HYPERCARBON CHEMISTRY

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Mookie, the Olahs' new cocker spaniel enlightens this otherwise wasted page (photo by Mark Sassaman).

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To the universality of chemistry,
the science of compounds of all elements,
including carbon

Rather than ask why it has taken some 30 years for these concepts to become widely known, one can be amazed that the background for this fine book developed at all. It is due in no small part to reluctance of chemists to adapt to the dynamic changes of chemistry. One can also hope that chemistry will recover from the recent neglect of support of research in mechanistic organic chemistry and synthesis of compounds of the main group elements. In addition, much of the molecular structure determination that is so central to these arguments had to await the newer methods of X-ray diffraction and nuclear magnetic resonance, and the theory had to await the modern developments in methods and computers. Thus the emergence of the depth and breadth of these concepts in this book is a tribute to the dedication of the authors and to the vitality of the ideas themselves.

WILLIAM N. LIPSCOMB

Harvard University
Cambridge, Massachusetts
May 1986

PREFACE

Organic chemistry is concerned with carbon compounds. Over 6 million such compounds are now known, and their number is increasing rapidly. They range from the simplest compound methane, the major component of natural gas, to the marvelously intricate macromolecules that nature uses in life processes.

Within such a rich and diverse subject, it is difficult for someone deeply familiar with one area to keep abreast of developments in others. This can hinder progress if discoveries in one field that can have significant impact on others are not recognized in a timely fashion. For example, developments in the chemistry of carbohydrates, proteins, or nucleotides are traditionally exploited by biochemists and biologists more than by organic chemists. Developments in organometallic chemistry, while increasingly attracting the attention of inorganic chemists, are not as well appreciated by mainstream organic chemists.

In this book we have attempted to alleviate this problem by pooling our diverse experience and backgrounds but centering on a common interest in the fascinating topic of hypercarbon chemistry. The book centers around the theme that carbon, despite its firmly established tetravalency, can still bond simultaneously to five or more other atoms. We refer to such atoms as *hypercarbon atoms* (short for hypercoordinated carbon atoms) since four valency (hence four coordination using normal two-center, two-electron type bonds) is the upper limit for carbon (being a first-row element it can accommodate no more than eight electrons in its valence shell). Since their early detection in bridged metal alkyls, where they helped advance the concept of the three-center, two-electron bond (and later the four-center, two-electron bond), hypercarbon atoms have now become a significant feature of

organometallics, carborane, and cluster (carbide) chemistry, as well as of acid catalyzed hydrocarbon chemistry and the diverse chemistry of carbocations.

First we survey the major types of compounds that contain hypercarbon. The relationships that link these apparently disparate species are demonstrated by showing how the bonding problems they pose can be solved by use of three- or multicenter electron-pair bond descriptions or simple MO treatments. We also show the role played by hypercoordinated carbon intermediates in many familiar reactions (carbocationic or otherwise). Our aim here is to demonstrate that carbon atoms in general can increase their coordination numbers in a whole range of reactions.

In our original plans for the book, we were privileged to have our friend and colleague Paul v. R. Schleyer participate, and we regret that other obligations made it impossible for him to continue. We gratefully acknowledge his many suggestions and thank him for his continued encouragement. We have mainly focused our attention on experimentally known hypercarbon systems and are not discussing only computationally studied ones (these are reviewed by Paul Schleyer elsewhere).

Most chemists' familiarity with chemical bonding evolved in electron-sufficient systems, where there are enough electrons not only for ($2e$–$2c$) bonds but also for nonbonded electron pairs. Hypercarbon atoms are generally found in electron-deficient systems where electrons are in short supply and thus have to be spread relatively thinly to hold molecules or ions together. A relative deficiency of electrons is not uncommon in chemistry, particularly in the chemistry of the metallic elements. The ($3c$–$2e$) and multicenter bonding concept of boranes and carboranes, pioneered by Lipscomb, further emphasizes this point. Thus it is not surprising that the concept of hypercarbon bonding was accepted by inorganic and organometallic chemists earlier than by their organic colleagues. The well-publicized spirited debate over the classical–nonclassical nature of some carbocationic systems preceded their preparation and their spectroscopic study under long-lived stable ion conditions, which unequivocally established their structures. Debate and even controversy is frequently an essential part of the "growing pains" of a maturing field, and they should be welcomed as they help progress in finding answers. The importance of hypercoordination in carbocations and related hydrocarbon chemistry is now firmly established. At the same time hypercoordinate carbocations are but one aspect of the much wider field of hypercarbon chemistry.

It is significant to note that almost all carbocations have known isoelectronic and isostructural neutral boron analogs. Boron compounds also provide useful models for many types of intermediates (transition states) of electrophilic organic reactions.

The field of hypercarbon chemistry is already so extensive that it is impossible to give an encyclopedic coverage of the topic. Instead we have taken the liberty of organizing our discussion around selected topics with representative examples to emphasize major aspects. Our choices were arbitrary and we apologize for inevitably omitting much significant work.

Multiauthor books frequently lack the uniformity that a single-author book is able to convey. Our close cooperation, made possible by the Loker Hydrocarbon Research Institute, has helped us give a homogeneous presentation that merges our individual viewpoints to reflect our common goal. If we have succeeded in calling attention to

the ubiquitous presence of hypercarbon compounds, breaching the conventional boundaries of chemistry, and have aroused the interest of our readers, we shall have achieved our purpose.

We thank Ms. Cheri Gilmour for typing the manuscript and our editor, Dr. Theodore P. Hoffman, for helping along the project in his always friendly and efficient way. Many friends and colleagues offered helpful comments and suggestions and we are grateful to them all.

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HYPERCARBON CHEMISTRY

chapter 1

INTRODUCTION AND GENERAL ASPECTS

1.1. AIMS AND OBJECTIVES

The chemistry of carbon compounds is generally referred to as organic chemistry. This book is intended to draw attention to an important but generally neglected area of carbon chemistry that has recently undergone a period of extremely rapid growth, yet which is still hardly touched on in most organic textbooks. This is the chemistry of compounds in which carbon atoms are covalently bonded to more neighboring atoms than can be explained in terms of classical, two-center, electron-pair bonds. We refer to such carbon atoms as *hypercarbon atoms*[1a] (short for *hypercoordinated carbon atoms*) because of their *unexpectedly high coordination numbers*.

Carbon contains four atomic orbitals (AO's) in its valence shell (the $2s$, $2p_x$, $2p_y$, and $2p_z$ AO's), and so can accommodate at most four bonding electron pairs (in accordance with the "octet rule").[1b] Commonly, these electron pairs are used to form four single bonds (as in alkanes), two single bonds and one double bond (as in alkenes), one single and one triple bond (as in alkynes), or two double bonds (as in cumulenes). With only four bond pairs, carbon atoms cannot bond covalently to more than four neighboring atoms using only two-center, electron-pair bonds. If attached to more than four neighboring atoms, they must resort to some form of *multicenter* σ *bonding*, in which the bonding power of a pair of electrons is spread over more than two atoms. All carbon atoms with coordination numbers greater than four are therefore necessarily hypercoordinated, and compounds containing such atoms (of which there are now many known examples) will be the main concern of this book. However, there are circumstances in which carbon atoms with only three or four

neighbors may participate in multicenter sigma bonding to two or even three of these neighbors, and we shall include them in our discussion where appropriate.

We have four main objectives:

1. *To illustrate the wide and developing scope of hypercarbon chemistry* by indicating the variety of compounds now known to contain hypercarbon atoms (carbocations,[2] organometallics,[3] carboranes,[4] and other cluster compounds,[5,6] carbides), including many familiar systems such as alkyllithium reagents $(LiR)_n$[7-10] (n = 4 or 6) in which the hypercoordinated nature of the carbon atoms (and, by implication, the roles that the attached metal atoms play in their chemistry) is often ignored.

2. *To discuss ways in which the bonding in such systems can be described.* Notably, in terms of three-center, electron-pair bonds as well as classical two-center bonds, but also in terms of simple molecular orbital (MO) treatments that shed useful light on some of the more symmetrical systems.

3. To demonstrate that, far from being exotic species remote from mainstream organic chemistry, *hypercarbon compounds are closely related to many classically bonded systems, and to aromatic systems,* comparisons with which are of mutual benefit.

4. To show how *the study of hypercarbon compounds helps us to understand the mechanisms of many organic reactions.* These are reactions in which carbon atoms become hypercoordinated in intermediates or transition states, even though the reagents and products of these reactions contain only normally coordinated carbon atoms.

In introducing the subject in Section 1.2, we define some of the terms we shall be using. In Section 1.3 we illustrate the various types of hypercarbon compounds now known. Since we shall rely heavily on the concept of the three-center, electron-pair bond in our discussion of their bonding, and since the usefulness of this concept is perhaps less widely appreciated in organic chemistry than in inorganic or organometallic chemistry, we devote Section 1.4 of this introductory chapter to discussion of the three-center bond concept and illustration of its value for treating specific systems. We also demonstrate the relevance and value of some simple MO arguments applied to hypercarbon systems (Sections 1.4 and 1.5), and conclude this introductory chapter by indicating the types of reactions that are now thought to involve hypercarbon systems. More detailed treatments of particular types of systems, and of specific reactions, follow in subsequent chapters.

1.2. SOME DEFINITIONS

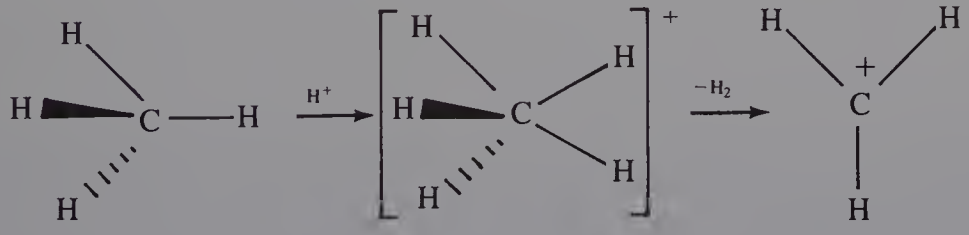
Throughout this book we shall be concerned with the twin issues of coordination and bonding. The terminology by which chemists refer to these issues tends to vary

considerably from area to area. It is, therefore, important to define and to illustrate the sense in which certain terms will be used here.

The *coordination number* of an atom is defined here as the *number of neighboring atoms* by which that atom is directly surrounded, and to each of which it is attached by the direct sharing of electronic charge. All the coordinating atoms may not be at the same distance—some may be bonded more strongly than others, and so be closer to the atom under consideration—but all will be located in directions and at distances that indicate some sharing of electronic charge with the central atom, rather than linkage to the central atom via a second neighboring atom.

On occasions, the term "valence" is used as if it were synonymous with "coordination number." We shall not use it in that sense here. We define the *valence of an atom* as the *number of bonding electron pairs* used by that atom. Normally, carbon is *tetravalent* (i.e., the octet rule is obeyed), and hypercarbon compounds are no exception. On the other hand, in hypervalent compounds the number of valence electrons exceeds the number of bonding orbitals available. Carbon being a small first row element cannot expand its valence shell (vide infra). In the same way that the carbon atom of methane is tetravalent in forming four two-center, two-electron ($2c$–$2e$) bonds to the neighboring four hydrogen atoms, so it is tetravalent but pentacoordinate in the product of protonation of methane. The methonium cation (CH_5^+) is an energetic, highly reactive species[11] believed to have a structure in which three hydrogen atoms are at a normal single bond distance while the other two are at a greater distance.[11,12] In contrast, the methyl cation (CH_3^+) into which CH_5^+ decomposes contains a triply coordinated, *trivalent* carbon atom (Scheme 1.1).

Scheme 1.1



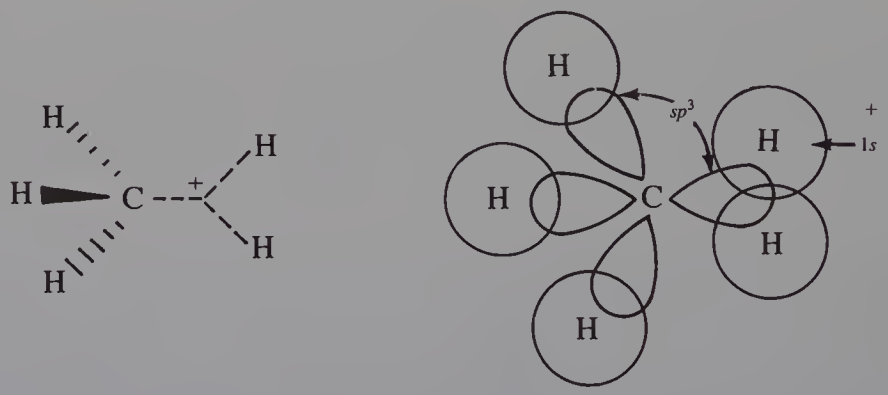
(The lines in the structural diagrams used in Scheme 1.1 represent links to the coordinating hydrogen atoms, *not* bonds in the classical electron-pair sense.) The carbon atom in the last example, CH_3^+, is said to be *coordinatively unsaturated*, a term we shall use in connection with any atom that can readily expand its coordination number, either (as in the case of the carbon atom of CH_3^+) by bonding to another *ligand* (coordinating atom or group), which supplies electrons for the purpose (e.g., $CH_3^+ + X^- \longrightarrow CH_3X$), or by using electrons that were previously *nonbonding*, as occurs when coordinately unsaturated carbanions are protonated, that is, when nonbonding lone-pair electrons are converted into bond pairs (Scheme 1.2).

Scheme 1.2

$$R_3{-}C^- \xrightarrow{H^+} R_3CH$$

When discussing bonding, we shall find it convenient to retain wherever practicable the concept of single, double, and triple bonds, that is, links between pairs of atoms that involve the sharing between those atoms of two, four, or six electrons, respectively, and shall refer to them as two center, two electron [i.e., (2*c*–2*e*)] bonds, two center, four electron (2*c*–4*e*) bonds, and two center, six electron [i.e., (2*c*–6*e*)] bonds. However, as already indicated, we shall find it necessary, in discussing hypercarbon compounds, to use the concept of *multicenter σ bonds*, bonds in which the bonding power of a pair of electrons is considered to extend over three or occasionally four atoms. In CH_5^+, for example, a three-center, two-electron (3*c*–2*e*) bond can account for the bonding between the carbon atom and the two hydrogen atoms furthest from the carbon atom, represented as follows in Scheme 1.3.

Scheme 1.3



For simplicity it is suggested[2a] that three-center bonds be depicted by triangular dotted lines drawn from and meeting each other between the three participating atoms; full straight lines are generally used to symbolize two-center, two-electron bonds. Such a formulation best illustrates the overlap of bonding orbitals; however, it must be remembered that the point of branching of the dotted lines does not represent an additional atom. Alternatively, the three-center bonds can also be represented by a triangle of lines joining all three atoms. This notion may avoid misunderstandings assuming an atom at the "junction" of the branched dotted line symbols. As, however, by definition a three-center bond joins three atoms and does not usually represent equal bonding character between them (in CH_5^+ the "long bond" indeed indicates CH_3^+ bound to H_2), the former symbol is preferred and is gaining acceptance.

Such a bond is envisaged as resulting from the mutual overlap of a suitable AO

from each of the atoms involved, an sp^3 hybrid AO on carbon and a 1*s* AO on each hydrogen atom, as illustrated in Scheme 1.3.

It should be stressed that although such a three center, two electron bond shares the bonding pair of electrons between three atoms instead of two as in classical bonds and therefore is sometimes referred to as delocalized, the description of the bonding in CH_5^+ by three (2*c*–2*e*) bonds and one (3*c*–2*e*) bond is nevertheless a description in terms of *localized bonds*. It is a valence bond description of this cation that attempts to account for the distribution of the atoms and the internuclear distances by allocating pairs of electrons to localized regions between pairs of atoms or within triangular arrays of three atoms. A *delocalized* bonding description of this cation would allocate the four pairs of electrons to MOs embracing all six atoms, each or most making some contribution to all of the pairwise interactions, bonded or nonbonded, in CH_5^+, but generating overall much the same electron density in particular regions as the localized bond model. Thus, electron density corresponding to essentially one pair of electrons would be found in each of the "normal" C−H bonds, but the electron density associated with each long C−H link, and also in the H−H link between the two anomalous (hypercoordinated) hydrogen atoms, would approximate to two thirds of an electron apiece (for electron bookkeeping purposes, the sharing of a pair of electrons between three atoms, as in a (3*c*–2*e*) bond, corresponds to the allocation of two thirds of an electron to each edge of the triangle defined by those three atoms).

An additional term that we may occasionally find useful, though we shall restrict its use to avoid ambiguity, is *electron deficient*. This term has at least three different senses in which it has been used in connection with organic systems. It is often applied as meaning "center for nucleophilic attack" to refer to carbon atoms bearing electron-withdrawing substituents. Secondly, it is also used in referring to compounds with coordinatively unsaturated carbon atoms like those of carbenium ions, R_3C^+, which can accommodate an extra pair of electrons. The third usage[13,14a] is as a label for molecules, or sections thereof, that contain too few electrons to allow their bonding to be described exclusively in terms of two-center, electron-pair bonds. In this book we prefer to restrict our discussion to compounds wherein molecules or sets of atoms are held together by multicenter bonding (i.e., by electron-deficient bonding). Similarly, "electron precise"[14a] is a term that can be used as a label for systems in which there are exactly the right number of electrons to give each pair a two-center bonding role, as in CH_4. "Electron rich" systems are those containing nonbonding (lone-pair) electrons, as in H_3C^-, NH_3, or H_2O.

A molecule or polyatomic ion can often be identified as *electron deficient* from its formula, if it contains fewer than $(n - 1)$ valence shell electron pairs, where n is the number of atoms in the molecule or ion in question. This is because at least $(n - 1)$ two-center covalent links will be needed to hold n atoms together, whatever the structure may be. Thus, the methonium ion, CH_5^+, with six atoms held together by only four valence shell electron pairs, is clearly electron deficient in this sense. In the CH_6^{2+} dication[14b] seven atoms are involved, further increasing the electron deficiency.

1.3. THE STRUCTURES OF TYPICAL HYPERCARBON SYSTEMS

Before exploring the various bonding situations that occur in hypercarbon systems, it is helpful to illustrate the structures of some representative examples. These are shown in Figures 1.1–1.6, and include the following types.

Figure 1.1 shows the structures (most determined by X-ray crystallographic studies) of some *bridged metal alkyls*, and related aryl, alkenyl, and alkynyl compounds.[7-10,13,15-21] It was compounds of this type that were instrumental in establishing the ability of the carbon atoms of typical monovalent organic groups to participate in multicenter σ bonding. Note that, in all of the structures shown, the hypercarbon atoms bond to either two or three metal atoms, and that, although the coordination numbers of the bridging carbon atoms in $(AlPh_3)_2$,[19] $(Al\textit{i}\text{-}Bu_2CHCH\textit{t}\text{-}Bu)_2$,[20] and $(MeBeCCMeNMe_3)_2$[21] are not unusual (4, 4, and 3, respectively), the $(MC)_2$ rings in these compounds (M represents the metal atom) resemble those in $(AlMe_3)_2$[15] and $(MgMe_2)_n$.[16]

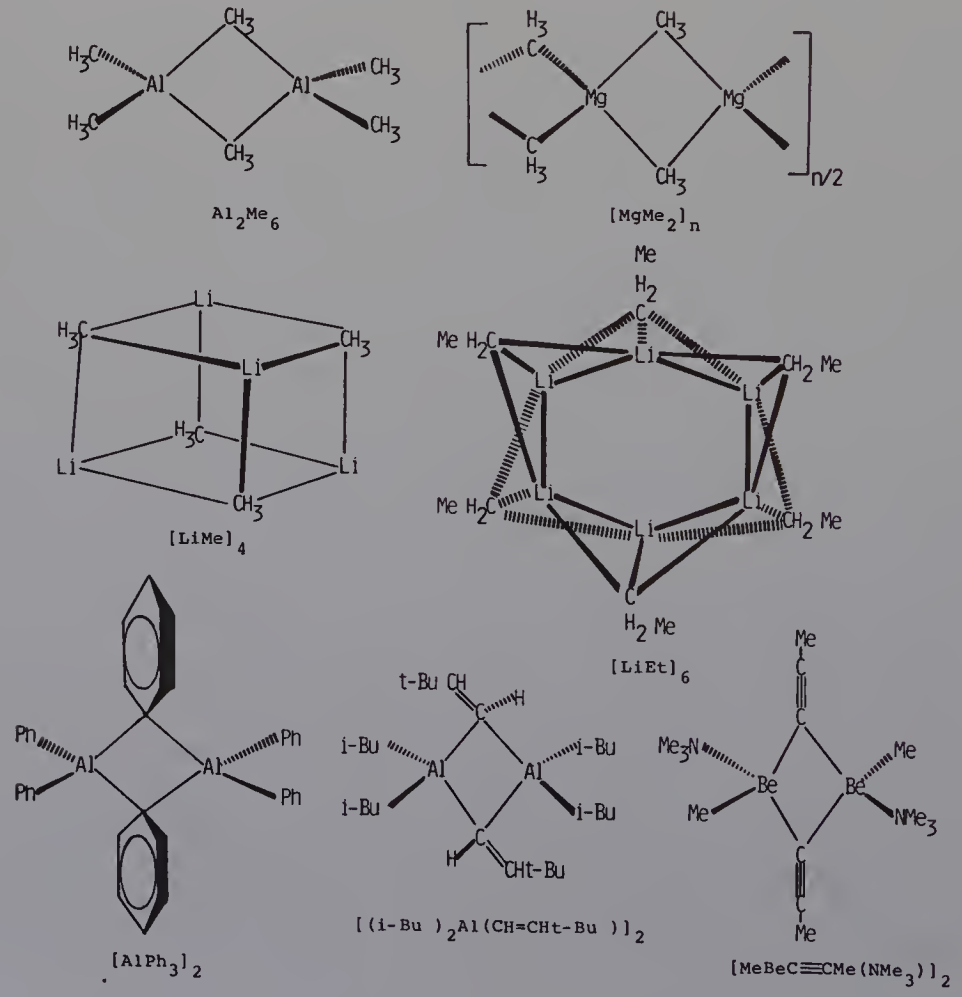


Figure 1.1. Bridged metal alkyls, aryls, alkenyls and alkynyls.

Figure 1.2 shows the structures of various types of carbocations, including the highly reactive, unstable methonium cation (CH_5^+),[11,12] the hydrogen-bridged 1,6-dimethylcyclodecyl cation ($Me_2C_{10}H_{17}^+$),[22] the pyramidal ions ($C_5Me_2H_3^+$)[23,24] and ($C_6Me_6^{2+}$),[25] and the homoaromatic cation ($C_6H_9^+$).[26] Although none of these structures has been determined by x-ray diffraction, there is good evidence from spectroscopic studies on their solutions and from theoretical calculations that the structures are as shown. Also shown in Figure 1.2 are the structures of the carbocationic transition states through which the classically bonded carbocations *i*-$PrCMe_2^+$ and *t*-$BuCMe_2^+$ can undergo degenerate rearrangement (a degenerate rearrangement is one in which migration of an atom or group from one atom to another generates a product equivalent but not identical to the original).

Figure 1.3 shows the structures of some deltahedral *carboranes*,[4,27-32] mixed hydride clusters of boron and carbon in which each carbon atom has a hydrogen atom attached to it by a bond pointing away from the center of the cluster, but otherwise

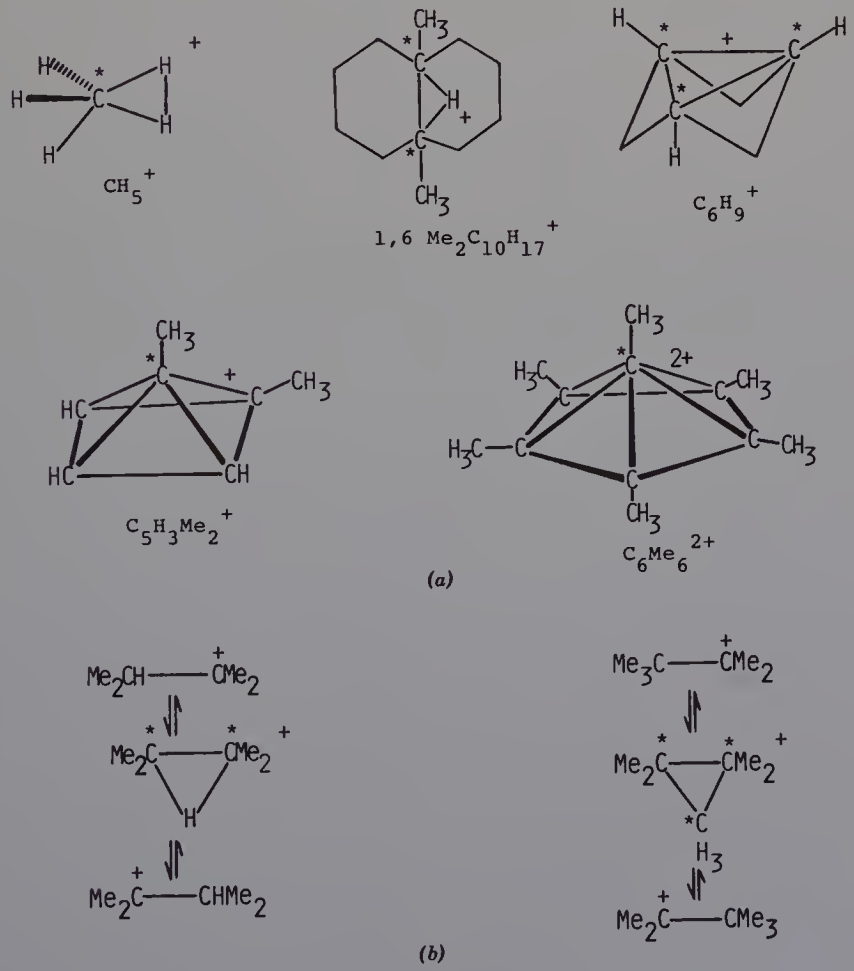


Figure 1.2. Carbocations containing hypercarbon atoms: (*a*) carbocations, (*b*) carbocationic intermediates or transition states (* denotes hypercarbons).

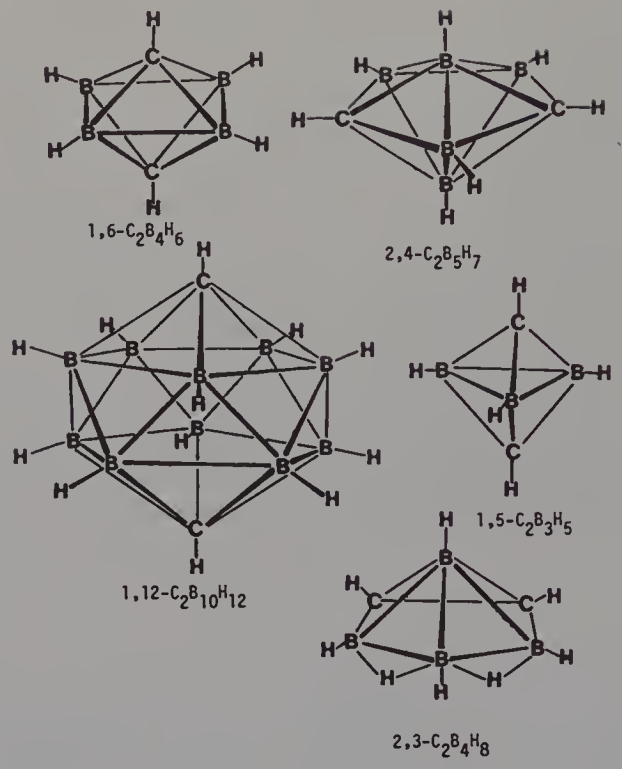


Figure 1.3. Carboranes.

uses its three remaining valences to bond to the four or five neighboring cluster atoms. Again, examples are chosen that include some highly coordinated carbon atoms ($C_2B_4H_6$, $C_2B_5H_7$, $C_2B_{10}H_{12}$) and others ($C_2B_3H_5$, $C_2B_4H_8$) where the environment (and presumably the bonding) of the carbon atoms is similar, although they are only four coordinate.

Figure 1.4 shows the structures of some mixed metal–carbon clusters.[5–7,13] Their shapes closely resemble those of the carboranes just mentioned, a resemblance we shall find of considerable significance. It is also apparent that the deltahedral examples chosen [$Fe_3(CO)_9C_2Ph_2$,[33] $Co_4(CO)_{10}C_2Et_2$,[34] $Fe_3(CO)_8C_4Ph_4$][35] have many features[36] in common with the cyclopentadienyl, cyclobutadiene, and butadiene metal complexes $(C_5H_5)Mn(CO)_3$, $(C_4H_4)Fe(CO)_3$, and $(C_4H_6)Fe(CO)_3$ also shown. The family relationship that extends from carboranes through mixed metal–carbon clusters to metal complexes of aromatic ring systems like the cyclopentadienide anion ($C_5H_5^-$) also extends to aromatic ring systems themselves.

In Figure 1.5, we show the structures of some metal carbide clusters,[5,6] compounds in which hypercarbon atoms are embedded in polyhedra (such as square pyramids,[37] octahedra,[38] trigonal prisms,[39] or square antiprisms[40]) of metal atoms. Although these carbon clusters may appear to be remote from typical organic systems, they illustrate clearly the capacity of carbon atoms to bond simultaneously to five, six, or even eight neighboring atoms, and provide useful models for what may

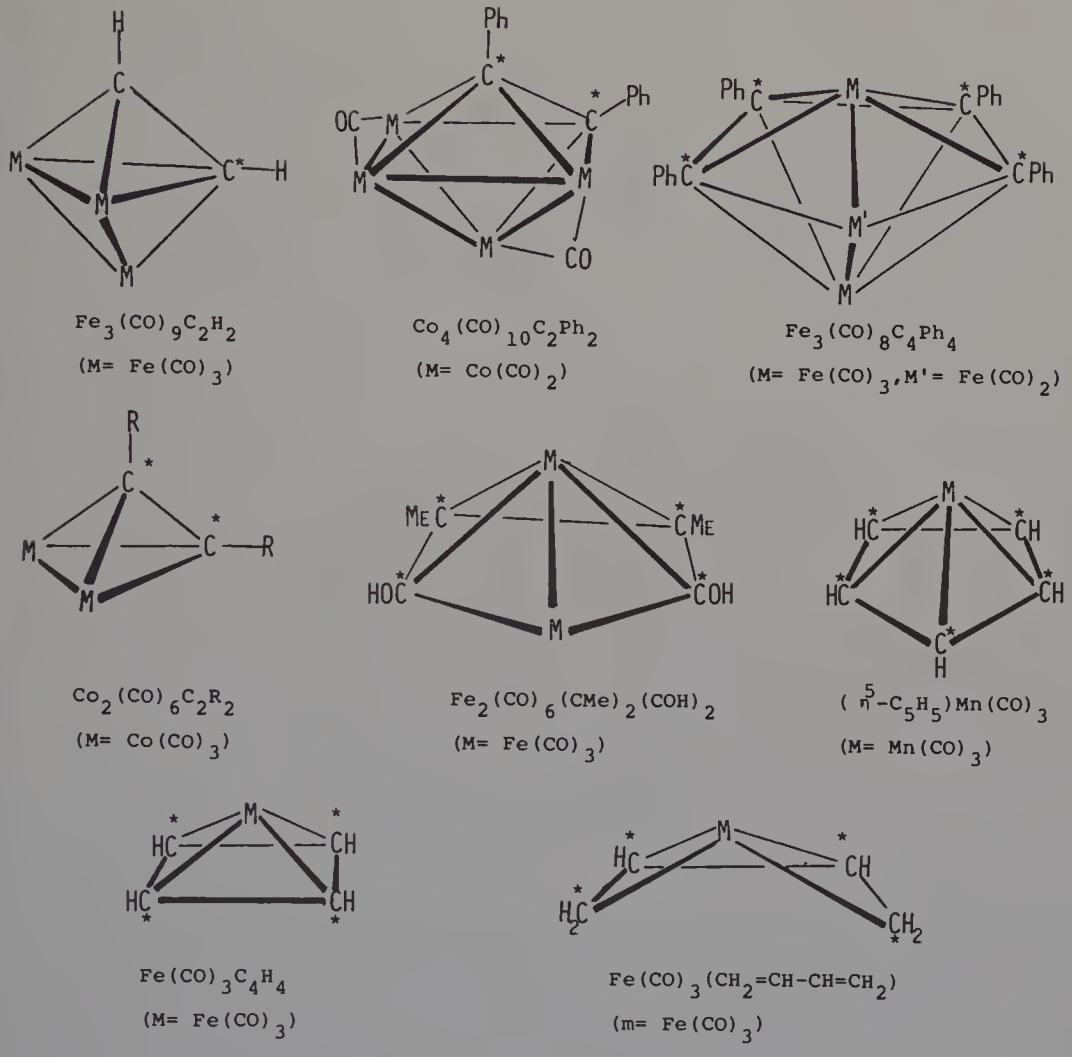


Figure 1.4. Mixed metal–carbon cluster compounds and metal–hydrocarbon π complexes ($*$ denotes hypercarbons).

be the key species in Fischer–Tropsch and related chemistry at metal surfaces. The carbon atoms of carbon monoxide may well undergo conversion at metal surfaces into carbide environments such as these, through which loss of the carbon to the bulk metal or ultimate conversion into hydrocarbons may well take place.

The carbon atoms of most binary metal carbides M_xC_y have hypercoordinated environments like those illustrated in Figure 1.5. In particular, octahedral carbon coordination is common in the interstitial carbides formed by many transition metals, materials of variable composition in which carbon atoms occupy interstices in the metal lattice that may suffer little distortion, even though the carbon valence shell electrons enter the metal valence band and so modify (and commonly strengthen) the metallic bonding. Both octahedral and distorted trigonal prismatic arrangements of

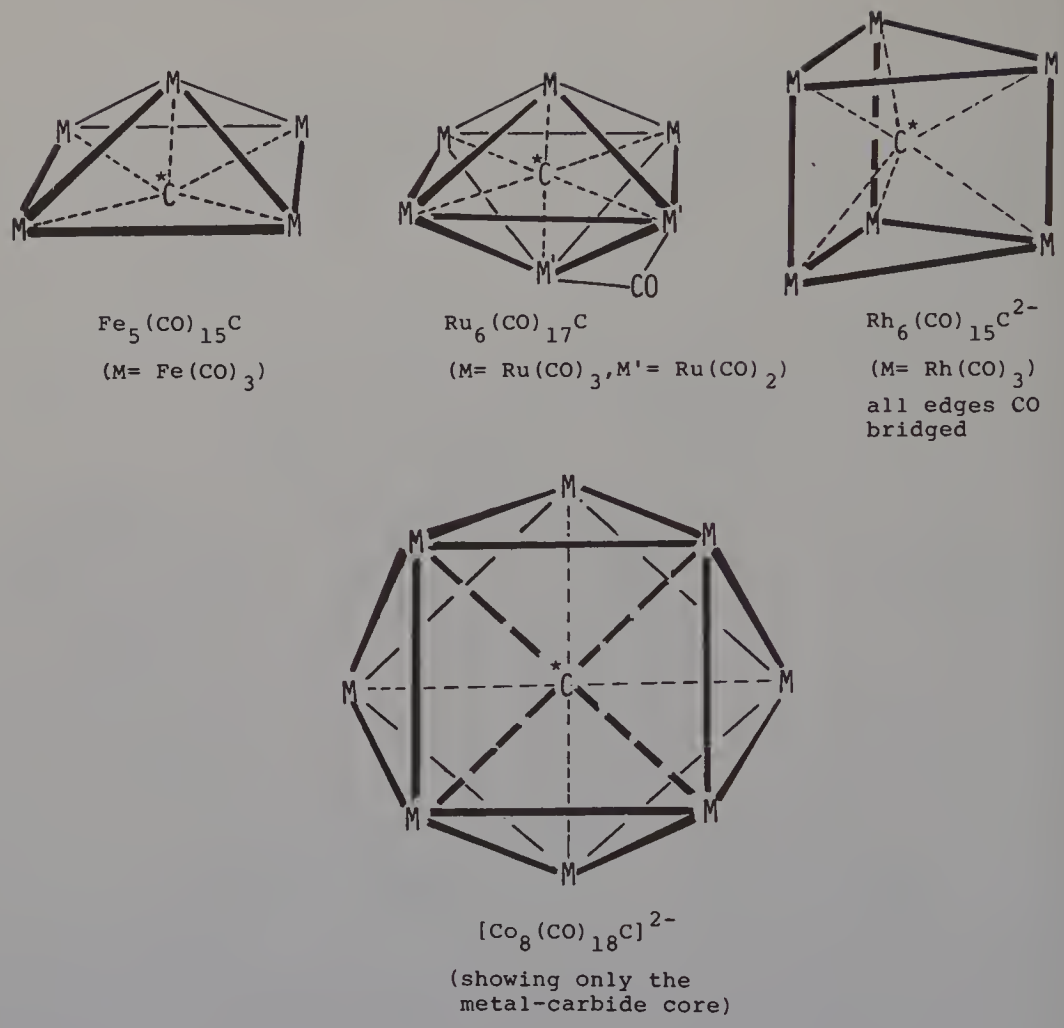


Figure 1.5. Metal Carbides, * denotes hypercarbons.

iron atoms about carbon atoms are believed to feature in the various iron carbide phases that are so important in iron and steel production. Mankind has thus been exploiting the beneficial effects of carbon hypercoordination, albeit unrecognized as such, since the dawn of the Iron Age.

Finally, Figure 1.6 shows examples of that category of hypercarbon compound that has seen the most rapid recent growth.[42-49] These are compounds in which *coordinatively unsaturated metal atoms* (metal atoms with fewer electrons in their valence shells than can be accommodated, that is, with a low energy vacant atomic orbital) form strong bonding interactions with neighboring C−H groups, effectively forming (3*c*–2*e*) CHM bonds (where M is the metal atom). Because the metal atom tends to distort the coordination sphere of the carbon atom involved, converting it from a normal carbon atom into a hypercarbon atom and drawing the C−H unit close to itself, the term "agostic" has been adopted in referring to these systems (from the Greek "to hold or clasp to oneself, as of a shield").[41]

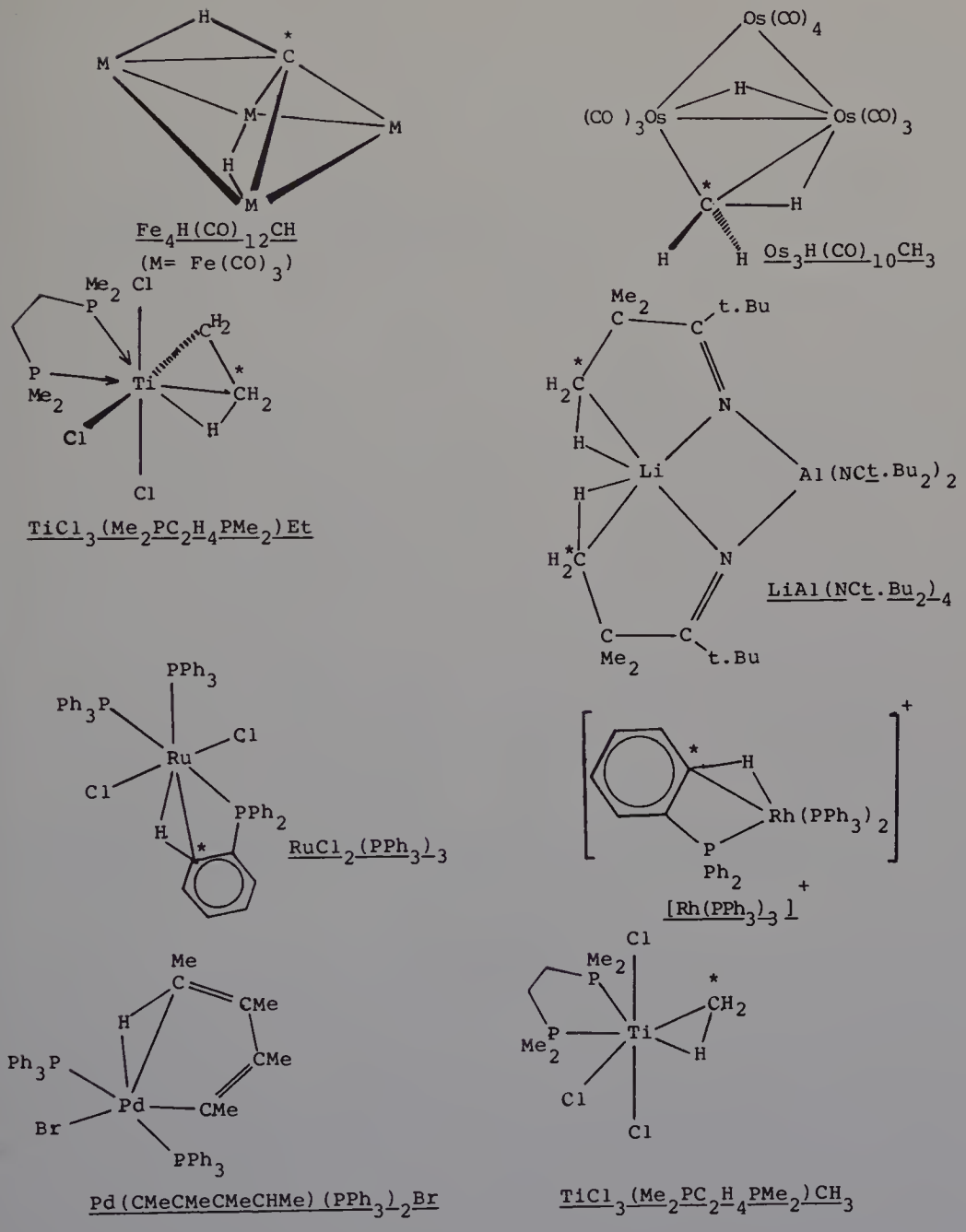


Figure 1.6. Systems containing carbon–hydrogen–metal ($3c$–$2e$) bonds (∗ denotes hypercarbons).

Among these agostic systems, which have attracted much interest because they illustrate the manner in which coordinatively unsaturated metal atoms may activate C−H bonds, there are examples of five-coordinate hypercarbon atoms (if the C−H bond is part of an alkyl group), and of four-coordinate hypercarbon atoms (if the C−H group in question is part of an alkenyl or aryl residue).

