathrm{H_2O}} \quad \mathrm{R_2TlX} \quad + \quad \mathrm{2B(OH)_3} \quad + \quad \mathrm{2HX} \qquad (18)$$

The organo-boron and -tin compounds are also useful for obtaining mixed diorganothallium compounds, as typically shown in equations (19) and (20).[5,34,35] On the other hand, ethyl and cyclohexyl Grignard reagents have been shown to react with $PhTlCl_2$ to give only a mixture of symmetrical diorganothallium chlorides, Ph_2TlCl and R_2TlCl (R = Me, cyclo-C_6H_{11}).[5] Methyl(phenylethynyl)thallium derivatives are obtained by the reaction of MeTlO with PhC≡CH in refluxing methanol in the presence of air (equation 21), followed by treatment of the resulting carbonate with appropriate anions.[5]

$$\mathrm{MeTl(O_2CPr^i)_2} \quad + \quad \mathrm{Bu_3(R)Sn} \quad \longrightarrow \quad \mathrm{Me(R)TlO_2CPr^i} \quad + \quad \mathrm{Bu_3SnO_2CPr^i} \qquad (19)$$

$$\mathrm{R = CH_2{=}CHCH_2,\ C_5H_5}$$

$$\mathrm{PhTlCl_2} \quad + \quad \mathrm{4\text{-}MeC_6H_4B(OH)_2} \quad \xrightarrow{\mathrm{H_2O}} \quad \mathrm{Ph(4\text{-}MeC_6H_4)TlCl} \quad + \quad \mathrm{B(OH)_3} \quad + \quad \mathrm{HCl} \qquad (20)$$

$$\mathrm{2MeTlO} \quad + \quad \mathrm{2PhC{\equiv}CH} \quad \xrightarrow{\mathrm{CO_2}} \quad \mathrm{[Me(PhC{\equiv}C)Tl]_2CO_3} \quad + \quad \mathrm{H_2O} \qquad (21)$$

Diazomethane reacts with $TlCl_3$ or $ArTlCl_2$ (Ar = Ph, 4-MeC_6H_4) to give $(CH_2Cl)_2TlCl$ or $Ar(CH_2Cl)TlCl$, respectively.[5,36]

Treating the diorganothallium halides with salts of silver(I) or thallium(I) is a very convenient way of obtaining diorganothallium salt-type compounds. Furthermore, the reaction of the halides with TlOH or TlOEt gives the organothallium hydroxides or ethoxides which serve, when treated with compounds containing an acidic hydrogen, as good starting materials for various organothallium salt and chelate-type derivatives.

The reaction of mesitylene- or polyfluorobenzene-sulfinate anions with $Tl(OAc)_3$ affords diarylthallium compounds *via* desulfination, as typically shown in equation (22).[37,38]

$$3NaO_2SR \quad + \quad Tl(OAc)_3 \quad \longrightarrow \quad R_2TlO_2SR \quad + \quad 2SO_2 \quad + \quad 3NaOAc \qquad (22)$$

$$R = 2,4,6\text{-}Me_3C_6H_2$$

Other methods of preparing the diorgano compounds of practical value include the reaction of $ArTl(O_2CCF_3)_2$ with trimethyl phosphite[39] (*cf.* Section 8.2.3.3) and those of the triorgano compounds described in Section 8.2.1.3.

Table 3 lists representative diorganothallium halides and their physical properties.

The lower dialkyl- (*e.g.* dimethyl- or diethyl-), divinyl- and diphenyl-thallium halides are stable solids of very high melting or decomposition points. These halides except the fluorides are not very soluble in water, alcohols or other common solvents except for pyridine or aqueous ammonia. The higher linear alkyl analogues, as well as $(Me_3YCH_2)_2TlCl$ (Y = C, Si), are likewise stable, and even more soluble. Other branched-chain alkyl analogues such as Pr^i_2TlCl, Bu^s_2TlCl and Bu^i_2TlCl decompose more easily when heated. Bis(pentafluorophenyl)thallium halides are more soluble than the diphenyl analogues.

Salts of dimethylthallium hydroxide and inorganic acids such as nitric, sulfuric, perchloric and chromic acids are soluble in water, but much less so in organic solvents.

Table 3 Diorganothallium Halides

Compound	*M.p.* (°C)	*Ref.*
Me_2TlF		1
Me_2TlCl	>280 dec.	2
Me_2TlBr	295 dec.	2
Me_2TlI	264–266 dec.	2
Et_2TlCl	205–206 dec.	2
Pr^n_2TlCl	198–202 dec.	2
Bu^n_2TlCl	240–250 expld.	3
Bu^s_2TlCl	150 expld.	3
$(Me_3CCH_2)_2TlCl$	>340	4
$(Me_3SiCH_2)_2TlCl$	238	4
$(cyclo\text{-}C_6H_{11})_2TlCl$	210–230 expld.	3
$(trans\text{-}MeCH{=}CH)_2TlCl$	>310	5
$(cis\text{-}MeCH{=}CH)_2TlCl$	>310	5
Ph_2TlCl	>310	6
$(C_6F_5)_2TlCl$	237–239	7
$(C_6Cl_5)_2TlCl$	314	8
$MeEtTlCl$	>250	9
$(4\text{-}MeC_6H_4)(CH_2Cl)TlCl$	265–266	10

1. E. Krause and A. von Grosse, *Ber.*, 1925, **58,** 272.
2. R. J. Meyer and A. Bertheim, *Ber.*, 1904, **37,** 2051.
3. E. Krause and A. von Grosse, *Ber.*, 1925, **58,** 1933.
4. H. Kurosawa, S. Numata, T. Konishi and R. Okawara, *Bull. Chem. Soc. Jpn.*, 1978, **51,** 1397.
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7. G. B. Deacon, J. H. S. Green and R. S. Nyholm, *J. Chem. Soc.*, 1965, 3411.
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9. M. Tanaka, H. Kurosawa and R. Okawara, *Inorg. Nucl. Chem. Lett.*, 1967, **3,** 565.
10. T. Abe and R. Okawara, *J. Organomet. Chem.*, 1972, **43,** 117.

8.2.2.2 Coordination chemistry

Most of diorganothallium salt-type compounds ionize in polar solvents to form a linear, more or less solvated cation, R_2Tl^+.[40] The ion Me_2Tl^+, being isoelectronic with Me_2Hg, is only a very weak aquo-acid, and the bonds to the water molecule in the first coordination sphere are very weak. A Raman spectrum of even Me_2TlOH in water is very similar to those of Me_2TlY ($Y = NO_3$, ClO_4), showing no lines attributable to $\nu(Tl—O)$.[41] The undissociated portion of the hydroxide may exist as ion pairs.

Other than undergoing ionic dissociation the diorgano compounds can form both intra- and inter-molecular coordination bonds. An increase of the coordination number for thallium appears to become prominent particularly in the solid state, as revealed by X-ray crystallography. In Table 4 are shown typical coordination geometries of diorganothallium compounds determined by X-ray structural studies.

Table 4 Coordination Geometry in Diorganothallium Compounds

Compound	*Geometry*[a]	*C.N.*[b]	*∠C—Tl—C* (°)	*Ref.*
$Ph_2TlS_2CNEt_2$	TD	4	148	1
Me_2TlOPh	TBP	4	173	2
Me_2TlSPh	TBP	4	163.5	2
$(Me_3SiCH_2)_2TlCl$	TBP	4	168	3
$(2,3,5,6\text{-}F_4C_6H)_2TlBr$	TBP	5	144.2 149.9	4
$(2,3,5,6\text{-}F_4C_6H)_2TlCl(Ph_3PO)$	TBP	5	140.6	5
$(C_6F_5)_2TlOH$	TBP	5	138.5	6
$(C_6F_5)_2Tl\{N(2\text{-pyridyl})_2\}$	TBP	5	127	7
Me_2Tl(tryptophanate)	OH	5	165.7	8
Ph_2Tl(tropolonate)	PBP	5	162.6	1
Me_2TlCl	OH	6	180	9
$[Me_2Tl][Me_3AlNCS]$	OH	6	177	10
Me_2TlCN	OH	6	180	11
Me_2TlN_3	OH	6	180	11
$Me_2TlC(CN)_3$	OH	6	178.7	12
Me_2TlO_2CMe	PBP	6	171.8	13
Me_2Tl(acac)	PBP	6	170.0	13
Et_2Tl(sal)	PBP	6	172	14
$[Me_2Tl(phen)]ClO_4$	PBP	6	168.3	15
Me_2Tl(L-phenylalaninate)	PBP	6	163.7 165.6	16
$Me_2TlSSCOMe$	PBP	7	170.9	17

[a] Most approximate geometry for thallium: TD, tetrahedral; TBP, trigonal bipyramidal; OH, octahedral; PBP, pentagonal bipyramidal. [b] Coordination number for thallium.

1. R. T. Griffin, K. Henrick, R. W. Matthews and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1980, 1550.
2. P. J. Burke, L. A. Gray, P. J. C. Hayward, R. W. Matthews, M. McPartlin and D. G. Gillies, *J. Organomet. Chem.*, 1977, **136**, C7.
3. F. Brady, K. Henrick, R. W. Matthews and D. G. Gillies, *J. Organomet. Chem.*, 1980, **193**, 21.
4. G. B. Deacon, R. J. Phillips, K. Henrick and M. McPartlin, *Inorg. Chim. Acta*, 1979, **35**, L335.
5. K. Henrick, M. McPartlin, R. W. Matthews, G. B. Deacon and R. J. Phillips, *J. Organomet. Chem.*, 1980, **193**, 13.
6. H. Luth and M. R. Truter, *J. Chem. Soc. (A)*, 1970, 1287.
7. G. B. Deacon, S. J. Faulks, B. M. Gatehouse and A. J. Jozsa, *Inorg. Chim. Acta*, 1977, **21**, L1.
8. K. Henrick, R. W. Matthews and P. A. Tasker, *Acta Crystallogr. (B)*, 1978, **34**, 935.
9. H. D. Hausen, E. Veigel and H. J. Guder, *Z. Naturforsch., Teil B*, 1974, **29**, 269.
10. S. K. Seale and J. L. Atwood, *J. Organomet. Chem.*, 1974, **64**, 57.
11. Y. M. Chow and D. Britton, *Acta Crystallogr. (B)*, 1975, **31**, 1922.
12. Y. M. Chow and D. Britton, *Acta Crystallogr. (B)*, 1975, **31**, 1934.
13. Y. M. Chow and D. Britton, *Acta Crystallogr. (B)*, 1975, **31**, 1929.
14. G. H. W. Milburn and M. R. Truter, *J. Chem. Soc. (A)*, 1967, 648.
15. T. L. Blundell and H. M. Powell, *Chem. Commun.*, 1967, 54.
16. K. Henrick, R. W. Matthews and P. A. Tasker, *Acta Crystallogr. (B)*, 1978, **34**, 1347.
17. W. Schwarz, G. Mann and J. Weidlein, *J. Organomet. Chem.*, 1976, **122**, 303.

It is notable that most of the C—Tl—C angles observed in the *dialkyl* derivatives deviate from linearity only slightly. This is the case even in discrete four-coordinate complexes where the ideal geometry around thallium may approach the tetrahedron. Furthermore, many of the observed Tl—ligand distances are much longer than the sum of the covalent radii for the thallium and donor atoms. These facts are again in line with the weakly polarizing effect of the dialkylthallium cation upon the ligands surrounding itself. On the other hand, due to the greater electronegativity of the *polyfluorophenyl* groups than those of the *alkyl* groups, cations such as $(C_6F_5)_2Tl^+$ would be expected to be stronger acids than the dialkylthallium cations.