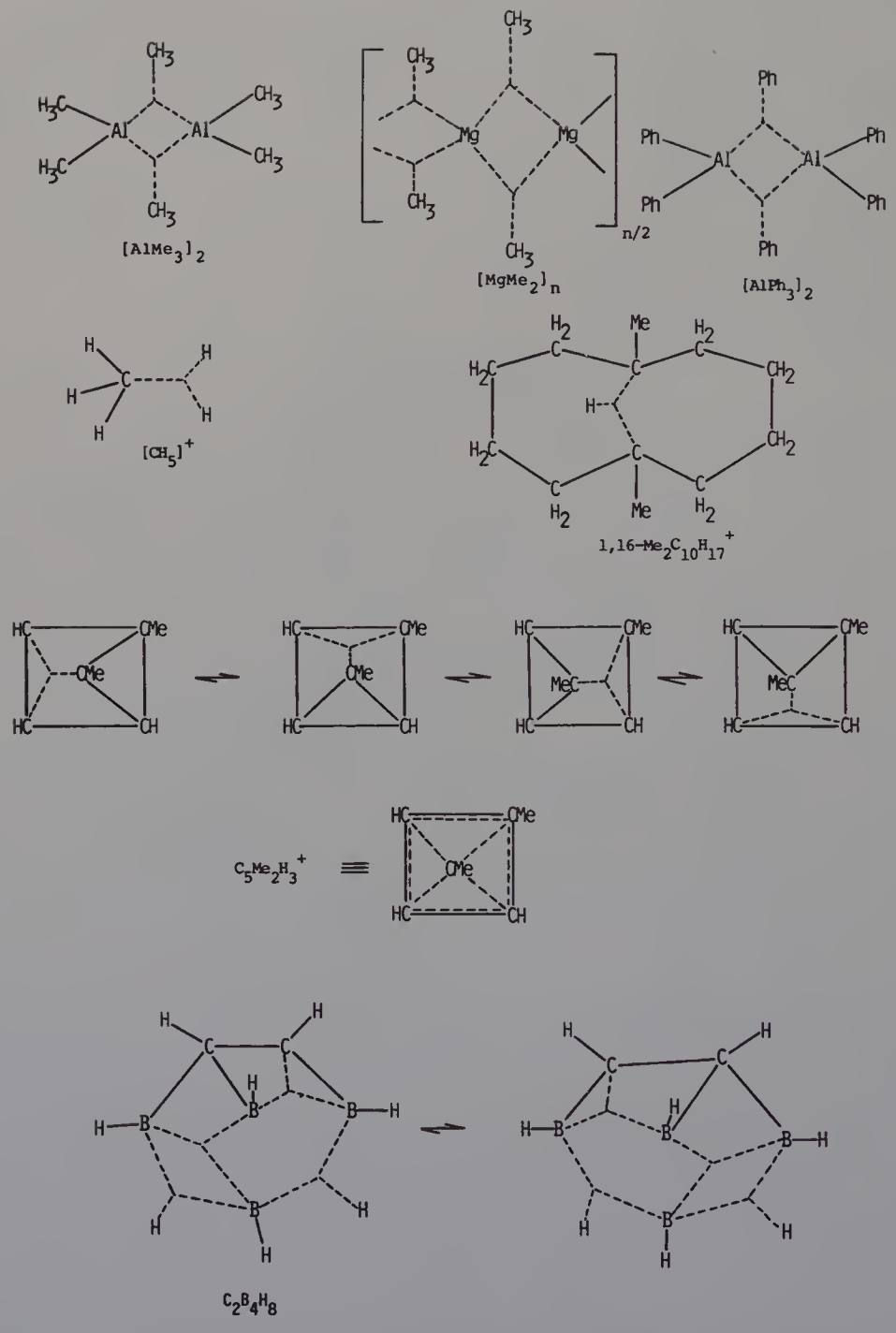
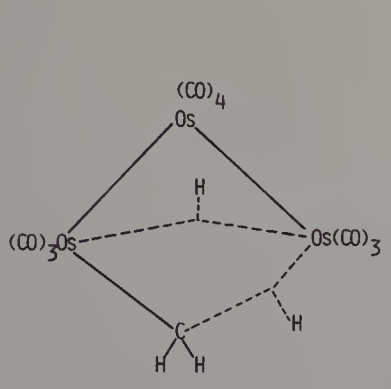
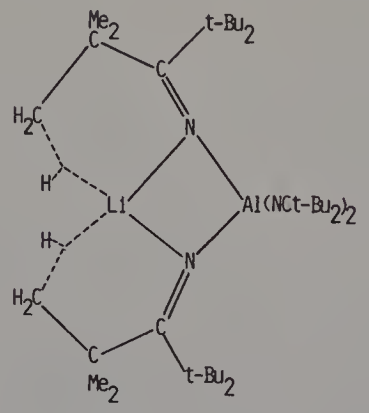


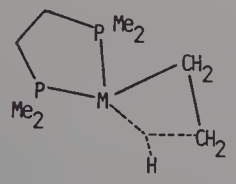
Figure 1.7. Two- and three-center two-electron bonding schemes for representative compounds from Figures 1.1–1.6.



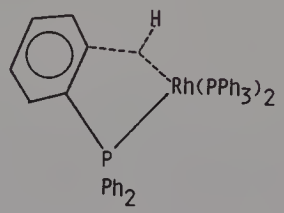
$Os_3H(CO)_{10}CH_3$



$LiAl(NCt\text{-}Bu_2)_4$



$M(Me_2PCH_2CH_2PMe_2)Et$, M= $TiCl_3$



$[Rh(PPh_3)_3]$

Figure 1.7 (continued).

1.4 THE THREE-CENTER BOND CONCEPT AND THE VARIOUS TYPES OF THREE-CENTER BONDS

In Section 1.2 we noted that the bonding in CH_5^+ could be described in terms of three (2*c*–2*e*) CH bonds and one (3*c*–2*e*) CHH bond. In Section 1.3 it was noted that (3*c*–2*e*) CHM bonds could account for the agostic systems that result when coordinatively unsaturated metals interact with CH groups. In a similar manner, (3*c*–2*e*) CMM bonds can be used to rationalize the structures of associated metal alkyls where the alkyl groups perform a bridging role between two metal atoms (Fig. 1.1). The hydrogen bridge across the middle of the cyclodecyl ring in $1,6\text{-}Me_2C_{10}H_{17}^+$ (Fig. 1.2)[22] can be explained by a (3*c*–2*e*) CHC bond. These bond schemes, illustrated in Figure 1.7, show that (3*c*–2*e*) CCC, CCB, or CBB bonds may help to describe the bonding in pyramidal carbocations or carboranes, though resonance between several canonical forms (delocalization) may need to be invoked for these more symmetrical species. That section of the molecule over which such delocalization of two- and three-center bonds occurs is often represented by broken lines as shown in Figure 1.7. The details of such bonding schemes are best left to later chapters dealing with specific categories of compounds. Here, however, it is appropriate to attempt to put such systems in perspective by noting their relationship to other examples of (3*c*–2*e*) bonding, and by noting the characteristic features of such systems.

The simplest known example of a (3*c*–2*e*) bond is the trihydrogen cation (H_3^+), the existence of which, in the gas phase, was first demonstrated by J. J. Thompson[50a] in 1911, even before G. N. Lewis formulated his electron-pair theory[51] of chemical bonding. Later, much additional evidence was obtained for H_3^+, even in solution chemistry (superacids).[50b] The H_3^+ ion is the most abundant ion present when hydrogen gas is subjected to an electrical discharge—its formation by the reaction $H_2 + H_2^+ \longrightarrow H_3^+ + H$ is some 40 kcal mol^{-1} (170 kJ mol^{-1}) exothermic,[52] and this illustrates the power of two electrons to hold together three atomic nuclei arranged at the vertices of an equilateral triangle calculated to have an edge length of 0.87 Å,[52,53] some 0.12 Å longer than the single, (2*c*–2*e*) bond length (0.75 Å) in the dihydrogen molecule, H_2. The (2*c*–1*e*) bond in H_2^+ is 1.08 Å in length.[54] These lengths reflect the lower electron density in the hydrogen–hydrogen linkage of H_2^+ and H_3^+ compared with H_2. In three-center bonded systems in general, interatomic distances typically exceed those in related (2*c*–2*e*) bonded systems by about 0.15–0.25 Å.[13]

The three hydrogen nuclei in H_3^+ are effectively held together by the electronic charge that accumulates where the three hydrogen 1*s* AO's mutually overlap (Fig. 1.8). A linear arrangement of the three nuclei would allow less effective overlap of the AO's involved, as the MO correlation diagram in Figure 1.8 indicates—note how

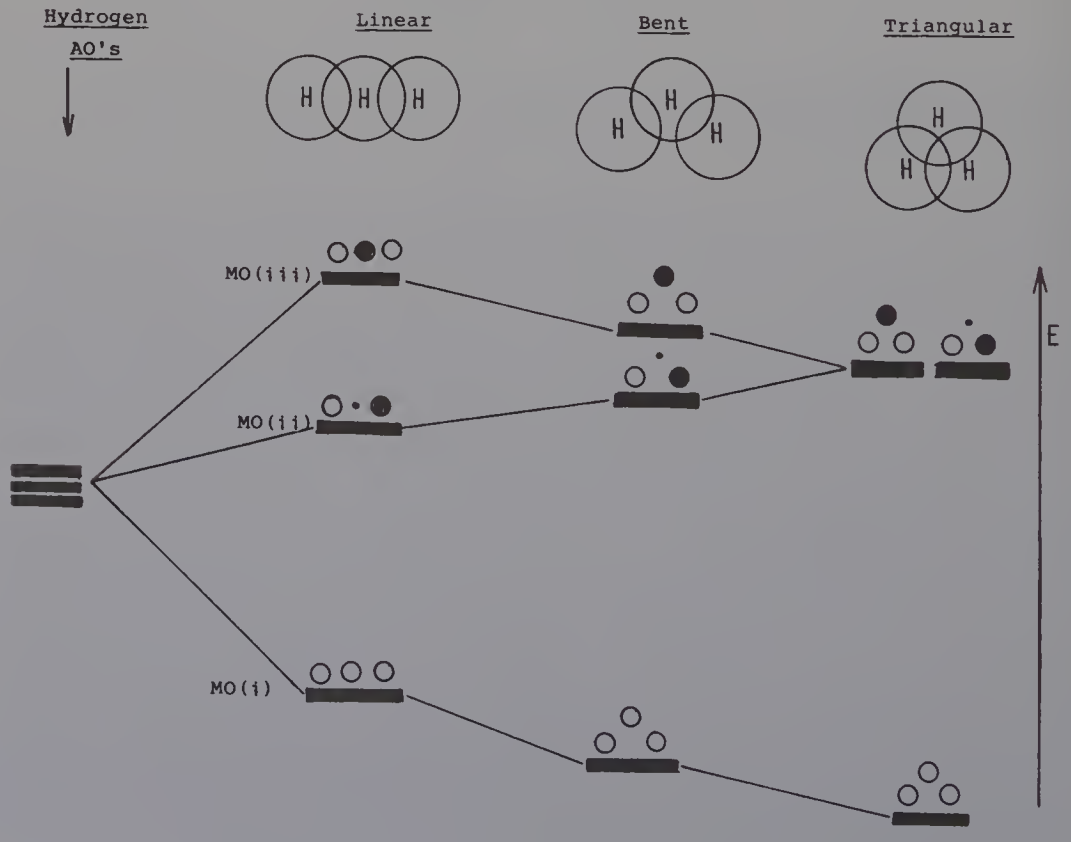


Figure 1.8. The H_3^+ cation. Possible geometries and MO energies.

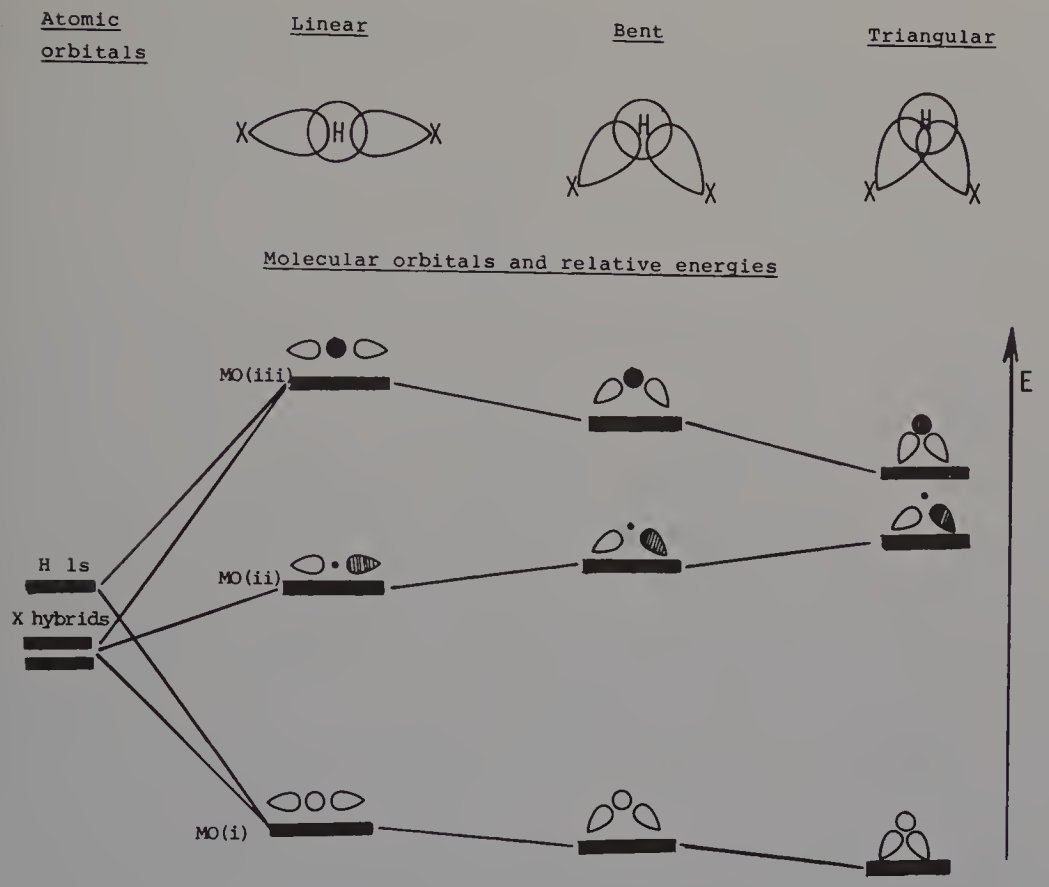


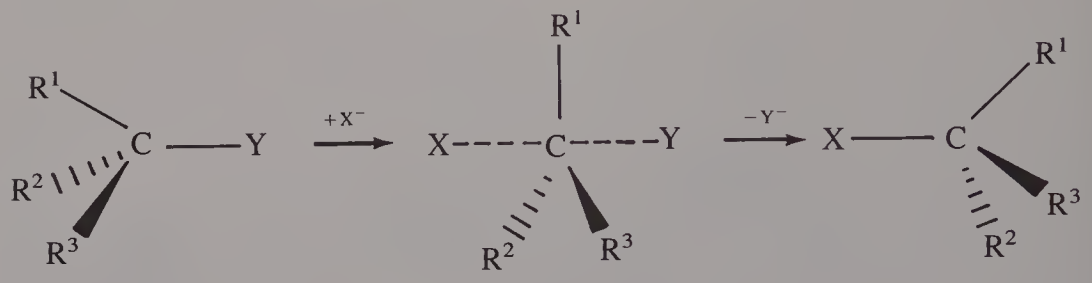
Figure 1.9. Triatomic XHX systems in which X uses a hybrid AO. Possible geometries and MO energies.

the energy of the bonding MO [that which corresponds to the (3*c*–2*e*) bond] decreases as the shape changes from linear to bent to equilateral triangular, strengthening the bonding interaction between what were initially the terminal hydrogen atoms. (Vibrational spectroscopic studies of H_3^+ have substantiated its equilateral triangular structure.)[50c]

A similar orbital correlation diagram could be constructed for other sets of three atoms contributing comparable AO's, in particular for XHX systems where the atom X, a carbon, boron or metal atom, for example, contributes a suitable *p* or *sp* hybrid AO (Fig 1.9), although MO (ii) and MO (iii) would not then become equal in energy in the triangular situation. Provided that the triatomic system needs to accommodate only one pair of electrons, a triangular arrangement is again preferred because this strengthens the (3*c*–2*e*) XHX bond [stabilizes orbital MO(i)] by increasing X----X bonding and retaining X---H bonding interactions. However, if two electron pairs have to be accommodated, as in the case of *classical hydrogen bonded*[55] systems containing N−H---N, O−H---O, F−H---F, or related hydrogen bonds, then both MO (i) and MO (ii) will be occupied, and there is no incentive for the XHX system to bend, since any stabilization in MO (i) is offset by a greater destabilization of MO (ii), which is exclusively X---X antibonding. In classical hydrogen-bonded systems,

where four electrons are involved, the unit XHX is linear, in contrast to the triangular shape we find preferred by the (3*c*–2*e*) systems.

A different triatomic system with which it is instructive to contrast these systems is the XCY linear triatomic entity involved as the transition state in S_N2 reactions.



The carbon atom in the transition state is five coordinated, and might at first sight appear to be pentavalent by accommodating five pairs of electrons in its valence shell. However, this is not the case (first-row elements like carbon have no suitable low energy AO's available to allow accommodation of 10 valence shell electrons).[56] In the transition state, the carbon atom can be assumed to use three sp^2 hybrid AO's to form classical (2*c*–2*e*) single bonds to the substituents R^1, R^2 and R^3, and we can treat it as a carbenium ion, $[R^1R^2R^3C]^+$, sandwiched between the incoming nucleophile, X^-, and leaving group, Y^-, with which it can interact using its vacant 2*p* AO. The MO diagram for this system is shown in Figure 1.10. Once again, there is one strongly bonding MO, MO(i), corresponding to a linear (3*c*–2*e*) bond. The next MO, MO(ii), has no contribution from the carbon 2*p* AO, because it consists of an in-phase combination of the orbitals on *X* and *Y*, a combination of the wrong symmetry to

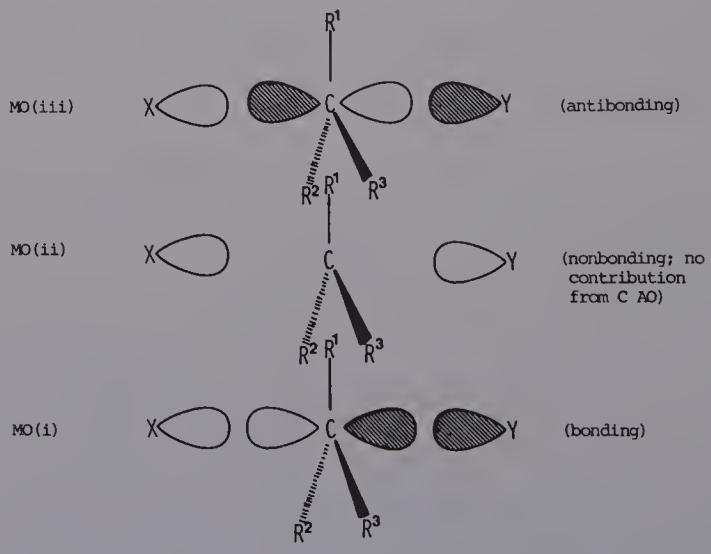


Figure 1.10. Molecular orbital description of the bonding to the five-coordinate carbon atom in the transition state in an S_N2 reaction.

combine with the carbon *p* AO. It is this MO that accommodates the second pair of electrons in the triatomic system (X^- and Y^- contribute a pair apiece) but the electrons it accommodates are shared between X and Y, and do not add to the four pairs of electrons already associated with the carbon atom's valence shell.

The $[XCR^1R^2R^3Y]^-$ system just discussed and the classical hydrogen bonds mentioned earlier are examples of triatomic systems that have to accommodate two pairs of electrons, each atom contributing a single atomic orbital. There are many other systems in which two pairs of electrons are fulfilling a bonding role between three atomic nuclei, but in which one or more of the atoms contributes more than one atomic orbital with which to bond to its two neighbors. The various possibilities for hydrocarbon systems are shown in Figure 1.11, together with some classically bonded systems. The numbers of electrons and AO's listed are those available for bonding between the three atoms concerned.

From Figure 1.11*a* (i), (ii), and (iii), it is apparent that (3*c*–2*e*) σ bonding can occur between three carbon atoms, or two carbon atoms and a hydrogen atom, in circumstances where (i) there is no other bonding between the atoms concerned, (ii) two of the atoms are linked by a (2*c*–2*e*) bond as well, or (iii) two of the atoms are linked by a (2*c*–4*e*) bond as well. *The requirements for (3c–2e) σ bonding are thus: Either all three atoms concerned contribute one AO apiece, or one of the atoms concerned contributes only one AO, and the total number of electrons available for bonding between the three atoms is one fewer than the number of AO's available.*

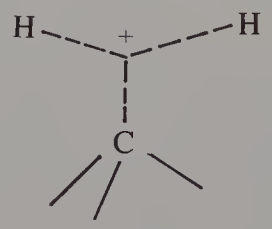
If each of the three atoms involved uses more than one AO, and if the number of electrons available is one fewer than the number of AO's, then (3*c*–2*e*) π *bonding* can occur, as shown by the examples of the allyl and cyclopropenium cations (Fig. 1.11 *b*). The difference arises because the establishment of a framework of (2*c*–2*e*) σ bonds between two or all three of the carbon atoms limits the three-center bonding to that arising from *p* AO's oriented perpendicular to the plane in which the carbon atoms lie.

Also shown in Figure 1.11*c*, for purposes of comparison, are three neutral classically bonded hydrocarbons, propane, cyclopropane, and cyclopropene. For these systems, and for electron-precise systems in general, the number of electrons available for bonding (*n*) is equal to the number of AO's available (and so adequate to fill the *n*/2 bonding MO's).

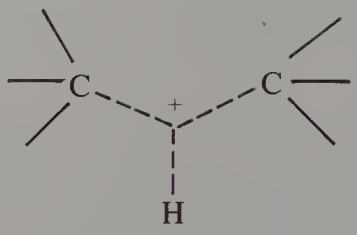
Note that the systems in Figure 1.11 that have (3*c*–2*e*) bonds, whether σ (*a*) or π (*b*), are *cationic*, as is necessary if the number of AO's is to exceed the number of electrons available. Noting this allows us to envisage carbocations and their neutral hydrocarbon precursors or products of their possible decomposition (Fig. 1.12), points that will prove relevant to a consideration of the mechanisms of reactions involving hypercarbon intermediates or transition states. Thus, protonation of a (2*c*–2*e*) C−H bond can be envisaged as a means of generating a (3*c*–2*e*) CHH bond, while protonation of a (2*c*–2*e*) C−C bond can in principle lead to a (3*c*–2*e*) CHC bond. Similar protonation of a carbon–carbon multiple bond, whether double or triple, converts a pair of carbon–carbon π-bonding electrons into a pair of three-center CHC σ-bonding electrons. Figure 1.12 also serves as a reminder that carbocationic species with structures requiring a (3*c*–2*e*) CHC or CCC bond may

(*a*)

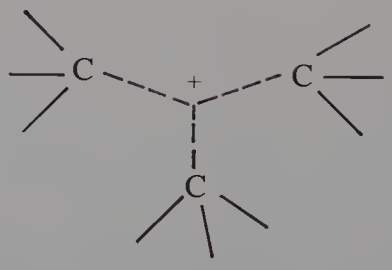
(i) (3*c*–2*e*) systems using three AO's



(alkonium ions such as CH_5^+)

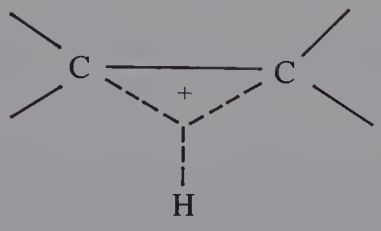


(H-bridged cations such as cyclodecyl)

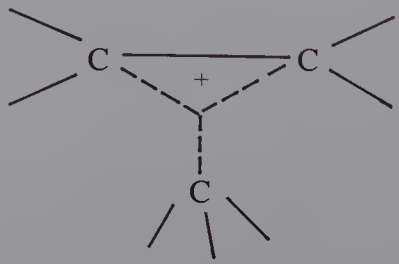


(trishomocyclopropenium type alkyl bridged cation)

(ii) (3*c*–4*e*) systems using five AO's



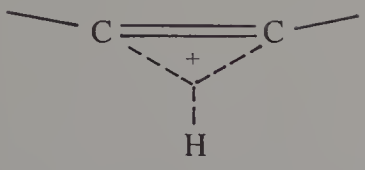
(protonated alkene)



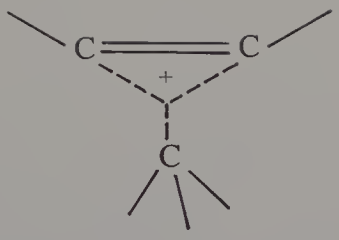
(2-norbornyl type or alkylated alkene cation)

Figure 1.11. Three-center bonding possibilities for carbocationic hydrocarbon systems: (*a*) 3*c*–2*e* σ-bonded systems (carbocations); (*b*) 3*c*–2*e* π-bonded systems (carbocations); and (*c*) hydrocarbons with classical 2*c*–2*e* bonds (electron precise).

(iii) (3*c*–6*e*) systems
using seven AO's

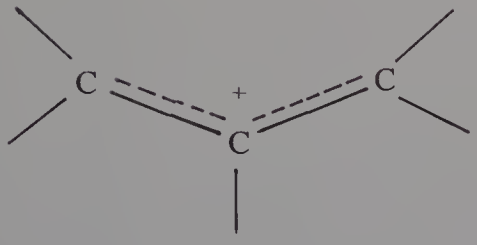


(protonated alkyne)

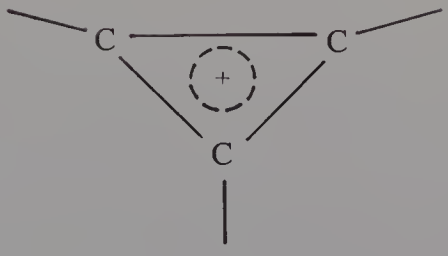


(alkylated alkyne)

(*b*)

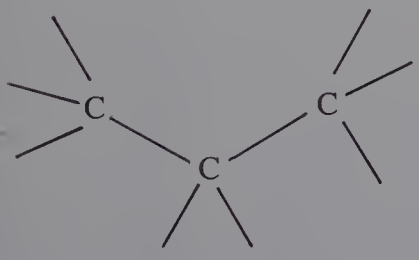


(allyl cation)

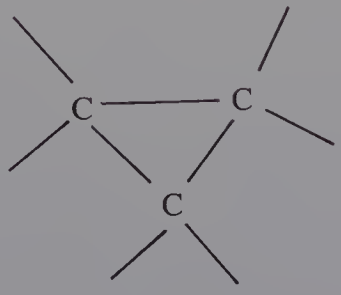


(cyclopropenium cation)

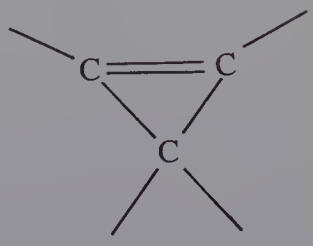
(*c*)



(propane)



(cyclopropane)



(cyclopropene)

Figure 1.11 (continued).

(*a*)

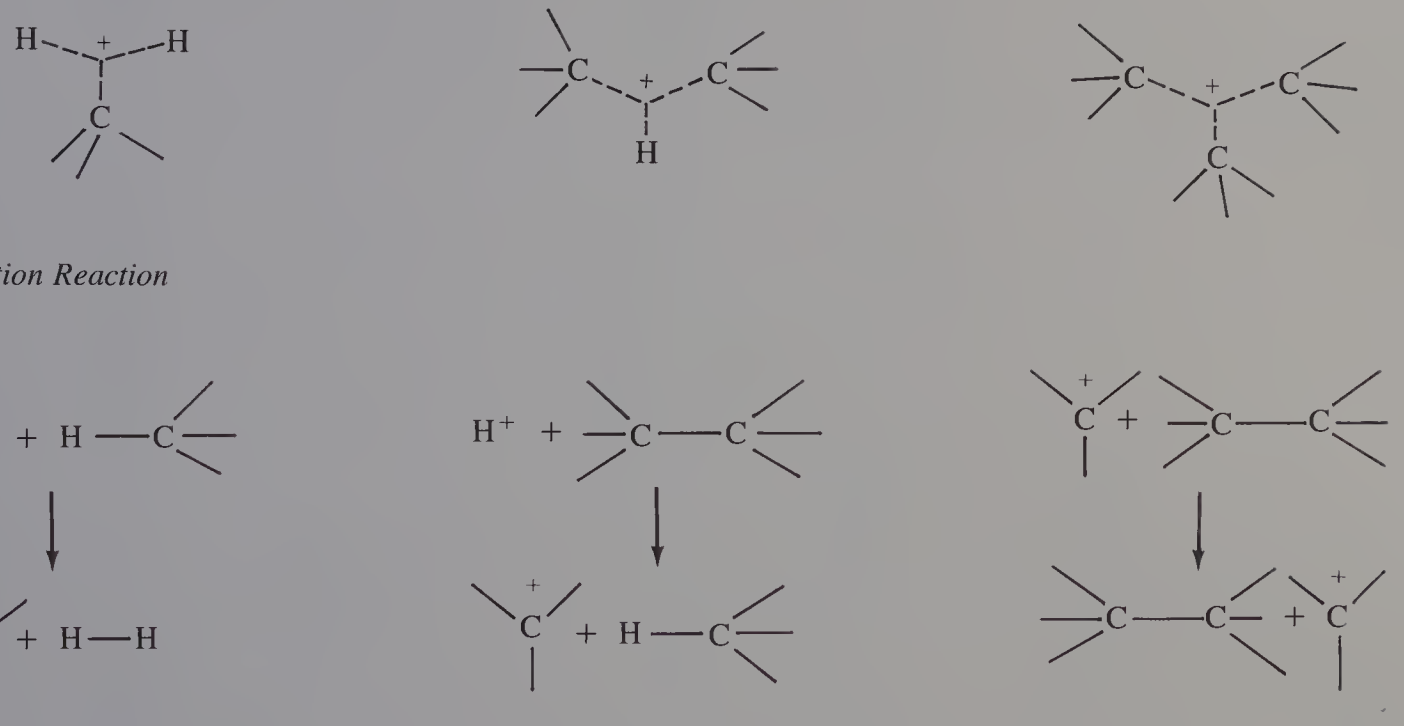
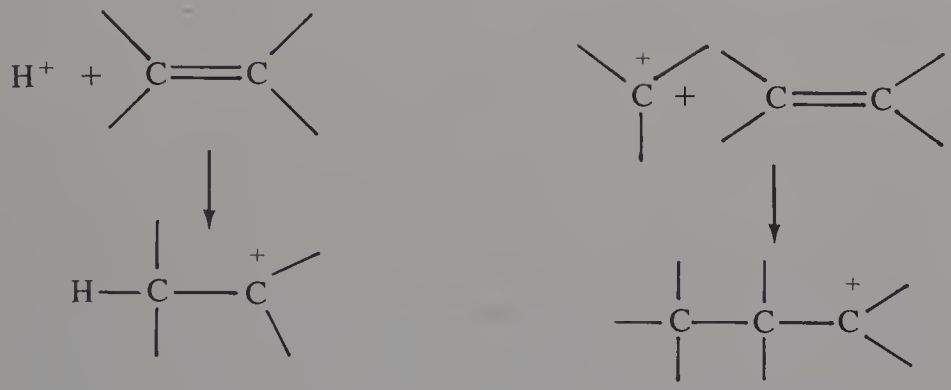


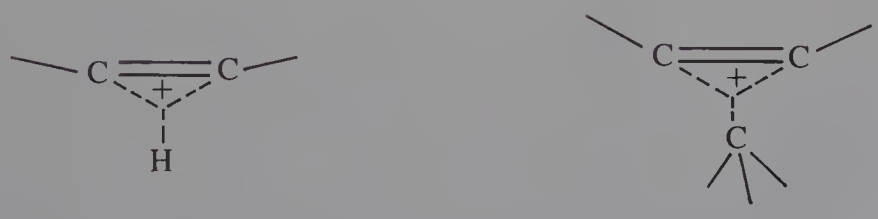
Figure 1.12. Different types of hypercoordinated carbocations, their formation from hydrocarbon precursors either by protonation or alkylation and their cleavage products (*a*) (3*c*–2*e*) bonded carbocations.

(*b*)

Formation Reaction



(*c*)



Formation Reaction

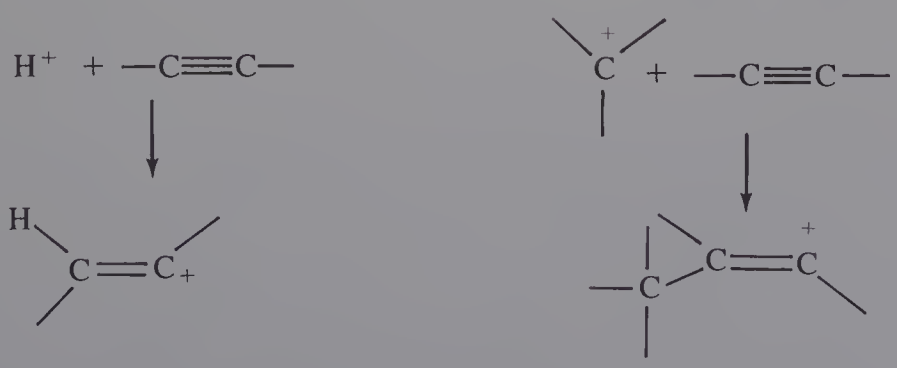
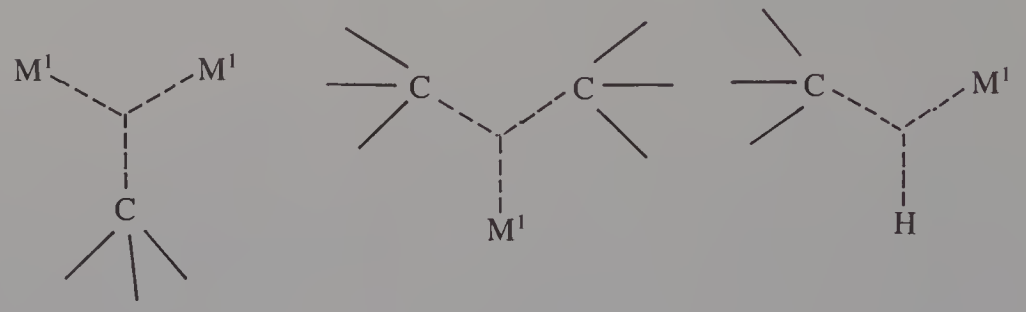


Figure 1.12 (continued). (*b*) (3*c*–4*e*) bonded carbocations; and (*c*) (3*c*–6*e*) bonded carbocations.

revert to, or indeed be less stable than, a classically bonded carbenium ion structure in which one of the available AO's remains unused (as a $2p$ AO on the carbocationic center, oriented perpendicular to the plane of the σ bonds to that center).

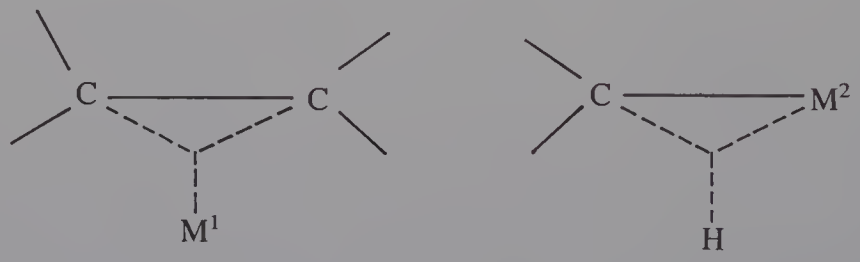
Before turning from a consideration of three-center bonded systems to systems in which the bonding is more delocalized, it is worth noting briefly what other types of systems exhibit ($3c$–$2e$) σ bonding, to set these carbon systems in a more general context. We have already noted that bridged metal alkyls, and so on, exhibit ($3c$–$2e$)

($3c$–$2e$) systems



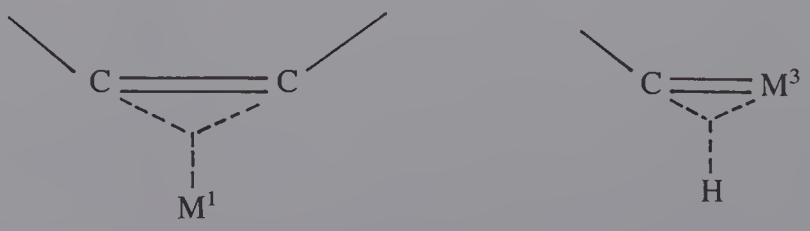
bridged metal alkyls metallated C−C bond metallated C−H bond

($3c$–$4e$) systems



metal–alkene π complex protonated metal–carbene complex

($3c$–$6e$) systems



metal–alkyne π complex protonated metal–carbyne complex

Figure 1.13. Three-center bonding possibilities for organometallic systems. M^n represents a metal-containing unit where the superscript number "n" indicates the number of metal AO's that unit contributes to bond the other two atoms.

MCM bonding (where M is an electropositive metal atom) (Fig. 1.1), and that coordinatively unsaturated metal atoms can convert (2*c*–2*e*) C−H bonds into (3*c*–2*e*) CHM bonds (Fig. 1.6). These and the various other three-center bonding possibilities open to organometallic systems are summarized in Figure 1.13, which shows the relationship between the systems already mentioned and metal–alkene or metal–alkyne complexes, and protonated metal–carbenes and metal–carbynes. It should be mentioned, however, that, although the metal–alkene and metal–alkyne interactions shown in Figure 1.13 indicate the type of weak bonding that the coordinatively unsaturated aluminum atoms of aluminum trialkyls (AlR_3) can participate in with alkenes or alkynes, they do not adequately represent the type of bonding that occurs in the relatively stable complexes of alkenes and alkynes with transition metals, as in the earliest reported such complex, $KPtCl_3(C_2H_4)H_2O$ (Zeise's salt).[57,58] Very stable alkene complexes such as this are formed by metal atoms that can contribute not only the vacant AO into which to draw electronic charge from the filled carbon–carbon π-bonding MO [Fig. 14*a* (i)], but also a filled *pd* hybrid MO that can transfer electronic charge back to the alkene's empty π-antibonding MO [Fig. 1.14*a* (ii)].[59] The net result is to convert the MC_2 triatomic system from a four electron, five AO system in the case of a metal like aluminum

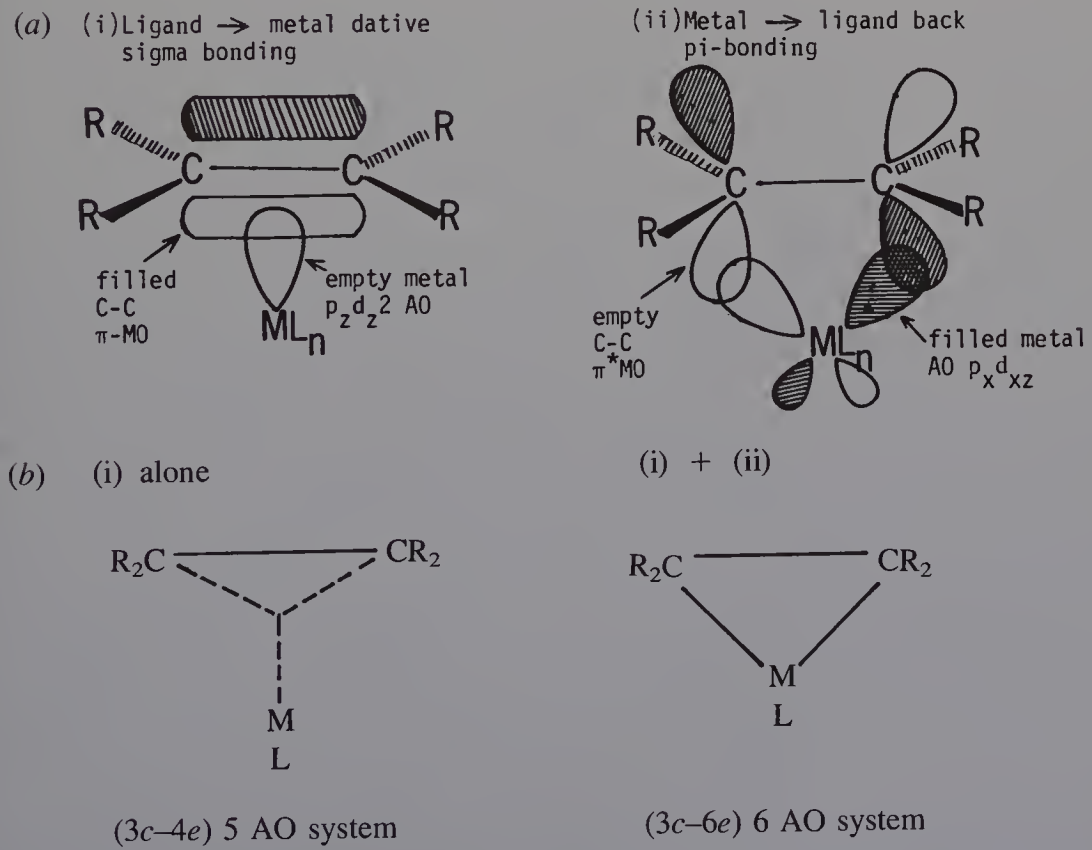


Figure 1.14. Bonding in transition metal–alkene complexes: (*a*) orbitals involved; and (*b*) valence bond representation.

[Fig. 14*b* (i)] into a six electron, six AO system for a metal like platinum, for which an electron-precise bonding description is possible [Fig. 14*b* (ii)].

To place these (3*c*–2*e*) carbon systems in perspective, it should be acknowledged that (3*c*–2*e*) σ bonding is widespread in inorganic chemistry, principally in the chemistry of elements to the left of carbon in the periodic table, that is, in the chemistry of boron and the metallic elements in general.[3-10,54] This is because such elements generally have more valence shell AO's than electrons, so need to spread the bonding power of these electrons over a larger number of centers than elements with equal numbers of electrons and valence shell AO's (like carbon) or with more electrons than valence shell AO's (like the nonmetallic elements of Groups 5–7). Indeed, the concept of three-center, two-electron σ bonding, which had been suggested tentatively earlier, really first made a significant impact in the 1940s and 1950s when it proved invaluable, as emphasized by Longuet-Higgins[60] and

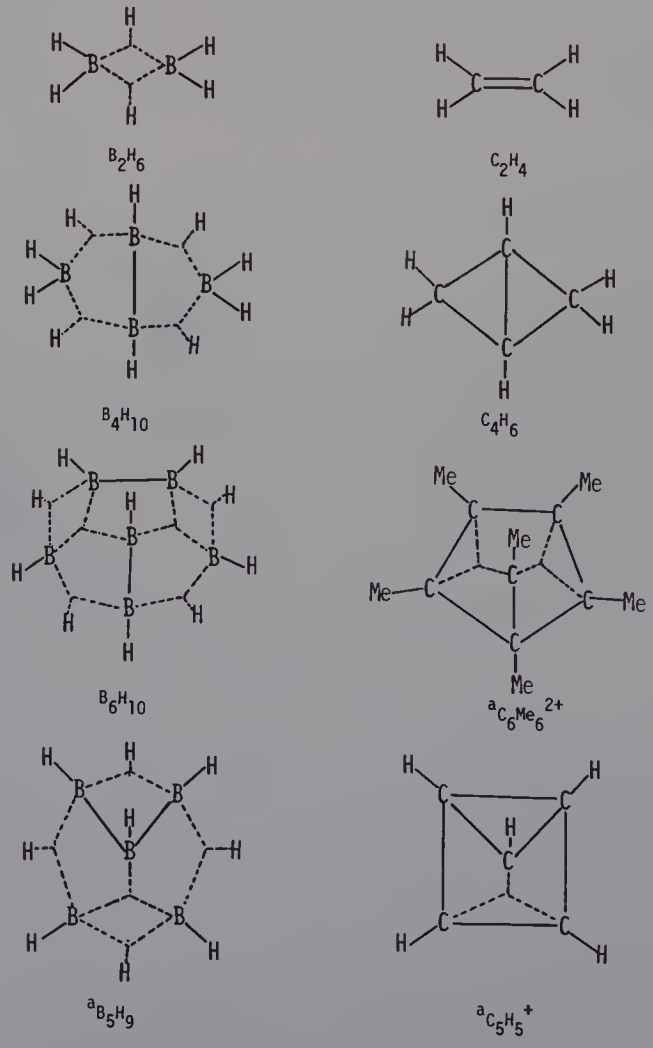


Figure 1.15. Two- and three-center bond networks in some boron hydrides and their hydrocarbon counterparts; [a] indicates structures that are one of the several possible canonical forms.

Lipscomb[61] in explaining the intricate networks of atoms revealed by structural studies on boron hydrides such as B_2H_6, B_4H_{10}, B_5H_9, and B_6H_{10}, where localized (3*c*–2*e*) BHB and BBB bonds, together with (2*c*–2*e*) BH and BB bonds, neatly accounted for structures that defied description solely in terms of (2*c*–2*e*) bonds.

Since analogies between hypercarbon systems and their isoelectronic polyborane counterparts will provide a recurrent theme in this book we illustrate some representative boron hydride bond networks in Figure 1.15 alongside their organic counterparts (generated in principle by replacement of BH units by isoelectronic carbon atoms). Note that where (3*c*–2*e*) BBB bonds are needed to explain the structure of a boron hydride, (3*c*–2*e*) CCC bonds are needed to explain the structure of the analogous hydrocarbon system. Since (3*c*–2*e*) bonds between carbon atoms and other carbon atoms, or between carbon atoms and hydrogen, metal and/or boron

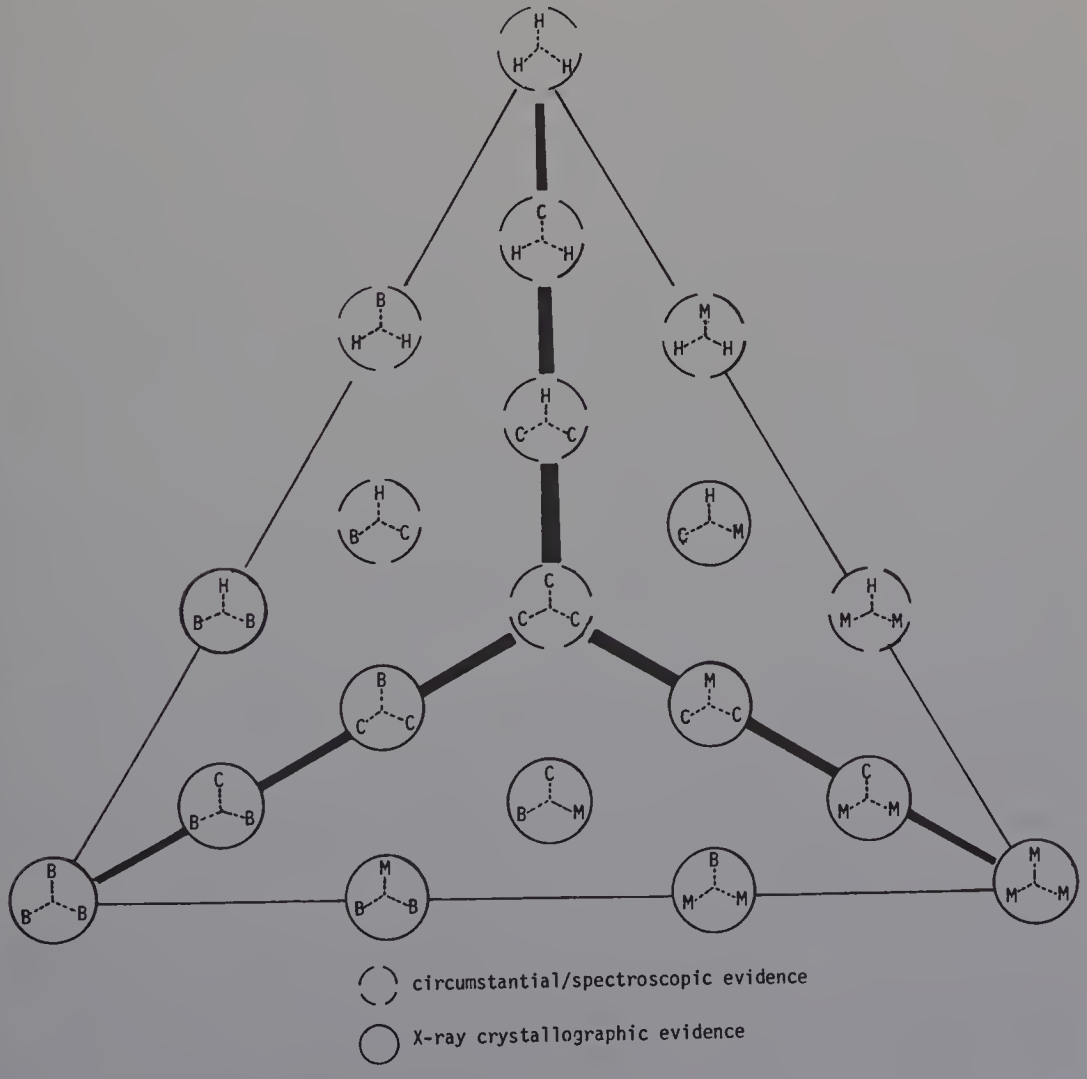


Figure 1.16. The various triatomic arrangements of carbon, hydrogen, metal, and/or boron atoms that can be linked by (3*c*–2*e*) σ bonds.

atoms, will be featured throughout this book, we illustrate in Figure 1.16 the various types of trinuclear systems that can be envisaged for these four types of elements. X-ray crystallographic evidence for most of these systems is now available, and there is either spectroscopic or circumstantial evidence for the existence of the remainder, even if short-lived.

1.5. THE BONDING IN MORE HIGHLY DELOCALIZED SYSTEMS

Thus far, in our discussion of the bonding in hypercarbon systems, we have considered various types of three-center bonding situations, varying according to the spatial arrangement of the three atoms (linear, bent, or triangular) and the numbers of electrons and AO's available to hold those atoms together. Such three-center bonding descriptions can be applied to a wide range of hypercarbon systems, notably to bridged metal alkyls, many carbocations, and agostic systems in which coordinatively unsaturated metal atoms interact with suitably located C−H groups of their ligands. However, we have also seen that, when hypercarbon atoms participate in highly symmetrical systems such as pyramidal carbocations ($C_5H_5^+$, $C_6Me_6^{2+}$), then description of the bonding in terms of specific networks of two- and three-center, electron-pair bonds is unsatisfactory unless resonance between all the possible ways of locating these bonds is invoked. Such *resonance delocalization* of the two- and three-center bonds over a whole section of a molecule or ion clearly contributes to the stability of such systems, and must be taken into account if we are to get some feeling for the distribution of electron density over the network of atoms involved.

For example, for the square pyramidal cation ($C_5H_5^+$) and derivatives thereof (Fig. 1.11 and 1.15) there are four ways of assigning the (3*c*–2*e*) CCC bond and two (2*c*–2*e*) CC bonds that in localized bonding terms link the apical carbon atom to the basal atoms. For purposes of assessing how many electrons on average are assignable to each two-center C−C link between apical and basal atoms, or between basal atoms, we can regard a (2*c*–2*e*) bond as assigning one electron pair to the edge concerned, whereas a (3*c*–2*e*) CCC bond assigns one third of an electron pair to each of the three CC edges of the triangle in which it lies. Hence, on the average, each of the four two-center links holding the apical to the basal carbon atoms in $C_5H_5^+$ is associated with two thirds of an electron pair, and so can formally be regarded as a two-center bond of fractional bond order two thirds, that is, 0.67.

Each of the basal C−C links, already having a pair of electrons assigned to it because of the (2*c*–2*e*) σ bond along that edge, also gains on average one twelfth of an electron pair as its share of the (3*c*–2*e*) CCC bond pair, giving it an overall bond order of thirteen twelfths (Fig. 1.17).

Similar arguments applied to the pentagonal pyramidal dication $C_6Me_6^{2+}$, in which one (2*c*–2*e*) C−C bond and two (3*c*–2*e*) CCC bonds link the apical carbon atom to the basal atoms, lead to two-center bond orders of seven fifteenths between apical and basal atoms and seventeen fifteenths between basal atoms.

The usage of localized two- and three-center bond schemes gets progressively more complicated and less helpful as the symmetry of the system increases.

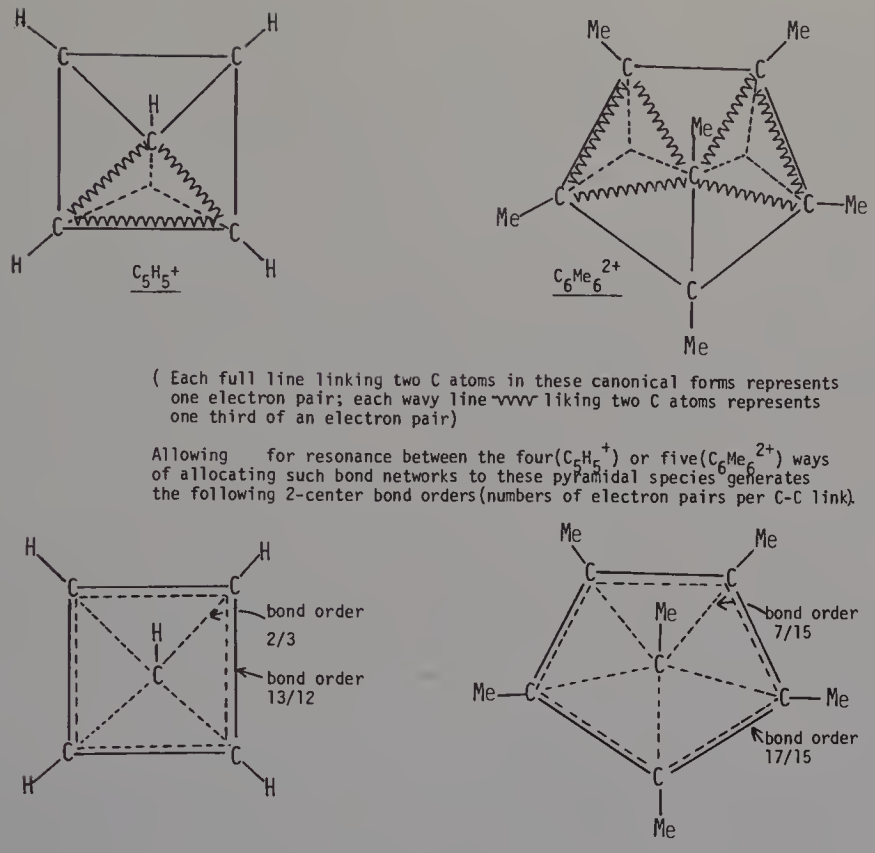


Figure 1.17. Bond orders in pyramidal cations $C_5H_5^+$ and $C_6Me_6^{2+}$ indicated by two- and three-center electron-pair networks.

Molecular orbital treatments are preferred in such cases. The manner in which these same cations, $C_5H_5^+$ and $C_6Me_6^{2+}$, can be treated in MO terms is worth illustrating here for the purpose of comparison with the localized bond schemes just discussed, and also to underline the relationship between these pyramidal species and normal aromatic ring systems.

The cations $C_5H_5^+$ and $C_6Me_6^{2+}$ are examples of species that would be described as *antiaromatic* if they had regular polygonal structures—with only four electrons to assign to the π system in each case, they would have triplet ground-state electronic configurations, with one electron in each of the doubly degenerate highest occupied molecular orbitals (HOMOs). [Cyclobutadiene (C_4H_4) if it had a D_{4h} square planar structure, would be another member of the same series.] The preferred pyramidal structures offer two main advantages: they generate closed shell electronic configurations, and provide a more strongly bonding role for the electrons in the HOMOs.

These points are illustrated in Figure 1.18*a* where we show how the doubly degenerate nature of the HOMO of the π system leads to triplet electronic configurations for D_{4h} C_4H_4, D_{5h} $C_5H_5^+$, and D_{6h} $C_6H_6^{2+}$ (or $C_6Me_6^{2+}$). In Figure 1.18*b* we show how the framework MO's, of square pyramidal (C_{4v}) $C_5H_5^+$ can in

principle be constructed by bringing the apical CH^+ unit along the fourfold axis of a basal square planar C_4H_4 residue. The apical CH^+ unit supplies a pair of electrons that can be considered, in the isolated unit, to occupy an *sp* hybrid AO pointing away from the C−H bond. This AO has the right symmetry to combine with the fully symmetric combination of *p* orbitals on the C_4H_4 species (the lowest energy π-bonding MO) to form a nondegenerate framework bonding MO. The pair of *p* AO's of the CH^+ unit perpendicular to the C−H bond interact with the half-filled degenerate HOMOs of C_4H_4 to convert them from the carbon–carbon *nonbonding* role they would play in D_{4h} C_4H_4 into a degenerate pair of MO's that considerably strengthen the bonding between the apical and basal atoms. The four electrons in the HOMOs of the basal C_4H_4 unit, together with the pair in the *sp* hybrid AO of the

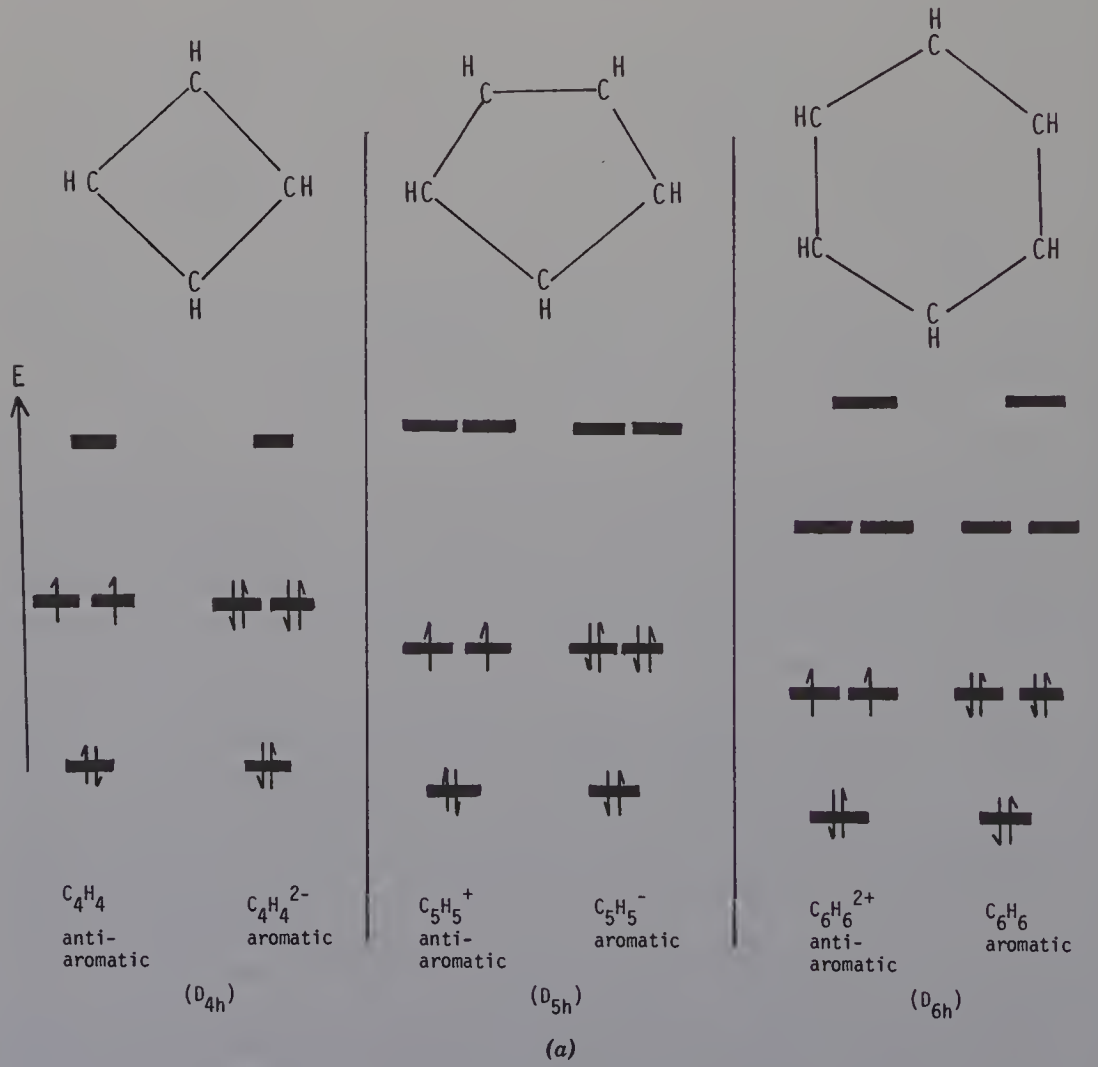


Figure 1.18. Molecular orbital diagrams showing how $C_5H_5^+$ and $C_6Me_6^{2+}$ would be antiaromatic if polygonal and how their framework bonding MO's use the π-bonding electrons of their basal C_4H_4 and C_5H_5 (equivalent to C_5Me_5) units: (*a*) Polygonal C_nH_n systems.

apical CH^+ unit, provide the three pairs needed for a closed shell electronic configuration.

A similar treatment of $C_6Me_6^{2+}$ considered to be generated by bringing an apical CMe^+ unit along the fivefold axis up to a pentagonal $C_5Me_5^+$ species, is illustrated in Figure 1.18*c*. Again, electrons that at best play a weakly bonding role in the case of the planar ring system $C_5Me_5^+$, acquire a strongly bonding role in the pyramidal cationic product.

These MO treatments of the bonding in pyramidal cations, exploring the interaction between the π MO's of the basal C_nH_n ring with the AO's of the capping CH^+ unit, closely parallel the normal treatment of the metal–carbon bonding in metal complexes of C_nH_n-ring systems.[5,9,62] The bonding in $C_5H_5^+$ thus closely resembles that in the iron carbonyl–cyclobutadiene complex $(C_4H_4)Fe(CO)_3$ (Fig. 1.4), while that in $C_6Me_6^{2+}$ resembles that in the pentamethylcyclopentadienyl–manganese carbonyl complex $(C_5Me_5)Mn(CO)_3$ (Fig. 1.4) or indeed in ferrocene, $Fe(C_5H_5)_2$. This is because such units as CH^+ and $Fe(CO)_3$ or $[Mn(CO)_3]^-$ have very similar frontier orbital characteristics, and thus capacities to bond to other units.[62] Though not isoelectronic, they are *isolobal*[63,64]: Their frontier orbitals have similar energies,

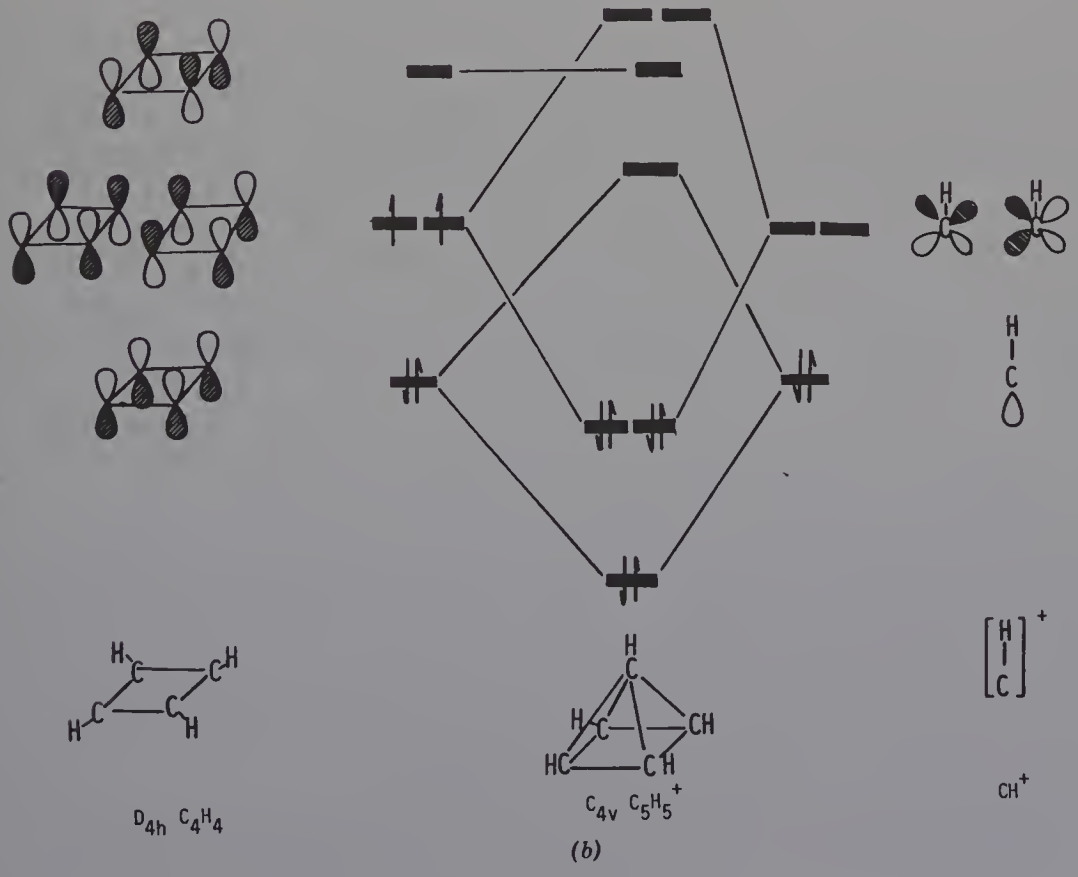


Figure 1.18 (continued). (*b*) Framework MO's of $C_5H_5^+$ generated from the π MO's of D_{4h} C_4H_4 and CH^+ units.

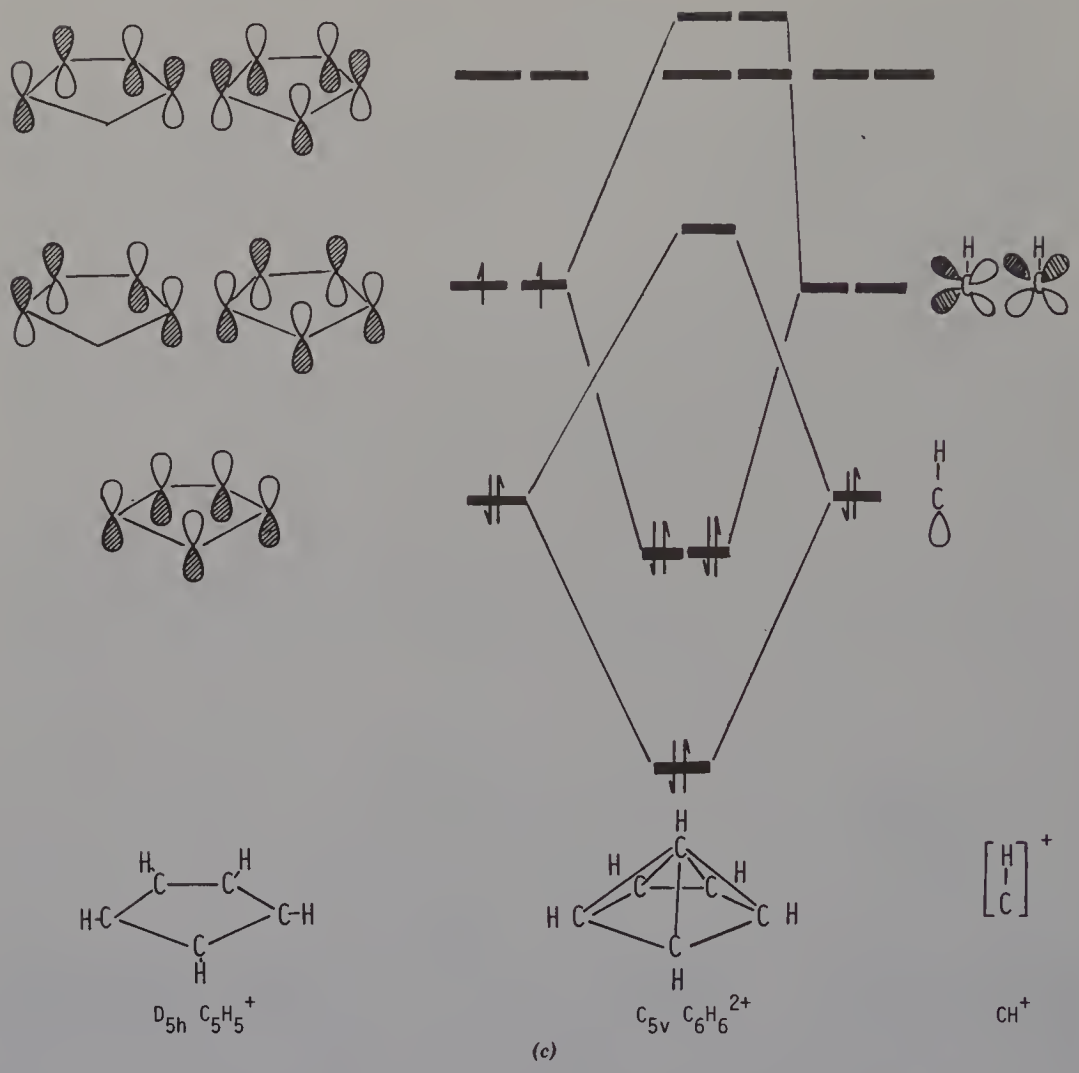


Figure 1.18 (continued). (*c*) Framework MO's of $C_6H_6^{2+}$ generated from π MO's of $C_5H_5^+$ and CH^+ units.

extensions in space, and lobal characteristics, which enable them to participate in the same types of bonding (Fig. 1.19) (The development of the concept of isolobality, as a means of recognizing the common bonding characteristics of what might seem to be quite disparate entities, owes much to the experimental studies of organometallic and metallacarborane systems containing hypercarbon atoms that showed what types of metal-containing residues might replace CH or BH units of C_nH_n rings or carboranes,[5,13,30,32] as will be discussed in Chapter 3.)

Further examples of the value of MO treatments of the bonding in hypercarbon systems will be found in later chapters of this book, notably in Chapters 3 and 4.

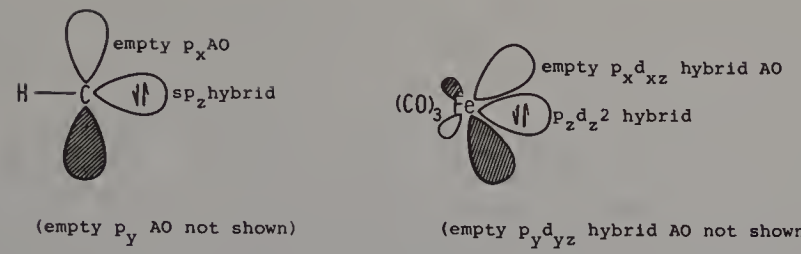
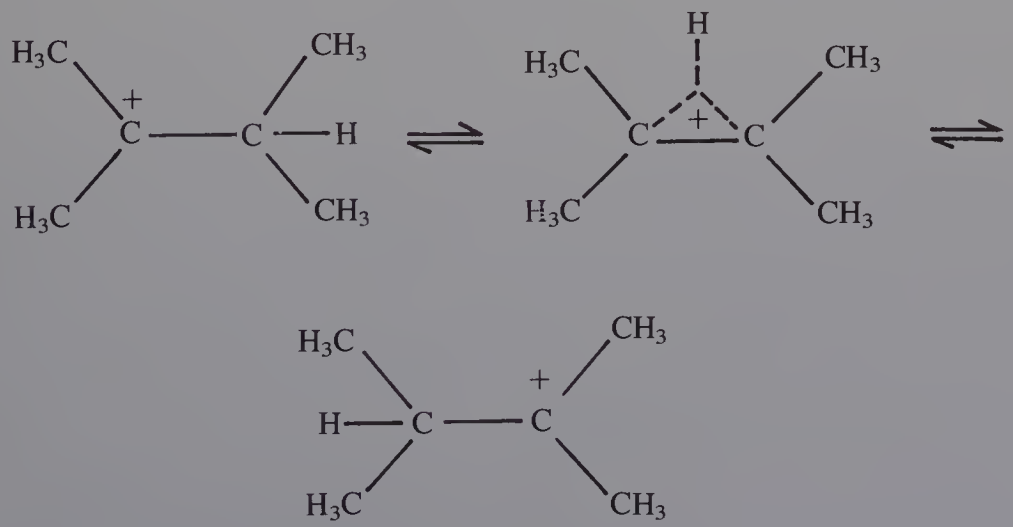


Figure 1.19. The isolobal relationship between a CH^+ unit and an $Fe(CO)_3$ unit.

1.6 REACTIONS INVOLVING HYPERCARBON INTERMEDIATES

For most of the systems discussed so far, hypercoordinated carbon atoms have featured in the most stable forms of the compounds in question. For example, the bridged metal alkyl structures found by x-ray studies on crystalline samples of such compounds as $(AlMe_3)_2$[15] or $(LiMe)_4$[17] persist in solutions of these substances in inert (hydrocarbon) solvents, and the shapes of the pyramidal cations $(C_5Me_2H_3^+)$[23,24] and $(C_6Me_6^{2+})$[25] have been deduced from ^{13}C and ^1H nuclear magnetic resonance (NMR) studies to be those adopted by such cations in solutions in acid media. For other systems, however, structures explicable solely in terms of classical (*2c–2e*) bonds may be more stable, although alternative structures involving hypercarbon atoms may be only a little less stable, and thus provide low energy transition states through which rearrangement reactions may occur, as in the degenerate rearrangement of the tetramethylethyl cation, a process for which $\Delta H^{\ddagger}$ is < 3 kcal mol^{-1} (Scheme 1.4).[65]

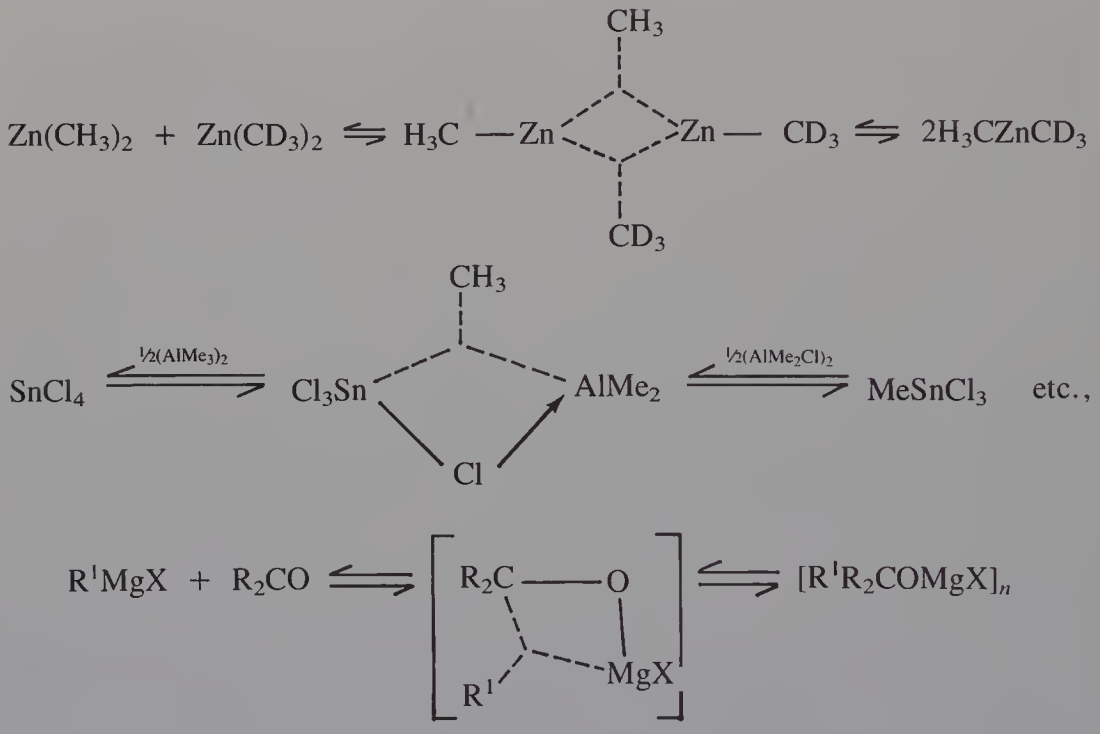
Scheme 1.4



In Chapter 7, we shall draw attention to the wide range of reactions now realized to involve hypercarbon intermediates. To indicate the scope of these reactions, some examples are illustrative.

The bridged structures of metal alkyls[3] such as $(AlMe_3)_2$ and $(MgMe_2)_n$, are not mimicked by their main group congeners $GaMe_3$ and $ZnMe_2$ (which are monomeric). Nevertheless, these bridged structures illustrate how alkyl groups can readily be transferred from one metal atom to another, or from a metal atom to a carbon atom, via hypercarbon intermediates or transition states (Scheme 1.5)

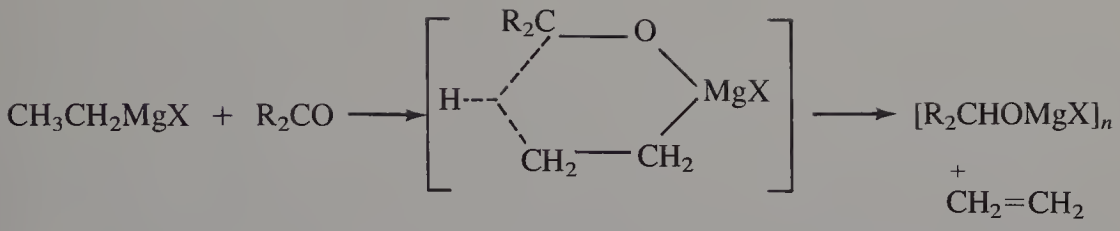
Scheme 1.5

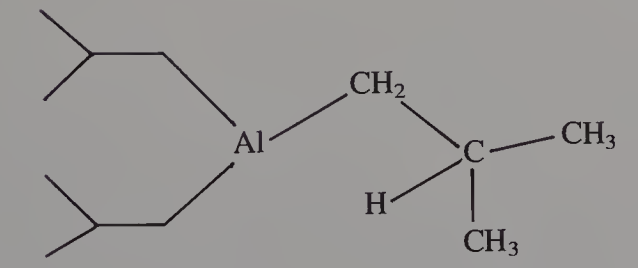


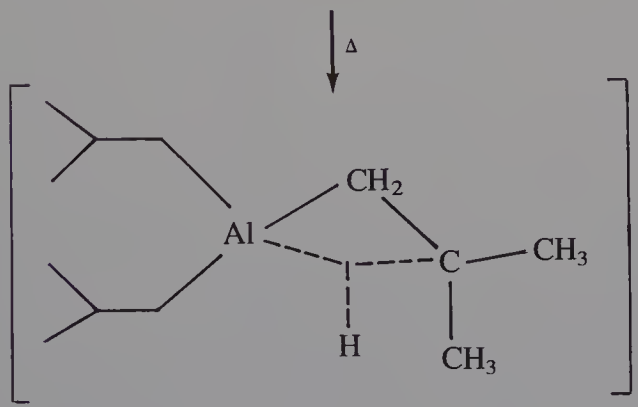
The manner in which ethyl Grignard reagents[66] (and many other metal alkyls with β-hydrogen atoms)[4] can function as reducing agents by alkene elimination and β-hydrogen transfer probably also involves hypercarbon species. Similarly alkyllithiums and alkylaluminums undergo analogous β-hydrogen elimination (Scheme 1.6). Similar hypercarbon intermediates must be considered in the case of the Meerwein–Ponndorf–Verley reduction[67] (Oppenauer oxidation), Scheme 1.7. A similar six membered ring option appears to be possible for the olefin exchange reaction of alkylboranes[68] (Scheme 1.8).

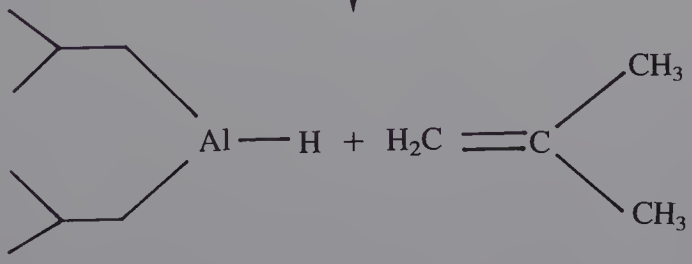
The involvement of hypercoordinated carbon species in S_N2 reactions was commented on in Section 1.4 (Fig. 1.10). Compounds have been synthesized[69] that keep the displaced and displacing atoms close to the carbon atom undergoing nucleophilic substitution, in order that the relative energies of the classically bonded

Scheme 1.6


CH3CH2MgX + R2CO
R2C
O
H
MgX
CH2
CH2
[R2CHOMgX]n
+
CH2=CH2

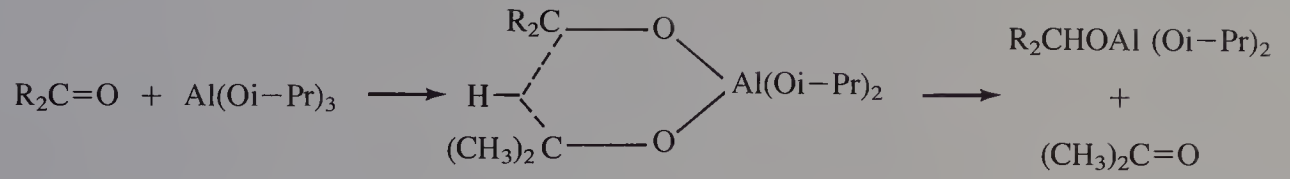

Al
CH2
C
CH3
H
CH3


Δ
Al
CH2
C
CH3
H
CH3

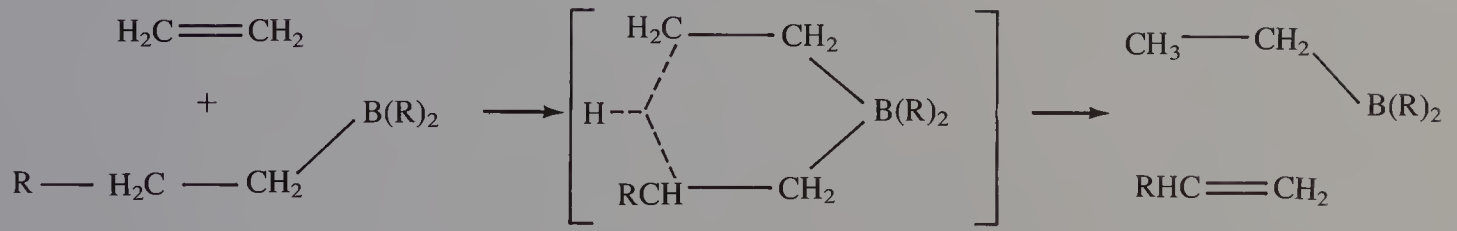

Al
H
+
H2C
C
CH3
CH3


CH3CH2CH2CH2Li
reflux
octane
CH3CH2CH
CH2
+
LiH

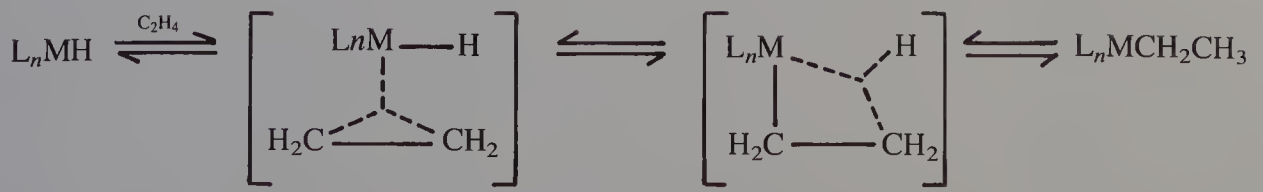
Scheme 1.7



Scheme 1.8



Scheme 1.9



reagent or product, and the hypercoordinated transition state, can be both more readily assessed and also modified (see Chapter 7).

The many reactions that involve insertion of carbon–carbon double or triple bonds into metal–carbon or metal–hydrogen bonds provide further examples of hypercoordinated carbon atoms.[70] For example, an alkene may coordinate to the coordinatively unsaturated metal atom of a metal hydride complex prior to inserting into the metal–hydrogen bond (Scheme 1.9). The hydroboration reaction, dehydroboration reaction[71] (not to be confused with olefin exchange reaction of alkylboranes) and organoborane rearrangement[72,73] reactions (in which boryl residues R_2B migrate along alkyl chains) are examples of this type of reaction (Fig. 1.20). The latter reaction is commonly supposed to entail successive dissociation and association steps in which a dialkylborane residue R_2BH separates from the hydrocarbon chain and then recombines in the reverse orientation.[71] That this mechanism is not general is shown by the way that in some cases, the hydrocarbon chain retains its stereochemical integrity,[72,73] a feature incompatible with the intermediacy of an alkene. The retention of the hydrocarbon stereochemistry poses no problem, however, if the boryl residue, R_2B, becomes attached to the next carbon atom along the chain before becoming detached from its original site (Fig. 1.20*b*). Its mode of travel along the hydrocarbon chain, "branch to branch," has aptly been described as "molecular brachiation."[74]

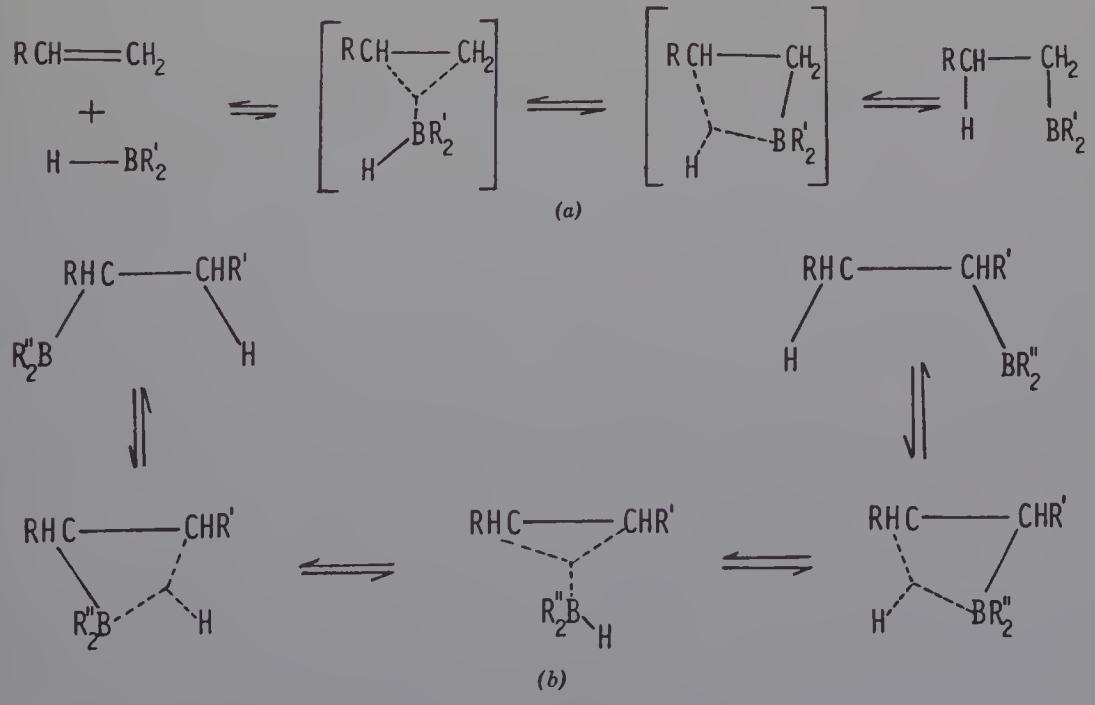
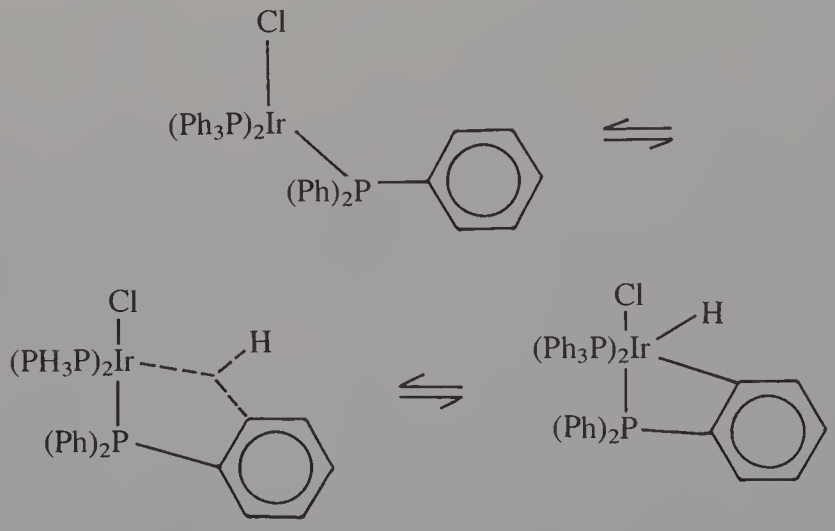


Figure 1.20. Involvement of hypercarbon intermediates in the hydroboration, dehydroboration and alkyl borane rearrangement: (*a*) Hydroboration–dehydroboration reaction; and (*b*) Alkyl borane rearrangement reactions (molecular brachiation).