Several adducts can be isolated by the reaction of Me_2Tl^+ with Lewis bases such as py, phen, bipy, DMSO and en.[5] The structure of $[Me_2Tl(phen)]ClO_4$ has been solved by an X-ray crystal study (Figure 2).[42] This is a distorted pentagonal-bipyramidal structure with one equatorial position vacant. The Tl—N bonds are short enough to permit partial covalent character, but the two oxygen atoms are located at distances appropriate for an electrostatic bond. Complexation also occurs between Me_2Tl^+ and dicyclohexyl-18-crown-6 to give the rigid compound [Me_2Tl(crown)]picrate (**7**).[43] The rigidity of the complexation in (**7**) is such that the two methyl groups can be distinguished from each other in proton NMR spectra.

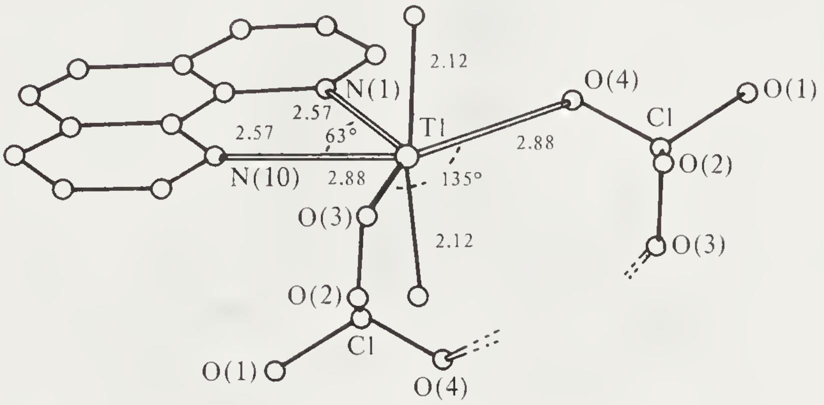
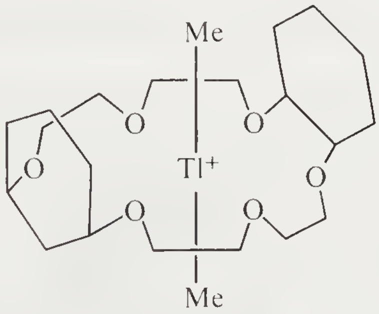


Figure 2 The structure of $[Me_2Tl(phen)]ClO_4$ (From *Chem. Commun.*, 1967, 54).



(**7**)

The crystal structure of a polymeric compound, Me_2TlCl, consists of layers where a linear Me_2Tl group is surrounded by four chlorines and each chlorine atom is surrounded by four Me_2Tl cations (Figure 3).[44] The observed Tl—Cl distance is 3.029 Å. The corresponding bromide and iodide have the same overall structure.[5] Crystals of dimethylthallium cyanide, azide, cyanate and thiocyanate have distorted sodium chloride structures similar to those of the halides, all containing the octahedral thallium atom.[45]

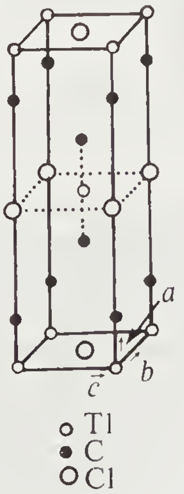


Figure 3 Unit cell of Me_2TlCl (From *Z. Naturforsch., Teil B*, 1974, **29**, 269).

Crystals of another polymer, (2,3,5,6-C_6HF_4)$_2$TlBr, contain a thallium atom with a different type of coordination, namely a distorted trigonal bipyramid with two carbons and one bromine occupying the equatorial positions, as shown in Figure 4.[46] The Tl—Br interaction (3.214 and 3.172 Å) between the dimeric [R_2TlBr]$_2$ units shown in Figure 5 gives rise to a polymeric chain. This compound, as well as (C_6F_5)$_2$TlX (X = Cl, Br), dissociates into dimers in benzene solution. These halides also form adducts with bipy, phen, py, Ph_3E and Ph_3EO (E = P, As), presumably resulting in depolymerization of the polymer chains.[47] In fact an X-ray structural study of (C_6HF_4)$_2$TlCl(Ph_3PO) has revealed a chlorine-bridged dimeric structure with a five-coordinate thallium atom.[48] An overall geometry around the thallium is similar to that of (C_6HF_4)$_2$TlBr shown in Figure 4.

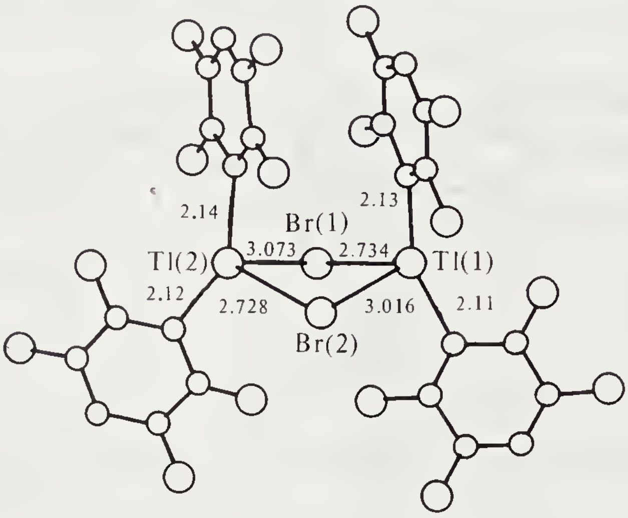


Figure 4 The two crystallographically independent (2,3,5,6-F_4C_6H)$_2$TlBr units (From *Inorg. Chim. Acta*, 1979, **35**, L335).

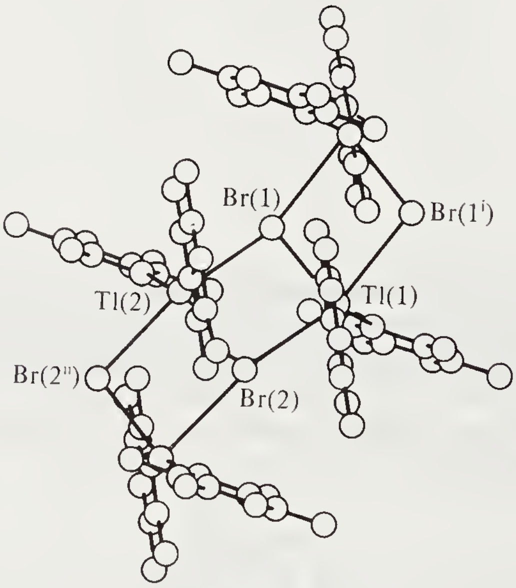


Figure 5 Part of the polymeric chain of (2,3,5,6-F_4C_6H)$_2$TlBr (From *Inorg. Chim. Acta*, 1979, **35**, L335).

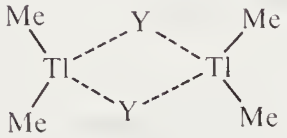
Occurrence of a discrete dimeric structure in the solid state of (Me_3SiCH_2)$_2$TlCl has been confirmed by an X-ray crystal study.[49] Molecular weight measurements indicated that Bu$^{i}_{2}$TlCl and (Me_3CCH_2)$_2$TlCl also are dimeric in solution.[50] A possibility of dimerization of Me_2TlCl in the vapor phase has been presented by mass spectral studies.[51]

Addition of halide anions to solutions of diorganothallium halides leads to isolation of solid complexes containing the anion $[R_2TlX_2]^-$ (R = Ph, C_6F_5; X = Cl, Br, I, NCS) and $[Me_2TlX_3]^{2-}$ (X = Cl, Br, I).[5] It has been suggested from an electrophoretic study that the increasing order of the acidity of the cations towards Cl^- is $Tl^+ < Me_2Tl^+ < Ph_2Tl^+ < PhTl^{2+} < Tl^{3+}$.[52]

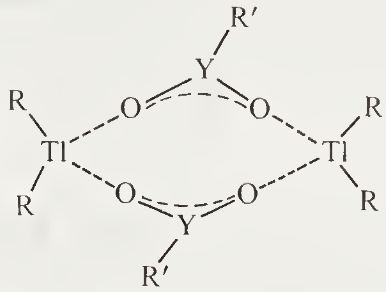
Diorganothallium fluorides, R_2TlF (R = Bu^{i}, i-C_5H_{11}, n-C_6H_{13}, C_6F_5), are associated in solution,[5,53] but little is known about the nature of the thallium–fluoride interaction.

Molecular weight measurements show that intermolecular bridging by oxygen, sulfur, selenium and nitrogen occurs in solutions of Me_2TlY (Y = OMe, OEt, OBu^t, $OSiMe_3$, OPh, SMe, SPh, SeMe, NMe_2) to form the dimer (**8**).[22,54,55] Occurrence of this type of dimerization in the solid state of Me_2TlY (Y = OPh, OC_6H_4Cl-2, SPh) has been confirmed by X-ray crystallography.[55] Significantly, the C—Tl—C angles in these compounds (173, 166.2, 163.5°, respectively) do not deviate much from linearity. The coordination for the thallium is better envisaged as distorted trigonal bipyramidal with one equatorial site vacant. On the other hand, the crystal structure of $(C_6F_5)_2TlOH$ contains infinite chains of dimers quite similar to those of $(C_6HF_4)_2TlBr$ shown in Figure 4.[56]

Several diorganothallium sulfinates and carboxylates are also dimeric in solution through bridging *O*-sulfinato and carboxylato groups (**9**)[57,58] (see later, however, for the solid state structure of Me_2TlOAc).



(**8**)



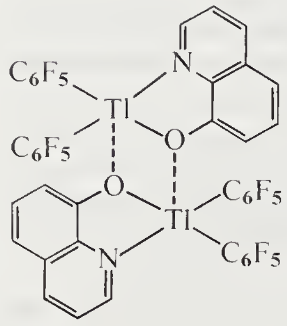
(**9**) Y = S, C

Intramolecular chelate bond formation occurs in some diorganothallium derivatives both in solution and in the solid state. A cation R_2Tl^+ forms a 1:1, but no 1:2, complex with β-diketonate anions, $[RCOCHCOR']^-$ (R = R′ = Me; R = R′ = Ph; R = Me, R′ = Ph; R = CH_2COPh, R′ = Me or Ph), in dioxane/water.[59] The formation constant for a given β-diketonate ligand increases in the order $Me_2Tl^+ < Et_2Tl^+ < Pr^n_2Tl^+ < Ph_2Tl^+$. This result can be best correlated with the hydrophobic character of the organothallium cation. As the chain length of the alkyl group increases, this character would increase and this should be paralleled by an increasing ease of displacement of solvent molecule by the chelate ligand.

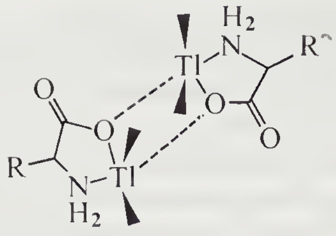
Thallium atoms in certain chelate compounds can attain a coordination number greater than four as a result of extra intermolecular association. Rather a small number of chelate compounds have been found to be monomeric in solution. Typical examples include $R_2TlS_2CNEt_2$ (R = Me, Ph),[60] $R_2TlS_2PR'_2$ (R = Et, Ph; R′ = Et, OMe)[60–62] and $(C_6F_5)_2Tl$(β-diketonate).[63] An X-ray study of $Ph_2TlS_2CNEt_2$ has revealed that the bent C—Tl—C angle (148°) is among the smallest for non-fluoro-alkyl- and -aryl-thallium derivatives.[64] Many other diorganothallium β-diketonates, dithiophosphinates, 8-hydroxyquinolinates, salicylaldehydates and tropolonates are more or less associated in solution,[60,62,63,65,66] the apparent degree of association being usually between 1 and 2. A five-coordinate structure (**10**) can be assigned to the dimer of $(C_6F_5)_2Tl(ox)$ (ox = 8-hydroxyquinolinate).[63] A rigid dimerization of chelate units has been confirmed by the X-ray structural determination of dimethylthallium tryptophanate, as schematically shown in (**11**).[67] This is a distorted octahedral complex with a vacant equatorial site. Also determined by X-ray crystallography was a dimeric structure of Ph_2Tl(tropolonate)[64] (*cf.* a further association of the dimethyl analogue shown below).

Even polymerization of the chelate units occurs in the solid state of Me_2TlY (Y = acac, OAc, tropolonate) and $Et_2Tl(sal)$, as schematically shown in (**12**). The structures of all of these compounds have been determined by X-ray studies,[68,69] a detailed geometry for Me_2TlOAc being shown in Figure 6. This is again a distorted pentagonal bipyramidal structure with one equatorial site vacant. The other compounds in (**12**) have an almost similar overall geometry around thallium. Dimethylthallium phenylalaninate is also polymeric in the solid state where a unit similar to (**11**), namely (**13**), is linked *via* the carboxylate bridge, so that each thallium is six coordinate.[70]

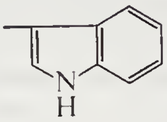
A more complex intermolecular association exists in the solid state of Me_2TlS_2COMe, as shown in (**14**).[71] Thallium in this compound is apparently seven coordinate with two methyl groups occupying apical sites of a distorted pentagonal bipyramid.



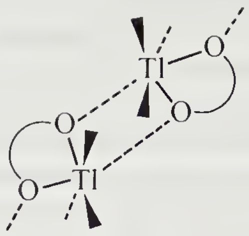
(10)



(11) R = CH_2—



(13) R = CH_2Ph .



(12) O⌒O ≡ acac, OAc, sal, tropolonate

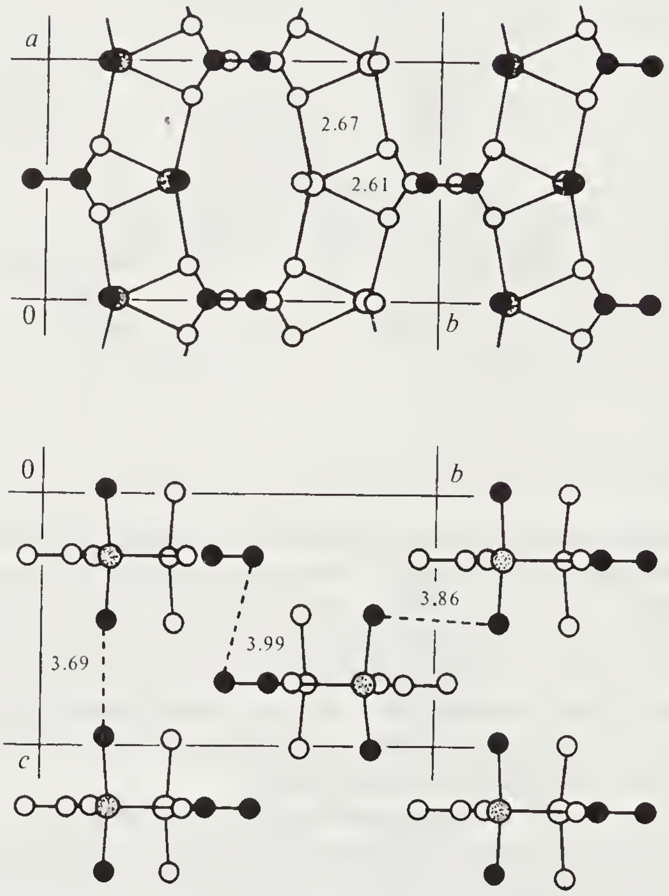
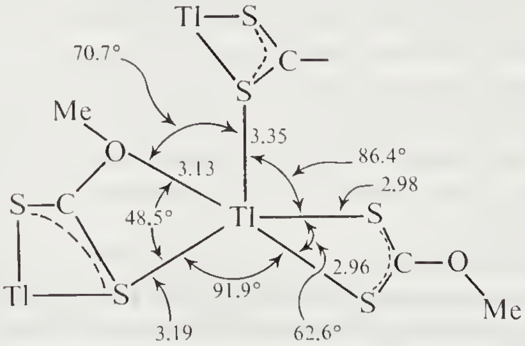


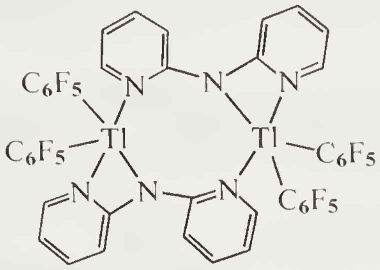
Figure 6 The structure of Me_2TlOAc. Top, view along *c*; bottom, view along *a*. Large atoms are Tl; small open atoms are O; small solid atoms are C. All atoms in molecules that are to the rear in each view are left open (From *Acta Crystallogr.* (*B*), 1975, **31**, 1929).



(14)

The increase of the coordination number in the chelate compounds is made possible by not only the intermolecular association of chelate units but also coordination of a Lewis base to thallium. Thus the compounds $(C_6F_5)_2TlY$ (Y = acac, hfacac, tfacac, benzoylacetonate, ox) react with Ph_3EO (E = P, As), bipy or phen to form five- or six-coordinate adducts, $(C_6F_5)_2TlYL$ or

$(C_6F_5)_2TlYL_2$.[63] Another pentafluorophenyl chelate compound having a five-coordinate thallium atom (**15**) has been prepared, and its structure determined by X-ray crystallography.[72] This is a very distorted trigonal-bipyramidal structure with two pyridyl nitrogen atoms at apical positions.



(**15**)

Notable in this structure is the relatively small C—Tl—C angle (127°) which, together with those of $(C_6F_5)_2TlOH$, $(C_6HF_4)_2TlBr$ and $(C_6HF_4)_2TlCl(Ph_3PO)$, contrasts well with the nearly linear C—Tl—C angles found in many five- and six-coordinate *dialkyl*-thallium compounds.

8.2.2.3 Reactions

Although the Tl—C bonds in diorganothallium compounds are much less labile than those in the triorgano and monoorgano counterparts, several reactions of the diorgano compounds are known in which the cleavage of the Tl—C bond(s) occurs with considerable ease.

(*i*) *Reductive Tl—C bond cleavage*

The Tl—C bonds in the diorgano compounds can undergo several types of reductive cleavage reactions. The electrochemical one-electron reduction of the cation R_2Tl^+ (R = Me, Et, Pr^n, Bu^n, n-C_5H_{11}, Ph) is thought to afford an intermediate radical, R_2Tl (equation 23).[23,73] This radical then either disproportionates to R_3Tl and metallic thallium (equation 24), or is further reduced to give the carbanion (equation 25). The disproportionation presumably is related to the finding that the action of sodium in liquid ammonia on Ph_2TlBr gives Ph_3Tl and metallic thallium.[5] A somewhat complicated kinetic aspect would be expected in polarography of R_2Tl^+ at a mercury electrode, for Ph_2TlBr readily reacts with mercury in non-electrochemical systems to give Ph_2Hg and TlBr (equation 26).[74] Based on a chronopotentiometric study, a plausible intermediate in equation (26) has been suggested as (**16**). In pyridine and ethylenediamine such Hg/Tl exchange occurs mainly *via* the homogeneous reaction with dissolved mercury, while in DMSO the contribution of the homogeneous reaction is nearly the same as that of the heterogeneous reaction.[75]

$$R_2Tl^+ + e^- \longrightarrow R_2Tl \tag{23}$$

$$3R_2Tl \longrightarrow 2R_3Tl + Tl \tag{24}$$

$$R_2Tl + 2e^- \longrightarrow 2R^- + Tl \tag{25}$$

$$Ph_2TlBr + Hg \longrightarrow Ph_2Hg + TlBr \tag{26}$$

$$[Ph{-}Tl{-}Hg{-}Ph]^+$$

(**16**)

Diaryl- and divinyl-thallium chlorides react with $SnCl_2$ to give the corresponding organotin compounds (*e.g.* equation 27).[5] The stereochemistry of the propenyl group is retained during this reaction. The polyfluorophenyl analogues such as $(C_6F_5)_2TlBr$ are particularly prone to undergo the aryl transfer reaction to elements (Hg, Sn, P, S, I, Br, Cl, Zn, Ge, As) and metal complexes in the reduced form.[76,77] The metal complexes which accept two C_6F_5 groups include $SnCl_2$, $M(PPh_3)_2$ (M = Ni, Pd, Pt), AuXL (X = Cl, Br, I; L = PPh_3, $AsPh_3$, PhNC), $RhCl(PPh_3)_2$ and $MCl(CO)(PPh_3)_2$ (M = Rh, Ir). A cobalt(II) Schiff base complex can accept one C_6F_5 group according to equation (28).[78]

$$(MeCH{=}CH)_2TlCl + SnCl_2 \longrightarrow (MeCH{=}CH)_2SnCl_2 + TlCl \qquad (27)$$

$$(C_6F_5)_2TlBr + 2CoL \longrightarrow 2C_6F_5CoL + TlBr \qquad (28)$$

L = salen, *N*,*N*′-bis(acetylacetone)ethylenediamine, *N*,*N*′-bis(salicylaldehydo)phenylenediamine

The original claim that the reaction of $(C_6F_5)_2TlBr$ with $PdCl_2(PPh_3)_2$ affords the Pd(IV) complex $Pd(C_6F_5)_2Cl_2(PPh_3)_2$, has been denied by the later study.[79] In fact mixtures of $Pd_2(C_6F_5)_2Cl_2(PPh_3)_2$ and $Pd(C_6F_5)Cl(PPh_3)_2$ have been confirmed to be present in the reaction products.

Irradiating diarylthallium compounds, $Ar_2TlO_2CCF_3$, in benzene gives unsymmetrical biphenyls, ArC_6H_5.[80] Aryl radicals may be involved as intermediates in this transformation.

(*ii*) *Alkyl exchange*

The diorganothallium compounds undergo some alkyl exchange reactions. Attempts to isolate dimethylthallium compounds, Me_2TlY [Y = $Co(CO)_4$, $Cr(CO)_3Cp$, $Fe(CO)_2Cp$] all failed owing to occurrence of the disproportionation shown in equation (29).[26] This corresponds to the reverse of equation (9).