The *oxidative–addition* reactions of transition metal complexes with C−H bonds of either saturated or unsaturated organic groups, whereby organometallic hydrides are formed, and their reverse reactions, *reductive eliminations*, provide yet further examples of important reactions that involve hypercoordinated carbon atoms. The largest group of such reactions, *orthometallation reactions*, involves intramolecular formation of a metal–carbon bond to the nearest carbon atom of an aromatic ring already linked to the metal atom through another atom (Scheme 1.10).[75]

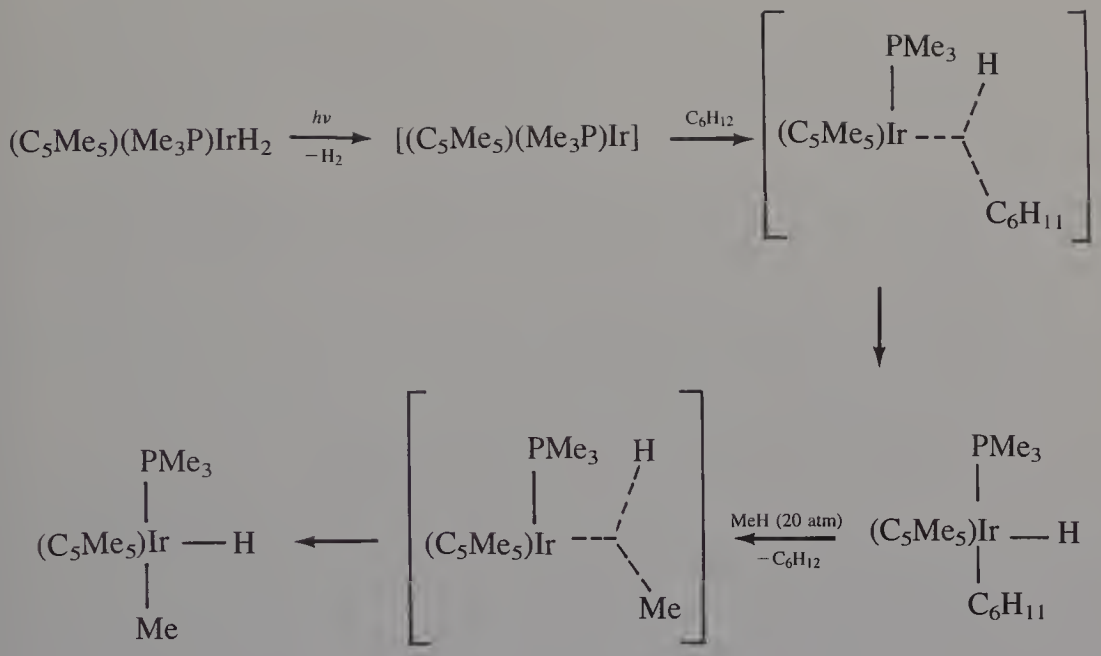
Scheme 1.10



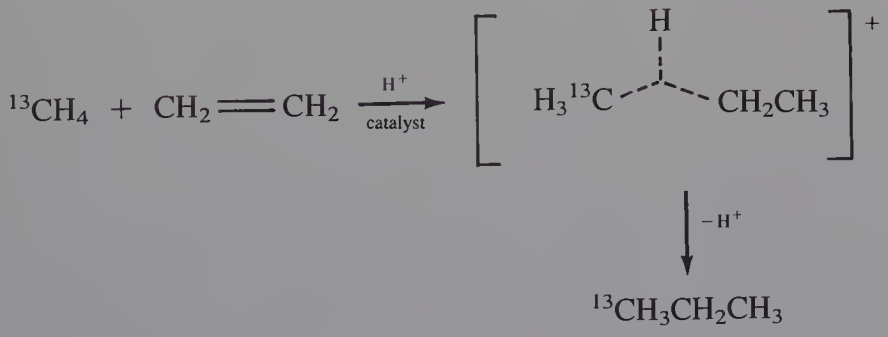
Intermolecular reactions between coordinatively unsaturated metal atoms and the C−H groups of relatively unreactive hydrocarbons such as cyclohexane and even methane have been reported (Scheme 1.11).[76] Insertion reactions of carbenes, R_2C: (generated from diazo alkanes, R_2CN_2) into C−H or other bonds are clearly of the same type, the carbene carbon atom playing the role of the coordinatively unsaturated metal in the reactions just cited (see also insertion reactions of nitrenes, etc.). Typical electrophilic substitution reactions of alkanes, including methane, are exemplified in the ethylation of the latter (labeled with ^{13}C) with ethylene over superacid catalyst (Scheme 1.12).[77] The key step is the insertion of the highly electron-deficient trivalent ethyl cation into a C−H bond forming the pentacoordinate carbocation. Similar substitutions of methane include electrophilic chlorination,[78] nitration, and related reactions[2c] (Scheme 1.13).

These and other reactions believed to involve hypercarbon intermediates are discussed in Chapter 7.

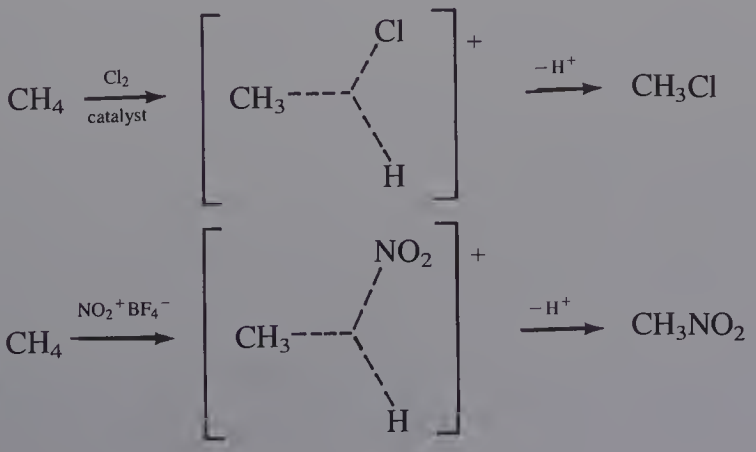
Scheme 1.11



Scheme 1.12



Scheme 1.13



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chapter 2

BRIDGED (ASSOCIATED) METAL ALKYLS

2.1. INTRODUCTION

One area of organic chemistry in which higher coordinated carbon atoms are found as normal features of typical molecules is in the organometallic chemistry of the more electropositive metals.[1–3] The many x-ray crystallographic studies that have been carried out on such substances have shown that the simple alkyl and aryl derivatives of such metals as aluminum,[4–7] beryllium,[8–9] copper,[10,11] lithium,[12,13] magnesium,[14,15] manganese,[16] yttrium, and various lanthanons[17,18] have structures in which the metal-attached carbon atoms can use three of their four valencies to bond in the usual manner to other atoms (usually carbon and/or hydrogen atoms) in the alkyl or aryl residue, while using the fourth to bond simultaneously to two or more metal atoms. Crystalline trimethylaluminum, for example, contains dimeric molecules, $(AlMe_3)_2$, in which two of the six methyl groups perform a bridging role between the two metal atoms, as shown in structure **1**.[19,20] These dimers persist in solutions of trimethylaluminum in inert (paraffinic) solvents and even in the vapor, though dissociating into monomers, **2**, at elevated temperatures.

The complete range of metals capable of forming such associated alkyls has yet to be established. Those already known to do so are identified in the periodic table in Figure 2.1. They tend to have electronegativities in the range 1.0–1.5 on the Pauling scale, and form small, highly polarizing cations. They also have more orbitals than electrons in their valence shells. By forming associated structures, their alkyl derivatives make better use of these orbitals than monomeric alkyls would, increasing the metal–carbon bond energy of the systems. For example, the total energy of the

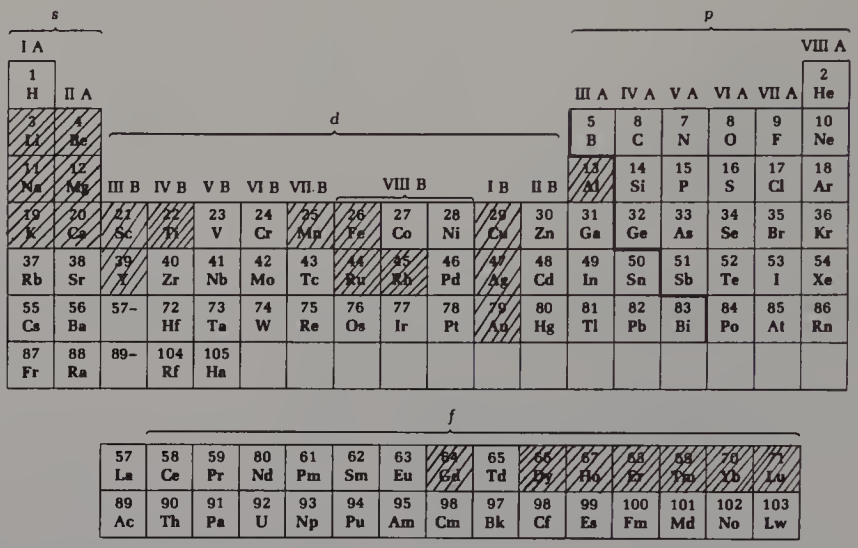
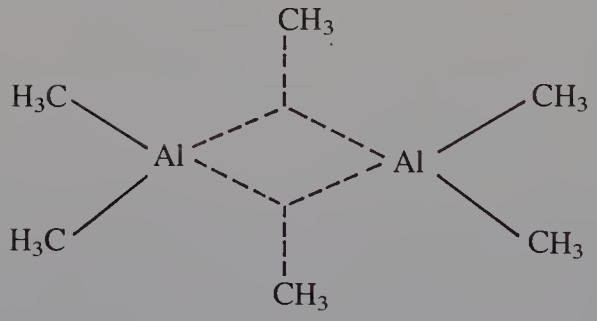
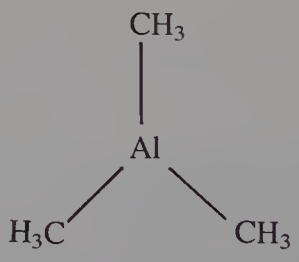


Figure 2.1. Elements known to form bridged alkyl or aryl derivatives.



1



2

four terminal two-center Al−C bonds and two bridging three-center Al−C−Al bonds of the trimethylaluminum dimer, **1**, is some 19.1 kcal mol^{-1} greater than that of the six terminal two-center Al−C bonds of two monomeric molecules of $AlMe_3$, **2** (note that each metal atom of **1** participates in four bonds, whereas the metal atom of **2** is involved in three).[21–23] Each three-center Al−C−Al bridge bond of structure **1** is thus 9.55 kcal mol^{-1} stronger than its two-center Al−C terminal counterpart in structure **2**, sufficient to make **1** the thermodynamically preferred species at normal temperatures, but not enough to prevent cleavage of the dimer by Lewis bases such as ethers or tertiary amines, in which trimethylaluminum dissolves as the monomer (Scheme 2.1).

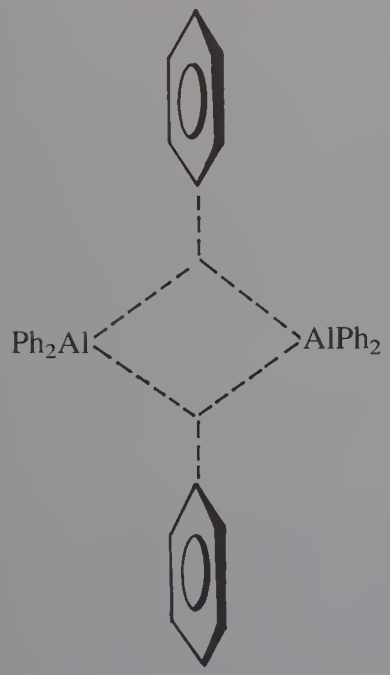
The dative two-center bonds in the adducts formed in such solutions make much better use of the fourth metal orbital than do the three-center Al−C−Al bridge bonds they replace. For this reason, in studies of systems in which metal atoms are bridged by hypercarbon atoms, it is advisable to avoid or restrict exposure of the system to

Scheme 2.1

$$Al_2Me_6 + 2Et_2O \longrightarrow 2Et_2O{\cdot}AlMe_3$$

Lewis bases, though in this chapter we shall consider some associated metal alkyls that remain associated even in the presence of an excess of Lewis base.

In the following pages we shall consider some representative systems in detail. Although attention will be focused on bridged metal alkyls, in which the bridging carbon atoms have a coordination number of five or more, we shall also discuss some closely related systems containing μ_2-bridging aryl (e.g., phenyl), alkenyl ($-CH{=}CHR$), or alkynyl ($-C{\equiv}CR$) groups, in which the coordination number of the bridging carbon atom is four, four, or three, respectively. Examples include the triphenylaluminum dimer (Al_2Ph_6), **3**,[24] and the bridged alkenyl, $Al_2i\text{-}Bu_4(CH{=}CHt\text{-}Bu)_2$, **4**.[25]



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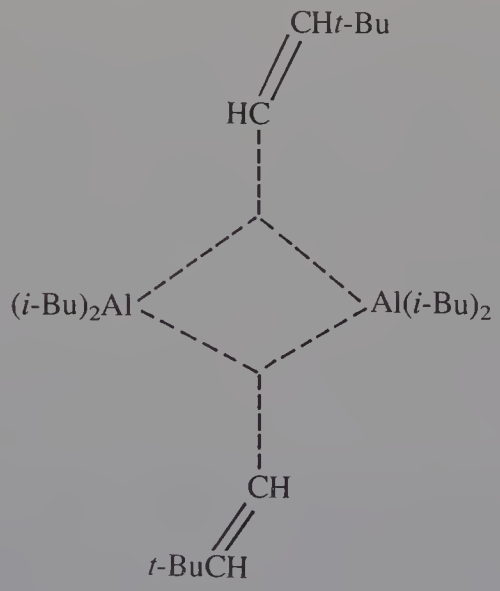

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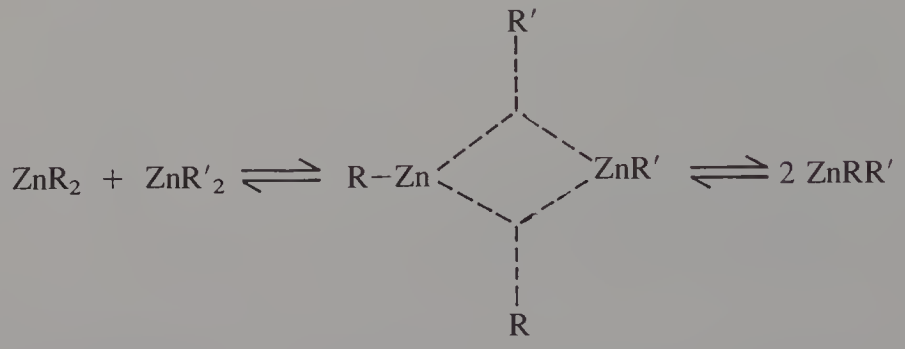
Although the coordination numbers are unexceptional, and strictly do not justify treatment of these systems as examples of hypercoordinate carbon, we shall see that the bonding of their carbon atoms is very similar to that of the hypercoordinate atoms in associated alkyls, in that three carbon valencies are essentially occupied in bonds within the bridging ligand, while the remaining valency is used to form a three-center metal–carbon–metal bond.

Our concern here is primarily with those metal alkyls for which associated structures are thermodynamically more stable than monomeric structures. There are many other metal alkyls for which the reverse is just barely true. For example,

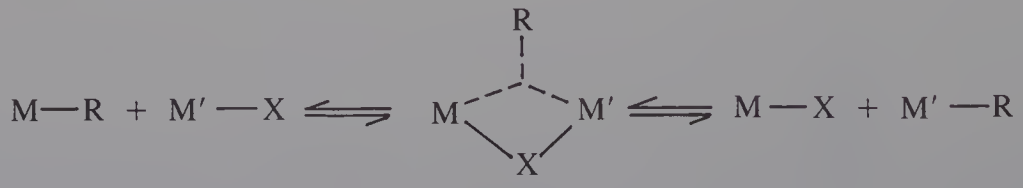
although they are monomeric, zinc dialkyls (ZnR_2) exchange alkyl groups between molecules so readily, as to suggest that associated structures are energetically readily accessible (Scheme 2.2).[26]

Scheme 2.2



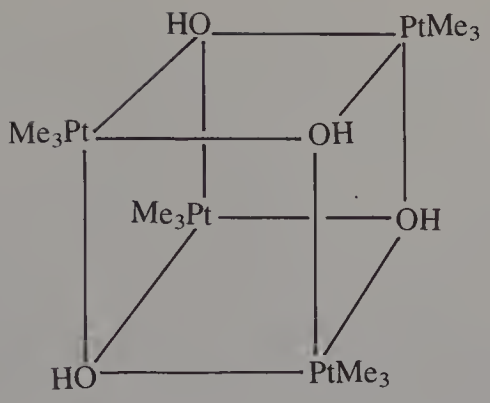
The thermodynamically stable bridged species we shall be considering thus provide the model for the intermediate or transition state through which metal atoms exchange alkyl groups. These reactions are exceedingly important not only for the synthesis of metal alkyls in general (Scheme 2.3), but are also important in many of their reactions. This point will be taken up in Chapter 7.

Scheme 2.3



Interestingly, the compound that was once thought to provide the first example of a bridged metal alkyl to be structurally characterized by x-ray diffraction turned out to be a case of mistaken identity. This was the compound $(Me_3PtOH)_4$, the tetrameric molecule that contains a cubane arrangement of its skeletal platinum and oxygen atoms, **5**. At the time of the structural study[27] it was thought to be tetramethyl platinum ($PtMe_4$)- the μ_3-bridging OH groups (which contain enough electrons to assign a pair to each Pt–O bond) were thought to be μ_3-bridging methyl groups, which contain the same number of electrons.

In our survey of bridged metal alkyl structural types, and bonding rationales for them, it is convenient to begin by considering some aluminum systems that involve hypercarbon atoms in a relatively simple environment, that is, one in which they form three normal two-center bonds to the neighboring atoms in the alkyl groups, and one

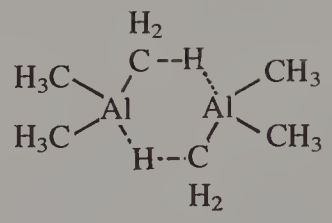


5

three-center bond to two metal atoms, as in structure **1**. These aluminum systems also allow a comparison to be made between three-center Al−C−Al and two-center Al−C bonds in the same molecule. Similar three-center M−C−M bonds are featured in associated transition metal alkyls and lanthanon alkyls, and account for the polymeric structures of the dialkyls of beryllium and magnesium. In alkyllithium chemistry, by contrast, four-center Li_3C bonds involving six-coordinate carbon atoms predominate: These allow each lithium atom to use at least three AO's. If restricted to three-center Li−C−Li bonding, the metal atoms of unsolvated lithium alkyls, LiR, would be only two-coordinate and use only two orbitals apiece.

2.2. BRIDGED ORGANOALUMINUM COMPOUNDS

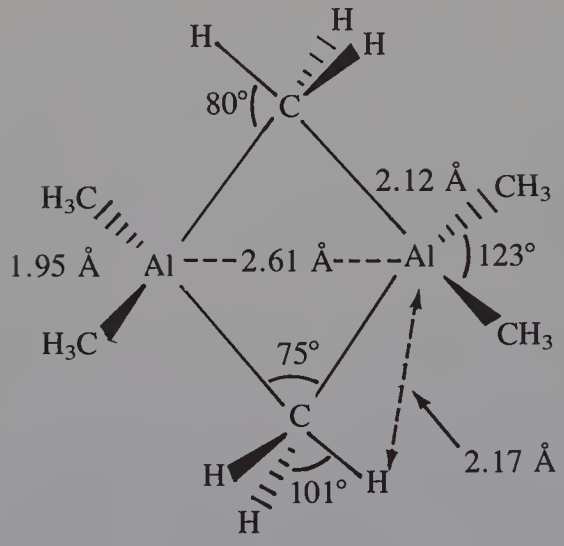
Some indication that aluminum alkyls, AlR_3, tend to associate to form dimers, $(AlR_3)_2$, was obtained from very early work on these systems, too early for the valence problem that they posed to be apparent.[28] That trimethylaluminum is dimeric in the gas phase at moderate temperatures was established in 1941 by gas density measurements[29] also showing that the enthalpy of dissociation, $(AlMe_3)_2 \longrightarrow 2\ AlMe_3$, was about 20.04 kcal mol^{-1}. That the structure was bridged like that of aluminum chloride (Al_2Cl_6) rather than ethane-like, was deduced from its vibrational spectra,[30–32] although these did not reveal whether the hydrogen atoms of the bridging methyl groups were involved in the bridging. That is, whether association occurred through three-center Al−C−Al links as in structure **1** or three-center C−H−Al links, as in structure **6**. It was known that the degree of association of aluminum alkyls (AlR_3) in inert solvents decreases in the sequence R=Me > Et > *i*-Pr > *t*-Bu. One possible explanation for the *t*-butyl derivative, Al(*t*-Bu)$_3$, being monomeric, was that association involved Al−C---H---Al links, the scope of which would progressively decrease, and finally be eliminated, as the α-hydrogen atoms were replaced by methyl groups. The earliest x-ray crystallographic studies on $(AlMe_3)_2$,[19,20] did not locate the hydrogen atoms, so although they were strongly



6

suggestive of symmetrical Al---C---Al bridges, the data were arguably also compatible with the unsymmetrical bridging that Al−C---H---Al links would require.[33,34]

Further x-ray crystallographic work[35] with data collected at low temperatures located the hydrogen atoms of the bridging methyl groups with sufficient precision to confirm that the structure was indeed the symmetrically bridged form, which was also indicated by ^{27}Al NQR (nuclear quadrapole resonance) studies.[36]



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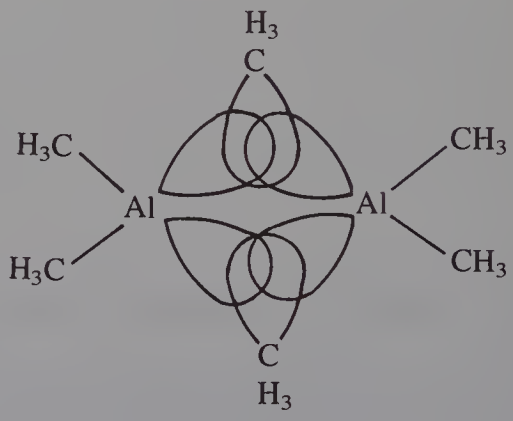

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Details of this are given in structure **7**. The greater length of the bridging Al---C links than the terminal Al−C bonds, the acute angle at the hypercoordinate bridging carbon atoms, and the orientation of the bridging methyl groups (with the hydrogen atoms pointing away from the Al---Al axis) are all consistent with the bonding scheme shown in structure **8**. Normal two-center electron-pair bonds link the metal atoms to the terminal methyl groups, and the carbon atoms to their substituent hydrogen atoms. The two three-center Al−C−Al bonds in the bridging region can be considered to result from overlap of suitably oriented metal and carbon sp^3 hybrid orbitals, as in structure **8**. The relatively short metal–metal distance across the $(AlC)_2$ ring of Al_2Me_6, and the acute angles at the hypercarbon atoms, are consequences of the cross-ring metal–metal bonding that is an implicit feature of the three-center

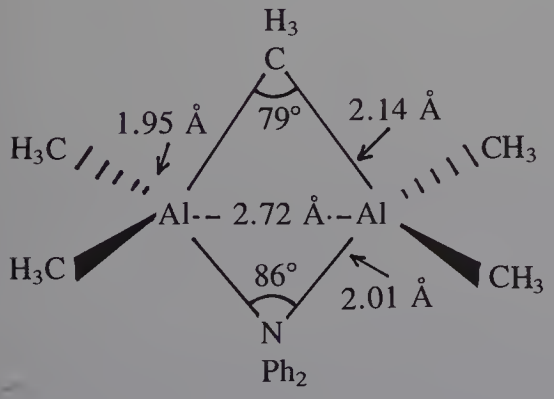
bonding description. In each three-center bond, the metal orbitals overlap and combine in phase with each other as well as with the carbon sp^3 hybrid orbital.

Alkyl bridges between metal atoms of the type found in Al_2Me_6 are commonly referred to as "electron deficient" in that there are fewer bonding electron pairs than points of contact between bonded atoms. The label is, however, misleading if it is taken to imply that more electrons are needed to hold the bridge together. The Al_2Me_6 molecule contains precisely the right number of electrons to fill all the bonding MO's. Adding an extra pair would cause the structure to change to one like ethane, with a single metal–metal bond and exclusively terminal methyl groups (Scheme 2.4).

Scheme 2.4

$$Me_2Al(\mu\text{-}Me)_2AlMe_2 \xrightarrow{+2e^-} [Me_3Al{-}AlMe_3]^{2-}$$

The distinctive features of the structure of $Me_2Al(\mu\text{-}Me)_2AlMe_2$ become more apparent when it is compared with the mixed-bridge compound $Me_2Al(\mu\text{-}Me)(\mu\text{-}NPh_2AlMe_2)$ (which contains three bridge bond pairs)[37] and the amino-bridged $Me_2Al(\mu\text{-}NMe_2)_2AlMe_2$ (which contains four bridge bond pairs).[38] Details of their structures are given in **9** and **10**. Localized bond representations are given in **11** and **12**.



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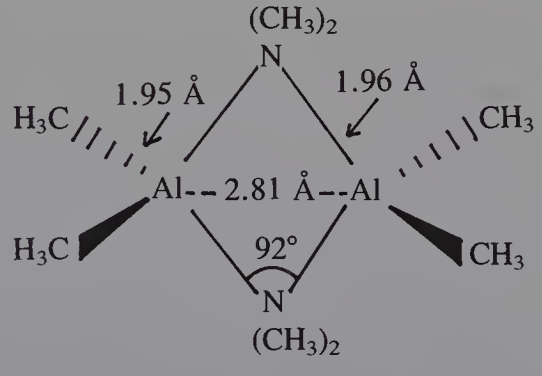

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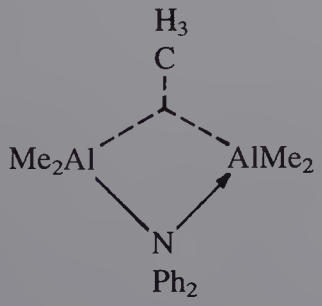

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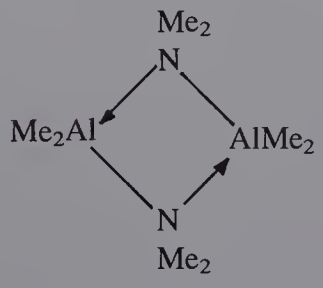


12

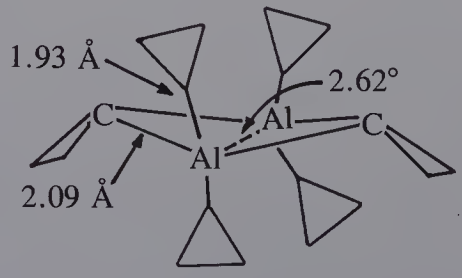
As the alkyl bridges (each of which supplies one electron and one AO for the bridge bonding) of structure **7** are progressively replaced by amino groups (each of which supplies three electrons and two AOs for bridge bonding) in structures **9** and **10**, the metal–metal distance across the bridge lengthens, even though the number of electrons associated with the bridge increases from two bond pairs in **7** to three bond pairs in **9** and four bond pairs in **10**. Also, the acute bridge bond angles at the hypercoordinate bridging carbon atoms of **7** and **9** give way to larger angles at the four-coordinate nitrogen atoms of **9** and **10**. Inspection of the bond distances from the metal atoms to the bridging atoms shows that the bonding effect of the extra electrons is channeled into these bonds at the expense of the admittedly weak metal–metal bonding of **7**.

A localized MO treatment[39,40] that provides an alternative rationalization of these changes to the localized bond treatments shown in structures **1**, **11**, and **12** is shown in Figure 2.2. The two electron pairs associated with the bridge bonding in Al_2Me_6, **7** are accommodated in MO's (i) and (ii), one of which is σ bonding, the other π bonding, with respect to metal–metal interactions. The C---C bonding character of MO(i) is offset by the C---C antibonding character of MO(ii), so there is no net bonding between the hypercoordinate carbon atoms.

As the bridging alkyl groups are progressively replaced by bridging amino groups, the extra AO these supply generate extra bridge bonding MO's, MO(iii) and MO(iv), that have metal–metal antibonding character. When both are occupied, as in the case of $Me_2Al(\mu\text{-}NMe_2)_2AlMe_2$, **12**, there remains no net metal–metal bonding.

The metal–metal distances across the bridges in these compounds should not be taken to imply that the bridge itself weakens as the metal–metal distance increases. The resistance to dissociation into monomers increases in the sequence $Al_2Me_6 < Al_2Me_5(NPh_2) < Al_2Me_4(NMe_2)_2$, that is, as the number of bonding electrons associated with the bridge increases. The increasing tendency for dissociation within the series of alkyls, $Al_2Me_6 < Al_2Et_6 < Al_2i\text{-}Pr_6$ already noted, probably reflects the increased nonbonded repulsions as the bulk of the bridging group increases (dissociation enthalpies for the process $Al_2R_6 \longrightarrow 2AlR_3$ are about 20, 16.9, and 8.1 kcal mol^{-1} for R=Me, Et, and *i*-Bu, respectively).[21,22]

Structural studies on other dimers $(AlR_3)_2$ or mixed derivatives $(AlR'_2R^2)_2$ have provided further evidence of the relative bridging capacities of various groups R, and have consistently indicated Al---C---Al rather than Al−C---H---Al bridging interactions. The structure of the cyclopropyl derivative $Al_2c\text{-}Pr_6$, **13**[41] is particularly



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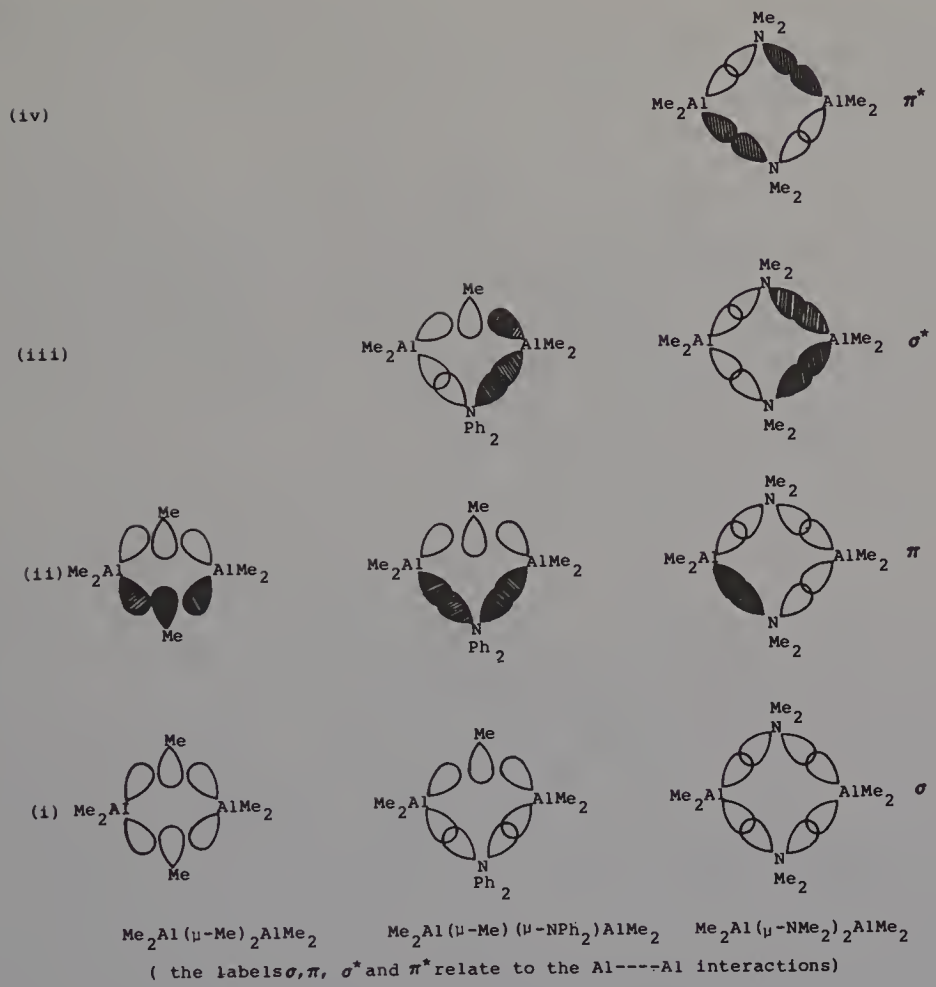
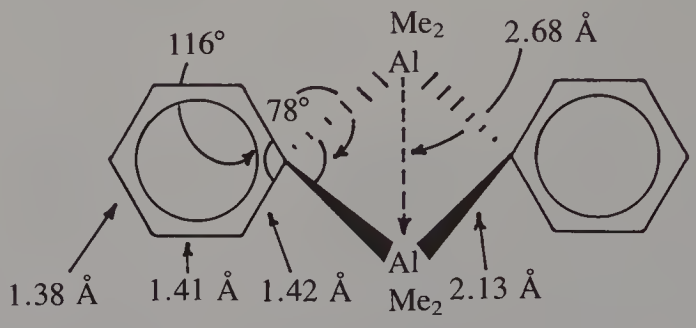


Figure 2.2. Localized MO for the bridge bonding in Al_2Me_6, $Al_2Me_5NPh_2$, and $Al_2Me_4(NMe_2)_2$. The labels σ, π, σ^*, and π^* relate to the Al---Al interactions.

interesting in that, although it could in principle form an Al−C---H---Al bridge by use of the one hydrogen atom attached to the α-carbon atom, the orientation of the carbon–carbon bonds formed by this same carbon atom clearly precludes C---H---Al interactions. The $(AlC)_2$ ring in this molecule differs from those already discussed in being slightly folded (dihedral angle 32°) apparently to reduce nonbonding repulsions involving the bridging cyclopropyl groups, both of which lean to the same side of the $(Al-C)_2$ ring (dihedral angle 135° between the cyclopropyl ring planes and the Al−C−Al planes). Structural details about the hypercoordinate carbon atoms, again indicative of the formation of three normal two-center bonds and one three-center bond, are given in structure **13**.

When phenyl groups act as bridges between aluminum atoms (which they do more effectively than methyl groups—the compound $Al_2Me_4Ph_2$[42] has phenyl, not methyl, bridges) Al−C---H---Al bonding cannot occur because the bridging carbon atom has no hydrogen substituent, and the phenyl ring orientation—perpendicular to the

$(Al-C)_2$ ring plane—precludes Al−C−C---H---Al bridging through the ortho hydrogen atoms. Structural information on Al_2Ph_6 and $Al_2Me_4Ph_2$ is shown in structures **14** and **15**.[42]



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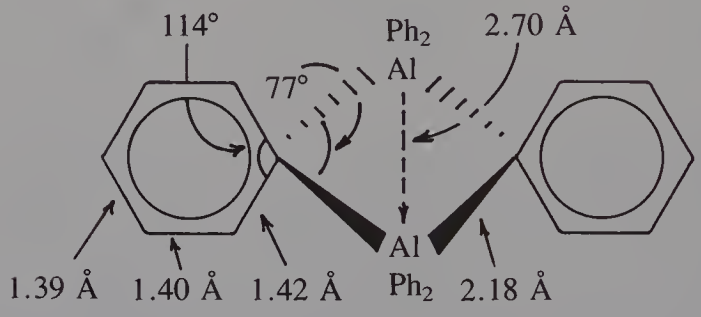
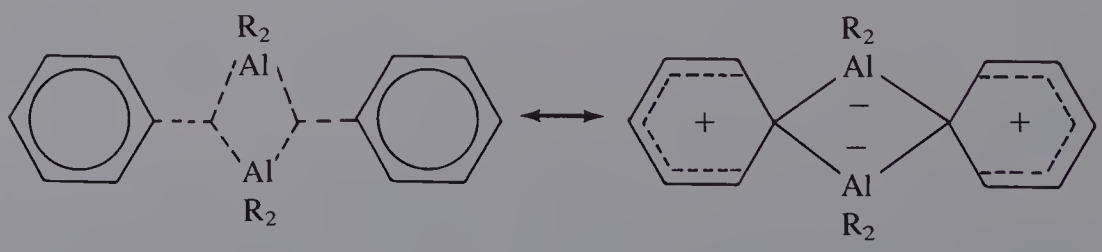


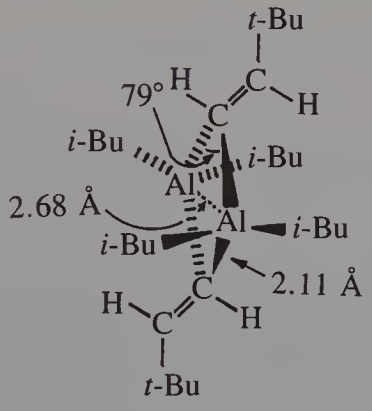
15

These reveal the long Al−C links to the bridging carbon atoms indicative of three-center Al−C−Al bonding, though the slight distortion of the bridging rings in the neighborhood of the bridging carbon atom, and the greater metal–metal distance than in Al_2Me_6, **7**, both indicate some delocalization of the benzene ring π-electron density into the $(Al-C)_2$ ring, suggesting contributions from two canonical forms (Scheme 2.5).

Scheme 2.5



In MO terms, this corresponds to some drainage of electron density into MO(iii) and MO(iv) of Figure 2.2, from the appropriately orientated *p* AO of the bridging carbon atom. It is this extra bridge-bonding electron density that an aryl or other unsaturated group can provide that probably accounts for the stronger bridges that they form compared with alkyl groups. Bridging in the mixed alkyl–alkenyl derivative, $Al_2i\text{–}Bu_4(CH{=}CHt\text{-}Bu)_2$, **16**,[25] for example, involves the alkenyl groups, which, like the bridging phenyl groups of structures **13** and **15**, are oriented so as to allow the C=C π-bonding *p* AO of the bridging atom to lie parallel to the Al---Al axis, the alignment that maximizes its contribution to the bridge bonding and incidentally minimizes the likelihood of Al−C---H---Al bonding (and also minimizes nonbonding repulsions):



16

NMR studies have been used to explore the solution behavior of bridged organoaluminum species,[1,4] for example, to determine the ease with which bridging and terminal groups exchange sites in the systems Al_2R_6, or to identify the bridging groups in mixed derivatives $Al_2R'_2R''_4$.[4,43–45] Such studies showed that the bridging capacity of different groups decreases in the sequence $R_2N > RO > Cl > Br >$ $PhC{\equiv}C > RCH{=}CPh > Me > Et > i\text{-}Pr > t\text{-}Bu$. Three-electron ligands thus form stronger bridges than do one-electron ligands of the type considered here. The relative bridging capacities of the alkyl groups are the reverse of the sequence expected from inductive effects, and presumably reflect bulk effects.

The ease with which groups exchange between terminal and bridging sites in species Al_2R_6 in solution in hydrocarbon solvents means that all the alkyl groups appear equivalent at room temperature, though separate resonances due to terminal and bridging ligands can usually be distinguished in spectra recorded at low temperatures. For example, solutions of Al_2Me_6 in cyclopentane give only one proton resonance at normal temperatures, though two sharp signals, of intensity ratio 2:1, are found at temperatures below about −55 °C, the lower intensity signal due to the bridging groups appearing at a higher field.[46,47] Similarly, in the ^{13}C NMR

spectrum, Al_2Me_6 in toluene gives only one absorption at δ-7.31 (quartet, J_{C-H} 114.6 Hz) at +30° C, whereas at −75° C two well resolved carbon signals can be observed at δ-8.22 (quartet, J_{C-H} 112.7 Hz) and −5.63 (quartet, J_{C-H} 115.3 Hz) relative to external $SiMe_4$.[41,45]

The aryls, Al_2Ph_6 and $Al_2(p\text{-tolyl})_6$, likewise give NMR spectra at +37 °C that show their aryl groups to be exchanging between terminal and bridging sites too rapidly to be distinguished, though at low temperatures signals due to both types of ligand are obtained.[4,43–45] Resonances due to the ipso carbon atoms, whether terminal or bridging, appear in the range characteristic of carbon atoms in aromatic systems, though the effect of the three-center bond on the bridging carbon atom is apparent in its relatively low chemical shift relative to $SiMe_4$.