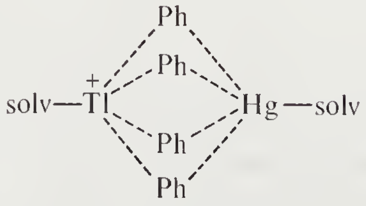
$$3Me_2TlY \longrightarrow 2Me_3Tl + TlY_3 \qquad (29)$$

No facile intermolecular exchange of organic groups takes place between diorganothallium cations in aqueous solution. However, the reversible redistribution reaction (equation 30) occurs in refluxing toluene solution when Y is SMe, SPh, ox, sal and tropolonate.[66] The dithiocarbamate $MeEtTlS_2CNMe_2$ is quite stable under similar conditions. Proton NMR spectroscopy indicates that the η^1-allyl group in $Me(CH_2{=}CHCH_2)TlO_2CPr^i$ undergoes neither intermolecular exchange nor intramolecular rearrangement.[34] Similarly, there is no intermolecular exchange of the η^1-C_5H_5 group in $Me(C_5H_5)TlO_2CPr^i$, as revealed by the observation of the spin–spin couplings between thallium and the C_5H_5 protons,[35] in marked contrast to the rapid exchange of the C_5H_5 group in $Me_2(C_5H_5)Tl$.[14] In the former system a rapid intramolecular shift of the Tl—C bond around the C_5H_5 ring is evident on the NMR time scale.

$$Me_2TlY + Et_2TlY \rightleftarrows 2MeEtTlY \qquad (30)$$

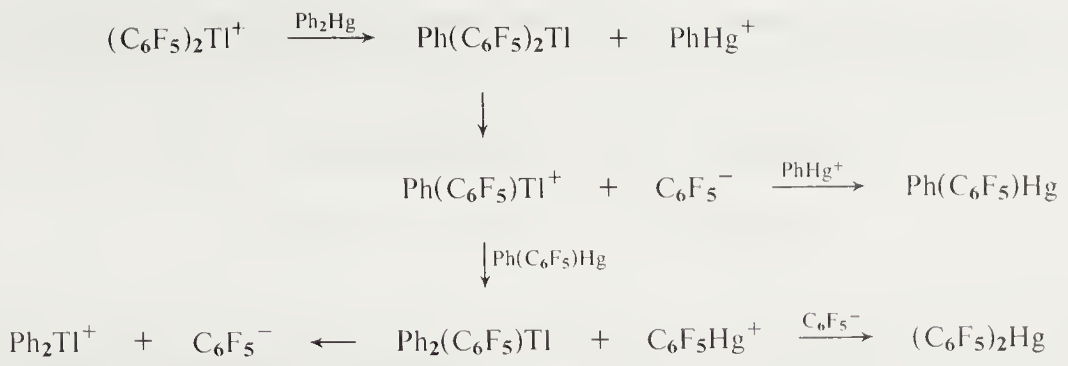
Exchange of organic groups proceeds not only within the thallium compounds but with other organometallic compounds. Thus a second-order phenyl exchange occurs between Ph_2TlBr and Ph_2Hg in pyridine (equation 31), the kinetics having been examined by the use of ^{14}C-labelled Ph_2TlBr.[81] The transition state (**17**) has been proposed on the basis of activation parameters and the simultaneous exchange of all the phenyl groups. For an apparently analogous exchange between $(C_6F_5)_2TlBr$ and Ph_2Hg (equation 32) a different, stepwise mechanism may be assumed (Scheme 1), since it is possible to isolate the intermediate $Ph(C_6F_5)Hg$ from the product mixtures.[53] Continuation of electrophilic attack by an organothallium cation on the phenyl–mercury bond

$$Ph^*_2Tl^+ + Ph_2Hg \rightleftarrows Ph_2Tl^+ + Ph^*_2Hg \qquad (31)$$



(**17**)

$$(C_6F_5)_2TlBr + Ph_2Hg \longrightarrow Ph_2TlBr + (C_6F_5)_2Hg \qquad (32)$$



Scheme 1

and the liberation of the most electronegative group, $C_6F_5^-$, would ultimately give Ph_2Tl^+, which is precipitated as the bromide. The insolubility of this compound would drive the reaction to completion. The bromide $(C_6F_5)_2TlBr$ similarly reacts with $NaBPh_4$ and Ph_3Bi to give Ph_2TlBr.

Tetramethyltin can replace the organic group R in $MeRTlO_2CPr^i$ in methanol solution, as shown in equation (33).[34,82] The reaction occurs only when R is Ph, $CH_2{=}CH$, $CH_2{=}CHCH_2$ and $PhC{\equiv}C$, but not when it is Et. There is no reaction if the solvent is dichloromethane or chloroform. The reaction may proceed *via* a Me/O_2CPr^i exchange, giving $Me_3SnO_2CPr^i$ and Me_2RTl. The latter compound then reacts with methanol, preferentially losing R which is more prone to the electrophilic attack of methanol. Alternatively, the methylation by Me_4Sn and the attack by methanol may take place in a concerted fashion.

$$MeRTlO_2CPr^i + Me_4Sn \xrightarrow{MeOH} Me_2TlY + Me_3SnY + RH \qquad (33)$$

$$Y = O_2CPr^i \text{ and/or } OMe$$

(*iii*) *Electrophilic Tl—C bond cleavage*

Electrophilic attack on the carbon in the diorgano compounds can afford either monoorganothallium or inorganic thallium derivatives. Both dialkyl- and diaryl-thallium carboxylates react with mercury(II) carboxylates at room temperature to afford monoorganothallium dicarboxylates (equation 34).[5] This reaction is used as the most convenient way of preparing monoalkylthallium compounds. Diarylthallium compounds react with thallium(III), lead(IV) and palladium(II) salts as well, transferring the aryl group to these metals. In particular, the transfer to lead(IV) or palladium(II) which leads to phenol or olefin synthesis[80,83] constitutes a class of transformations useful for organic synthesis (*cf.* Section 8.2.3.3 and Chapter 47).

$$R_2TlOAc + Hg(OAc)_2 \longrightarrow RTl(OAc)_2 + RHgOAc \qquad (34)$$

$$R = Me, Ph$$

Bromination of $(Me_3YCH_2)_2TlCl$ (Y = C, Si) (equation 35) has been used to obtain the monoalkylthallium compounds possessing uniquely high stability (*cf.* Section 8.2.3.3).[50,84] The reaction of $Ar_2TlO_2CCF_3$ with excess iodine in a refluxing chloroform solution (equation 36)

$$(Me_3YCH_2)_2TlCl + Br_2 \longrightarrow Me_3YCH_2TlClBr + Me_3YCH_2Br \qquad (35)$$

$$Y = C, Si$$

$$Ar_2TlO_2CCF_3 + I_2 \longrightarrow 2ArI + TlO_2CCF_3 \qquad (36)$$

serves as a procedure for the conversion of aromatic chlorides and bromides to iodides *via* Grignard reagents.[80] The reaction may proceed stepwise, as shown in equations (37) and (38).

$$Ar_2TlO_2CCF_3 \quad + \quad I_2 \quad \longrightarrow \quad ArTlI(O_2CCF_3) \quad + \quad ArI \tag{37}$$

$$ArTlI(O_2CCF_3) \quad \longrightarrow \quad ArI \quad + \quad TlO_2CCF_3 \tag{38}$$

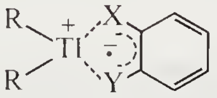
Treatment of $(C_6F_5)_2TlY$ (Y = F, Cl, Br, NO_3, CN, O_2CR) with iodide anion in methanol, ethanol and water results in the formation of TlI_4^- (under acidic condition) and C_6F_5H as shown in equation (39).[85] One possible reaction mechanism is that the nucleophilic attack of iodide anion on thallium occurs first, followed by the electrophilic cleavage of the Tl—C_6F_5 bonds. Alternatively, the reversed order of these processes is possible.

$$(C_6F_5)_2Tl^+ \xrightarrow{\text{excess } I^-/H^+} 2C_6F_5H + TlI_4^- \tag{39}$$

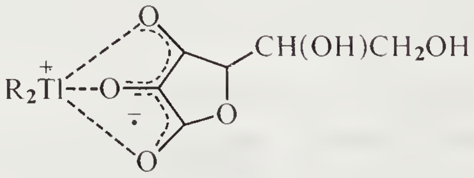
(*iv*) *Reactions without Tl—C bond cleavage*

There are known many reactions of diorganothallium compounds in which the Tl—C bonds remain intact. Most of these are trivial metathetical or adduct formation reactions. Here emphasis is put on some reactions of basic diorganothallium derivatives such as the hydroxide, alkoxide or amide.

The reaction of diorganothallium hydroxides with acids to give salt-type compounds has already been described. With diphenols, aminophenols and *o*-phenylenediamines, R_2TlOH (R = Ph, C_6F_5, Me, Et, Bu^n, $CH_2{=}CH$) give the paramagnetic complexes (**18**) which have been suggested by ESR spectra to be ion pairs of R_2Tl^+ and semiquinones or their NH analogues.[86,87] Similarly, R_2TlOH react with ascorbic acid to show the ESR signals attributable to the ion pairs of R_2Tl^+ and paramagnetic anions of ascorbic acid, namely (**19**).[88]

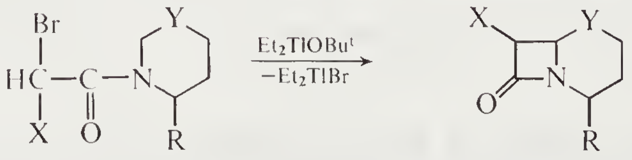


(**18**) X, Y = O and/or NH



(**19**)

In the reaction of dialkylthallium amides and alkoxides with polychloromethanes such as dichloromethane and chloroform in the presence of cyclohexene, dialkylthallium chlorides and dichloronorcarane are formed, suggesting the formation of the $:CCl_2$ carbene.[89] In another carbene reaction the alkoxide Et_2TlOBu^t and the polyhalogen compounds (**20**) give the fused lactams (**21**) (equation 40).[90]

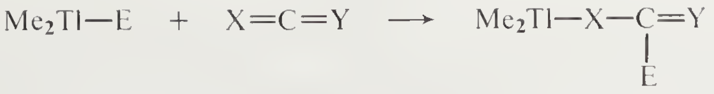


(40)

(**20**) X = Br, Cl

(**21**) Y = S, R = CO_2Me;
Y = CH_2, R = H

Heterocumulene molecules such as CO_2, COS, CS_2, PhNCX (X = O, S) insert into the Tl—O or Tl—N bond of Me_2TlOEt or Me_2TlNMe_2 to form stable adducts as shown in equation (41).[30,91] Similarly, insertion reaction of SO_2 with Me_2TlOR (R = Et, Ph) affords $Me_2TlOS(O)OR$.[30] The Tl—P bonded compound Me_2TlPPh_2 also reacts with PhNCX (X = O, S) in a manner similar to equation (41) to give the adducts, $Me_2Tl{-}X{-}C({=}NPh)PPh_2$.[92]



$$\mathrm{Me_2Tl{-}E} + \mathrm{X{=}C{=}Y} \longrightarrow \mathrm{Me_2Tl{-}X{-}\underset{\displaystyle E}{\underset{|}{C}}{=}Y} \qquad (41)$$

X = O, Y = O, NPh; X = S, Y = O, S, NPh

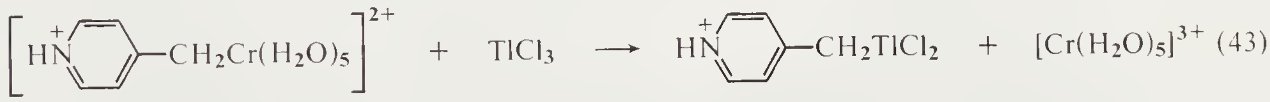
8.2.3 Monoorganothallium Compounds

8.2.3.1 Preparation and properties

Aryl- and vinyl-thallium dichlorides are usually prepared by the reaction of aryl- and vinylboronic acids with excess $TlCl_3$ in aqueous solution (equation 42).[5] Aryl and vinyl derivatives of mercury(II) and tin(IV) also transfer the organic group to TlY_3 (Y = halogen, O_2CR) to give the corresponding monoorganothallium compounds. Various arylthallium dicarboxylates can be obtained very conveniently through thallation of aromatic hydrocarbons with $Tl(O_2CCF_3)_3$[6] (see also Chapter 47).

$$RB(OH)_2 + TlCl_3 \xrightarrow{H_2O} RTlCl_2 + B(OH)_3 + HCl \qquad (42)$$

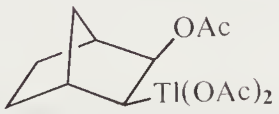
The monoalkyls are best prepared from the dialkyl derivatives through equations (34) and (35). Another method of preparing methyl- and ethyl-thallium compounds of the type RTl(CN)(OAc) (R = Me, Et) is the reaction of $Tl(OAc)_3$ with the alkyltin compounds or $(NH_4)_2[MeSiF_5]$ in the presence of cyanide ion.[5] In the absence of cyanide ion the monoalkyl species react further with the alkyltin compounds to give dialkylthallium compounds. The pyridiniomethylthallium chloride is obtained by the reaction of $TlCl_3$ with the organochromium(III) ion in aqueous solution (equation 43).[5]