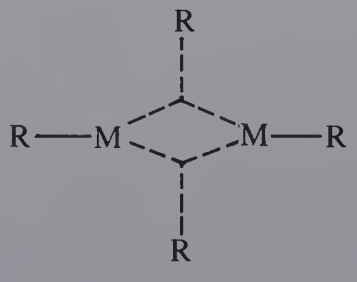
2.3. BERYLLIUM AND MAGNESIUM COMPOUNDS

Of the Group IIA metals, beryllium[9] and magnesium[15] show the greatest tendency to form derivatives containing hypercoordinated carbon atoms. Their dialkyls, MR_2, generally have associated structures in which at least half if not virtually all of the metal-attached carbon atoms are hypercoordinated. Of the other Group IIA metals, calcium, strontium, and barium[15] form dialkyls that are essentially ionic $M^{2+}(R^-)_2$, while zinc,[26] cadmium,[26] and mercury[49] form covalent monomeric molecular dialkyls, MR_2, whose linear structures, **17**, are held together by two-center, two-electron metal–carbon bonds that use only two metal valence shell AO's:

R—M—R

17

More extensive use of the metal orbitals is made in most beryllium and magnesium dialkyls, the degree of association of which, like that of aluminum trialkyls, is a function of the size of the alkyl groups. Very bulky groups may prevent any association—*t*-Bu_2Be, for example, is monomeric both in the vapor and in benzene solution and its vibrational spectra are consistent with a linear structure **17**.[50,51] The neopentyl derivative $Be(CH_2t\text{-}Bu)_2$ exists as a mixture of monomer and dimer in



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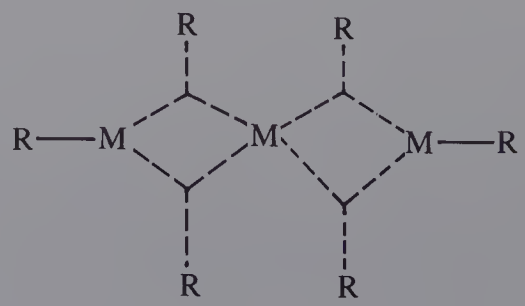
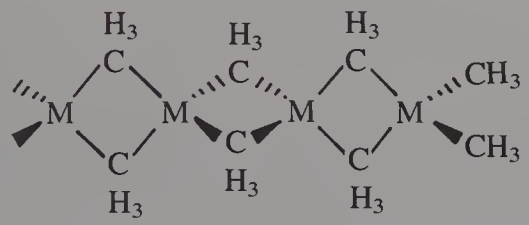


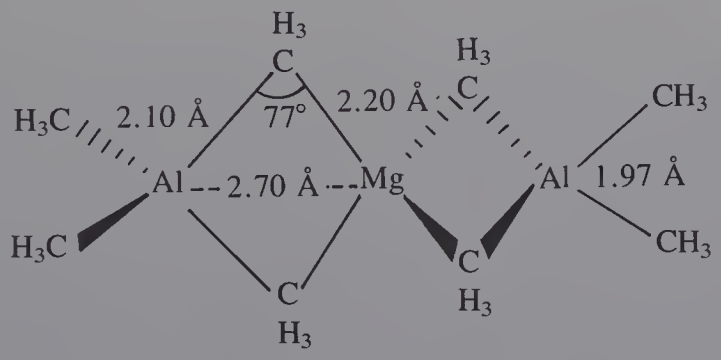
19

solution,[52] the latter presumably having structures of type **18**, in which half of the metal-attached carbon atoms are hypercoordinated, and each metal atom uses three valence shell AO's. Yet higher degrees of association are found as the bulk of the alkyl groups is reduced. Association to trimers $(MR_2)_3$ of the type in structure **19** allows the central metal atoms to use all four of its valence shell AO's in four three-center M−C−M bonds, thus making all four carbon atoms attached to this metal atom hypercoordinated. Exclusive hypercoordination of *all* the metal-attached carbon atoms is a characteristic of the structure of $BeMe_2$[53] and $MgMe_2$.[54] Their polymeric chain structures, held together only by three-center M−C−M bonds, have been established by x-ray crystallographic studies that revealed the interatomic distances and angles shown in structures **20** and **21**.



		M−C(Å)	M−M(Å)	MCM angle
20	$(BeMe_2)_n$	1.93	2.09	66°
21	$(MgMe_2)_n$	2.24	2.72	75°

Although their hydrogen atoms were not located, their relatively short metal–metal distances and acute M−C−M angles at the hypercoordinated carbon atoms show the metal–carbon bonding to resemble that in Al_2Me_6 discussed previously. This resemblance to the aluminum system is underlined by the structure of the mixed metal methyl $Mg(AlMe_4)_2$, **22**, also established by an x-ray study.[55]



22

In all of these systems, the metal–carbon distances involving hypercoordinated carbon atoms are significantly longer than those involving the four-coordinate carbon atoms of the terminal alkyl groups (monomeric $BeMe_2$ has a Be−C distance of 1.70

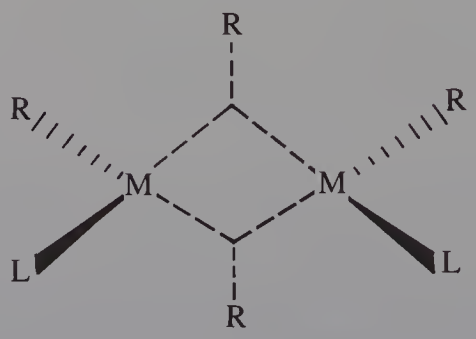
Å, as shown by an electron diffraction study of the vapor,[56] while two-center Mg–C bonds are typically about 2.16–2.17 Å in length). Magnesium diethyl ($MgEt_2$) has a polymeric structure like that of $(MgMe_2)_n$, **21**, with interatomic distances Mg–C, 2.26 Å and Mg–Mg, 2.67 Å, and a bond angle MgCMg of 72° at the hypercoordinated carbon atom.[54]

As is the case with alkyl bridges between aluminum atoms, these bridges between beryllium or magnesium atoms are relatively weak, and the metal orbitals are put to better use by addition of Lewis bases, L, which cleave the polymer chains, forming monomeric molecules MR_2L_2, in which the carbon atoms are no longer hypercoordinated (Scheme 2.6).

Scheme 2.6

$$(MR_2)_n + 2nL \longrightarrow nMR_2L_2$$

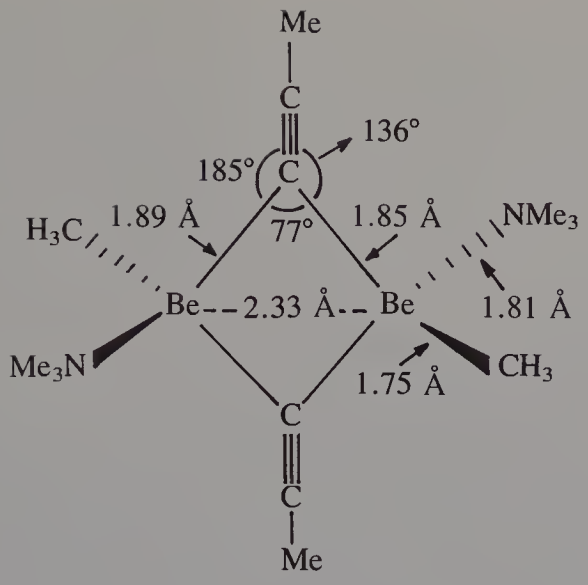
In weakly basic solvents, dimers, **23** that retain alkyl bridges (and so hypercoordinated carbon atoms) may be formed.



23

Monoalkylberyllium or monoalkylmagnesium compounds of the Grignard reagent type, RMX, where X is a halogen or some other electronegative residue, may also have dimeric structures, $(RMX)_2$, but these do not contain hypercoordinated carbon atoms, since bridging in such derivatives invariably involves the halogen or electronegative group X functioning as a three-electron ligand.

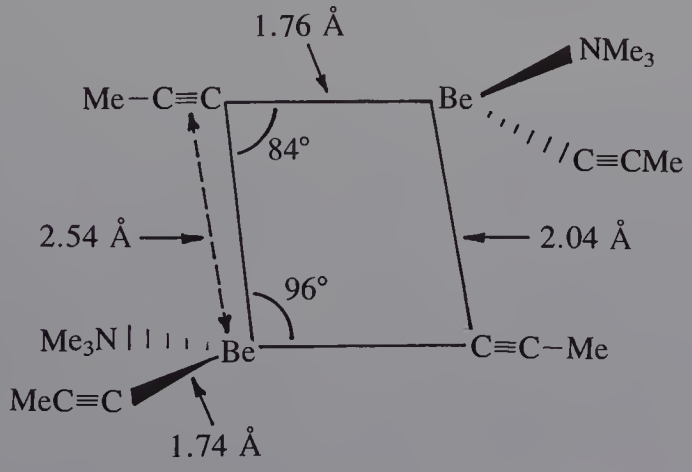
Studies on aryl, alkenyl, and alkynyl derivatives of beryllium and magnesium though fewer than those on related aluminum systems, have nevertheless shown that such unsaturated groups are more effective than alkyl groups at bridging these metals through carbon atoms that use essentially only one valency for the purpose. The mixed alkyl–alkynyl, $[BeMe(C{\equiv}CMe)(NMe_3)]_2$, **24**, for example, associates through its propynyl groups, which are orientated almost perpendicular to the metal–metal axis.[57]



24

Comparison of the $(BeC)_2$ ring geometry in **24** with that in $(BeMe_2)_n$, **20**, shows that the greater strength of the propynyl bridges is indicated both by the shorter Be−C bonds in structure **24**, and by its greater Be---Be distance, consistent with the bonding interpretation discussed previously in connection with the unsaturated organoaluminum systems, **14–16**.

The bis(propynyl)beryllium compound $[Be(C{=}CMe)_2NMe_3]_2$ is unusual in crystallizing with two types of dimeric molecule in the lattice, one of which has a diamond shaped $(Be-C)_2$ ring very similar to that of **24**.[58] The other structure, **25**, has a nearly rectangular $(Be-C)_2$ ring, explicable in terms of donation of charge from the alkynyl triple bond into the available metal orbital:[58]



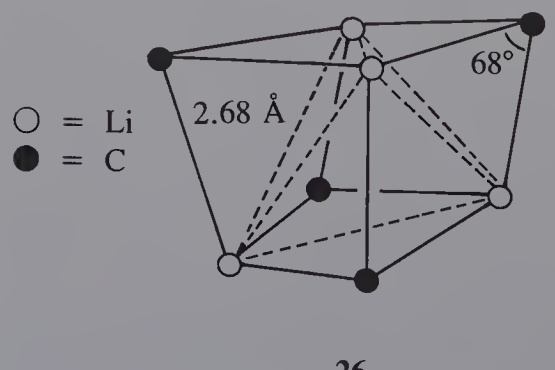
25

A similar type of bridge has been found in the propynyl–aluminum compound, $(Ph_2AlC{\equiv}CPh)_2$.[59] Coordination of metals to the C≡C π-bonding electrons of alkynes is of course a familiar feature of transition metal organometallic chemistry, where simultaneous transfer of electronic charge from filled metal orbitals into a vacant π* orbital of the alkyne can strengthen the metal–carbon bonding, which in structure **25** is clearly relatively weak along the long edges of the $(Be-C)_2$ rectangle.

2.4. ORGANOLITHIUM COMPOUNDS

Of the main group metals, lithium has the greatest capacity to stabilize hypercoordinate carbon. This is because lithium contains only one electron in its valence shell. In bonding to a one-electron one-orbital ligand like an alkyl group, therefore, it must indulge in multicenter bonding if it is to use more than one of its valence shell orbitals. Dimerization of lithium alkyls by formation of three-center M−C−M bonds of the type already discussed would still involve only two metal orbitals, and it is significant that lithium alkyls typically adopt tetrameric or hexameric structures $(LiR)_4$ or $(LiR)_6$ in which each lithium atom is directly bonded to *three* carbon atoms, and each metal-attached carbon atom is directly bonded to three metal atoms in addition to the three other carbon and/or hydrogen atoms in the alkyl residue.[12,13]

For example, methyl–lithium exists in solution and in the crystal as the tetramer $(LiMe)_4$, the structure of which was deduced from x-ray powder data.[60] The slightly distorted cubic arrangement of the four lithium and four carbon atoms in the molecular skeleton, **26**, effectively consists of two interpenetrating tetrahedra, the larger defined by the four carbon atoms, the smaller defined by the four metal atoms. The methyl groups thus cap the four faces of the Li_4 tetrahedron. The bonding is conveniently described by assuming that both metal and carbon atoms are sp^3



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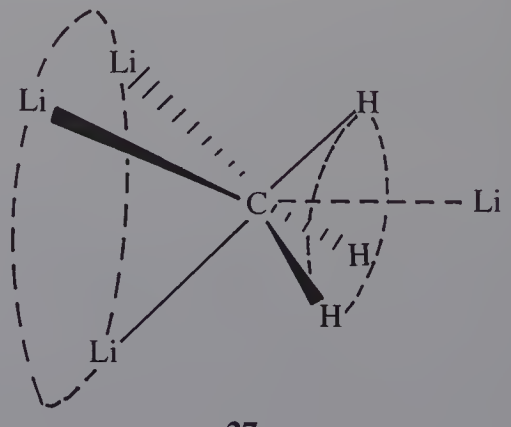


27

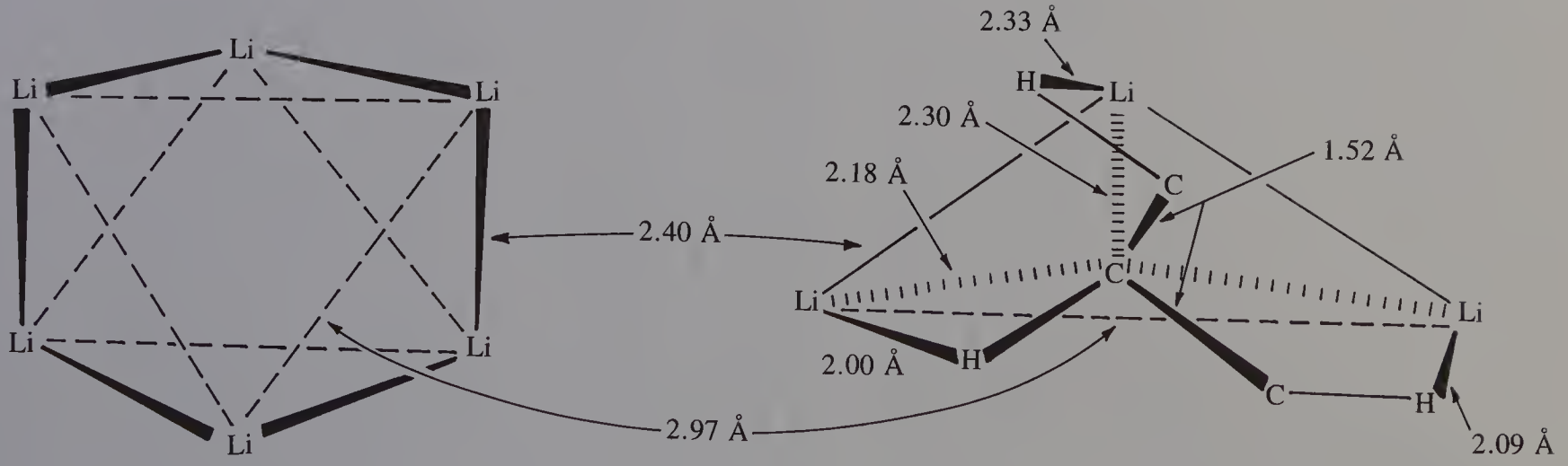
hybridized. Three of the four sp^3 hybrid orbitals associated with each metal atom point over the faces of the Li_4 tetrahedron, in which direction they overlap the carbon sp^3 hybrid orbitals, in four-center, two-electron bonds. The remaining metal orbital, pointing away from the center of the molecule, is available to bond a Lewis base such as an ether molecule. (Methyllithium dissolves as the tetramer in basic solvents that clearly make use of these remaining metal orbitals.) In crystalline uncoordinated $(LiMe)_4$, the tetrameric molecules pack in a manner that places a methyl group of one tetramer opposite to the metal atom of another tetramer, rendering the carbon atoms effectively seven-coordinate, **27**, if one includes the weak intermolecular Li---C interaction, which could use the spare metal orbital just discussed.

The crystal structure of the tetramethylethylenediamine (TMEDA, $Me_2NCH_2CH_2NMe_2$) adduct of methyllithium, $(LiMe)_4(TMEDA)_2$, has also been determined by x-ray diffraction.[61] Despite the presence of the strongly basic, potentially chelating TMEDA ligands in this adduct, the lithium alkyl retains its tetrameric state of association. The bidentate TMEDA molecules act as bridges between tetramers, coordinating to the metal atoms by making use of the spare *exo*-directed metal orbitals. The hypercoordinated carbon atoms in this adduct are six coordinate, each forming three normal two-center, two-electron bonds to the three hydrogen atoms, and a four-center, two-electron bond to the three lithium atoms some 2.23–2.27 Å away (compare **27**, but without the *exo* C---Li interaction). The lithium–lithium distance is 2.57 Å, and the Li−C−Li angles range from 60–70° (mean 66°).

Rather less symmetrical tetrameric molecules, $(LiEt)_4$, have been found (by x-ray diffraction[62]) in crystalline ethyllithium, again held together by hypercoordinate carbon atoms forming four-center bonds to three neighboring metal atoms located 2.19–2.47–Å distant. The Li---Li distances range from 2.42–2.63 Å and the Li−C−Li angles from 66–67°.

Methylsodium, NaMe, is believed, on the basis of an x-ray study of the powder,[63] to have a tetrameric structure like that of $(LiMe)_4$. The more electropositive alkali metals form essentially ionic alkyls in which the carbon atoms are presumed to be pyramidally coordinated.[63,64]

Ebullioscopic, cryoscopic, and NMR spectroscopic studies on solutions of lithium alkyls in hydrocarbon solvents have shown not only that tetrameric aggregates $(LiR)_4$ persist in solution, but that higher aggregates, particularly hexamers, are also present. The cyclohexyl derivative crystallizes from benzene as the hexamer, (Li cyclohexyl)$_6 \cdot 2C_6H_6$, features of the structure of which are shown in structure, **28** and **29**.[65] The six metal atoms define the vertices of an octahedron compressed along one threefold axis so as to generate a trigonal antiprism with two large equilateral triangular faces and six smaller isosceles triangular faces. This is shown in **28** viewed along the threefold axis in question—the edges of the large equilateral triangular faces are shown by broken lines. Each isosceles triangular face is bridged by a cyclohexyl group: The environment of the bridging hypercoordinate carbon atom is shown in structure **29**.


Li
Li
Li
Li
Li
Li
2.40 Å
2.97 Å
2.33 Å
H
Li
2.30 Å
2.18 Å
C
1.52 Å
C
Li
Li
2.00 Å
H
C
H
2.09 Å

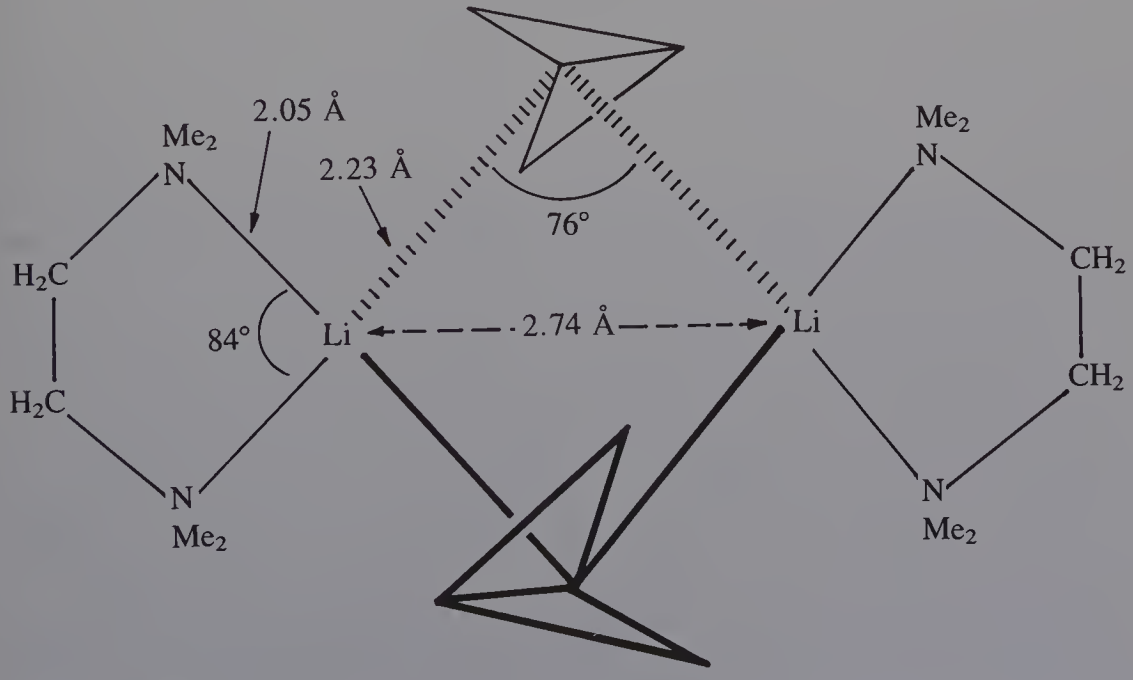
28 **29**

Again, as in $(LiMe)_4$, **26**, the hypercoordinate carbon atom forms three normal two-center bonds within the alkyl group and one multicenter bond to the bridged metal atoms. The molecules of benzene of crystallization are located over the equilateral triangular faces of the Li_6 antiprism.

A further feature of interest in the structure of (Li cyclohexyl)$_6 \cdot 2C_6H_6$ is that the hydrogen atom attached to the hypercoordinate carbon atom is close enough (about 2.00 Å) to one of the bridged metal atoms to be regarded as forming a highly unsymmetrical C−H---Li three-center bonding interaction with that metal atom. Some of the β-hydrogen atoms of (Li cyclohexyl)$_6 \cdot 2C_6H_6$ also appear to be involved in similar C−H---Li interactions, which, by bonding the carbon atom in question to an extra atom (the metal atom), render them hypercoordinate as well, and incidentally control the orientation of the cyclohexyl rings. Further examples of carbon atoms that achieve hypercoordination through C−H---metal bonding are discussed later.

It is worth noting that trimethylsilyllithium, $LiSiMe_3$, also crystallizes as a hexamer, $(LiSiMe_3)_6$,[66] based on an Li_6 trigonal antiprism like that of (Li cyclohexyl)$_6$, held together by μ_3-trimethylsilyl groups in which the silicon atoms are effectively hypercoordinate, forming three normal two-center Si−C bonds and one four-center $SiLi_3$ bond.

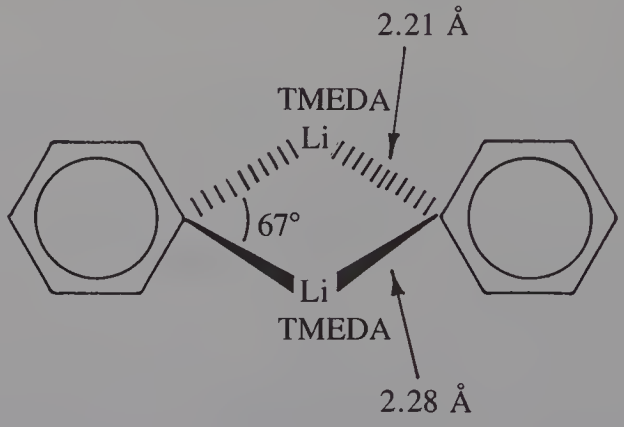
Although rarer than triply bridging alkyl groups, doubly bridging alkyl groups containing five-coordinate carbon atoms are known in organolithium chemistry, either in derivatives in which the bulk of the alkyl residue prevents a higher degree of association, or in cases where chelating bases restrict the number of bonding interactions open to the metal atoms. An example of the latter type is provided by the lithiobicyclobutane–tetramethylethylenediamine adduct, $LiC_4H_5 \cdot$ TMEDA, which crystallizes as the dimer, **30**.[67]



30

This compound is of particular interest in that the hypercoordinate carbon atom is a tertiary (bridgehead) carbon atom. Prior to its structural characterization, all known bridged metal alkyls had at least one hydrogen atom in the coordination sphere of the hypercoordinate bridging carbon atom, allowing the possibility of M−C---H---M bridging interactions. Such interactions are clearly ruled out in **30**, in which the hypercoordinate carbon atom forms three normal two-center bonds to the other carbon atoms of the bicyclobutyl group, and one three-center bond to the two metal atoms. The relative length of the Li---Li and Li---C distances in **30** [both might have been expected to be shorter, when compared with $(LiMe)_4$, **26**, or $(Li\ cyclohexyl)_6$, **28**] probably reflects the effect of the chelating TMEDA ligands in limiting these interactions.

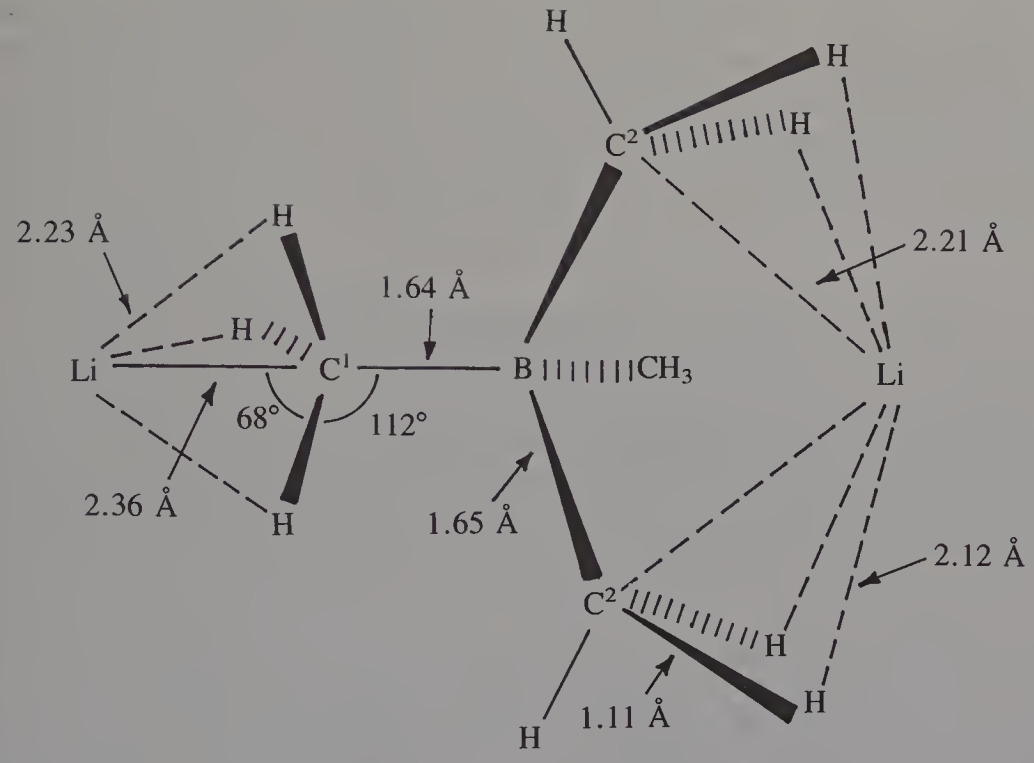
A similar dimeric structure has been established for the phenyllithium tetramethylethylenediamine adduct $(LiPh \cdot TMEDA)_2$,[68] in which the μ_2-phenyl ligands assume their normal bridging orientation, lying in a plane perpendicular to the plane of the M_2C_2 ring, **31** (see the aluminum systems discussed earlier in structures **14**, and **15**).



31

Though technically not hypercoordinate in that they are only four coordinate, the bridging carbon atoms of structure **31** resemble those of **30** in that they use three of their four valencies to bond to the neighboring carbon atoms in the ligand, employing the fourth to bond to the two bridged metal atoms (3*c*-2*e* bond).

Another organolithium compound whose structural characterization significantly advanced our understanding of the ways that carbon atoms can become highly coordinated was the tetramethyl borate $(LiBMe_4)$ crystals that have been subjected to both x-ray and neutron diffraction investigations.[69] The crystalline compound is polymeric, and the association between $LiBMe_4$ units is strong enough to allow tetramers, $(LiBMe_4)_4$, to persist in the vapor. In the crystal, all of the carbon atoms are hypercoordinated, though in two distinct ways that are illustrated in structure **32**. From **32**, it is apparent that the methyl groups that act as bridges between lithium and boron in $(LiBMe_4)_4$ do so in a manner that involves their hydrogen atoms. In the first type, where the hypercoordinate carbon atom is labeled C^1 in **32**, the metal atom lies



32

on the threefold axis of the methyl group, colinear with the C−B bond, equidistant from all three hydrogen atoms of the methyl group. The coordination about C^1 is thus trigonal bipyramidal, with equatorial hydrogen atoms and axial lithium and boron atoms, the carbon atom being displaced slightly out of the equatorial H_3 plane towards the boron atom. This environment places the lithium atom not only within a bonding distance of C^1 but also within a bonding distance of its substituent hydrogen atoms, and thus allows Li---H_3C interactions of the same type that occur between tetramers in crystalline $(LiMe)_4$ (cf. structure **27**).

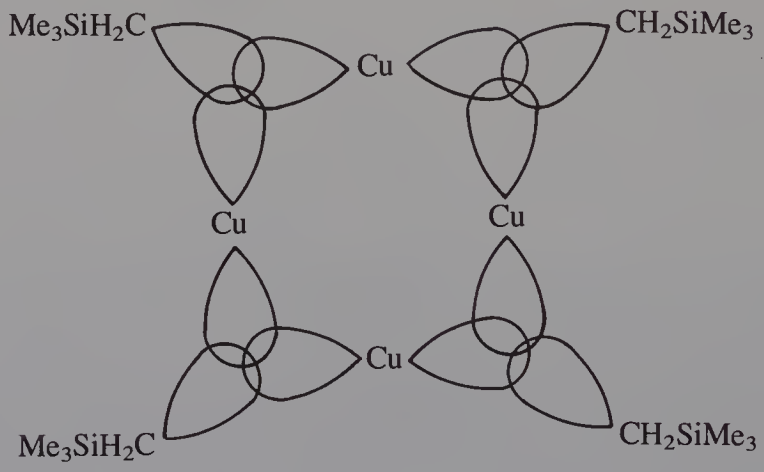
The coordination about the second type of hypercoordinate carbon atom in $(LiBMe_4)_4$, C^2, also evidently involves the methyl hydrogen atoms, but only two of them. The BCLi bond angle at that carbon atom (82°) appears compatible with the three-center BCLi bonding. However, this is precluded by the boron–carbon distance of 1.65 Å, appropriate for a two-center B−C bond, and by the orientations of C−H bonds, two of which place these hydrogen atoms only 2.12 Å from the lithium atom, although there appears to be negligible lengthening of the C−H bonds. Indeed, the coordination about C^2 is best interpreted as near normal for the $B-CH_3$ unit, but with the coordinatively unsaturated lithium atom within a weakly bonding distance of the carbon atom and two of the hydrogen atoms.

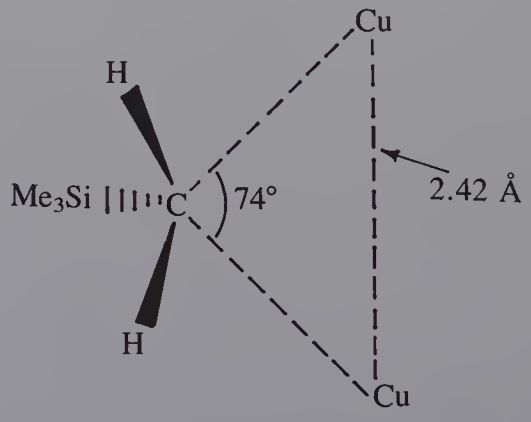
Although highly coordinated carbon atoms are to be found in crystals of alkyls of the heavier alkali metals, the more ionic nature of their metal–carbon bonding makes it preferable to regard most of them as composed of close-packed arrays of metal cations and alkyl anions. For example, whereas methylsodium crystallizes in

tetramers, $(NaMe)_4$, similar in shape and bonding to those of methyllithium, ethylsodium crystallizes in a double-layer structure in which the methylene groups of the alkyl residues have trigonal pyramidal arrays of sodium ions as near neighbors.[70] Methylpotassium (KMe) has a nickel arsenide-type crystal structure, in which the methyl groups, effectively carbanions (CH_3^-) with C_{3v} pyramidal shapes, are surrounded by trigonal prismatic arrays of potassium ions.[71]

2.5. ORGANO-COPPER, SILVER, AND GOLD COMPOUNDS

Copper is another metal with a strong tendency (in its +1 oxidation state) to participate in multicenter metal–carbon bonding, though the thermal instability of its alkyl derivatives has limited the number that have been structurally characterized. The trimethylsilylmethyl derivative $(CuCH_2SiMe_3)_4$ is tetrameric in the crystal, with a square planar arrangement of the metal atoms, bridged by the μ_2-trimethylsilylmethyl groups, **33**.[72]

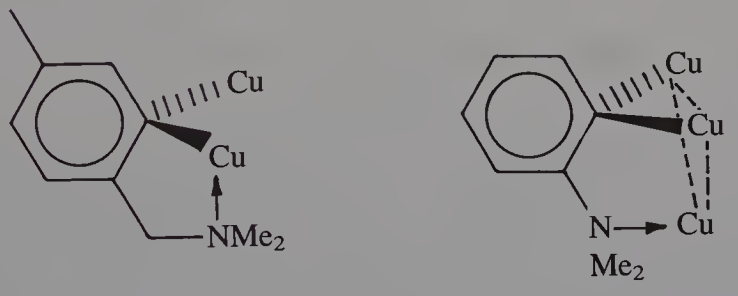




33

The hypercarbon atom environment in this compound, with one silicon atom, two hydrogen atoms, and two copper atoms in the carbon coordination sphere, with a CuCCu bond angle of 74°, is consistent with the formation of the three two-center, two-electron bonds to the silicon and hydrogen atoms, and a three-center, two-electron bond to the two metal atoms. This open cyclic structure, which may be contrasted with the more compact tetrahedral structures of typical tetrameric lithium alkyls, suggests that the metal atoms are *sp* hybridized, unable to make use of as many AO's as lithium atoms can.

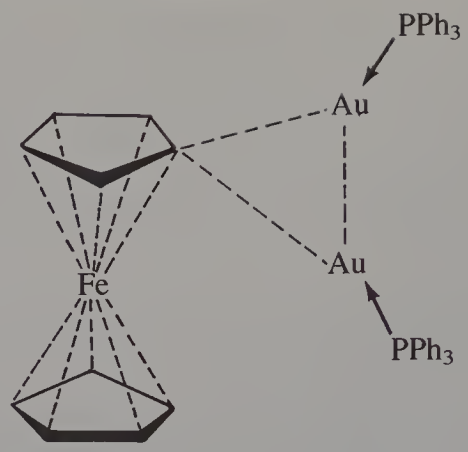
Nevertheless, higher coordination of the metal atoms of organocopper compounds can be achieved if donor groups are incorporated in their organic residues, and this leads to greater thermal stability and lower reactivity. Several arylcopper compounds with donor substituents (e.g., dimethylaminomethyl or dimethylamino groups) in the ortho position have been found to have tetrameric $(Cu\ aryl)_4$ or hexameric $(Cu\ aryl)_6$ structures in which the aryl groups perform a μ_2-or μ_3-bridging role, **34**.



(a) **(b)**

34

For example, the 2-dimethylaminomethyl-5-methylphenyl copper tetramer, $[CuC_6H_3(2\text{-}CH_2NMe_2)(5\text{-}Me)]_4$, contains μ_2-ligands of the type shown in structure **34(a)**, and a butterfly-shaped arrangement of its four metal atoms,[73] whereas the μ_3-ligand environment shown in **34(b)** is found in 2-dimethylaminophenyl copper compounds.[74,75] In both types of compound, pairs of copper atoms are bridged by (hypercoordinate) carbon atoms of the type already noted in $Al_2Me_4Ph_2$, **14**, Al_2Ph_6, **15**, and so on. Similar aryl bridges between pairs of copper[76], silver,[11,77] or gold atoms[78,79] or between lithium and copper, silver, or gold atoms[11] have also been structurally characterized. The ferrocenyl–gold compound, **35**,[79] provides an interesting example of a hypercarbon atom that is not only part of an aromatic cyclopentadienyl ring system, in which it is bonded to two other carbon atoms, but also bonds simultaneously to the sandwiched iron atom and (by a three-center, two-electron bond) to the two gold atoms.



35

2.6. SCANDIUM, YTTRIUM, AND LANTHANIDE COMPOUNDS

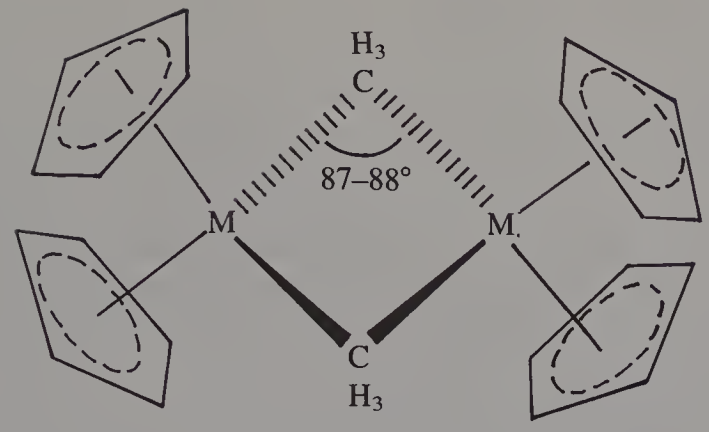
Although electron-deficient bridging of pairs of metal atoms by the hypercarbon atoms of alkyl groups is less familiar for *d*- or *f*-block metals than for *p*-block metals, evidence that the more electropositive transition metals can cause carbon atoms to become hypercoordinated is steadily accumulating, particularly in the case of scandium, yttrium, and the lanthanides. For example, the bis(cyclopentadienyl) metal alkyls of these elements, $(C_5H_5)_2MR$, form dimeric molecules typified by the yttrium and ytterbium methyl compounds, **36**, whose structures have been established by x-ray studies.[80] The resemblance between their dimeric molecules and those of the trimethylaluminum dimer, $Me_2Al(\mu\text{-}Me)_2AlMe_2$, structure **7**, is clearly close, a view reinforced by the fact that mixed metal compounds $(C_5H_5)_2M(\mu\text{-}R)_2AlR_2$, **37**, can readily be prepared containing alkyl bridges linking aluminum atoms to scandium, yttrium, or lanthanide atoms (Scheme 2.7).

Scheme 2.7

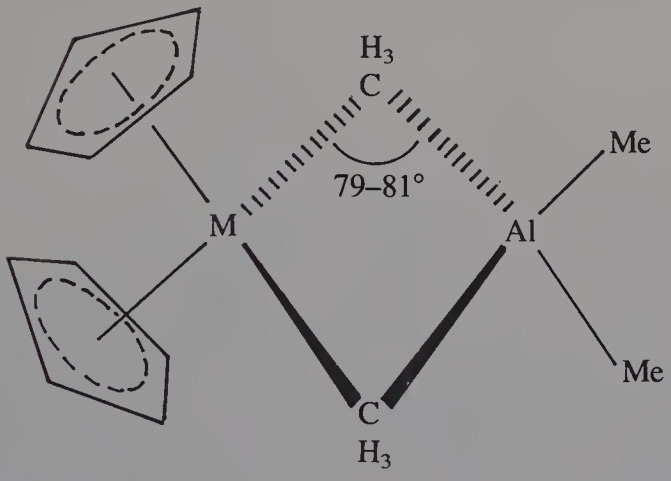
$$\frac{1}{2}[(C_5H_5)_2M(\mu\text{-}Cl)_2M(C_5H_5)_2]_2 + LiAlR_4 \longrightarrow (C_5H_5)_2M(\mu\text{-}R)_2AlR_2 + LiCl$$

R = Me, M = Sc,Y,Gd,Dy,Ho,Er,Tm,Yb; R = Et, M = Sc,Y,Ho

X-ray crystallographic studies on the yttrium[80] and ytterbium[81] compounds $(C_5H_5)_2M(\mu\text{-}Me)_2AlMe_2$ have established their structures as of the type in structure **37**, with the characteristic acute angle M−C−Al at the hypercarbon atom that shows it to be involved in a three-center, two-electron bond to the two metal atoms while bonding normally by three two-center, two-electron bonds to the methyl hydrogen atoms.



36



37

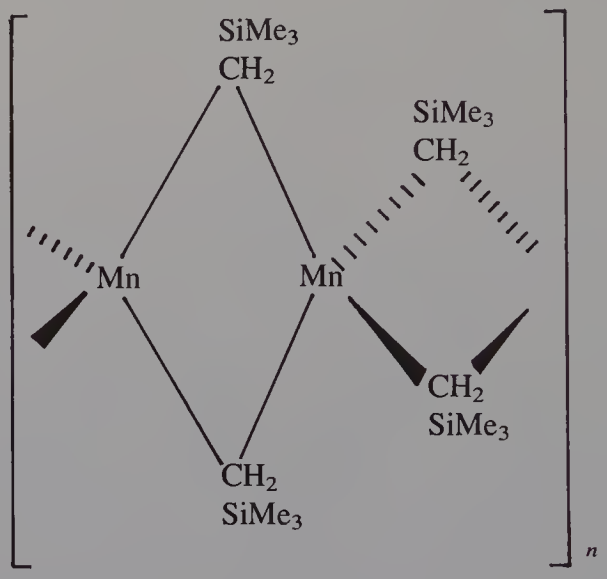
M = Y, Yb

The scandium, yttrium, or lanthanide atoms in these compounds evidently form such bridges to make better use of their valence shell electrons and orbitals. Monomers $(C_5H_5)_2MR$ would contain only 14 valence shell electrons (five from each cyclopentadienyl ligand, one from the alkyl group in addition to the three metal electrons), well short of the 16 or preferably 18 valence shell electrons characteristically present in stable organotransition metal compounds;[82] dimerization to $(C_5H_5)_2M(\mu\text{-}R)_2M(C_5H_5)_2$ raises the valence shell electron count to 16 and uses a metal orbital that would be vacant in the monomer.

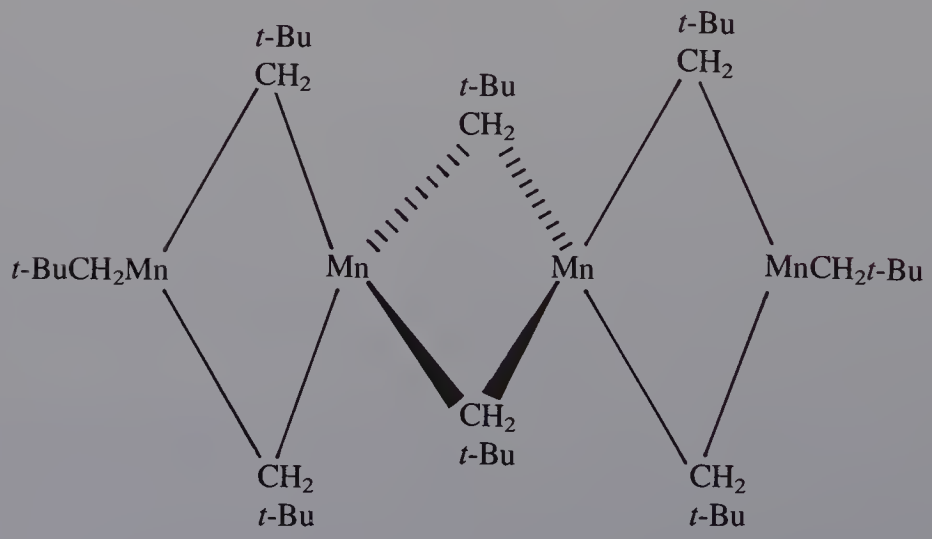
The relative strength of the methyl bridges in the mixed metal compound $(C_5H_5)_2Y(\mu\text{-}Me)_2AlMe_2$, **37**, has been demonstrated by variable temperature ^1H NMR studies of the activation energy, $\Delta G^{\ddagger}$, for exchange of the methyl groups between bridging and terminal positions.[80] These afforded a value of about 16 kcal mol^{-1} for $\Delta G^{\ddagger}$ [compare 11 kcal mol^{-1} for exchange of the methyl groups of $Me_2Al(\mu\text{-}Me)_2AlMe_2$ between bridging and terminal sites].

2.7. MANGANESE COMPOUNDS

Bulky alkyl groups $-CH_2R$(R = Ph, CMe_3, $SiMe_3$, or CMe_2Ph), which have no hydrogen atoms attached to the carbon or silicon atom in the β position, have been widely used to probe the alkyl chemistry of transition metals: their bulk protects the metal atoms from nucleophilic attack, while the absence of β hydrogen reduces the risk of decomposition by metal hydride formation and alkene elimination. The use of such ligands attached to manganese[83] has provided examples of hypercarbon atoms bridging pairs of metal atoms that are worthy of brief mention here.

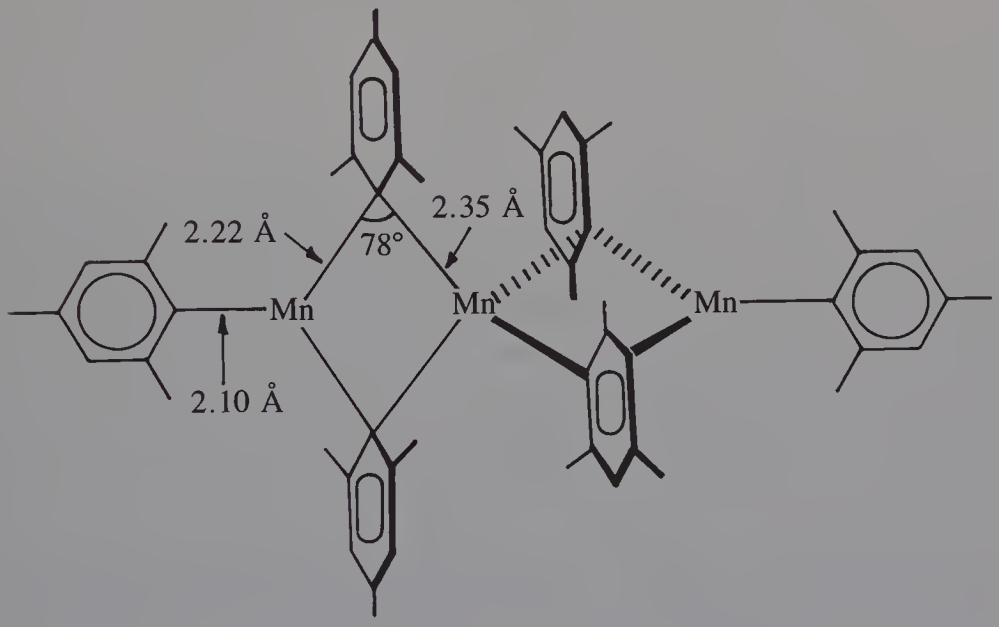


38



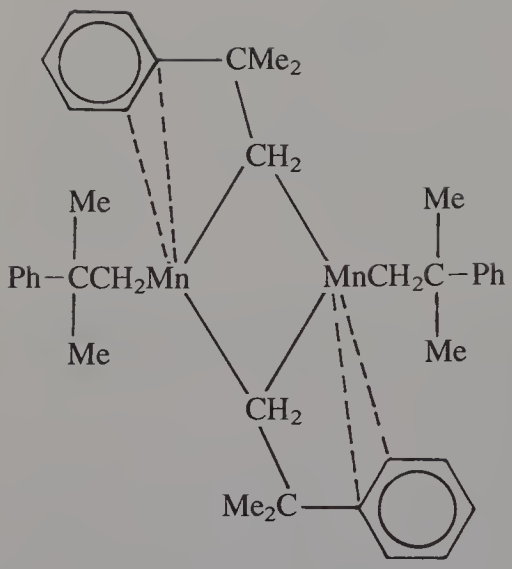
39

The compound $[Mn(CH_2SiMe_3)_2]_n$, for example, is polymeric in the crystal,[84] with a structure **38** like that of the beryllium and magnesium dialkyls, $(MR_2)_n$ (M = Be or Mg; R = Me or Et). Each metal atom, tetrahedrally coordinated, participates in four three-center, two-electron bonds, and all of the methylene carbon atoms are hypercoordinated.[84] The closely related neopentyl derivative, $[Mn(CH_2t\text{-}Bu)_2]_4$, has a tetrameric structure, **39**, in which half of the metal atoms are three coordinate, and so only three quarters of the methylene carbon atoms are hypercoordinate.[84] In this compound and in dimesitylmanganese, which crystallizes as the trimer $[Mn(mesityl)_2]_3$, **40**,[85] the degree of association is limited by the bulk of the substitutents. All of these systems show the characteristic features of three-center, two-electron Mn−C−Mn bridge bonding—greater Mn−C interatomic distances to the bridging (hypercoordinated) carbon atoms than to their terminal counterparts; sensitivity of the metal–carbon distance to the metal coordination number; and acute Mn−C−Mn bond angles at the hypercoordinated carbon atoms.

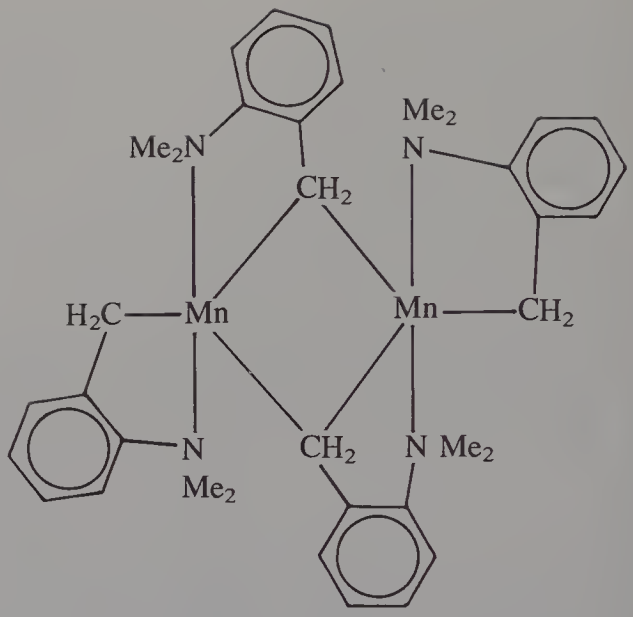


40

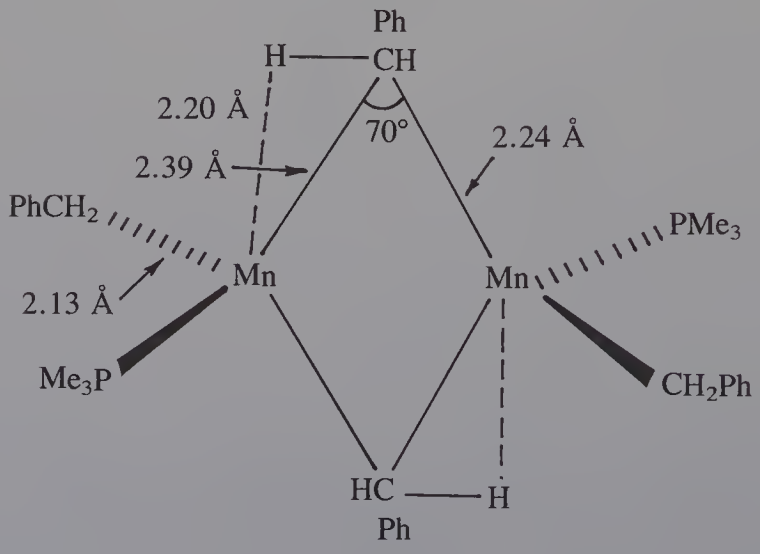
Several dimeric manganese dialkyls have been structurally characterized. They include two derivatives of dibenzylmanganese, $[Mn(CH_2CMe_2Ph)_2]_2$, **41**[84] and $[Mn(CH_2C_6H_4NMe_2)_2]_2$, **42**,[86] in which higher oligomer formation is inhibited by bonding interactions between the metal atoms and the phenyl groups of the bridging ligands, **41**,[84] or the ortho dimethylamino substituents thereon, **42**.[86] Phosphine ligands have also been used to stabilize dimers, and several adducts of stoichiometry $Mn_2R_4(PR'_3)_2$ have been structurally characterized.[87] The compounds $Mn_2(CH_2Ph)_4(PMe_3)$, **43**, and $Mn_2(CH_2SiMe_3)_4(PMePh_2)_2$, **44**, are typical of such adducts.


CMe2
CH2
Me
Me
Ph–CCH2Mn
MnCH2C–Ph
Me
Me
CH2
Me2C

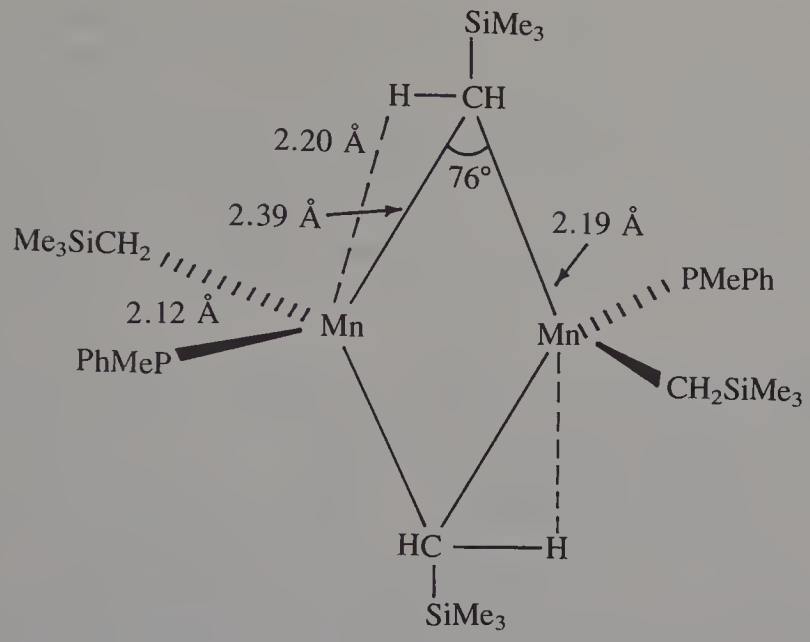
41


Me2N
Me2
N
CH2
H2C
Mn
Mn
CH2
N
Me2
CH2
N Me2

42


Ph
H
CH
2.20 Å
70°
2.24 Å
2.39 Å
PhCH2
PMe3
Mn
Mn
2.13 Å
Me3P
CH2Ph
HC
H
Ph

43



44

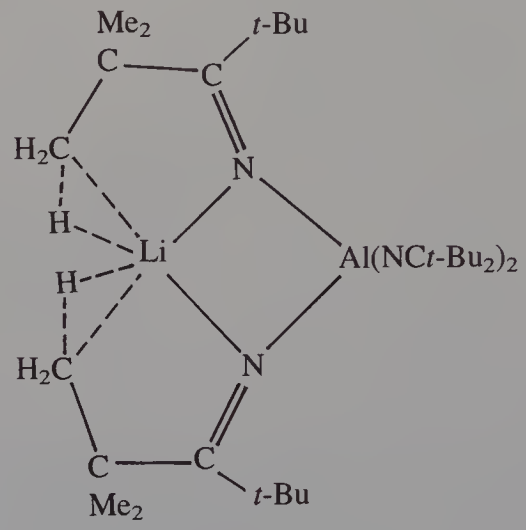
Interestingly, the bridges in these dimers are significantly asymmetric, containing two distinct metal–carbon distances to the bridging (hypercoordinated) carbon atoms. Moreover, one C–H bond of each bridging methylene unit is aligned roughly parallel to the metal–metal vector, bringing that hydrogen atom within a bonding distance of the metal atom furthest from the carbon atom in question. This structural feature is best interpreted in terms of a (3*c*–2*e*) C---H---Mn bonding interaction which, together with a (2*c*–2*e*) Mn–C bond to the nearer metal atom, accounts for the bridge bonding more satisfactorily than an explanation in terms of (3*c*–2*e*) Mn---C---Mn bonds.

2.8. MISCELLANEOUS SYSTEMS CONTAINING CARBON–HYDROGEN–METAL (3*c*–2*e*) BONDS

We have already seen in this chapter that although the association of two $AlMe_3$ units to form Al_2Me_6 does *not* involve (3*c*–2*e*) carbon–hydrogen–metal bonds,[33–36] such bonds are clearly indicated by the asymmetry of the bridges in the manganese compounds in structures **43** and **44** just discussed.[87] Moreover, we saw in our discussion of lithium alkyls in Section 2.4 that although (4*c*–2*e*) bonds provide the main rationale for their tetrameric, $(LiR)_4$, or hexameric, $(LiR)_6$, states of association, several lithium alkyls have structures in which carbon–hydrogen–metal bonding interactions help to explain the short metal–hydrogen distances present. These are not isolated, obscure examples of a rare phenomenon, but are members of a large, rapidly growing family of compounds in which (3*c*–2*e*) carbon–hydrogen–metal bonds are well-established, structurally characterized

features. Transition metal systems incorporating such bonds were surveyed by Brookhart and Green in 1983.[88] A few further examples are considered here.

The compound $LiAl(N{=}Ct\text{-}Bu_2)_4$,[89] **45**, provides another example of coordinatively unsaturated lithium interacting with C−H bonding electrons. Two of the ketimino ligands, $N{=}C(t\text{-}Bu)_2$, in this compound bridge the metal atoms by normal (*2c–2e*) bonds, leaning over towards the lithium to place two of their methyl groups so close to the metal atom as to imply quite strongly bonding C---H---Li interactions.



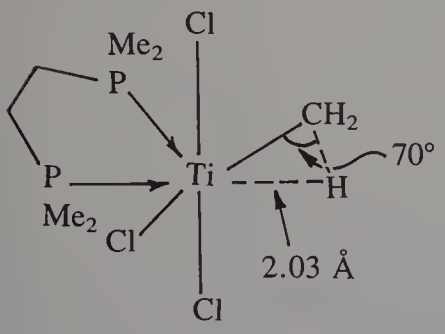
$LiAl(NCt\text{-}Bu_2)_4$

45

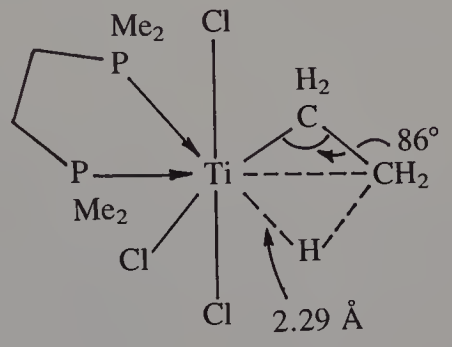
Two features of this structure are worthy of comment as being typical of such systems. One is that, without the C---H---metal interactions, the metal atom would be coordinatively unsaturated (bonding in this case only to the two nitrogen atoms). The other is that the ligands lean over perceptibly towards the lithium atom. The manner in which the metal atom draws the ligand towards itself, as a warrior might hold a shield to his body, prompted the labeling of such systems as "agostic" (from the Greek).[88]

The number of atoms separating the ligand C−H groups in structure **45** from the lithium atom via the azomethine group is sufficient to allow them to be drawn towards the metal atom without significant bond angle distortion, except at the bridging nitrogen atoms. Some agostic systems show very marked distortion of the ligand from its normal shape. The alkyltitanium chloride complexes, **46**,[90] and **47**,[91] contain alkyl groups that fold back towards the metal atoms which, though six-coordinate, would contain only 12 valence shell electrons if there were no Ti---H---C bonding. The methyl group of structure **46**, for example, has one hydrogen atom bent back towards the metal atom, the Ti---C---H angle being only 70° instead of the expected 109°,[90] while in structure **47**, the Ti---C---C angle of the ethyl group is only 86°.[91] Such

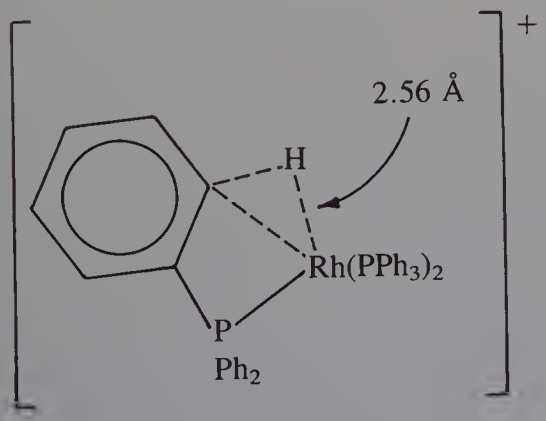
distortions of ligands are now recognized as highly likely when organic groups are attached to the relatively electropositive (and so strongly polarizing) metal atoms from the left-hand side of the transition series, particularly when the other ligands present are relatively electronegative and so unlikely to satisfy the metal atom's coordinative unsaturation and relative electron deficiency.



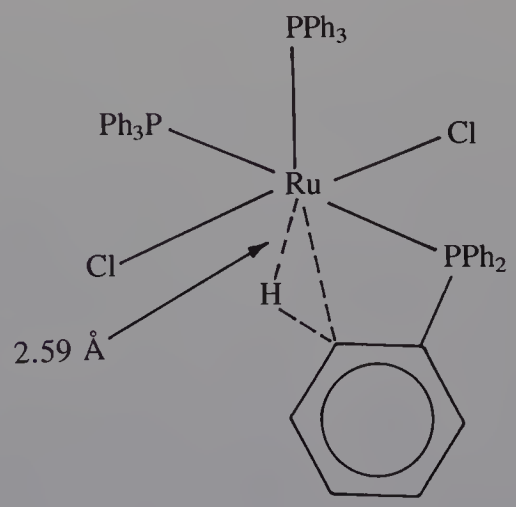
46 $MeTiCl_3(Me_2PCH_2CH_2PMe_2)$



47 $EtTiCl_3(Me_2PC_2H_4PMe_2)$



48[92] $[Rh(PPh_3)_3]^+$

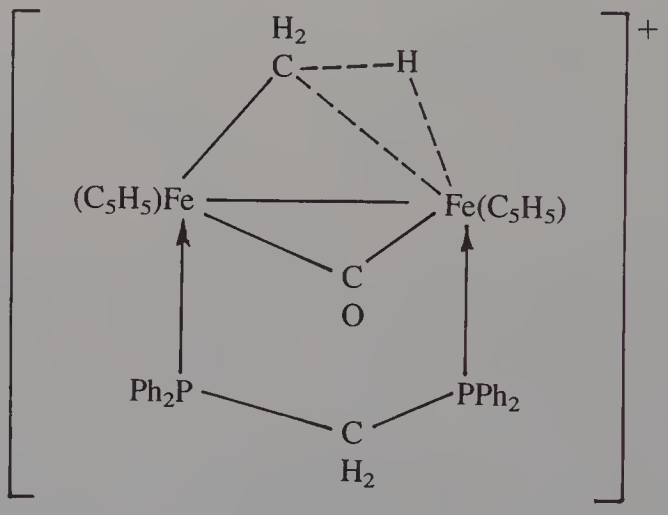


49[93] $RuCl_2(PPh_3)_3$

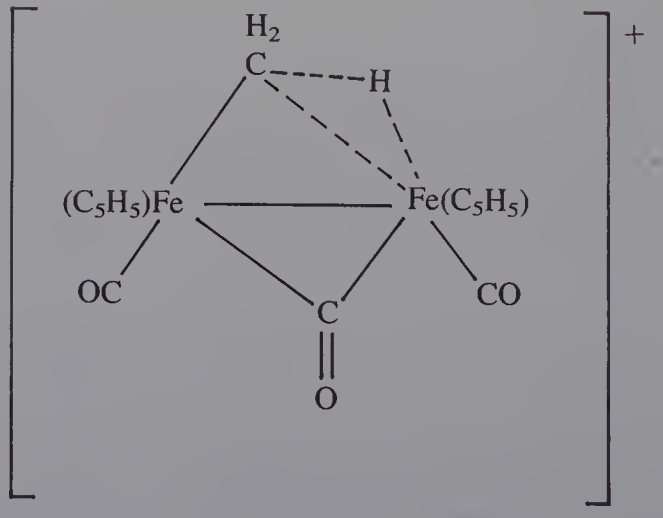
The compounds in structures **48**[92] and **49**[93] provide examples of another important category of compound showing (3*c*–2*e*) M---H---C bonding. These are systems in which the C–H bond in question is in the ortho position of an aryl group connected to the (coordinatively unsaturated) metal atom through one other atom (in both structures **48** and **49**, through a phosphorus atom). The normal bond angles of the ligands allow them to be orientated so as to place the ortho hydrogen atom over a

vacant coordination site of the metal atoms. Such systems effectively provide models of the intermediate through which ortho metallation of the aryl ring can occur.

The cations **50**[94] and **51**[95] are examples of dinuclear metal complexes in which a methyl group attached by a normal metal–carbon bond to one metal atom leans over towards the second metal atom to allow C---H---Fe bonding to ocur. This ensures that each of the iron atoms in each complex has the full complement of 18 electrons required for coordinative saturation.



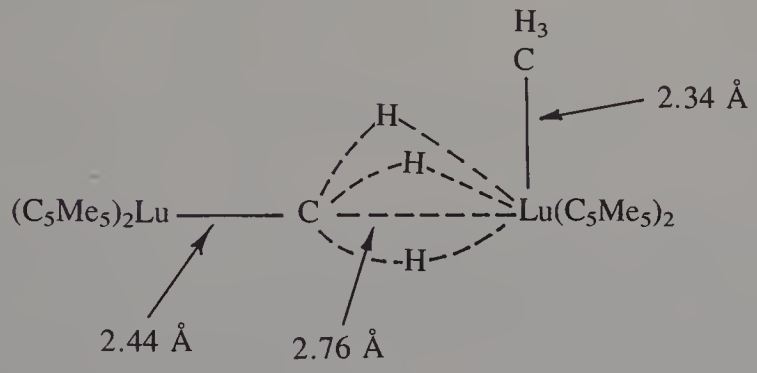
50[94]



51[95]

A final example of (3*c*–2*e*) C---H---metal bonding worth citing here is provided by the pentamethylcyclopentadienyl-lutetium methyl, $(C_5Me_5)_2LuMe$, which exists in

solution as an equilibrium mixture of monomer and dimer, and crystallizes as the dimer $(C_5Me_5)_4Lu_2Me_2$,[96] which has the unsymmetrical structure **52**, in which the methyl group of one molecule coordinates (by C---H---Lu bonds) to vacant metal orbitals of the second molecule.



52[96]

2.9. CONCLUSIONS

In this chapter we have shown that hypercarbon plays a key role in alkyl and aryl derivatives of main group metals, which associate through multicenter (electron-deficient) bonds. The compounds discussed are commonly referred to as electron deficient, in which sets of atoms are held together by fewer electrons than would be required if a pair would be allocated to each two-center link. Higher coordinate carbon atoms allow bonding in such compounds by participating in multicenter interactions. In the systems discussed, carbon atoms show coordination numbers ranging from five to eight (but not seven). In the following chapters examples of hypercarbon in carboranes, metal clusters, and carbocations will be discussed.

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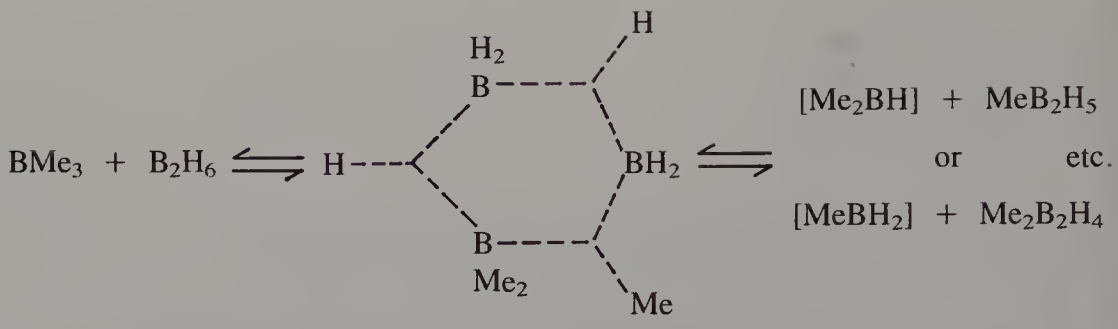
chapter 3

CARBORANES AND METALLACARBORANES

3.1. INTRODUCTION

Carbon forms two main types of mixed hydrides with boron.[1–5] In the first type, organic groups (e.g., alkyl or aryl groups) replace terminal hydrogen atoms of typical boron hydrides: the hydrocarbon and borane sections of the molecules are linked by normal (2*c*–2*e*) carbon–boron bonds. Examples of such organoboranes include the methyldiboranes $B_2H_{6-x}Me_x$ (where x can equal 1, 2, 3, or 4 but *not* 5 or 6—the bridging hydrogen atoms cannot be replaced by methyl groups) and similar derivatives of higher boranes, such as alkylpentaboranes ($B_5H_{9-x}R_x$) or alkyl decaboranes ($B_{10}H_{14-x}R_x$) (where R = an alkyl group and x is typically 1 or 2). In none of these does the organic group form an electron-deficient bridge between two or more boron atoms of the type described in Chapter 2, as normally found in alkyl derivatives of boron's more electropositive neighbors in the periodic table, namely, beryllium, magnesium, and aluminum. Such bridges necessarily entail greater internuclear repulsion forces (in the bridging region) than are present in the monomers: Evidently, the vacant 2*p* AO on boron in a monomeric trigonal planar trialkylborane like BMe_3 is not low enough in energy to form the strong (3*c*–2*e*) BCB bonds that would be needed to offset such internuclear repulsions. Nevertheless, methyl bridges between boron atoms are clearly formed readily enough to allow gaseous trimethylborane and diborane, when mixed at 20°, to generate the methyl diboranes ($B_2H_{6-x}Me_x$) (x=1 ⟶ 4) (Scheme 3.1).

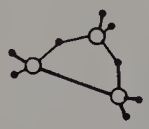
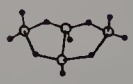
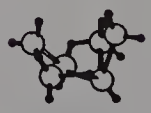
Scheme 3.1



It is, however, the second type of mixed hydride of carbon and boron, the *carboranes* (*carba-boranes*) that are the concern of the present chapter. In these, both boron and carbon atoms feature in the electron-deficient polyhedral molecular skeleton. The structures of a few examples were illustrated in Chapter 1, Figure 1.2. More comprehensive sets of examples, including the family of parent boranes, are shown in Figures 3.1–3.4

These remarkable compounds, which opened up a whole new area of organic chemistry, were a spin-off of the space race. The first carboranes[3b] were discovered during the early 1950s in the course of work aimed at the synthesis of organo derivatives of the higher boron hydrides as potential high-energy rocket fuels.[4–8] It was thought that, if simple organic groups were attached to boron hydride residues as in alkylpentaboranes ($B_5H_{9-x}R_x$) or alkyldecaboranes ($B_{10}H_{14-x}R_x$) (R = an alkyl group), then the products would have more suitable properties (liquid range, volatility, thermal stability, storage life, reactivity) for use as fuels than the parent boranes, most of which are extremely reactive, thermally unstable substances that tend to inflame spontaneously, if not actually explode, in contact with air. However, certain reactions between boranes and alkynes, instead of simply generating alkenyl or alkylboranes, afforded as the main products some hitherto unknown relatively unreactive, volatile, air and moisture stable substances. These were found to be of two main formula types, $C_2B_{n-2}H_n$ and $C_2B_{n-2}H_{n+2}$ ($n = 5 \longrightarrow 12$). Alkyl derivatives of these were also formed together with some monocarba species of the formula types $CB_{n-1}H_{n+1}$ or $CB_{n-1}H_{n+3}$. Although relatively few members of these series proved to be directly accessible by reactions between boranes and alkynes, methods of preparing the remaining members were quickly developed, and their derivative chemistry was soon opened up.[4]

Rarely in chemistry can a series of new compounds have created such an impact as did the carboranes. Their unprecedented polyhedral structures demonstrated the capacity of carbon atoms to bond simultaneously to as many as six neighboring atoms with astonishing strength. In particular, the reasonably accessible icosahedral carboranes ($C_2B_{10}H_{12}$) in which the carbon atoms can occupy adjacent (ortho), alternate (meta), or opposite (para) sites in the polyhedron, are so chemically robust as to be unreactive towards air, water, protic acids, and many powerful oxidizing agents, and so thermally stable as to undergo only slow isomerization in the

Closo species, $B_nH_n^{2-}$ [models for carboranes $CB_{n-1}H_{n+1}$, $C_2B_{n-2}H_n$]	Nido species, B_nH_{n+4} [models for carboranes $CB_{n-1}H_{n+3}$, $C_2B_{n-2}H_{n+2}$]	Arachno species, B_nH_{n+6} [models for carboranes $CB_{n-1}H_{n+5}$, $C_2B_{n-2}H_{n+4}$]
	$(B_4H_7^-)$	
$[B_5H_5]^{2-}$		$B_3H_8^-$
		
$B_6H_6^{2-}$	B_5H_9	B_4H_{10}
		
$B_7H_7^{2-}$	B_6H_{10}	B_5H_{11}
	(B_7H_{11})	
$B_8H_8^{2-}$		B_6H_{12}
		$(B_7H_{12}^-)$
$B_9H_9^{2-}$	B_8H_{12}	
		(B_8H_{14})
$B_{10}H_{10}^{2-}$	$B_9H_{12}^-$	
		
$B_{11}H_{11}^{2-}$	$B_{10}H_{14}$	B_9H_{15}
		
$B_{12}H_{12}^{2-}$	$B_{11}H_{13}^{2-}$	$B_{10}H_{14}^{2-}$

[ ] proposed structure, ( ) structure unknown,

Figure 3.1. *Closo*, *nido* and *arachno* Structures of Boranes of Formulas $B_nH_n^{2-}$, B_nH_{n+4} and B_nH_{n+6}, respectively.

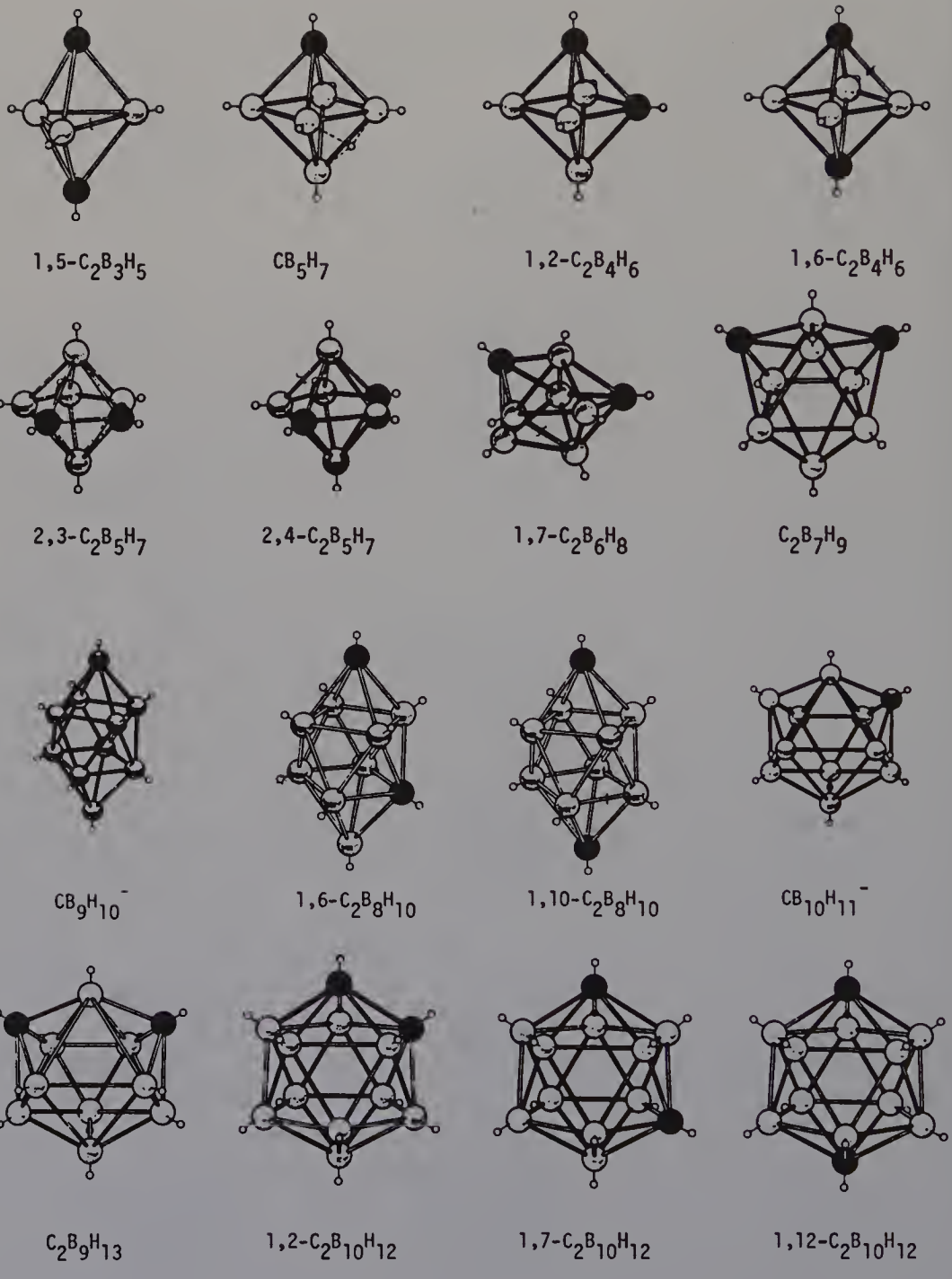


Figure 3.2. *Closo*-carboranes of formulas $CB_{n-1}H_{n+1}$ or $C_2B_{n-2}H_n$ (see *closo*-borane anions).

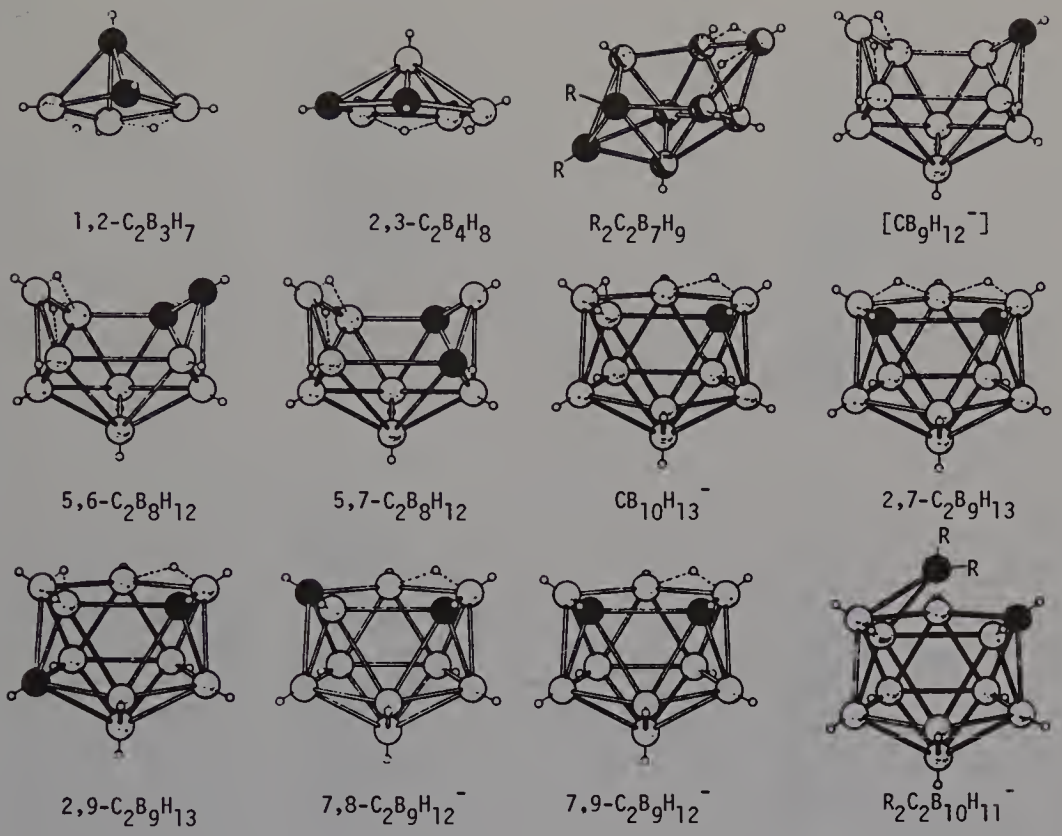


Figure 3.3. *Nido* carboranes of formulas $CB_{n-1}H_{n+3}$ or $C_2B_{n-2}H_{n+2}$ (see boranes B_nH_{n+4}).

temperature range 350–550 °C, degradation setting in at a significant rate only at higher temperatures than these. 1,10-$C_2B_8H_{10}$ is even more stable than the icosahedral carboranes. Such thermal stability, which exceeds that of typical organic compounds, has allowed several polyhedral carborane residues to be incorporated into the backbones of thermally stable polymers[9,10] for specialty high temperature applications.

The derivative chemistry of many of the polyhedral carboranes has revealed a remarkable similarity between their B—H and C—H bonds and those of aromatic ring systems, proving susceptible to substitution by similar reagents, for example, electrophiles. Indeed, most of the polyhedral carboranes may be regarded as three-dimensional aromatic systems. Their close family relationship to typical aromatic ring systems[11] will be illustrated later in this chapter.

Carboranes in general, and the icosahedral carboranes in particular, have another fascinating and highly significant type of derivative chemistry, that in which one or more of their BH units is replaced by another atom or group. The types of groups that have been found to be capable of replacing a BH unit include not only those such as AlEt, GaEt, $BeNMe_3$, or Sn atoms that are effectively isoelectronic with BH units, but also transition metal units [$Fe(CO)_3$, $Co(C_5H_5)$, $Ni(PPh_3)_2$, etc.] less obviously related to a BH unit.[11–13] Indeed, it was the existence of a wide range of

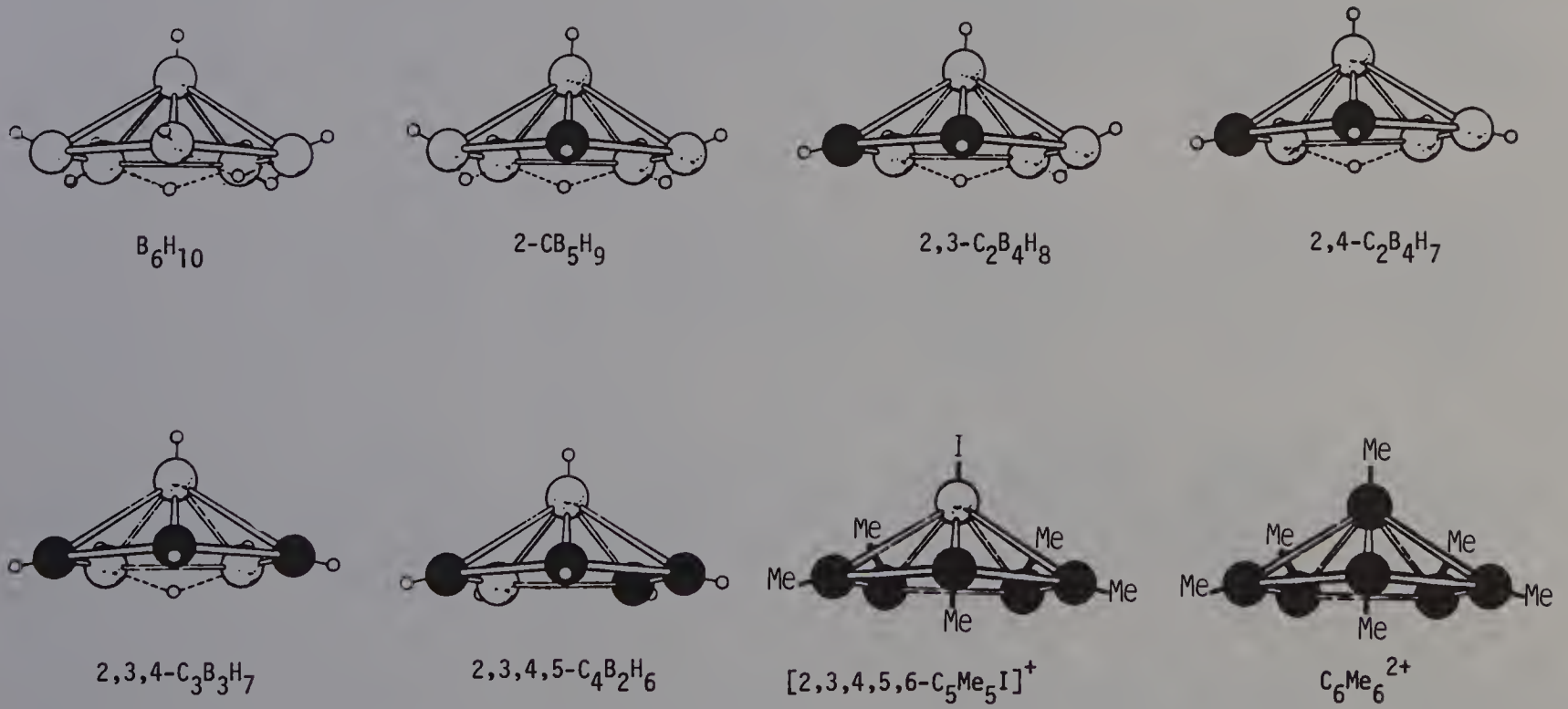


Figure 3.4. The family of *nido* carboranes $C_xB_{6-x}H_{10-x}$ related to B_6H_{10}.

metallacarboranes[2–5, 11–14] $C_2B_{n-3}H_{n-1}ML_x$ in which units ML_x (M = a metal atom to which assorted ligands, L_x, are attached) replaced a BH unit of the parent carborane $C_2B_{n-2}H_n$, that was to demonstrate clearly the bonding characteristics that such units shared with BH units and led to the concept of *isolobality*,[15–17] a concept that has provided a most useful device by which to rationalize the structures of organometallic systems and mixed metal–carbon clusters, and to correlate these with metal clusters, metal–carbene and metal–carbyne complexes, and borane clusters.[11–22] Units such as BH, $Fe(CO)_3$, $Co(C_5H_5)$, or $Ni(PPh_3)_3^{2+}$ are regarded as *isolobal* because their frontier orbitals—those with which they can bond to other species—are similar in number, energy, shape, and lobal characteristics (see Fig. 1.19).[15]

3.2. CARBORANE STRUCTURES

Carboranes and boranes form one comprehensive family of cluster compounds in which the structures[2–5,8,11,18–24] of the former may in principle be derived from their isoelectronic borane analogs by replacement of boron atoms by carbon atoms, with suitable charge adjustment (replace B^- by C or B by C^+), or loss of hydrogen atoms (replace a boron and a hydrogen atom by one carbon atom, or a boron and two hydrogen atoms by a CH unit). In order to illustrate the carborane structural pattern, it is helpful at this point to illustrate the pattern to which polyboranes themselves conform (Fig. 3.1) as a prelude to discussing the carboranes themselves. A representative selection of carborane structures is shown in Figures 3.2–3.4.