(43)

Another unique route to the monoalkyl derivatives is oxythallation of alkenes and alkynes (see also Chapter 47). Unlike the corresponding organomercury counterparts, the number of isolable oxythallation products is rather limited. Typical examples include adducts from $Tl(OAc)_3$ and bicyclic alkenes, *e.g.* (**22**) and (**23**),[5,93] or alkoxythallates of terminal alkenes or allenes, (**24**) and (**25**).[5,94] Some alkynes also give stable adducts, such as (**26**)–(**28**).[95,96] Note, however, a different type of reaction between terminal alkynes and $Tl(OAc)_3$ to give a formal diorganothallium compound (**29**).[97]

The stereochemistry of the oxythallation of the bicyclic alkenes is *cis-exo* for (**22**), and *trans* for (**23**), as has been revealed by proton NMR spectroscopy.[93,98] A proton NMR spectral study has also indicated the conformation of (**24**) obtained from *trans*-PhCH=CHD as (**30**), thus confirming the *trans* stereochemistry in oxythallation of styrene.[99]



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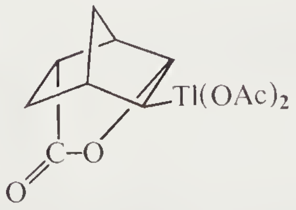
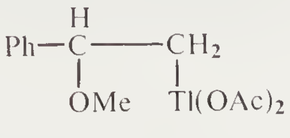
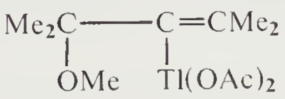


(23)



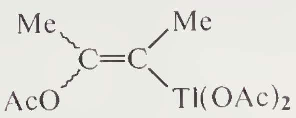
$$\mathrm{Ph{-}\overset{H}{\underset{OMe}{C}}{-}\underset{Tl(OAc)_2}{CH_2}}$$

(24)

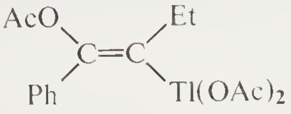


$$\mathrm{\underset{OMe}{Me_2C}{-}\underset{Tl(OAc)_2}{C}{=}CMe_2}$$

(25)



(26)



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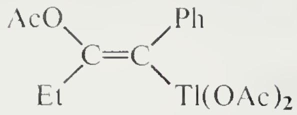

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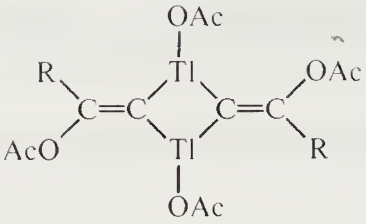
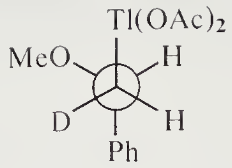


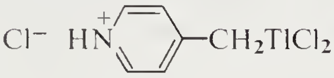
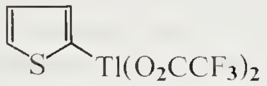
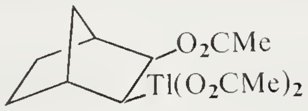
(29) R = Ph, Me, Bu^n, n-C_6H_{13}



(30)

Table 5 lists representative monoorganothallium compounds together with methods of preparation.

Table 5 Monoorganothallium Compounds

Compound	*M.p.* (°C)	*Prep.*[a]	*Ref.*
$Me_3CCH_2TlBr_2$		A	1
	98–100 dec.	B	2
$PhCH(OMe)CH_2TlCl_2$	146–147 dec.	C^b	3
$CH_2{=}CHTlCl_2$	170 dec.	D	4
$PhTlCl_2$	235 dec.	D	5
$PhTlBr_2$	149	D	5
$MeTl(O_2CMe)_2$	102–103 dec.	A	6
$MeTl(CN)(O_2CMe)$	150–160	E	7
$Me_3SiCH_2Tl(O_2CPr^i)_2$	144	A	8
$PhTl(O_2CCF_3)_2$	184–189	F	9
$PhTl(O_2CMe)(ClO_4)$		F	10
	194–196	F	9
$PhCH(OMe)CH_2Tl(O_2CMe)_2$	127–128 dec.	C	11
	150–151 dec.	C	12
$Ph(O_2CMe)C{=}C(Me)Tl(O_2CMe)_2$	169–171	C	13

[a] Method of preparation: A, dealkylation of R_2TlX; B, from the organochromium(III) compound; C, oxythallation; D, from $RB(OH)_2$; E, from methyltin(IV) compounds; F, thallation. [b] Followed by treatment with KCl.

1. M. D. Johnson, *Chem.Commun.*, 1970, 1037.
2. R. G. Coombes, M. D. Johnson and D. Vamplew, *J. Chem. Soc.* (*A*), 1968, 2297.
3. S. Uemura, A. Toshimitsu and M. Okano, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 2762.
4. A. N. Nesmeyanov, A. E. Borisov, I. S. Savel'eva and E. I. Golubeva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1958, 1490 (*Chem. Abstr.*, 1959, **53**, 13 045).
5. F. Challenger and B. Parker, *J. Chem. Soc.*, 1931, 1462.
6. H. Kurosawa and R. Okawara, *J. Organomet. Chem.*, 1967, **10**, 211.
7. T. Fukumoto, H. Kurosawa and R. Okawara, *J. Organomet. Chem.*, 1970, **22**, 627.
8. H. Kurosawa, S. Numata, T. Konishi and R. Okawara, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1397.
9. A. McKillop, J. S. Fowler, M. J. Zelesko, J. D. Hunt, E. C. Taylor and G. McGillivray, *Tetrahedron Lett.*, 1969, 2423.
10. K. Ichikawa, S. Uemura, E. Uegaki and T. Nakano, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 545.
11. H. J. Kabbe, *Liebigs Ann. Chem.*, 1962, **656**, 204.
12. K. C. Pande and S. Winstein, *Tetrahedron Lett.*, 1964, 3393.
13. S. Uemura, H. Tara, M. Okano and K. Ichikawa, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 2663.

Phenylthallium dihalides are more soluble in polar solvents than the diphenylthallium halides. However, the former compounds are much less stable in solution. They tend either to disproportionate into Ph_2TlX and TlX_3 (equation 44; X = Cl, Br) or to undergo reductive degradation to PhBr and TlBr. The lower alkylthallium dicarboxylates are also thermally unstable both in the

$$2PhTlX_2 \longrightarrow Ph_2TlX + TlX_3 \qquad (44)$$

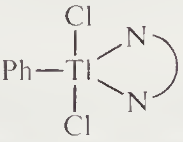
solid state and in solution. The cyanides RTl(CN)(OAc) and the dithiocarbamates $RTl(S_2CNMe_2)_2$ (R = Me, Et)[100] are much more stable than the dicarboxylates. The branched-chain compounds $Me_3CCH_2TlBr_2$ and $Me_3SiCH_2Tl(O_2CPr^i)_2$ do not decompose as readily as the lower alkyl analogues. The stability trends in these alkyl compounds are discussed in more detail in Section 8.2.3.3.

8.2.3.2 Coordination chemistry

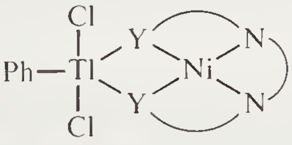
As already shown in Section 8.2.2.2, the acidity of $PhTl^{2+}$, and possibly also $(alkyl)Tl^{2+}$, towards base is thought to be greater than that of the diorganothallium cation. Phenylthallium dichloride is monomeric in methanol, and a non-electrolyte in acetone,[5] but its structure in the solid state has not yet been determined. Some 1 : 1 adducts are formed on treatment of $PhTlCl_2$ with donor molecules such as py, Ph_3P, Ph_3PO, phen, bipy and *N,N'*-bis(acetylacetone)ethylenediamine.[5] The complex $PhTlCl_2py$ is a non-electrolyte in acetone, and its IR spectrum in the solid state shows bands attributable to ν(Tl—Cl). A five-coordinate structure (**31**) may be postulated for the complexes containing the bidentate ligands. The five-coordinate adducts (**32**) are also formed on treating $PhTlCl_2$ with Ni(salen) or bis(β-mercaptoethylamine)nickel(II) complexes.[101] It should be noted, however, that treatment of $PhTlCl_2$ with sodium salts of Schiff bases in the dianion form gives a different type of compound, *e.g.* PhTl(salen).[102]

Phenylthallium dichloride reacts with free chloride ion in methanol to form $[PhTlCl_3]^-$ and $[PhTlCl_4]^{2-}$, as has been suggested by vapor-pressure measurements.[5] Isolated as solid samples are:[5] $[Me_4N][PhTlCl_3]$, $[Me_4N]_2[PhTlCl_4]$, $[Ph_4As][PhTlX_3]$ (X = Br, I), $K[PhTl(CN)_3]$ and $[Bu^n_4N][C_6F_5TlI_3]$.

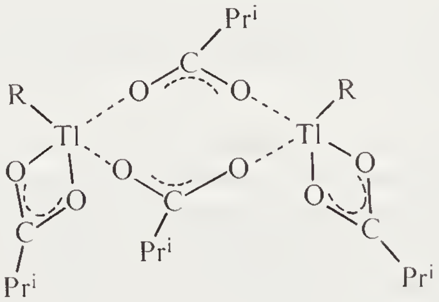
The dicarboxylates $RTl(O_2CPr^i)_2$ (R = Me, Et) are dimeric in chloroform solution.[58] Their IR spectra (particularly the COO stretching region) have been taken as evidence to suggest that the compounds contain both bridging and chelating carboxylate ligands in solution, giving rise to a five-coordinate thallium atom (**33**).



(**31**)



(**32**) Y = O or S



(**33**)

The crystal structure of $(cyclo\text{-}C_3H_5)Tl(O_2CPr^i)_2$ has been determined.[103] It reveals a fundamental aspect for the better understanding of the structure of the monoorganothallium dicarboxylates, for all of these compounds in the solid state exhibit common vibrational spectral characteristics in the COO stretching region. The cyclopropyl compound contains a linear polymeric chain (Figure 7) made through the bridge by one carboxylate group which acts as a chelate

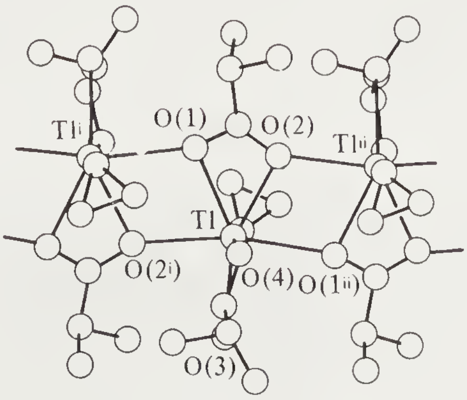


Figure 7 Part of the polymeric chain of $(cyclo\text{-}C_3H_5)Tl(OCOPr^i)_2$ (From *J. Organomet. Chem.*, 1979, **165**, 21).

ligand simultaneously. This type of intermolecular association is quite reminiscent of that found in Me_2TlOAc (Figure 6). Another carboxylate group makes an unsymmetrical chelate by O(3) and O(4) shown in Figure 8. The coordination for the thallium is thus approximately distorted pentagonal bipyramidal, as in Me_2TlOAc. However, one coordination site which remains vacant in the case of Me_2TlOAc is occupied by O(3) in the dicarboxylate. It is also notable that the C—Tl—O(4) angle is 168° and the Tl—O(4) distance (2.125 Å) is the shortest thallium–oxygen bond ever determined for organothallium compounds. Presumably the O(4) atom can best be considered to play a role somewhat similar to that played by one methyl group in Me_2TlOAc.