There are three main structural types of carborane and borane clusters, referred to as *closo* (closed-cage), *nido* (nest-like), and *arachno* (cobweb-like), of which the parent boranes have formulas $B_nH_n^{2-}$, B_nH_{n+4}, and B_nH_{n+6}, respectively. The formulas of typical examples are listed in Table 3.1. The structures of various *closo* carboranes are shown in Figure 3.2; Figure 3.3 illustrates representative *nido* systems, and Figure 3.4 shows the complete family of pentagonal pyramidal hexanuclear *nido* clusters formally related to B_6H_{10}.

The structural characteristics of each category of borane or carborane are as follows:

1. *Closo boranes and carboranes* (typical formulas $B_nH_n^{2-}$, $CB_{n-1}H_n^-$, $C_2B_{n-2}H_n$). The atoms in these clusters lie roughly on the surfaces of two concentric spheres, the skeletal boron and carbon atoms on the inner one, the terminal hydrogen atoms on the outer. The skeletal boron and carbon atoms form deltahedra (polyhedra with exclusively triangular faces), each skeletal atom having a single hydrogen atom attached to it, at a normal (2*c*–2*e*) bonded distance, by a bond that points in a direction (*exo*) radially outwards away from the cluster center.

In the *closo* carboranes of formulas $C_2B_{n-2}H_n$ or derivatives $C_2B_{n-2}H_{n-2}R_2$ where the substituents R are C– attached (several of which can be prepared from alkynes RC≡CR and boranes such as B_4H_{10}, B_5H_9, or $B_{10}H_{14}$)[24] the skeletal carbon atoms may occupy adjacent sites on the skeletal polyhedron. However, the thermodynamically preferred sites for the carbon atoms are of low coordination number and

TABLE 3.1. Carboranes and Boranes, Classified According to Their Formula and Structure Type

Number of Skeletal bond Pairs	Fundamental Polyhedron and Symmetry	*Closo* Species $B_nH_n^{2-}$ $CB_{n-1}H_{n+1}$ $C_2B_{n-2}H_n$	*Nido* Species B_nH_{n+4} $CB_{n-1}H_{n+3}$ $C_2B_{n-2}H_{n+2}$ and so on	*Arachno* Species B_nH_{n+6} $CB_{n-1}H_{n+5}$ $C_2B_{n-2}H_{n+4}$
6	Trigonal bipyramid (D_{3h})	$C_2B_3H_5$	$[B_4H_7^-]$ $[C_4t\text{–}Bu_4]$[a]	$B_3H_8^-$, $[C_3H_6]$[b]
7	Octahedron (O_h)	$B_6H_6^{2-}$ CB_5H_7 $C_2B_4H_6$	B_5H_9 $C_2B_3H_7$ $C_5Me_2H_3^+$	B_4H_{10}, $[C_4H_6]$[c] $[C_4H_4^{2-}]$[d]
8	Pentagonal bipyramid (D_{5h})	$B_7H_7^{2-}$ $C_2B_5H_7$	B_6H_{10} CB_5H_9 $C_2B_4H_8$ $C_3B_3H_7$ $C_4B_2H_6$ $C_5Me_5BI^+$ $C_6Me_6^{2+}$	B_5H_{11}, $[C_5H_5^-]$[e]
9	Dodecahedron (D_{2d})	$B_8H_8^{2-}$ $C_2B_6H_8$	$[B_7H_{11}]$	B_6H_{12}, $[C_6H_6]$[f]
10	Tricapped trigonal prism (D_{3h})	$B_9H_9^{2-}$ $C_2B_7H_9$	B_8H_{12}	$[B_7H_{12}^-]$
11	Bicapped square antiprism (D_{4d})	$B_{10}H_{10}^{2-}$ $CB_9H_{10}^-$ $C_2B_8H_{10}$	B_9H_{13} $C_2B_7H_{11}$	B_8H_{14}
12	Octadecahedron (C_{2v})	$B_{11}H_{11}^{2-}$ $CB_{10}H_{11}^-$ $C_2B_9H_{11}$	$B_{10}H_{14}$ $CB_9H_{12}^-$ $C_2B_8H_{12}$	B_9H_{15}, CB_8H_{14}, $C_2B_7H_{13}$
13	Icosahedron (I_h)	$B_{12}H_{12}^{2-}$ $C_2B_{10}H_{12}$	$B_{11}H_{13}^{2-}$ $CB_{10}H_{13}^-$ $C_2B_9H_{13}$ $C_2B_9H_{12}^-$	$B_{10}H_{14}^{2-}$, $C_2B_8H_{14}$

[a] A derivative of tetrahedrane.
[b] Cyclopropane.
[c] Bicyclobutane
[d] Cyclobutadiene dianion.
[e] Cyclopentadienide anion.
[f] Benzvalene.

nonadjacent if possible, as illustrated in Figure 3.2. This means that a carbon atom in a *closo* carborane, in addition to the bond it forms to the *exo* hydrogen atom, may also be bonded to from three (in $C_2B_3H_5$) to five (in $C_2B_{10}H_{12}$) neighboring skeletal atoms. Indeed, 1,5-$C_2B_3H_5$ is the only *closo* carborane in which carbon exhibits what may be regarded as a "normal" coordination number of four. For all the other *closo* carboranes, the overall coordination number of the carbon atom is either five (when the skeletal connectivity k—the number of neighboring atoms in the skeletal polyhedron—is four) or six (when $k = 5$). The boron–carbon bond distances are invariably longer than the single bond distance of about 1.58 Å.

2. *Nido boranes and carboranes* (typical formulas B_nH_{n+4}, $CB_{n-1}H_{n+3}$, $C_2B_{n-2}H_{n+2}$, etc.). These have "polyhedral fragment" structures that are clearly (Fig. 3.1) based on the same series of polyhedra as the *closo* compounds, but with one vertex (generally the one of highest skeletal connectivity, k) left vacant. The *nido* clusters with n skeletal atoms thus have structures that appear to be fragments of the *closo* system with $(n + 1)$ skeletal atoms. The carbon atoms usually occupy sites of lower connectivity adjacent to the vacant site, for example, a basal site in the pentagonal pyramidal series CB_5H_9, $C_2B_4H_8$, $C_3B_3H_7$, and $C_4B_2H_6$ (Fig. 3.4, which also shows two cationic members of this series). However, in these *nido* systems, the extra hydrogen atoms (additional to the one *exo* hydrogen atom that each skeletal atom still bears) lie on the same spherical surface as the skeletal atoms. They tend to occupy polyhedron edge-bridging positions adjacent to a vacant vertex, where they play B---H---B bridging roles, see Figure 3-4, (never B---H---C or C---H---C bridging roles, although such bridges have recently been observed elsewhere, see Chapter 5). The need to accommodate such extra hydrogen atoms may cause a carbon atom to occupy a more highly coordinated site (see, e.g., the structure of $C_2B_3H_7$ in Fig. 3.3, in which one carbon occupies an apical position, from which it would be expected to move on deprotonation to form $C_2B_3H_6^-$).[23,24]

3. *Arachno boranes and carboranes* (typical formulas B_nH_{n+6}, $CB_{n-1}H_{n+5}$, $C_2B_{n-2}H_{n+4}$, etc.).

These have yet more open structures than the *nido* compounds (Fig. 3.1), and can be regarded as based upon the same series of deltahedra as the *closo* and *nido* species, but with *two* vertices left vacant. There are too few *arachno* carboranes known at present to justify much discussion of these systems here. Those listed in Table 3.1 include some hydrocarbon species that may formally be classed as *arachno* carboranes though they contain no boron atoms. They include bicyclobutane (C_4H_6) (cf. B_4H_{10}, Fig. 1.15), the cyclobutadiene dianion ($C_4H_4^{2-}$), the cyclopentadienide anion ($C_5H_5^-$), and benzvalene (C_6H_6), all of whose structures conform to the pattern illustrated in Figure 3.1, though of course these systems do not contain hypercarbon atoms. We shall see later that aromatic ring systems in general can be classified as *arachno* members of the borane cluster family.

3.3. A LOCALIZED BONDING APPROACH TO THE SKELETAL BONDING IN *CLOSO* CARBORANES

Closo boranes ($B_nH_n^{2-}$) and carboranes ($CB_{n-1}H_n^-$ or $C_2B_{n-2}H_n$) can be regarded as aggregates of n BH and/or CH units held together by $(n + 1)$ pairs of electrons, since each BH unit can supply two electrons and each CH unit can supply three electrons for bonding to the rest of the cluster, (these are the numbers remaining after the boron or carbon atom has used one of its valence shell electrons to bond to the *exo* hydrogen atom). These $(n + 1)$ electron pairs are commonly referred to as the *framework* or *skeletal electron pairs* to distinguish them from the n pairs of ligand-bonding electrons involved in bonding the *exo* hydrogen atoms.

Since the deltahedral structures of the most stable *closo* compounds are those resulting from various methods of synthesis, including high temperature reactions between alkynes and boranes, it is evident that they are the thermodynamically preferred structures for these compounds, rather than accidental kinetic products of the synthetic routes used. A satisfactory bonding description must not only describe their bonding, but also explain why n trivalent BH or CH units held together by $(n + 1)$ pairs of electrons adopt such polyhedral structures in preference to alternatives. Molecular orbital treatments explain this much better than localized bond treatments. However, since localized two- and three-center bond schemes are so useful throughout hypercarbon chemistry in general, it is worth considering briefly at this point why they are of limited use when applied to *closo* boranes and carboranes.[25,26]

The problem is essentially one of complexity. There are so many ways of allocating two- and three-center bonds to the edges and faces of the *closo* deltahedra, particularly the more symmetrical ones, that it is difficult to ensure that all bond networks have been taken into account and that all opportunities for resonance delocalization of these bonds have been considered. The difficulty of representing three-dimensional polyhedra adequately in two-dimensional diagrams also complicates the problem. However, there are ways of systematizing the approach that offset some of these difficulties, and help to illustrate the carbon bonding environment one is dealing with. A CH unit has three electrons and three AO's with which it can bond to neighboring BH or CH units in carboranes. The ways in which it can use these, employing only (2*c*–2*e*) or (3*c*–2*e*) bonds or suitable combinations of these, to bond to from three to six neighboring atoms are shown in Figure 3.5.[26] [In constructing Fig. 3.5, it was assumed that each neighboring skeletal atom had to be accounted for either by a (2*c*–2*e*) bond to it, a (3*c*–2*e*) bond to it and a second neighboring atom, or two such (3*c*–2*e*) bonds. Bond schemes that placed a (3*c*–2*e*) bond in a face already edged by a (2*c*–2*e*) bond were not used, because they crowded the electrons unrealistically for such electron-deficient systems, though they may be appropriate for *nido* systems, as shown by Figures 1.7*a*, 1.15, and 1.17 in Chapter 1].

Some generalizations, apparent from Figure 3.5, are worth noting. First and rather obviously, as the skeletal connectivity k increases, so does the proportion of (3*c*–2*e*) bonds used. Since (3*c*–2*e*) bonds transfer more electronic charge from the central atom than do (2*c*–2*e*) bonds [as a crude approximation, one can allocate one third of an electron pair to each edge of the triangle of atoms bonded by a (3*c*–2*e*) bond], then

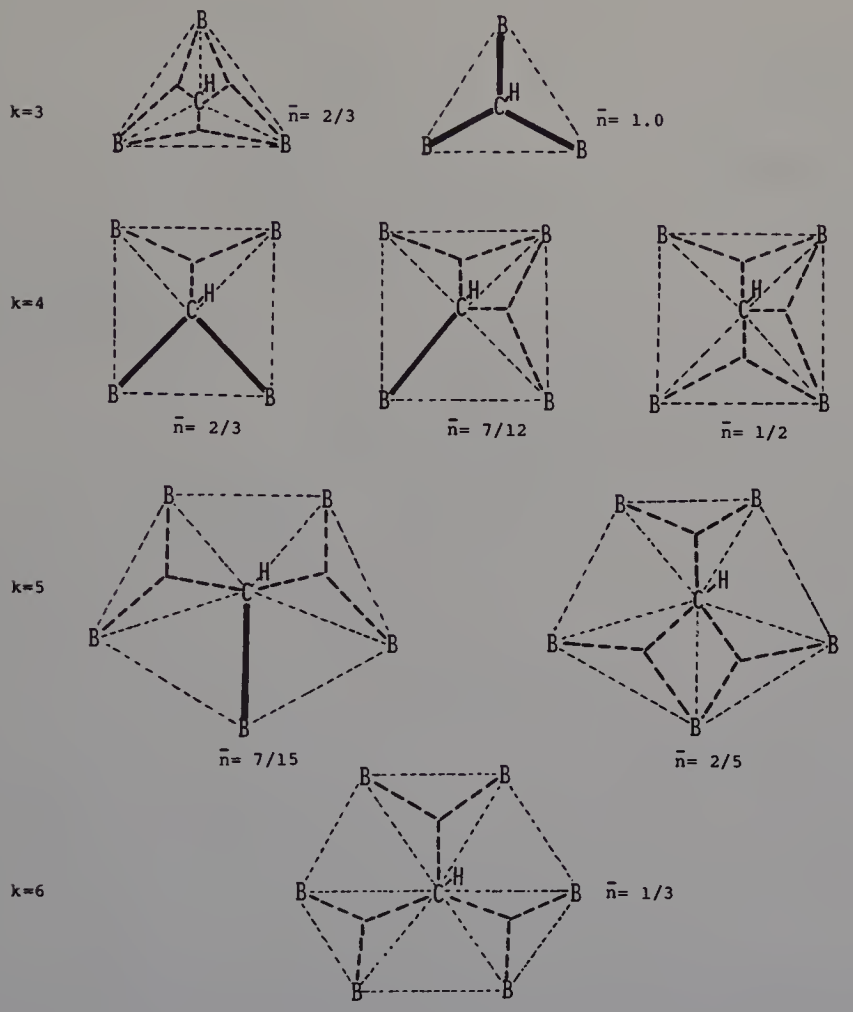


Figure 3.5. Two- and three-center bond arrangements possible for CH units of skeletal connectivity (k) 3,4,5, or 6 in carboranes. Bond orders n refer to the mean number of electron pairs per B−C edge for the bond network in question.

the *positive charge on the central carbon atom increases with its skeletal connectivity*, k. The *bond orders*, n, of the two-center links formed (numbers of electron pairs, or fractions thereof, that can be allocated to these two-center links) *decrease as k increases*, as does kn, the total number of electrons assigned to the k skeletal two-center links to the carbon atom in question. Such generalizations hold also for other hypercarbon systems than carboranes.

For the *closo* carboranes and related borane anions, $B_nH_n^{2-}$, if each skeletal atom is to participate in three skeletal bonds and so use all three of its valence shell AO's, then one must allocate the $(n + 1)$ skeletal bond pairs to three $(2c–2e)$ bonds (using six AO's) and $(n-2)$ $(3c–2e)$ bonds [using the remaining $(3n-6)$ AO's]. For the carborane $C_2B_3H_5$ (Fig. 3.6), this requires a skeletal bonding description in terms of three two-center and three three-center bonds, allocated to the two halves of the

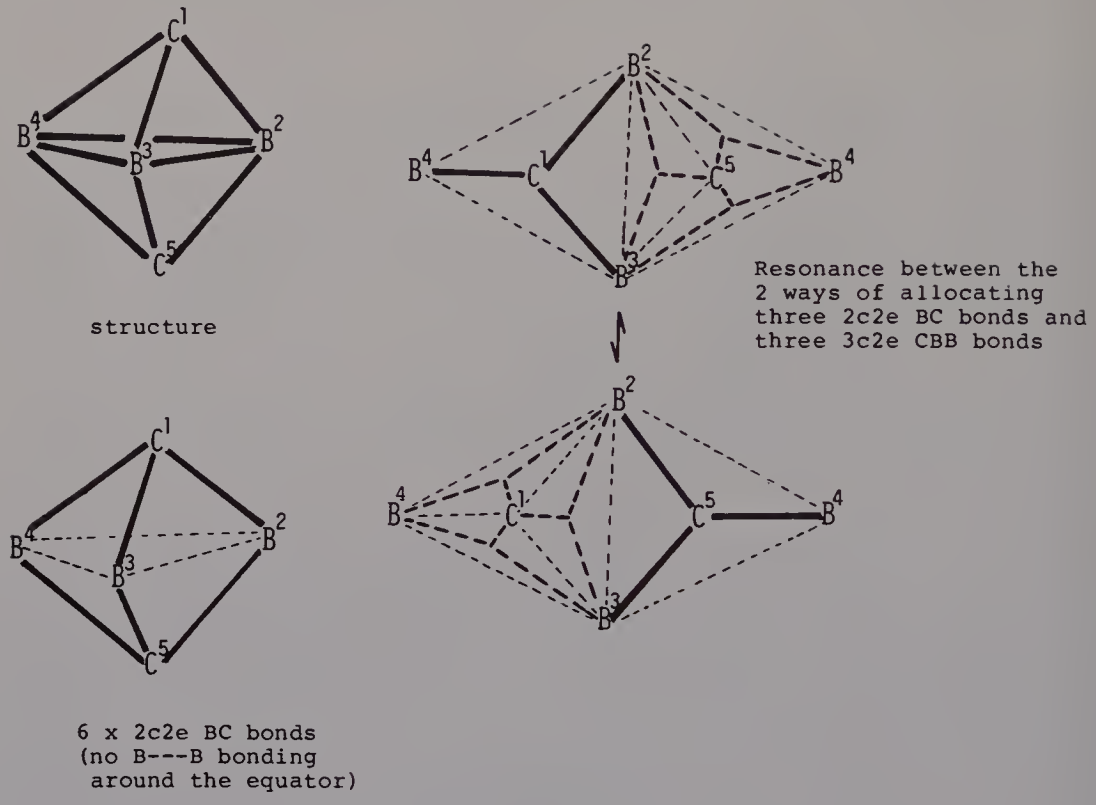
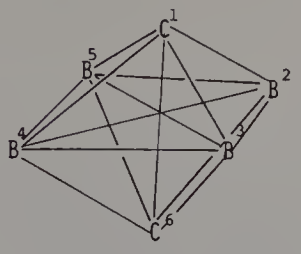
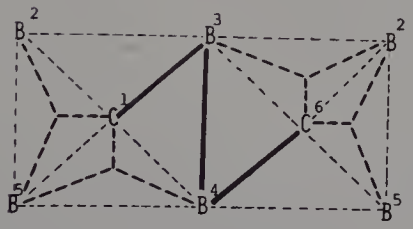


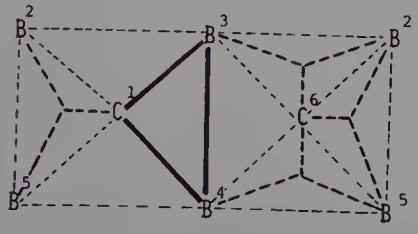
Figure 3.6. Two- and three-center bond treatments of the *closo* carborane, $C_2B_3H_5$.

trigonal bipyramid, respectively. Resonance between the two possible forms leads to formal edge bond orders n of five sixths for the axial edges and one third for the equatorial edges, making no allowance for the differing electronegativities of boron and carbon. This description is probably a little more appropriate than one using only (2*c*–2*e*) B−C bonds (Fig. 3.6), in which the boron atoms use only three of their four valence shell AO's, and indulge in no equatorial boron–boron bonding.

The scope for resonance increases dramatically if one turns to the pseudooctahedral (actually D_{4h}) carborane, 1,6-$C_2B_4H_6$, for which there are 32 ways of allocating three (2*c*–2*e*) and four (3*c*–2*e*) bonds to the skeleton (Fig. 3.7). For this and higher *closo* carboranes, localized two- and three-center bond schemes are generally too complicated to be of much use, though those with the patience to apply them will find the generalizations about the link between electron density and coordination number (Fig. 3.5) to be substantiated by the bond networks found to be compatible with the individual cluster geometries.[25,26] The seeming preference of the carbon atoms for the sites of lower connectivity may be understood as the natural "preference" of the more electronegative atom for the sites of maximum electron density. In other words, the assemblage of boron and carbon atoms is that which minimizes charge separations (i.e., maximizes charge smoothing).







(Skeleton shown opened out(about edge B^3B^4 as the hinge) for simplicity- atoms B^2 and B^5 therefore are shown twice)

Figure 3.7. Ways of allocating three (2*c*–2*e*) bonds and four (3*c*–2*e*) bonds to the skeletal bonds of the (D_{4h}) approximately octahedral *closo* carborane 1,6-$C_2B_4H_6$. (Skeleton shown opened out (about edge B^3B^4 as the hinge) for simplicity—atoms B^2 and B^5 therefore are shown twice).

One further weakness of localized two- and three-center bond schemes should be noted. This is that such schemes may lead us to expect the existence of clusters that MO schemes show to be unstable.[11] For example, it is possible to allocate six (3*c*–2*e*) bonds to six of the eight faces of a hypothetical octahedral species B_6H_6 or $C_2B_4H_6^{2+}$, or indeed to use six (2*c*–2*e*) bonds and two (3*c*–2*e*) bonds to describe the skeletal bonding in a hypothetical octahedral species, $B_6H_6^{4-}$ or $C_4B_2H_6$, still involving each skeletal atom in three skeletal bonds. That is, the localized bond treatment gives no indication as to why the *closo*-octahedral clusters $B_6H_6^{2-}$, CB_5H_7, or $C_2B_4H_6$ require seven skeletal bond pairs rather than six or eight, whereas MO treatments do allow us to understand how many skeletal electron pairs are needed, as follows.

3.4. MOLECULAR ORBITAL TREATMENT OF THE SKELETAL BONDING IN *CLOSO* CARBORANES

Many individual boranes and carboranes, including all the *closo* compounds, have been the subjects of MO calculations of various levels of sophistication.[27–37] All are agreed that the deltahedra in Figures 3.1 and 3.2 represent the most stable arrangements for their n BH (or CH) units when held together by $(n + 1)$ skeletal bond pairs in that they are more stable than alternative geometries, and have the correct symmetries to generate $(n + 1)$ bonding MO's from the $3n$ AO's available with a large HOMO–LUMO energy gap to the next available MO.

The basis for the systematic treatment of the bonding in *closo* boranes and carboranes, like so many important developments in bonding theory, was provided by Hofmann and Lipscomb.[29] They pointed out that the *exo* orientations of the BH and CH groups of *closo* species $B_nH_n^{2-}$ or $C_2B_{n-2}H_n$ allow each such group to contribute two types of atomic orbital for skeletal bonding purposes. One of these (Fig. 3.8*a*) is a radially orientated *s*, *p*, or *sp* hybrid AO pointing towards the center of the cluster (the counterpart of the *p*, *s*, or *sp* hybrid AO used in the *exo*-oriented BH or CH bond). The other type of AO provided by each BH or CH unit is the pair of *p* AO's orientated perpendicular to the BH or CH bond, tangential to the pseudospherical cluster surface (Fig. 3.8). Between them, these $3n$ AO's necessarily generate $3n$ MO's, of which only $(n + 1)$ are bonding for the known *closo* boranes and carboranes.

Of these $(n + 1)$ skeletal bonding MO's, one (common to all the *closo* systems) is unique: it is that MO of *A* symmetry, resulting from a fully in-phase combination of all of the radially orientated AO's, to which the tangentially orientated *p* AO's make no contribution because they have the wrong nodal characteristics. Such an orbital, illustrated for 1,6-$C_2B_4H_6$ in Fig. 3.8*c*, concentrates electronic charge just inside the cluster polyhedron. The remaining n bonding MO's, which concentrate electronic charge in the pseudospherical surface of the polyhedron, result primarily from interactions between the $2n$ tangentially orientated *p* AO's (Fig. 3.8*d–g*), stabilized where symmetry permits by suitable combinations of radially orientated AO's (Fig. 3.8*f* and *g*). No other bonding MO's arise *solely* from the radial AO's—their bonding combinations mix with similar symmetry bonding combinations of tangential AO's to stabilize such bonding MO's but not add to their number.

Figure 3.8 shows the form these bonding MO's take for 1,6-$C_2B_4H_6$. Note that there are three MO's that are effectively σ bonding, and three that are π bonding, around the equatorial B_4 belt of this cluster or around the two C_2B_2 rings generated by slicing this cluster in the two possible ways through both polar atoms and two equatorial atoms ($C^1B^2C^6B^4$ or $C^1B^3C^6B^5$). This feature underlines the relationship of this cluster to a four-membered ring aromatic system—its own three such four-membered rings are both σ and π bonded.

A further comment about these cluster bonding MO treatments is worth making. This concerns the way the skeletal bonding MO's can be classified irrespective of the point group to which a specific cluster belongs. This is by labeling them as *S*, *P*, *D*, and so on, according to how their lobal characteristics would match those of the set of AO's on a hypothetical atom at the center of the cluster. For example, the fully

symmetric combination of inward pointing orbitals (the A_{1g} MO shown in Fig. 3.8*c*) will always match the symmetry of an *S* AO on an atom at the center of the cluster, so it can be labeled as a skeletal bonding MO of type *S*. The A_{2u} and E_u skeletal bonding MO's shown in Figure 3.8*f* and 3.8*g* can similarly be labeled as type *P*, while the B_{2g} and E_g MO's (Fig. 3.8*d* and 3.8*e*), which would match the d_{xy}, d_{yz}, and d_{xz} AO's of an atom at the center, would be labeled as type *D* in a general approach to cluster bonding that has been developed by A.J. Stone using Tensor Surface Harmonic theory.[38–41] Stone's approach provides a mathematical explanation of why these clusters have exclusively triangular faces (their energies are governed by the numbers of polyhedral edges, which need to be maximized for maximum stability) and why

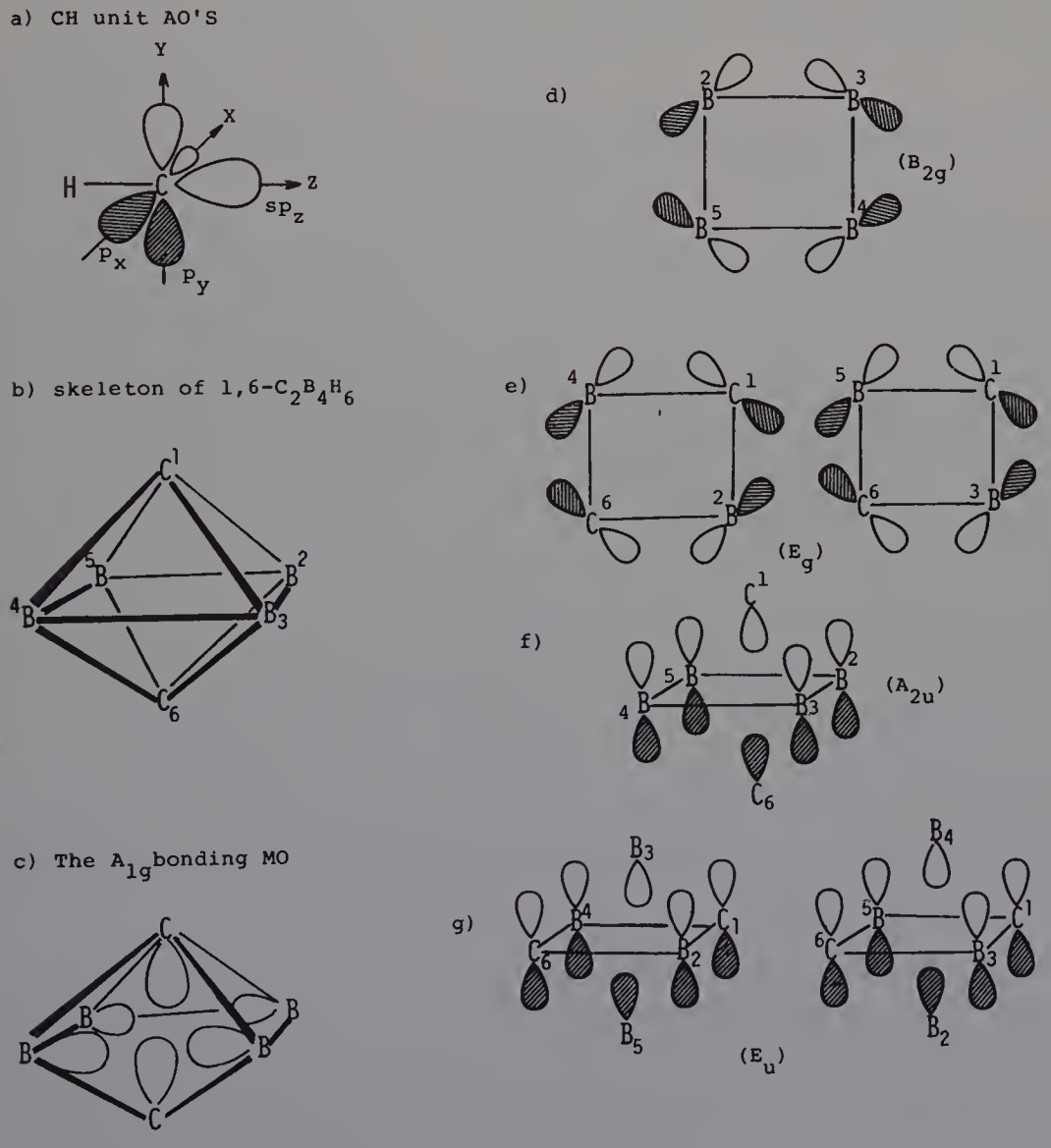


Figure 3.8. Orbitals that a CH or BH unit can use for cluster bonding, and the skeletal bonding MO's they generate in the case of 1,6-$C_2B_4H_6$.

they require $(n + 1)$ skeletal bonding electron pairs (endorsing the point already made here: That the n inward-pointing AO's generate only one bonding MO, while the remaining $2n$ tangentially oriented AO's generate the expected n bonding MO's). These generalizations apply to the whole series of *closo* boranes and carboranes from $C_2B_3H_5$ to $C_2B_{10}H_{12}$.

They do not, however, apply to such a molecule as the smallest possible deltahedron, the tetrahedron [as of tetrahedrane (C_4H_4)]. Uniquely among deltahedra, the tetrahedron has vertices exclusively of skeletal connectivity three, matching the skeletal valence of the atoms we have been considering. The molecule tetrahedrane (C_4H_4), with six skeletal bond pairs, can be described by six $(2c–2e)$ C−C edge bonds and the carbons are not examples of hypercoordinated carbon. In contrast, its boron relative, B_4Cl_4 (the chlorine atoms occupy *exo* positions), which also has a tetrahedral structure, may be considered as held together by four $(3c–2e)$ BBB face bonds.[42]

3.5. THE BONDING IN *NIDO* AND *ARACHNO* CARBORANES

As with *closo* carboranes, both localized (two- and three-center) bonding descriptions and MO treatments can be applied to *nido* and *arachno* carboranes.

Localized two- and three-center bonding treatments are generally more useful than was found to be the case for *closo* systems,[29–33] partly because their networks of atoms afford less scope for resonance, and partly because their polyhedral fragment shapes are more easily projected on to a plane (usually viewed through the open face) for representation in diagrammatical form. Figure 3.9 illustrates this by showing how the bonding in such pyramidal carboranes as 1,2-$C_2B_3H_7$, 2,3-$C_2B_3H_6^-$, 2-CB_5H_9, 2,3-$C_2B_4H_8$, 2,4-$C_2B_4H_7^-$, and 2,3,4-$C_3B_3H_7$ can be represented by two- and three-center bond networks. The compounds chosen may not adequately be represented by the single canonical form depicted. The various other ways of assigning the skeletal bonds need to be taken into account if local bond orders are to be assessed, when it should be borne in mind that, where there is a choice, carbon atoms will tend to be involved in as few three-center bonds as possible.

The anions 2,3-$C_2B_3H_6^-$ and 2,4-$C_2B_4H_7^-$ shown in Figure 3.9 incidentally contain carbon atoms in different sites from those in the parent neutral carboranes $C_2B_3H_7$ and $C_2B_4H_8$. This is to illustrate how they tend to move to preferred sites (from apical to basal sites, or from adjacent to separated basal sites) as the need to accommodate hydrogen atoms in BHB bridging positions is reduced.

Such localized bonding descriptions as those in Figure 3.10 can be found to give quite useful insight into the electron distribution in *nido* and *arachno* boranes and carboranes. However, they do not indicate *why* these compounds have the particular three-dimensional polyhedral fragment shapes they do. An understanding of this follows more directly from MO treatments. We saw in Section 3.4 that *closo*-borane anions $(B_nH_n^{2-})$ and carboranes $(CB_{n-1}H_n^-$ or $C_2B_{n-2}H_n)$ could be treated as sets of n CH and/or BH units held together by $(n + 1)$ skeletal electron pairs, and that their (nearly spherical) deltahedral shapes were those that made the best use of these

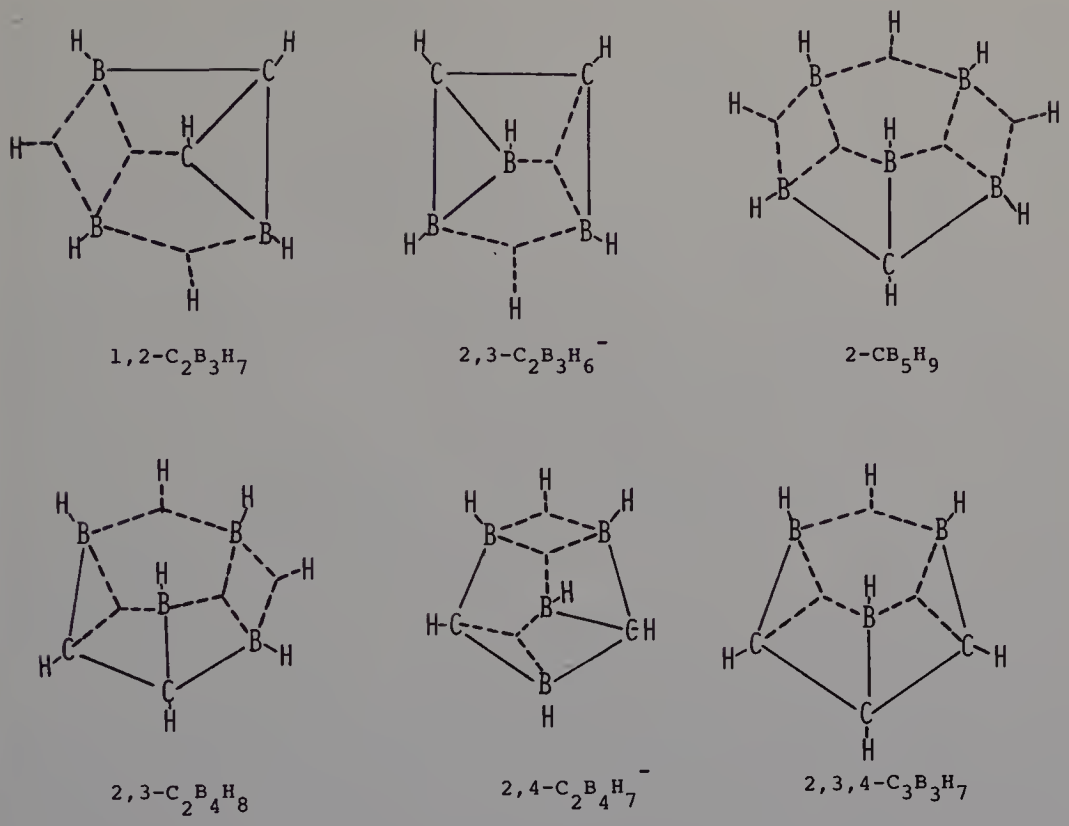


Figure 3.9. Localized bond schemes for square pyramidal and pentagonal pyramidal carboranes. Only one of the several possible canonical forms is shown in each case.

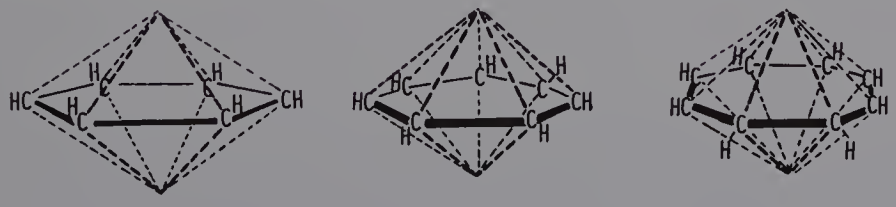


Figure 3.10. The hexagonal, heptagonal, and octagonal bipyramids as the parent polyhedra from which C_6H_6, $C_7H_7^+$, and $C_8H_8^{2+}$ are formally derived as *arachno* species.

electrons and the three AO's that each skeletal atom contributed. The key to an understanding of the structures of *nido* boranes (B_nH_{n+4}) and carboranes ($CB_{n-1}H_{n+3}$, $C_2B_{n-2}H_{n+2}$, and so on,) is to strip away their surplus hydrogen atoms (the ones that lie on the same spherical surface as the skeletal carbon and/or boron atoms, usually occupying BHB bridging sites but occasionally occupying *endo* terminal positions attached to one carbon or boron atom). If these are formally removed as protons (experimentally possible only in selected cases, when there are

only one or two such protons to remove), then the anions $B_nH_n^{4-}$, $CB_{n-1}H_n^{3-}$, $C_2B_{n-2}H_n^{2-}$, and so on, that are left have shapes that in principle might be derived from those of the *closo* species $B_{n+1}H_{n+1}^{2-}$, $CB_nH_{n+1}^{-}$, $C_2B_{n-1}H_{n+1}$, and so on, by removal of a BH^{2+} cationic unit from the most highly connected vertex possible. The *nido* species are thus clusters of n CH and/or BH units held together by $(n + 2)$ skeletal bond pairs, the appropriate number for the *closo* species they are formally derivable from by removal of a BH^{2+} unit.

MO treatments not only show that the *nido* deltahedral-fragment structures are indeed those that make better use of the available electrons than alternative hypothetical structures might have done; they also allow a direct comparison of the bonding orbitals of the *closo* system with those of the *nido* fragment. It is found that removal of the BH^{2+} unit from a *closo* species does not modify the total number of bonding MO's though one (the HOMO of the nido fragments $B_nH_n^{4-}$, $CB_{n-1}H_n^{3-}$, $C_2B_{n-2}H_n^{2-}$ etc.) rises in energy as it concentrates electronic charge around the open face of the fragment, which is where the protons were taken from in generating these hypothetical anions.

Similar arguments can be used to treat *arachno* species B_nH_{n+6}, $CB_{n-1}H_{n+5}$, $C_2B_{n-2}H_{n+4}$, and so on, as if these were derived from hypothetical anions $B_nH_n^{6-}$, $CB_{n-1}H_n^{5-}$, $C_2B_{n-2}H_n^{4-}$ and so on, which with n skeletal atoms and $(n + 2)$ skeletal bond pairs adopt structures based on those of *closo* parents $B_{n+2}H_{n+2}^{2-}$, $CB_{n+1}H_{n+2}^{-}$, $C_2B_nH_{n+2}$, and so on, but with *two* BH^{2+} units removed from highly connected vertices (Fig. 3.1 and Table 3.1).

Thus, for all three categories of borane and carborane clusters (*closo*, *nido*, and *arachno*) the structure adopted is based on a deltahedron that has one vertex fewer than the number of electron pairs available for skeletal bonding. All of the vertices are occupied by carbon and/or boron atoms in the case of *closo* systems; the most highly coordinated vertex is left vacant in the case of *nido* systems; and a second adjacent vertex is left vacant in the case of *arachno* systems.[11,23,24]

The picture of *nido* and *arachno* boranes and carboranes as derivable from a *closo* parent by removal of BH^{2+} units (or CH^{3+} units), with subsequent protonation to neutralize the negative charge generated can be combined with the information obtained from MO treatments, leading to a localized electron-pair view of the skeletal electron pairs that can be quite helpful. This view allocates skeletal electron pairs to polyhedron *vertices* rather than edges [(2*c*–2*e*) bonds] or faces [(3*c*–2*e*) bonds].[43] For example, we know from the *A* symmetry bonding MO that one electron pair is spread symmetrically just inside the polyhedron. Subsequent allocation of the remaining n electron pairs, one to each vertex of the polyhedron, is quite apt for *closo* anions, $B_nH_n^{2-}$, when each vertex pair will have a BH^{2+} unit embedded in it, and be used for skeletal bonding. The charge distribution implied needs some modification for carboranes, $C_2B_{n-2}H_n$, in which the more electronegative carbon atoms will draw more electronic charge towards themselves than the pair formally allocated. However, the relative electron deficiency of the carbon atoms compared with those in normal organic systems is nevertheless indicated by this treatment. Moreover, it can usefully be extended to *nido* and *arachno* systems, where the electron pairs allocated to vertices from which BH^{2+} units have been removed become the HOMOs of these

systems, spreading out towards the adjacent nuclei, which need to number as many as possible for maximum stability. It is these "vacant vertex" electrons that provide the electron density for protonation when the hypothetical anions $B_nH_n^{4-}$, $CB_{n-1}H_n^{3-}$, $C_2B_{n-2}H_{n+2}^{2-}$, and so on, are reconverted into their neutral actual *nido* species.

It is instructive to conclude this discussion of the bonding in *nido* and *arachno* carboranes by considering briefly some systems that can technically be classified as members of the carborane family (Table 3.1), although they contain no boron atoms. For example, among *nido* systems, one might include the pyramidal carbocations $C_5H_3Me_2^+$ [44–46] and $C_6Me_6^{2+}$,[47] while the term *arachno* could justifiably be applied to the aromatic ring units cyclobutadiene dianion ($C_4H_4^{2-}$) and the cyclopentadienide anion ($C_5H_5^-$) as systems of n CH units held together by $(n + 3)$ skeletal bond pairs. Molecular Orbital treatments of the pyramidal cations that illustrate their relationship to aromatic systems were discussed in Chapter 1; see Figure 1.18. Indeed, aromatic systems in general that contain six π electrons $C_4H_4^{2-}$, $C_5H_5^-$, C_6H_6, $C_7H_7^+$, or even $C_8H_8^{2+}$ and related ring systems in which n atoms are held together by n σ-bonding electron pairs and three π-bond pairs may be regarded as *arachno* species. This is because the bipyramidal polyhedra from which the last three are formally derived by leaving both axial sites vacant (the hexagonal, heptagonal, and octagonal bipyramids, Fig. 3.10) are suitable deltahedra to generate the requisite number of skeletal bonding MO's (one more than the number of vertices). With respect to electron count, they resemble the D_{2d} dodecahedron of $B_8H_8^{2-}$ (the *closo* parent for benzene's isomer, benzvalene), the D_{3h} tricapped trigonal prism of $B_9H_9^{2-}$, and the bicapped square antiprism of $B_{10}H_{10}^{2-}$, though these latter, being more nearly spherical than the former, are preferred for *closo* systems. Although aromatic ring systems like $C_5H_5^-$, C_6H_6, and $C_7H_7^+$ do not contain hypercarbon atoms, they do so once a capping atom changes them from *arachno*-ring systems into pyramidal *nido* systems, as when $C_5Me_5^-$ is converted into the cation $C_6Me_6^{2+}$, or indeed when any of these aromatic ring systems coordinate to metal atoms or ions to generate π complexes such as the manganese carbonyl complex $(C_5H_5)Mn(CO)_3$, ferrocene $(C_5H_5)_2Fe$, or dibenzenechromium, $(C_6H_6)_2Cr$ as illustrated in Figures 4.1 and 4.2 in Chapter 4.