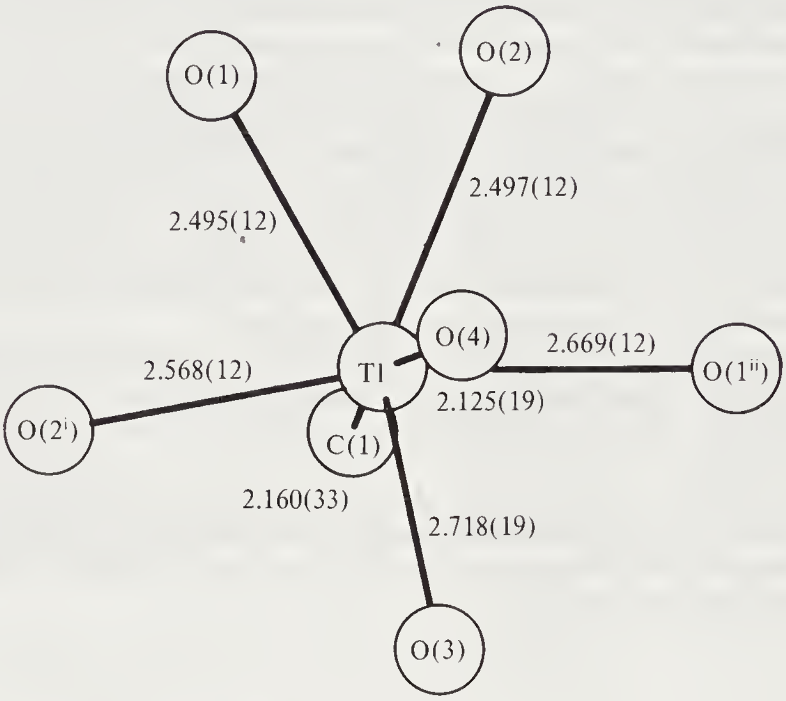
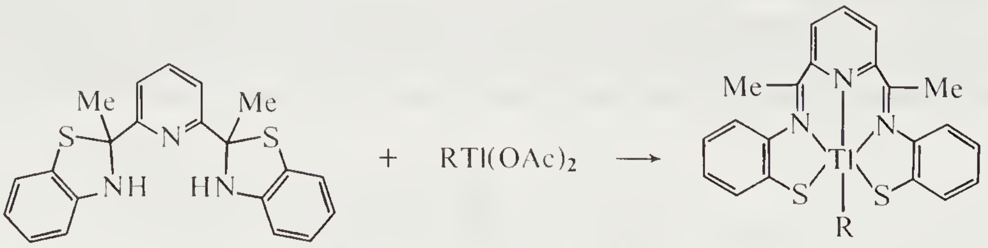


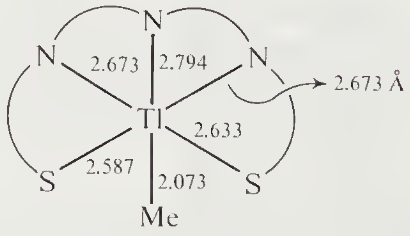
Figure 8 Coordination geometry around Tl in (cyclo-C_3H_5)Tl($OCOPr^i$)$_2$ (From *J. Organomet. Chem.*, 1979, **165**, 21).

The chelate compounds $RTlY_2$ (R = Me, Et, Ph; Y = ox, tropolonate, S_2CNMe_2, S_2PPh_2) are monomeric in solution with the coordination number of thallium being five.[58,61,100] Another interesting chelate compound having a six-coordinate thallium can be prepared from $RTl(OAc)_2$ (R = Me, Et) and 2,6-bis(2-methyl-2-benzothiazolinyl)pyridine through rearrangement and deprotonation of the ligand (equation 45).[104] An X-ray crystal study of (**34**) has shown that it has a highly distorted pentagonal-pyramidal geometry with the methyl group occupying the apical position [see (**35**) for structural parameters]. The crystal structural study of a related complex, MeTl(TPP) (TPP = tetraphenylporphinate), has revealed a square-pyramidal geometry with thallium being displaced from the porphyrin plane by 1.11 Å.[104a]



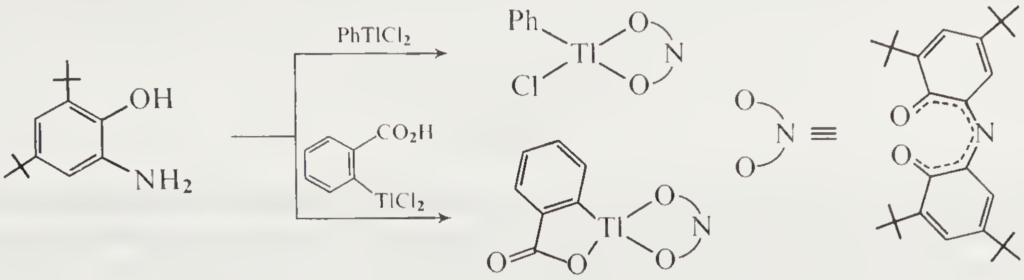
(45)

(**34**)

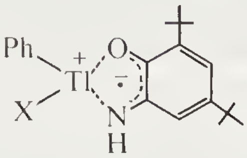


(**35**)

Complexes containing an eight-membered chelate ring can be obtained from the reaction of $PhTlCl_2$ or $(2\text{-}C_6H_4CO_2H)TlCl_2$ with two molecules of 2-amino-4,6-di-*t*-butylphenol as shown in Scheme 2.[105] Measurements of ESR spectra of the reaction mixture from $PhTl(O_2CCF_3)_2$ and the aminophenol have indicated the existence of paramagnetic intermediates such as (**36**), a species closely related to the ion pair shown as (**18**) in Section 8.2.2.3.



Scheme 2



(**36**)

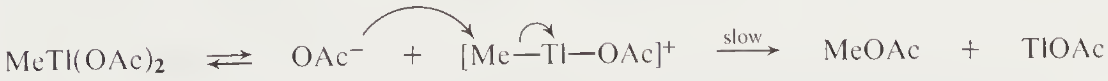
8.2.3.3 *Reactions*

Most of the reactions of the monoorgano compounds described in this section are those involving Tl—C bond cleavage. The only reaction without Tl—C bond cleavage worthy of note is that between the monoorgano compounds and other organometallic compounds, which affords the mixed diorgano compounds (equations 19 and 20).

(*i*) *Reductive Tl—C bond cleavage*

The monoorganothallium compounds are particularly liable to undergo reductive cleavage of the Tl—C bond. The methyl compound $MeTl(OAc)_2$ decomposes in various solvents slowly at room temperature, and rapidly when heated, to give methyl acetate and thallium(I) acetate (equation 46). The reaction rate decreases in the solvent, $H_2O > MeOH > MeNO_2 >$ dioxane.[106] In THF and chloroform, autocatalysis due to the formation of TlOAc occurs. A kinetic analysis of the reaction based on the OAc^- dependency of the rate and the conductivity data is best accommodated by the S_N2 mechanism shown in Scheme 3. When pyridine is added to a methanol solution of $MeTl(OAc)_2$, more than 90% of *N*-methylpyridinium acetate is produced, possibly *via* an S_N2 attack of pyridine at the methyl group of the $[MeTlOAc]^+$ intermediate.[107]

$$MeTl(OAc)_2 \longrightarrow MeOAc + TlOAc \tag{46}$$



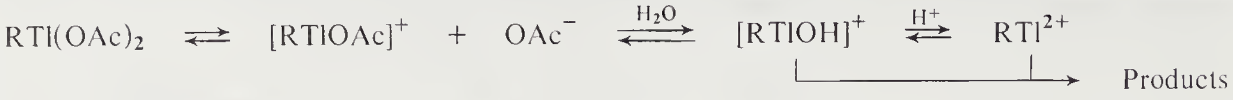
$$MeTl(OAc)_2 \rightleftarrows OAc^- + [Me{-}Tl{-}OAc]^+ \xrightarrow{\text{slow}} MeOAc + TlOAc$$

Scheme 3

The decomposition of the acetate (**24**) in aqueous methanol involves phenyl migration, forming phenylacetaldehyde and its dimethyl acetal (equation 47). The reaction is again first order with respect to the alkylthallium species, and may proceed *via* a reactive species, $[RTlOH]^+$, and a

$$PhCH(OMe)CH_2Tl(OAc)_2 \xrightarrow{MeOH/H_2O} PhCH_2CHO + PhCH_2CH(OMe)_2 + TlOAc \tag{47}$$

more reactive one, RTl^{2+}, under acidic conditions (Scheme 4).[108] Apparently the alkyl group in the cationic intermediates must be very susceptible to attack by nucleophiles, which eventually drives a pair of electrons used in the Tl—C bond on to the thallium atom.



$$RTl(OAc)_2 \rightleftarrows [RTlOAc]^+ + OAc^- \xrightleftharpoons{H_2O} [RTlOH]^+ \xrightleftharpoons{H^+} RTl^{2+} \longrightarrow \text{Products}$$

R = $PhCH(OMe)CH_2$

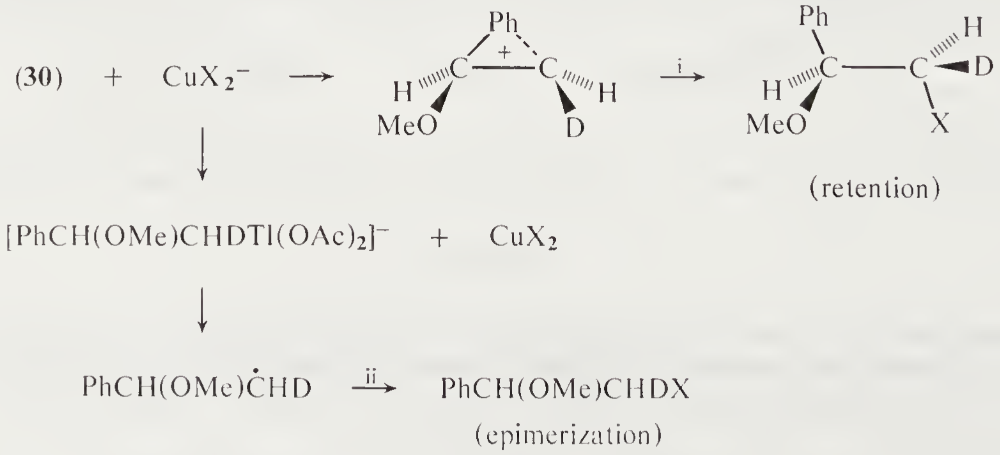
Scheme 4

With the proposed mechanism for the decomposition of the monoalkylthallium compounds in mind, it is anticiapted that those monoalkyl compounds which contain less ionizable and/or better electron-donating ligands exhibit higher stabilities with respect to the reductive decomposition. Also, bulkier alkyl groups would be expected to exert a barrier to the S_N2 attack. These anticipations have been realized in the stable compounds $RTl(CN)(OAc)$ and $RTl(S_2CNMe_2)_2$ (R = Me, Et), and $Me_3SiCH_2Tl(O_2CPr^i)_2$. The role of the ionic dissociation (*e.g.* Schemes 3 and 4) in promoting the reductive decomposition of the monoalkyl compounds is clearly one of the primary bases on which the broader utility of the salts TlY_3 (Y = NO_3, ClO_4, O_2CCF_3) compared with $Tl(OAc)_3$ and $TlCl_3$ as oxidants in organic synthesis has been explored (see Chapter 47).

Methylthallium diacetate can be decomposed by the addition of chloride, bromide and iodide ions to give methyl halides and thallium(I) halides.[58] The 4-pyridiniomethyl compound decomposes similarly in aqueous solution containing chloride ion to give 4-pyridiniomethyl chloride (equation 48).[109] On the other hand, neopentylthallium dibromide is stable in pyridine at room temperature, and decomposes only slowly at 65 °C without rearrangement to give neopentyl bromide. Apparently the S_N2 displacement of the thallium moiety by bromide ion would be unfavorable in the bulky alkyl compound.

(48)

Addition of CuX (X = Cl, Br) to a mixture of (**24**) and KX in acetonitrile facilitates formation of $PhCH(OMe)CH_2X$.[110] A mechanistic study of this reaction employing spin-trapping reagents and (**30**) or its diastereomer has indicated occurrence of two competing pathways:[111] one is an ionic path involving anchimeric assistance by the phenyl group which predominates at lower temperatures, and the other a radical path which predominates at higher temperatures (Scheme 5). More detail is given later concerning the radical reactions of the monoalkylthallium derivatives. The two pathways compete also in the reaction of *erythro*-$Oc^nCH(OMe)CHDTl(OAc)_2$ with CuCl/KCl, although the ionic path in this case results in the inversion of configuration at the α-carbon. Heating an acetonitrile solution of (**24**) with CuX/KX (X = I, CN, SCN, SeCN) likewise affords $PhCH(OMe)CH_2X$ in fair yields.[110,112]



i, X^- and/or CuX_2^-; ii, CuX_2

Scheme 5

Phenylthallium dichloride is stable with respect to spontaneous reductive decomposition. The dibromide $PhTlBr_2$ when heated decomposes rapidly into PhBr and TlBr. Treatment of $PhTlX_2$ ($X = Cl, O_2CCF_3$) with KI results in almost immediate formation of PhI and TlI (equation 49).[5] Although the exact mechanism is not known, the great ease of equation (49) has been applied, when combined with a facile thallation of a variety of aromatic compounds with $Tl(O_2CCF_3)_3$, to a simple synthesis of aromatic iodides with a great orientation control.[6]

$$PhTlX_2 \quad + \quad 2I^- \quad \longrightarrow \quad PhI \quad + \quad TlI \tag{49}$$

$$X = Cl, O_2CCF_3$$

The formation of aryl chlorides, cyanides, thiocyanates and selenocyanates from $ArTl(OAc)(ClO_4)$ is effected by treating the aryl compounds with the copper(II) salts, CuX_2 (X = Cl, CN, SCN, SeCN), as typically shown in equation (50).[112-115] The reaction is solvent dependent, with the best result being obtained in pyridine for the cyanide and dioxane for the other three cases. The aryl cyanides and thiocyanates can alternatively be obtained in fair yields by irradiating aqueous solutions of $ArTl(O_2CCF_3)_2$ containing KCN and KSCN, respectively.[116,117] Photolysis of a suspension of these arylthallium compounds in benzene results in the formation of unsymmetrical biphenyls.[118]

$$PhTl(OAc)(ClO_4) \quad + \quad CuCl_2 \quad \longrightarrow \quad PhCl \quad + \quad TlClO_4 \quad + \quad Cu(OAc)Cl \tag{50}$$

The monoorganothallium compounds can also be decomposed by obvious reductants. Electrochemical reduction of $PhTl(ClO_4)_2$ in aqueous solution at a mercury electrode gives Ph_2Hg and metallic thallium, possibly through one- and two-electron processes (equations 51 and 52).[119]

$$PhTl^{2+} \quad + \quad e^- \quad \longrightarrow \quad PhTl^+ \quad \xrightarrow{Hg} \quad Ph_2Hg \quad + \quad Tl^+ \tag{51}$$

$$PhTl^+ \quad + \quad e^- \quad \longrightarrow \quad PhTl \quad \xrightarrow{Hg} \quad Ph_2Hg \quad + \quad Tl \tag{52}$$

Ascorbic acid and hydrazine react with the acetates $RTl(OAc)_2$ ($R = Me, n\text{-}C_8H_{17}, Ph$) as well as (**24**) under an inert atmosphere to give R_2TlOAc and TlOAc, as shown in equation (53).[120,121] The spin-trapping experiment based on ESR spectroscopy suggested intervention of alkyl radical intermediates during these reductions. In the reaction of $RTl(OAc)_2$ with ascorbic acid under O_2, the alcohols ROH [$R = n\text{-}C_8H_{17}, PhCH(OMe)CH_2$] can be obtained in good yields. Furthermore, extensive epimerization at the α-carbon of the alkyl group occurs during the formation of $\{PhCH(OMe)CHD\}_2TlOAc$ when the compound (**30**) is allowed to react with the reductants. A possible mechanism for equation (53) involving alkyl radical intermediates is shown in Scheme 6. Presumably one-electron reduction of RTl^{2+} to give RTl^+ plays a key role. Homolysis of the Tl—C bond in RTl^+ then produces the radical $R\cdot$ which reacts with RTl^+ or RTl^{2+} to give R_2Tl^+ eventually.

$$2RTl(OAc)_2 \quad \xrightarrow{\text{red.}} \quad R_2TlOAc \quad + \quad TlOAc \tag{53}$$

$$\text{red.} = \text{ascorbic acid}, NH_2NH_2$$

$$RTl^{2+} \quad \xrightarrow{\text{red.}} \quad RTl^+ \quad \longrightarrow \quad R\cdot \quad + \quad Tl^+ \quad \xrightarrow{\text{i, ii, iii}} \quad R_2Tl^+$$

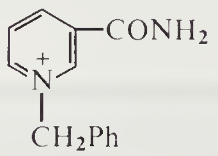
$$\text{i}, RTl^+; \text{ ii}, RTl^{2+}; \text{ iii, red.}$$

Scheme 6

The one-electron reduction of RTl^{2+} and subsequent homolysis of the Tl—C bond may also be involved in hydrodethallation of $RTlX_2$ with *N*-benzyl-1,4-dihydronicotinamide (BNAH) in methanol or THF (equation 54).[122] The formation of a good yield of $PhCH(OMe)CH_3$ from (**24**) and BNAH can be contrasted to a dominant formation of styrene in the reduction of (**24**) by $NaBH_4$ in aqueous alkaline methanol.[123] The yield of $PhCH(OMe)CH_3$ in the latter reduction ranges only from 10 to 6%. It is also interesting that the hydrogen source for forming this ether in equation (54) is mainly BNAH, but not methanol, while it is the acidic hydrogen of methanol and water in the reduction with $NaBH_4$. In connection with the latter result, effective introduction of deuterium into aromatic compounds is made possible through the reaction of $ArTl(O_2CCF_3)_2$ with $NaBH_4$ in EtOD solution (equation 55).[124]

$$\mathrm{RTlX_2} + \mathrm{BNAH} \longrightarrow \mathrm{RH} + \mathrm{TlX} + [\mathrm{BNA}]\mathrm{X} \qquad (54)$$

R = Me, n-C_8H_{17}, $PhCH(OMe)CH_2$, 4-MeC_6H_4; $[BNA]^+$ =



$$\mathrm{ArTl(O_2CCF_3)_2} \xrightarrow[\mathrm{EtOD}]{\mathrm{NaBH_4}} \mathrm{Ar{-}D} \qquad (55)$$

Ar = 4-RC_6H_4 (R = Pr^n, OMe), 2-RC_6H_4 (R = CO_2Me, CO_2H, CH_2CO_2H)

These reactivity patterns in the reduction of $RTlX_2$ with $NaBH_4$ differ significantly from those in the reduction of RHgX compounds with $NaBH_4$. The latter reaction involving a typical radical process can serve as the Markownikov conversion of alkenes to ethers or alcohols when applied to oxymercuration adducts of alkenes, with the hydrogen source for replacing the mercury predominantly originating from $NaBH_4$.[125]

The spontaneous disproportionation of $PhTlCl_2$ into Ph_2TlCl and $TlCl_3$ is already described in equation (44), and the dicarboxylate $PhTl(O_2CCF_3)_2$ also undergoes a similar reaction in a hot acetone or aqueous solution to give $Ph_2TlO_2CCF_3$.[39] Treatment of $PhTl(O_2CCF_3)_2$ with $P(OMe)_3$ without solvent likewise affords the diphenyl compound.[39] The stoichiometry of this reaction in acetone/methanol (5:1) has been confirmed as that shown in equation (56).[126] The methyl compound $MeTl(OAc)_2$ also undergoes the same reaction quite rapidly at room temperature.

$$\mathrm{2RTl(OAc)_2} + \mathrm{P(OMe)_3} \xrightarrow{\mathrm{MeOH}}$$

$$\mathrm{R_2TlOAc} + \mathrm{TlOAc} + \mathrm{O{=}P(OMe)_3} + \mathrm{AcOH} + \mathrm{AcOMe} \qquad (56)$$

R = Me, Ph

It has been assumed in considering the mechanism for such an interesting disproportionation reaction mediated by $P(OMe)_3$ that there is a spontaneous equilibrium reaction (equation 57) which lies far to the left, although actual formation of R_2TlOAc in the absence of $P(OMe)_3$ could not be confirmed by proton NMR spectroscopy.[126] The mechanism proposed is that the rate-determining disproportionation, namely the forward path of equilibrium (57), is followed by a rapid removal of $Tl(OAc)_3$ by $P(OMe)_3$ from the equilibrium. However, occurrence of this type of equilibrium, with the rate of the forward path comparable to the overall rate of equation (56), appears highly unlikely at least for $MeTl(OAc)_2$, for it has been found that there occurs no reaction at all between Me_2TlOAc and $Tl(OAc)_3$ under similar conditions.[5] As for the mechanism of equation (56), other possibilities such as disproportionation induced by direct electron transfer to $RTl(OAc)_2$ must also be taken into serious consideration. In this connection it should be noted that the action of $P(OMe)_3$ on (**30**) in THF/methanol gave 84% yield of $\{PhCH(OMe)$-$CHD\}_2TlOAc$ which contained *ca.* 70% of the epimerized alkyl group.[121]

$$\mathrm{2RTl(OAc)_2} \rightleftharpoons \mathrm{R_2TlOAc} + \mathrm{Tl(OAc)_3} \qquad (57)$$

(*ii*) *Electrophilic Tl—C bond cleavage*

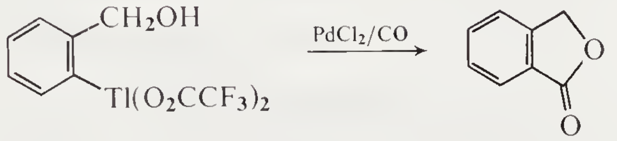
The Tl—C bond in the monoorganothallium compounds is susceptible to certain electrophiles as well. Exchange of the phenyl group occurs between $PhTl^{2+}$ and Tl^{3+} in aqueous perchloric acid, as shown in equation (58), and has been examined by the use of radioactive thallium.[5] Transfer of the organic group of $RTlX_2$ to mercury(II) and lead(IV) is also a facile process, with the latter acceptor having been used as a reagent for a simple phenol synthesis from $ArTl(O_2CCF_3)_2$[116] (*cf.* Chapter 47).

$$PhTl^{2+} + {}^*Tl^{3+} \rightleftarrows Ph^*Tl^{2+} + Tl^{3+} \qquad (58)$$

Palladium(II) salts are also versatile reagents in synthetic reactions when reacted with $ArTl(O_2CCF_3)_2$, particularly in the presence of alkenes or carbon monoxide, as typically shown in equations (59) and (60).[83,127] The carbonylation shown in equation (60) proceeds at room temperature under atmospheric pressure of carbon monoxide. On the other hand, in the carbonylation of $PhTl(OH)(NO_3)$ and $PhTlX_2$ ($X = Cl, O_2CPr^i$) in the absence of the palladium(II) salts, it requires very high temperatures and high pressures to obtain a moderate yield of benzoic acid or its derivatives.[128] The alkyl compound (**24**) also reacts with $PdCl_2$ in methanol containing NaOAc to give acetophenone and metallic palladium.[129] Perhaps an alkylpalladium(II) intermediate, $PhCH(OMe)CH_2PdX$, is formed initially.

$$PhTl(O_2CCF_3)_2 \xrightarrow{Li_2PdCl_4/RCH{=}CHR'} PhC(R){=}CHR' \qquad (59)$$

$$R = H, R' = CO_2Me;\ R = Ph, R' = H$$



(60)

In contrast to the reduction of $ArTl(O_2CCF_3)_2$ with $NaBH_4$ (equation 55), the dicarboxylates react with B_2H_6 in THF to give intermediates possibly containing the Ar—B bond.[130] These intermediates give, on oxidation with alkaline H_2O_2 or hydrolysis by water, good yields of phenols or arylboronic acids, respectively.

Other electrophilic reactions at the Ar—Tl bond of the monoarylthallium compounds which are of synthetic interest include nitrosodethallation with NOCl to give nitrosoarenes,[131] and bromination with bromine to give aryl bromides.[132]

8.3 THALLIUM(I) COMPOUNDS

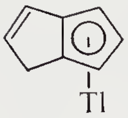
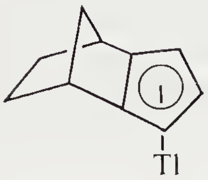
Monoalkyl- and monoaryl-thallium(I) compounds have been proposed as intermediates in several reactions, *e.g.* the preparation of triorganothallium compounds by the use of Grignard or lithium reagents and TlX,[5] electrochemical reduction of RTl^{2+},[119] or thermal decomposition of Ph_3Tl.[15] None of these intermediates, however, has been isolated. The only organic derivatives of thallium(I) to be isolable are cyclopentadienylthallium and its analogues, the borinates, $(C_5H_5BR)Tl$,[133] and thallium(I) salts of dicarbaundecaborane anions, $[B_9C_2H_9RR']^{2-}$.[134]

8.3.1 Preparation and Properties

Cyclopentadienylthallium can best be prepared from cyclopentadiene and TlOH or thallium(I) salts in the presence of alkali in aqueous solution.[5] The ring-substituted analogues are obtained in a similar way. The pentachloro analogue C_5Cl_5Tl can be prepared by the direct reaction of C_5Cl_6 with thallium amalgam or by the reaction of TlOEt with C_5Cl_5H in pentane at −78 °C.[135] The reaction of TlCl and alkali metal borinates in acetonitrile gives $(C_5H_5BR)Tl$ (R = Me, Ph).[133] Table 6 shows representative organothallium(I) compounds.

The parent compound C_5H_5Tl is moderately soluble in polar solvents, and considerably stable in air or water. The alkyl-substituted analogues are more air sensitive. The chloro analogue C_5Cl_5Tl is unstable even at room temperature, and ignites spontaneously in air. The borinates show similar stability trends to those of C_5H_5Tl.

Table 6 Organothallium(I) Compounds

Compound	*M.p.* (°C)	*Ref.*
C_5H_5Tl	>270	1
MeC_5H_4Tl	109–110	2
$Me_3SiC_5H_4Tl$	116	2
$(3\text{-}FC_6H_4)C_5H_4Tl$	123–125 dec.	3
$(4\text{-}FC_6H_4)C_5H_4Tl$	149–151 dec.	3
$(CN)_2C{=}C(CN)C_5H_4Tl$	175 dec.	4
	86–90	2
	163–164	2
C_5Cl_5Tl		5
	149–150	6
	193–194	6

1. F. A. Cotton and L. T. Reynolds, *J. Am. Chem. Soc.*, 1958, **80**, 269.
2. H. P. Fritz and F. H. Köhler, *J. Organomet. Chem.*, 1971, **30**, 177.
3. A. A. Koridze, N. A. Ogorodnikova and P. V. Petrovsky, *J. Organomet. Chem.*, 1978, **157**, 145.
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5. G. Wulfsberg and R. West, *J. Am. Chem. Soc.*, 1972, **94**, 6069.
6. G. E. Herberich, H. J. Becker and C. Engelke, *J. Organomet. Chem.*, 1978, **153**, 265.

8.3.2 Structure and Bonding

The structure of C_5H_5Tl in the solid state has been suggested by an X-ray crystal study to contain linear polymeric chains, similar to those of C_5H_5In, which are composed of alternating rings and metals (· · ·M· · ·C_5H_5· · ·M· · ·).[22] In the structure of C_5H_5In the ring is situated in the midst of two neighboring indium atoms with the ring–indium distances being 3.19 Å. The ring–thallium distances in C_5H_5Tl may not be very different from the corresponding values in the indium analogue. The crystal structure of $(CN)_2C{=}C(CN)C_5H_4Tl$ (**37**) (see later for preparation) has also been determined by a low-temperature single X-ray study (Figure 9).[136] In (**37**) essentially the same structural characteristics as those in C_5H_5In are retained. The ring–thallium distances are 3.014 and 3.065 Å.

The microwave spectrum of C_5H_5Tl in the vapor phase has suggested an open-face half-sandwich structure with the carbon–thallium distances being 2.7 Å. This is smaller than the sum of the van der Waals radius of carbon and the ionic radius of Tl^+ (3.1 Å). The mass spectrum of C_5H_5Tl exhibits peaks corresponding to monomeric species.[5] Presumably the thallium–carbon bonds in C_5H_5Tl in the vapor phase contain a higher degree of covalent character than in the solid state and in solution.

An SCF calculation based on the theory of effective potentials has been carried out for gaseous C_5H_5Tl in its experimental equilibrium conformation.[137] The result has indicated that the thallium atom is nearly neutral with an overall electron distribution of $s^{1.75}p^{0.45}d^{0.71}$ as obtained from a Mulliken population analysis. Furthermore, bonding between thallium and C_5H_5 is principally due to the highest-filled molecular orbital pair of E_1 symmetry based primarily on p–d combination of thallium orbitals (see **38**) and p of carbon, constituting π-symmetry interaction with respect to the thallium–ring axis.

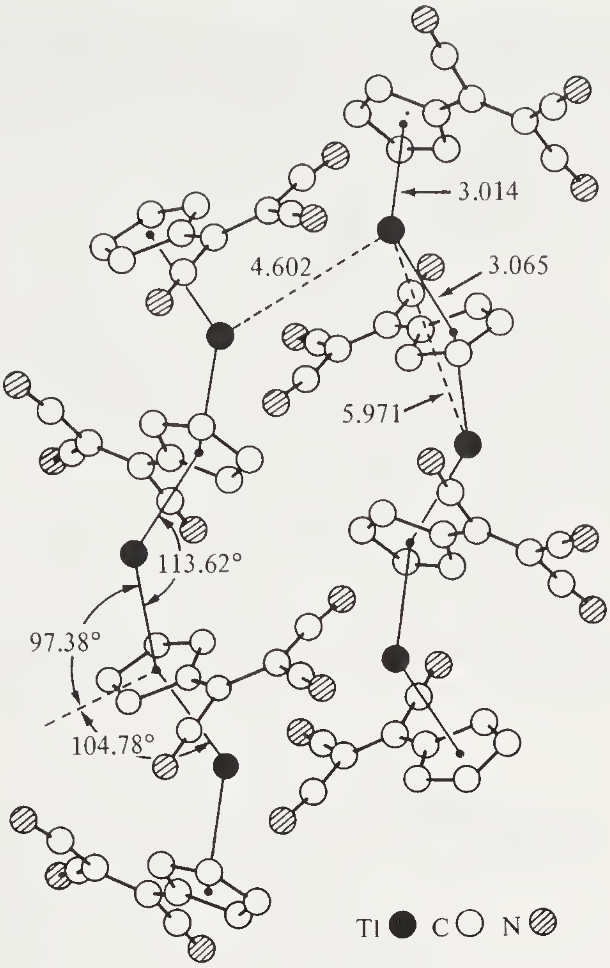
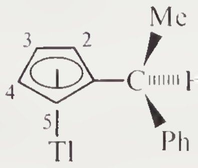


Figure 9 The crystal structure of $(CN)_2C{=}C(CN)C_5H_4Tl$ (From *J. Am. Chem. Soc.*, 1977, **99**, 5194).

The mass spectra of the borinates also show the monomeric parent ion peaks.[134]

The ^1H and ^{13}C NMR spectra of several substituted cyclopentadienylthallium analogues show no spin–spin coupling between Tl and ^1H or ^{13}C nuclei.[138,139] Further, the ^{13}C spectra of the thallium(I) derivative of a chiral ligand (**39**) in benzene, dichloromethane or THF show only one signal for a formally diastereotopic pair of carbons, 2 and 5 or 3 and 4, unlike the rigid, ferrocene-type compound $Fe(C_5H_5)(C_5H_4CHMePh)$.[139] These results indicate the cyclopentadienylthallium derivatives either to undergo a very rapid intermolecular exchange or to dissociate into free ions or ion pairs. Comparison of the ^{19}F chemical shifts of (3- or 4-$C_6H_4F)C_5H_4Tl$ with those of Fe(II), lithium and sodium analogues also suggests a considerable ionic character in the thallium compounds in solution.

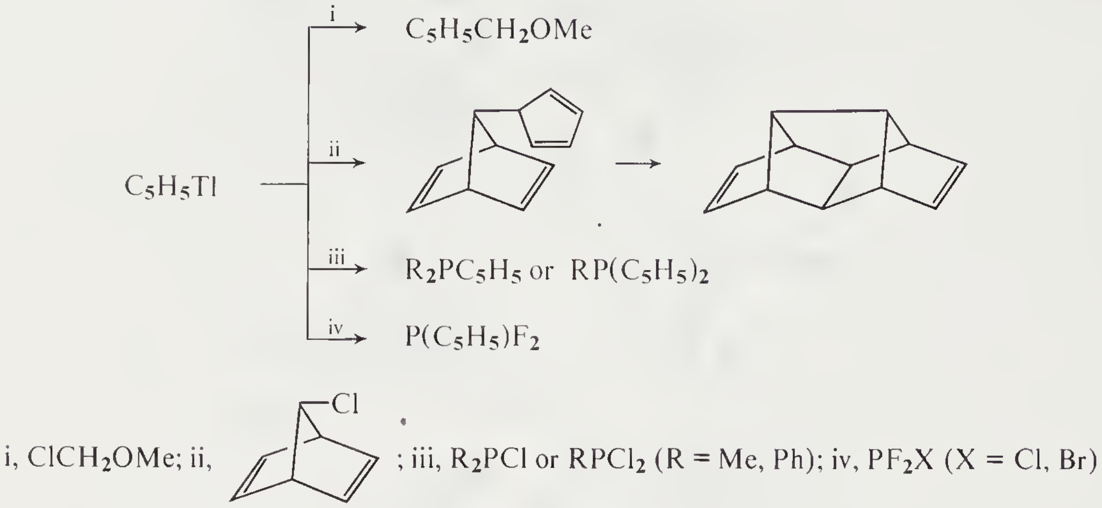
(**38**)



(**39**)

8.3.3 Reactions

The cyclopentadienyl derivatives of thallium(I) find wide application as donors of the cyclopentadienyl groups to not only metal complexes (especially those of transition metals), but several organic moieties. The latter examples are shown in Scheme 7.[140–143] The reaction of C_5H_5Tl with tetracyanoethylene gives a tricyanovinyl-substituted analogue (**37**), as shown in equation (61).[136] The new compound (**37**) also serves as a tricyanovinylcyclopentadienyl group-transfer reagent to Mn(I), Cu(I) and Fe(II) complexes.



i, $ClCH_2OMe$; ii, ; iii, R_2PCl or $RPCl_2$ (R = Me, Ph); iv, PF_2X (X = Cl, Br)

Scheme 7

$$C_5H_5Tl + (NC)_2C{=}C(CN)_2 \longrightarrow \underset{(\mathbf{37})}{(CN)_2C{=}C(CN)C_5H_4Tl} + HCN \qquad (61)$$

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