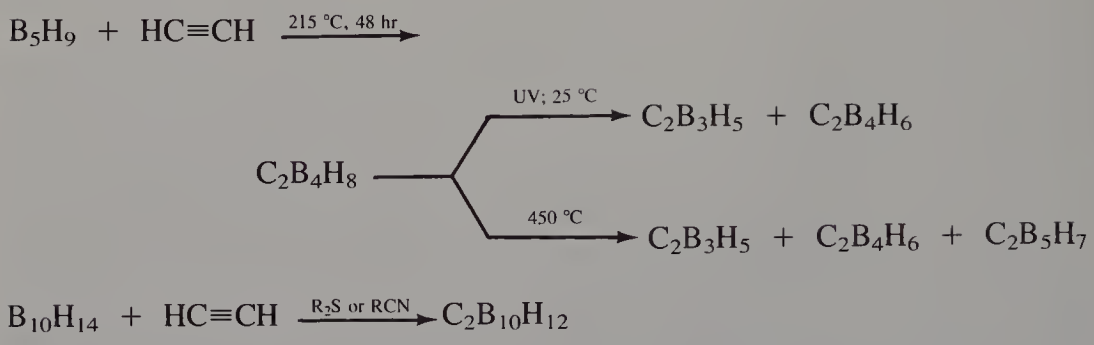
3.6. METHODS OF SYNTHESIS AND INTERCONVERSION REACTIONS

Although the main concern of this book is to survey the structures and bonding of hypercarbon systems, it is appropriate here to note briefly the routes by which carboranes have been synthesized, and methods by which one carborane can be converted into another. Section 3.7 indicates the types of reaction that can occur at the highly coordinated carbon atoms of carboranes.

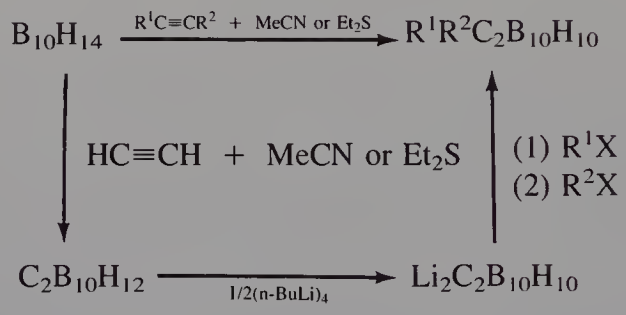
The first carboranes were discovered[3,5] among the products of reactions between *alkynes* and *boron hydrides*, and such reactions remain the best routes to dicarba species (Scheme 3.2).[3–7,48]

Derivatives bearing substituents at the carbon atoms are accessible from suitable alkyne precursors $R^1C{\equiv}CR^2$, or by reactions of the carborane (Scheme 3.3).

Scheme 3.2

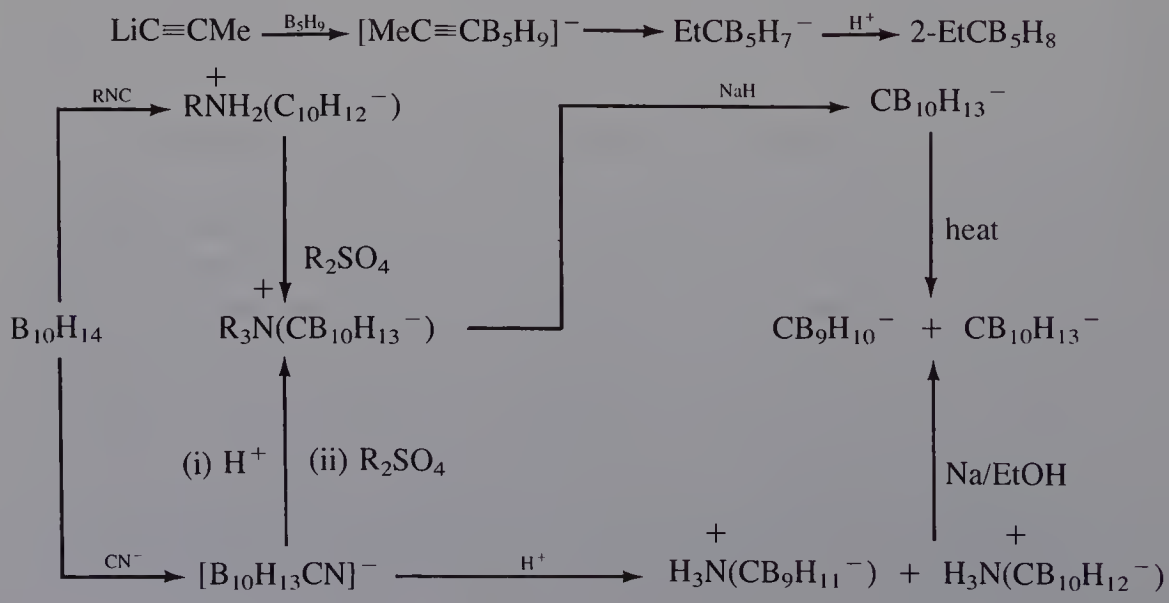


Scheme 3.3



Monocarba-boranes can be prepared from boranes and acetylides, cyanides, or isonitriles (Scheme 3.4).

Scheme 3.4



Cage closure from *nido* or *arachno* to *closo* commonly occurs on heating, though *disproportionation* may occur simultaneously (Scheme 3.5).

Scheme 3.5

$$C_2B_{n-2}H_{n+3} \xrightarrow{-H_2} C_2B_{n-2}H_n \text{ or } C_2B_{n-3}H_{n-1} \text{ or } C_2B_{n-1}H_{n+1}$$

$$2,3\text{-}C_2B_4H_8 \xrightarrow{450°C} 1,5\text{-}C_2B_3H_5 + 1,6\text{-}C_2B_4H_6 + 2,4\text{-}C_2B_5H_7$$

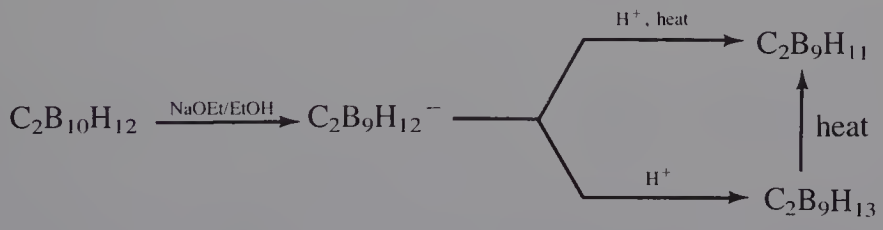
Reaction with diborane effects *cage growth* in several cases, including intermediate-sized *closo* carboranes (Scheme 3.6).

Scheme 3.6

$$1,7\text{-}C_2B_6H_8 \xrightarrow[-H_2]{\frac{1}{2}\,B_2H_6} 1,6\text{-}C_2B_7H_9 \xrightarrow[-H_2]{\frac{1}{2}\,B_2H_6} 1,10\text{-}C_2B_8H_{10}$$

Cage *degradation* is achieved by stepwise removal of BH units, using sodium ethoxide in ethanol. The alkoxide ions EtO^- attack a boron atom that is connected to one or both carbon atoms (Scheme 3.7).[3–7,13,48]

Scheme 3.7



Such reactions make the intermediate-sized carboranes accessible from $C_2B_{10}H_{12}$.

Isomerization reactions, whereby adjacent carbon atoms in carborane polyhedra move apart, allow more stable isomers to be prepared from the less stable by heating (Scheme 3.8).

Scheme 3.8

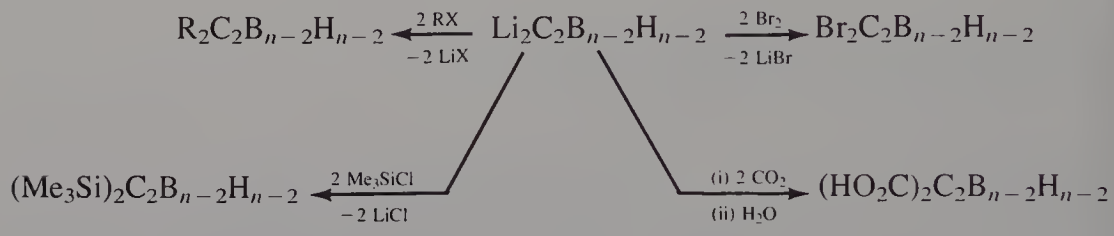
$$1,2\text{-}C_2B_4H_6 \longrightarrow 1,6\text{-}C_2B_4H_6$$

$$1,2\text{-}C_2B_{10}H_{12} \longrightarrow 1,7\text{-}C_2B_{10}H_{12}$$

3.7. REACTIONS AT THE CARBON ATOMS OF CARBORANES

The weakly acidic nature of the *C*-attached hydrogen atoms of *closo* carboranes is shown by their reactions with butyllithium or Grignard reagents, which afford *C*-metallated products, themselves useful intermediates through which to attach a variety of substituents to the cage carbon atoms (Scheme 3.9).

Scheme 3.9



The *C*-lithio or *C*-magnesium intermediates are of interest in their own right as organometallic derivatives of metals that commonly participate in metal-alkyl or metal-aryl bridge formation (Chapter 2, Sections 2.3 and 2.4), thus rendering the bridging carbon atoms hypercoordinated. Barring steric restrictions, similar bridging of *C*-lithio derivatives of the icosahedral carborane $C_2B_{10}H_{12}$ would raise the carbon coordination number from six to seven (if the carboranyl residue were doubly bridging) or eight (if it were triply bridging). The compounds [PMDETA)Li(Me)$C_2B_{10}H_{10}$ (PMDETA = the tridentate ligand, $MeN(CH_2CH_2NMe_2)_2$] and (dioxane)$_2$Mg[$MeC_2B_{10}H_{10}]_2$ are not bridged, however, and contain normal (2*c*–2*e*) metal–carbon bonds to their hypercoordinated carbon atoms (Fig. 3.11).[49]

Like other aromatic systems, *closo* carboranes undergo *electrophilic substitution reactions*, but these occur preferentially at the boron atoms rather than at the carbon

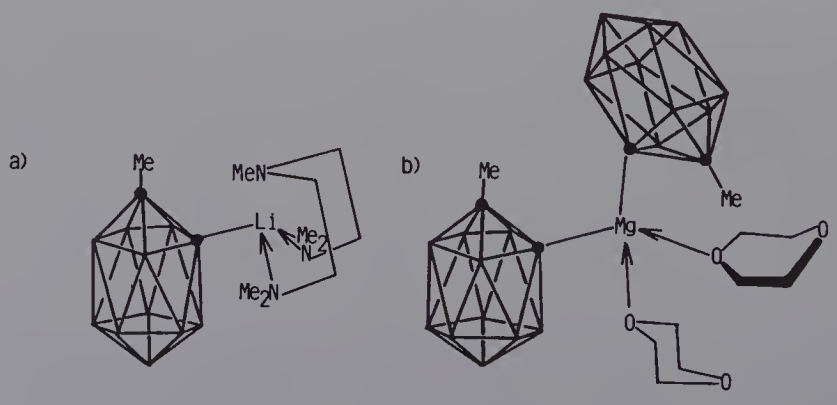


Figure 3.11. Structures of the terminally (*exo*) metallated icosahedral carboranes (*a*) [$MeN(CH_2CH_2NMe_2)_2$]Li[$MeC_2B_{10}H_{10}$] and (*b*) [dioxan]$_2$Mg[$MeC_2B_{10}H_{10}]_2$.

atoms. The boron atoms most remote from the carbon atoms tend to be those first substituted, as they are the most negatively charged atoms (those next to carbon suffer depletion of electronic charge towards carbon which, however, remains relatively positive because it has donated one more electron than has boron to the skeletal bonding). Thus, 2,4-$C_2B_5H_7$ suffers methylation under Friedel–Craft conditions preferentially at equatorial sites 5,6, followed by 1,7 and then 3 (Fig. 3.2); 1,2-$C_2B_{10}H_{12}$ suffers bromination in the presence of aluminum bromide at the sites indicated in the following sequence: 9,12 > 8,10 > 4,5,7,11 > 3,6 > 1,2, that is, the carbon atoms are the last to be so substituted.[4]

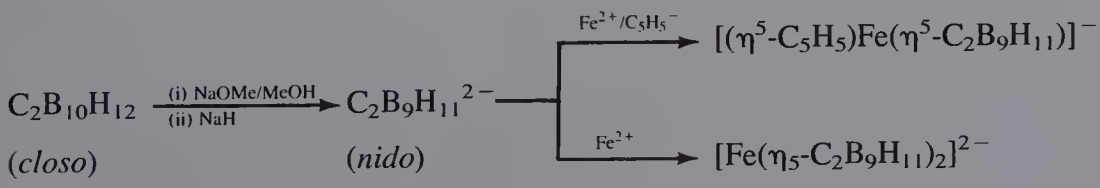
3.8. METALLACARBORANES

In the previous section we noted that lithium and magnesium atoms can replace hydrogen atoms as the *exo* substituents on the carbon atoms of carboranes. Many other *C*-metallated compounds of this type have been prepared, and are generally referred to as metall*o*carboranes. Their metal carbon bonds are normal [albeit polar, M(δ+)—C(δ−)] (2*c*–2*e*) bonds, external to the skeletal carborane bonding. Involvement of metal atoms *in the skeletal bonding* is also possible in compounds in which metal as well as carbon and boron atoms occupy polyhedral vertex sites. They are generally referred to as metall*a*carboranes,[11–14] because they are formally derivable from carboranes by replacement of BH and/or CH units within the various carboranes by one or more metal containing units.

Their discovery[13,50,51] was of major importance not only for carborane chemistry, but also for organometallic and cluster chemistry in general. This was because they illustrated the various types of units, other than the CH and BH units of carboranes, that could participate in cluster formation. First they made it possible to understand some metal cluster structures that had appeared puzzling. Second, they facilitated the prediction of the structures of others from their formulas by analogy with known polyborane or carborane structures. And third, they made it possible to plan syntheses and degradation reactions of metal clusters and of mixed metal carbon clusters.

The breakthrough came with the discovery that the *nido* anion $C_2B_9H_{11}^{2-}$ (an icosahedral fragment prepared by removal of a BH^{2+} unit from 1,2-$C_2B_{10}H_{12}$ by means of its reaction with sodium methoxide in methanol) could coordinate strongly to transition metal cations in a manner similar to that of the cyclopentadienide anion, $C_5H_5^-$ (Scheme 3.10).[50]

Scheme 3.10



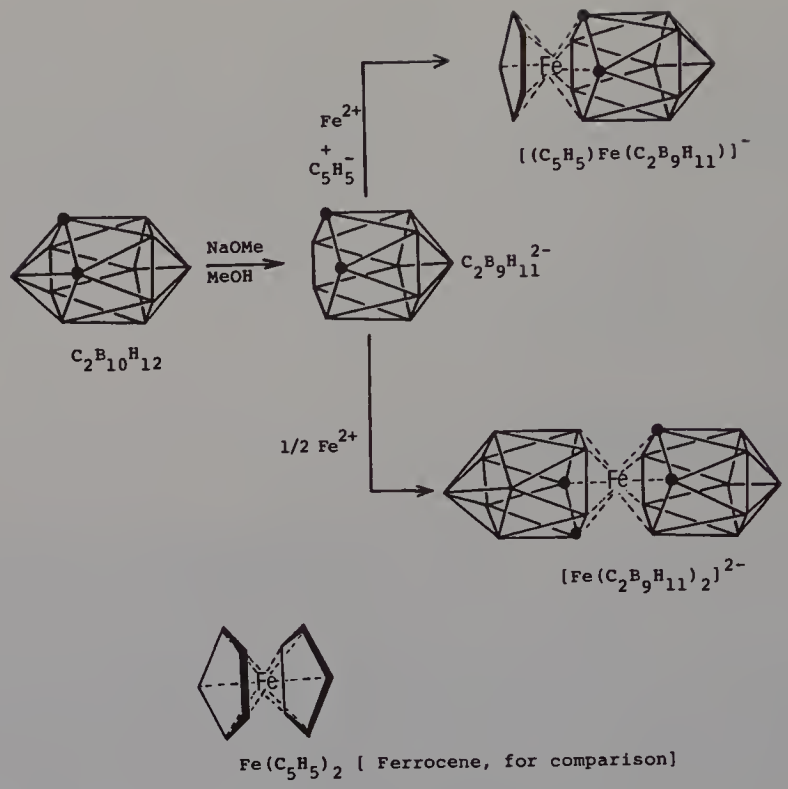


Figure 3.12. Incorporation of an iron atom in an icosahedral carborane cluster.

The structures of the products[13] (Fig. 3.12) show that the iron atom effectively plugs the gap created by removal of a BH^{2+} cationic unit from the *closo* carborane. As this BH^{2+} unit was one of the two that were adjacent to the two carbon atoms, the *nido*-carborane anion ($C_2B_9H_{11}^{2-}$) coordinates to the metal atom through these two carbon atoms and three boron atoms. The coordination sphere of each of the carborane carbon atoms consists of one (*exo*) hydrogen atom on one side, at a normal (2*c*–2*e*) bonded distance, and one carbon, one iron, and three boron atoms on the other (cluster) side in a distorted pentagonal array (distorted because carbon, boron, and particularly iron atoms have different radii).

The structure of ferrocene, $Fe(\eta^5\text{-}C_5H_5)_2$, is included in Figure 3.12 for comparison with these carborane complexes. [The symbol η^5 (eta-five) in these formulas denotes the *hapticity* of the ligands in question—the number of *atoms* they contribute to the metal coordination sphere (the number through which they evidently bond to the metal atom].

The bonding in the anions $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_2B_9H_{11})]^-$ and $[Fe(\eta^5\text{-}C_2B_9H_{11})_2]^{2-}$ can be viewed in various ways. In organometallic chemistry it is customary to view the metal–carbon bonding in transition metal complexes of aromatic ring systems as involving the ring π electrons, which therefore contribute to the total in the metal valence shell. A filled transition metal valence shell, and so coordinative saturation of the metal, normally corresponds to the presence of 18 electrons (the 18 electron rule) as 9 electron pairs are needed to fill the 9 metal AO's

(one *s*, three *p*, and five *d* AO's) or the MO's derived therefrom.[52] The coordinative saturation of the metal atom in ferrocene, $Fe(\eta^5\text{-}C_5H_5)_2$, for example, is apparent if it is viewed as an iron(II) cation, Fe^{2+}, (which contains 6 valence shell electrons) sandwiched between two $C_5H_5^-$ anions (each of which uses its aromatic sextet to bond to the metal ion).

Treating the anions $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_2B_9H_{11})]^-$ and $[Fe(\eta^5\text{-}C_2B_9H_{11})_2]^{2-}$ similarly, we conclude that the open pentagonal B_3C_2 face of the *nido*-carborane anion $C_2B_9H_{11}^{2-}$, like a cyclopentadienide anion, $C_5H_5^-$, can function as a source of six electrons for the metal valence shell. The reason for this is simple: six electrons would be required to fill the three *empty* AO's that a cluster forming unit would need to furnish in order to occupy the empty vertex of a *nido* species without causing any change in the number of skeletal bonding electrons.

Conversely, the anion $[Fe(\eta^5\text{-}C_2B_9H_{11})_2]^{2-}$ can be treated as a system in which the Fe^{2+} cation occupies a site that is the one shared vertex of two overlapping FeC_2B_9 icosahedra (Fig. 3.12). As such, it must make three AO's available for skeletal bonding in each icosahedron, leaving three valence shell AO's to accommodate six spare (cluster nonbonding) valence shell electrons. Hence its formal oxidation state, iron (II), is intelligible. Ferrocene itself consists of two *nido* (pentagonal pyramidal) FeC_5 clusters, sharing a common vertex (the iron atom).

A third viewpoint is to note that, by comparing icosahedral $C_2B_{10}H_{12}$ with $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_2B_9H_{11})]^-$, treating the latter anion as an icosahedral FeC_2B_9 cluster, a neutral BH unit in the former has been replaced by an *anionic* $[(\eta^5\text{-}C_5H_5)Fe]^-$ unit in the latter. Evidently the capacities of these two units, BH and $[(\eta^5\text{-}C_5H_5)Fe]^-$, to participate in cluster bonding are similar. Each can function as a source of two electrons, and three AO's, for use in skeletal bonding.

Such electron bookkeeping methods as these were quickly developed to help understand the structures of new metallacarboranes as the field was rapidly opened up by the generation of assorted *nido* carborane anions, and the reaction of these with suitable cationic metal residues.[13] Some hundreds of metallacarboranes, virtually all containing hypercarbon atoms, are now known.[12] Tables 3.2 and 3.3 give the formulas of some *closo* and *nido* species, respectively, that have been subjected to x-ray crystallographic study, and Figure 3.13 shows a representative selection of their structures in skeletal form. From these, it is apparent that not just one BH unit, but two or three, occasionally more BH units of a carborane are in practice capable of being replaced by such metal-containing units as the following: $[\eta^5\text{-}C_5H_5)Fe]^-$, $(\eta^5\text{-}C_5H_5)Co$, $[(\eta^5\text{-}C_5H_5)Ni]^+$, $[Mn(CO)_3]^-$, $Fe(CO)_3$, $[Co(CO)_3]^+$, Be, Sn, Pb, Tl^-, $BeNMe_3$, AlEt, $Ni(PPh_3)_2$, $Pt(PPh_3)_2$, and so on.

What these have in common, in the parlance of transition metal chemists, is that these transition metal units are "14-electron systems" (i.e., they contain 14 valence shell electrons). Such groups, if required to make 3 valence shell AO's available for cluster bonding, will contribute two electrons, just like a BH unit. The main group examples are "4-electron systems," atoms or units that can also furnish 3 valence shell AO's and 2 electrons for use in skeletal bonding.

It is somewhat artificial to view these cluster-forming units solely in terms of the requirements of a BH unit. A better method, for the dual purposes of electron

TABLE 3.2. Examples of Metallacarboranes and Metallaboranes with *Closo* Structures

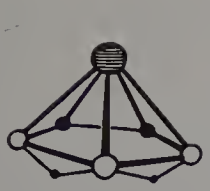
N^a	Shape	Examples
6	Octahedron	$C_2B_3H_5CoCp$; $C_2B_3H_5Fe(CO)_3$; $B_4H_6(CoCp)_2$; $B_3H_5(CoCp)_3$
7	Pentagonal bipyramid	$C_2B_4H_6ML_n$[ML_n = $Fe(CO)_3$, CoCp, $Ni(PPh_3)_2$, $Pt(PEt_3)_2$, GaR]; $C_2B_3H_5(ML_n)_2$[ML_n = $Fe(CO)_3$, CoCp]; $C_3B_3H_5MeMn(CO)_3$; $C_4BH_3R_2[Mn(CO)_3]_2$
8	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	$C_2B_{10}H_{12}(CoCp)_2$; $C_4B_8H_8Me_4(FeCp)_2$

^aN = number of skeletal atoms.

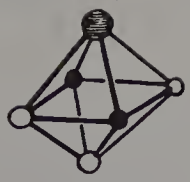
TABLE 3.3. Metallacarboranes and Metallaboranes with *Nido* Structures

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	$[(B_{10}H_{12})_2Zn]^{2-}$; $[B_{10}H_{12}NiCp]^-$; $B_9H_{10}SPtH(PEt_3)_2$

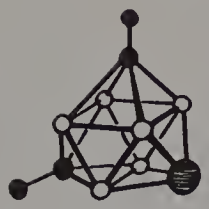
^aN = number of skeletal atoms.



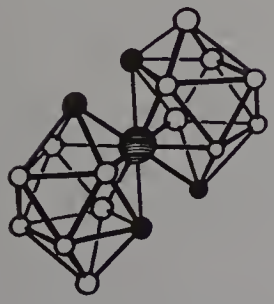
$C_2B_3H_7Fe(CO)_3$



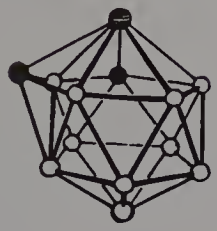
$C_2B_3H_5Fe(CO)_3$



$(Me_3P)_2PtC_2Me_2B_6H_6$



$[Co(C_2B_7H_9)_2]^-$

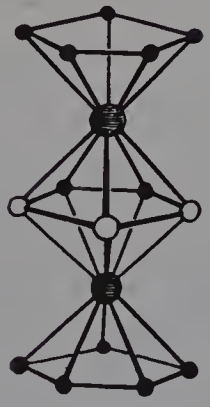


$(C_5H_5)Co(C_2B_{10}H_{12})$

$C_2B_9H_{11}ML_n$

ML_n = $Fe(CO)_3$, $(C_5H_5)Co$, Sn, AlMe, $BeNMe_3$, etc

$(C_5H_5Co)_2C_2B_6H_8$



$C_2B_3H_5[Co(C_5H_5)]_2$

Figure 3.13. Typical metallacarborane skeletons (B○, C ●, M or ML_n ○).

bookkeeping and for predicting structures from molecular formulas, is to treat each potential cluster unit as a neutral entity and simply assess how many electrons it can contribute for skeletal bonding. To do this, one counts how many electrons there are altogether in the valence shell of the potential cluster atom by adding any ligand electrons (x) to that atom's own valence electrons (v); one then subtracts two in the case of main group elements (because one AO is used for an *exo* bond or lone pair), or twelve in the case of transition elements (when six AO's can be used other than for skeletal bonding). Thus, an MgR unit would supply one electron, an AlR unit two electrons, and an SiR unit three electrons for cluster bonding. Similar contributions would be made by $Mn(CO)_3$, $Fe(CO)_3$, and $Co(CO)_3$ units, respectively. These and

further examples are listed in tabular form, for convenience, in Tables 3.4 and 3.5.[11,20]

TABLE 3.4. 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 3.5. Skeletal Electron Contributions $(v + x - 2)^a$ 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.

Note that a CH_2 unit can in principle function as a source of four electrons for cluster bonding if it is orientated so that one of the C−H bonds points in an *exo* direction, the other in an *endo* direction, thus placing its hydrogen atom on the spherical surface containing the skeletal atoms. Then the electrons in the *endo*-C−H bond are formally among those available for skeletal bonding. This situation arises in bicyclobutane, C_4H_6, for example, whose butterfly shape (compare its *arachno*-boron analog, B_4H_{10}) has two wing-tip hydrogen atoms oriented *exo*, the others *endo*.

Theoretical justification for the electron-bookkeeping device of treating CH and $Co(CO)_3$ or $Ni(\eta^5\text{-}C_5H_5)$ units as similar sources of three AO's and two electrons for

cluster forming use followed from an analysis of the frontier-orbital (HOMOs and LUMOs) characteristics of the conical transition metal units by Hoffmann[15,17] and Mingos and co-workers,[15] who coined the term "isolobal" to describe their relationship to a CH unit. Though the transition metal units can use *pd* hybrid orbitals where a CH unit can use only *s* and *p* AO's or hybrids thereof, the numbers, energies, extensions in space, and lobal characteristics of these various units are very similar, so they are described as isolobal, written CH $\leftrightarrow$ $Co(CO)_3$ $\leftrightarrow$ $Ni(\eta^5\text{-}C_5H_5)$. (Compare Fig. 1.19 in Chapter 1).

Although, for bookkeeping purposes, a vee-shaped nickel bis(phosphine) unit such as $Ni(PPh_3)_2$, or its platinum analog $Pt(PPh_3)_2$, can in principle function [like $Fe(CO)_3$ or $Co(\eta^5C_5H_5)$] as a source of three AO's and two electrons for cluster bonding use, its C_{2v} symmetry makes its frontier orbitals capable of discriminating nodal features of carborane residues that conical fragments cannot. Accordingly, the orientations of such vee-shaped metal units with respect to the five-membered open

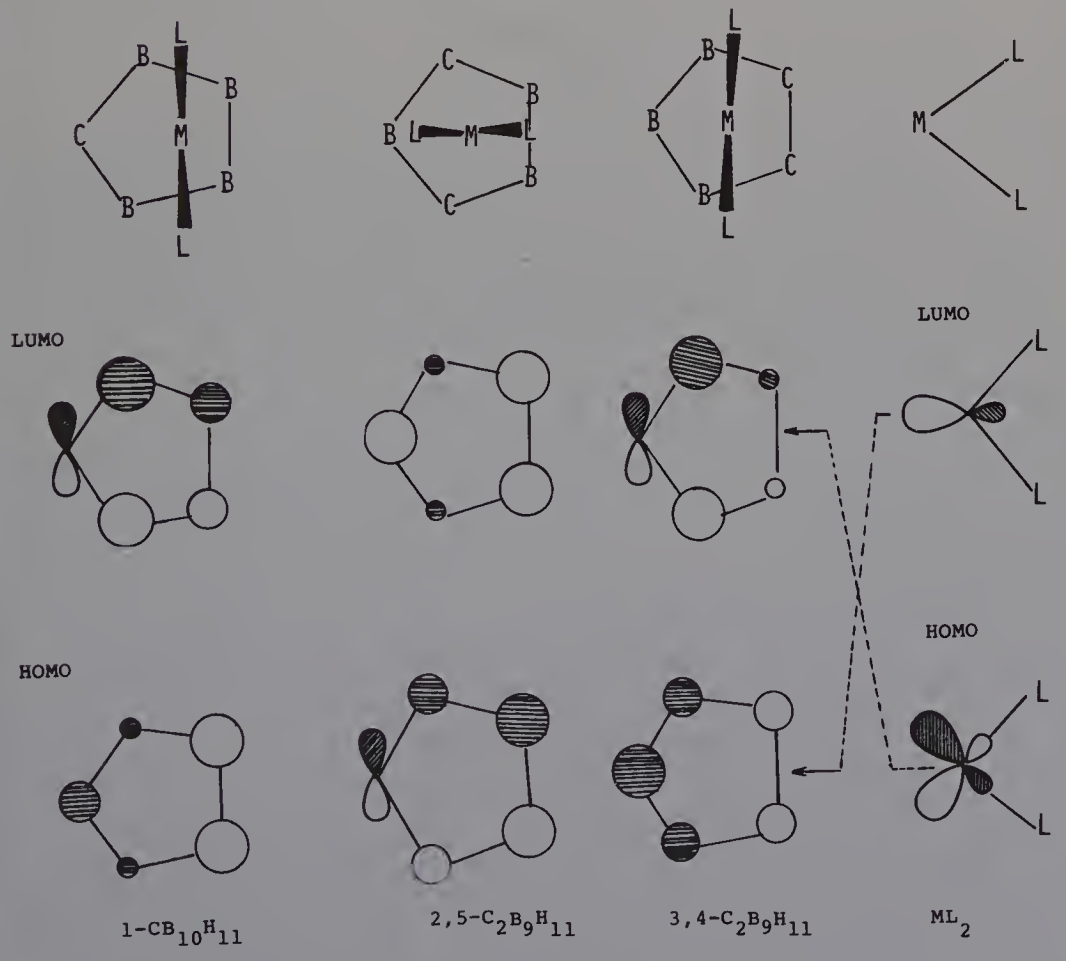


Figure 3.14. Orientations possible for a vee-shaped ML_2 unit (M = Pd or Pt; L = CNR or PR_3) over the open pentagonal face of a *nido*-carborane residue as a function of the positions of the carbon atoms in the face and the frontier orbitals involved.

faces of *nido*-carborane residues such as $C_2B_9H_{11}^{2-}$ or $CB_{10}H_{11}^{3-}$ may vary in a systematic manner that reflects differences between the nodal characteristics of the carborane fragment's frontier orbitals (Fig. 3.14).

3.9. CONCLUSIONS

Carboranes and metallacarboranes are important categories of carbon compounds, that are of substantial interest, not least because of their relative stability despite the highly coordinated states of their skeletal carbon atoms. A wealth of structural information, mostly X-ray crystallographic, has accumulated to show that carbon coordination numbers of five or six are exceedingly common in such systems. In this short survey it has been possible only to illustrate the main structural types and to discuss the bonding environments of their carbon atoms. Readers interested in their general chemistry are advised to consult the texts cited.

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chapter 4

MIXED METAL–CARBON CLUSTERS AND METAL CARBIDES

4.1. INTRODUCTION

In the previous chapter, the similarity between the metal environment in ferrocene, $Fe(\eta^5\text{-}C_5H_5)_2$, and that in the complex anion $[Fe(\eta^5\text{-}C_2B_9H_{11})_2]^{2-}$ was noted (Fig. 3.13).[1–6] In both species the 10-coordinate iron(II) cation is sandwiched between two anionic five-membered ring systems that formally contribute 6 electrons apiece for the metal–ligand bonding, completing the 18-electron configuration needed for coordinative saturation of the metal atom. Although the carbon atoms in ferrocene are 4 coordinate, while those in the carborane derivative are 6 coordinate, the metal–carbon bonding in both systems is clearly similar. In our previous comparison of these systems we also noted that ferrocene itself could be regarded as a mixed metal–carbon cluster species in which two *nido* pentagonal pyramidal FeC_5 units shared a common vertex, the iron atom.[7,8]

These are not isolated specific examples. Metal–hydrocarbon π complexes in general,[9] of which ferrocene is an example, and in which unsaturated organic groups or molecules coordinate to metal atoms by using their carbon–carbon π-bonding electrons to form the metal–carbon bonds, have structures that may be regarded as mixed metal–carbon clusters, the shapes of which clearly reflect the numbers of electrons available[7,10] as do the mixed boron–carbon cluster shapes of carboranes. All are members of the same family of hypercarbon systems.

The scope of the present book does not permit us to give a detailed survey of the structures and bonding of metal–hydrocarbon π complexes. This subject is itself vast, and is dealt with in considerable detail in many specialist texts,[9–15] and in some detail

in standard inorganic texts.[16–19] Our intention here (in Sections 4.2 and 4.3) is to illustrate the principal types of structural unit found in metal–hydrocarbon π complexes in which a single metal atom interacts with the ligand π system, to note their structural relationship to *nido* or *arachno* carborane-type clusters, and to consider briefly the type of bonding their hypercarbon atoms participate in.

In the next section (Section 4.4) we then survey some systems in which unsaturated organic residues coordinate to two or more metal atoms, and show how their M_xC_y skeletons place their carbon atoms in bonding environments like those in carboranes.

In the concluding section of the chapter (Section 4.4) we turn to some metal carbide systems in which carbon atoms are encapsulated in polyhedra of metal atoms,[20–22] such as the ruthenium carbonyl carbide, $Ru_6(CO)_{17}C$, in which the carbon atom is surrounded by an octahedron of metal atoms,[23] the rhodium carbonyl carbide anion, $[Rh_6(CO)_{15}C]^{2-}$, in which the carbon coordination is trigonal prismatic,[24] and the cobalt carbonyl carbide anion, $[Co_8(CO)_{18}C]^{2-}$, in which the environment is square antiprismatic.[25] In such systems as these, which illustrate the

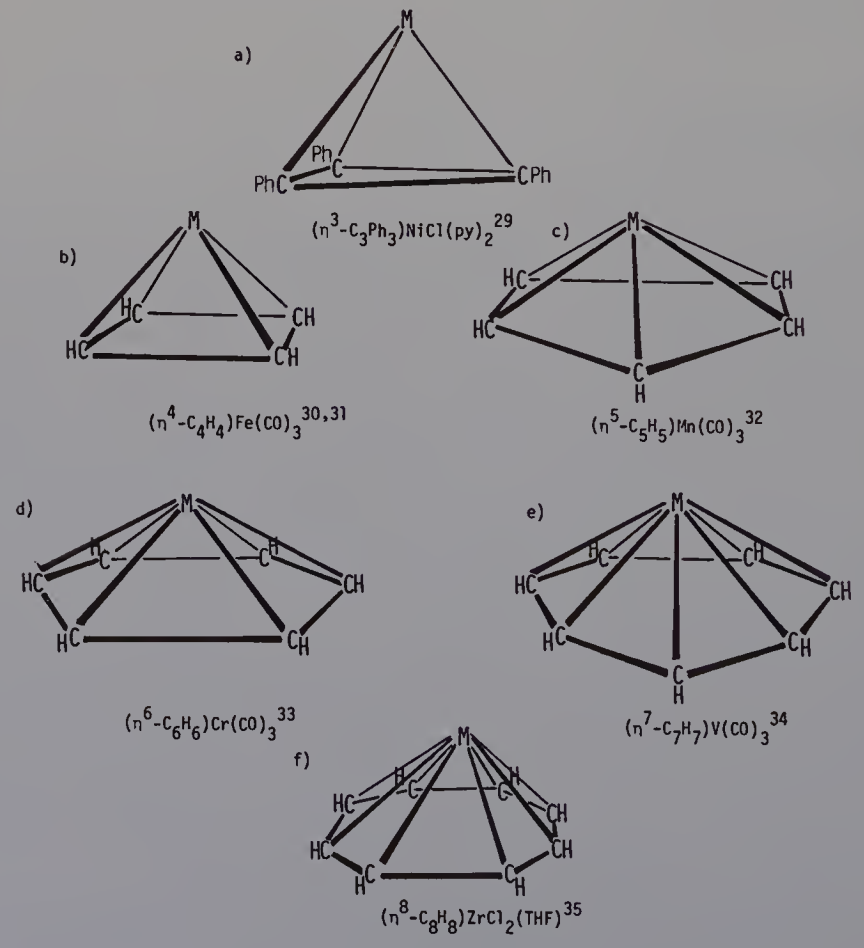


Figure 4.1. "Half-sandwich" complexes of C_nH_n ring systems.

types of carbon environment also found in the extended lattices of many metal carbides,[26–28] the arrangements of the metal atoms themselves show the same sensitivity to electron numbers as do the carbon and boron atoms of carboranes.

4.2 COMPLEXES OF C_nH_n-RING SYSTEMS WITH A METAL ATOM

In Figures 4.1 and 4.2 we show the structures of some typical metal complexes of C_nH_n-ring systems.[9–19,29–41] The former shows some "half-sandwich" compounds in which a unit ML_x (containing a transition metal atom, M, and x other ligands, L) coordinates to the C_nH_n ring by taking up a position above the plane of the ring, on the n-fold symmetry axis, so generating a pyramidal MC_n skeleton.[29–35] The latter shows some sandwich compounds in which metal atoms, generally with no other ligands attached, are sandwiched between pairs of C_nH_n rings.[36–41] Their structures thus contain two MC_n pyramids sharing a common apex, the metal atom.

Stability in such systems is generally associated with the presence of 18 electrons in the metal valence shell (or 16 electrons for such metals as palladium or platinum), because nine pairs of electrons are needed to fill the low energy MO's available. The examples illustrated are 18-electron systems. Each CH unit of a C_nH_n ring can contribute one electron for metal–carbon bonding [the remaining two electrons a CH

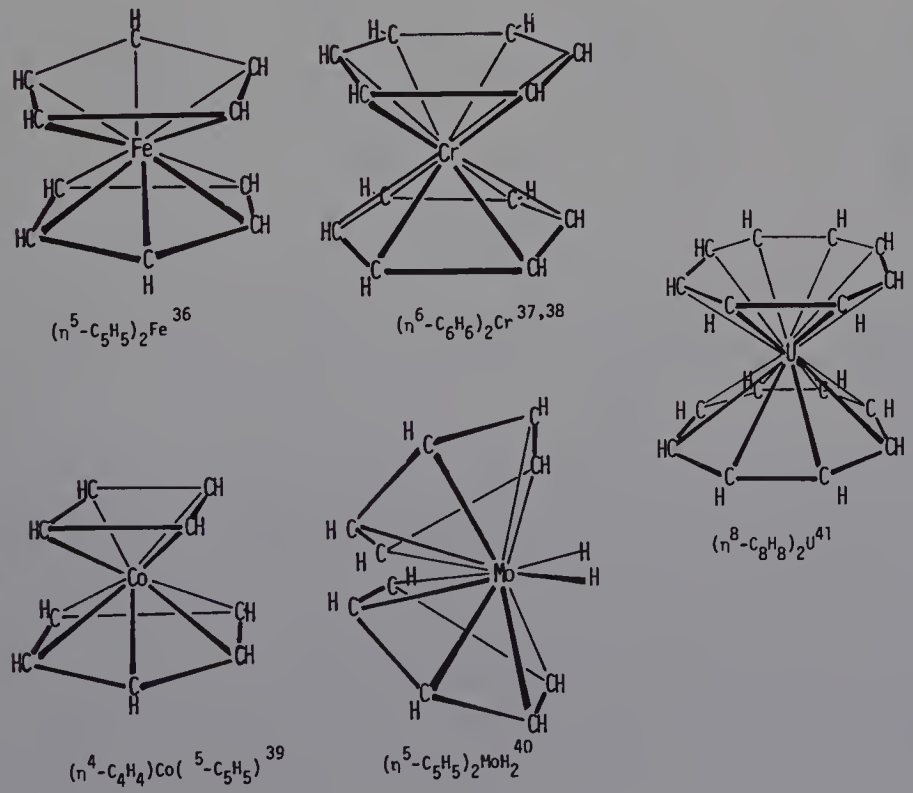


Figure 4.2. Sandwich complexes of C_nH_n ring systems.

unit can furnish are used to form the (2*c*–2*e*) σ bonds to its neighbors in the ring], so an *n*-membered C_nH_n ring system functions as an "*n*-electron" ligand to the metal atom on its *n*-fold axis. Added to the metal valence shell electrons and the electrons supplied by the other ligands on the metal atom, these total 18 for most of the systems in Figures 4.1 and 4.2.

For example, in $(\eta^3\text{-}C_3Ph_3)NiCl(py)_2$ (py = pyridine) (Fig. 4.1),[29] the C_3Ph_3 ligand supplies 3 electrons, the chlorine atom supplies 1 electron, and each pyridine ligand supplies 2 electrons. Added to the 10 electrons in the nickel atom valence shell, this generates a total of 18 electrons. In the case of the sandwich compound, $(\eta^6\text{-}C_6H_6)_2Cr$, dibenzenechromium (Fig. 4.2),[37,38] 6 electrons from each benzene ligand may be added to the 6 electrons in the metal valence shell to generate the total of 18 electrons.

In order to appreciate how many of these electrons are really involved in bonding the metal atoms to the C_nH_n ring systems, and the bonding environment of their hypercarbon atoms, it is convenient to consider the benzene complexes $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ (Fig. 4.1)[33] and $(\eta^6\text{-}C_6H_6)_2Cr$ (Fig. 4.2).[37,38] The metal–carbon distances to the benzene rings in these two compounds are very similar, so they presumably contain very similar metal–carbon bonds. Although, as it happens, the former compound contains just enough valence shell electrons to allocate a pair to each of the nine metal–carbon bonds (six to ring carbon atoms, three to carbonyl ligand carbon atoms), the latter compound certainly does not, and localized (2*c*–2*e*) bonding descriptions are unsuitable for both compounds.

If a hexahapto benzene ligand is not to coordinate to the metal atom by means of six (2*c*–2*e*) metal–carbon bonds, it might be thought that, as it functions as a six-electron ligand, it may do so by donating the three pairs of π-bonding electrons, using them to form three (3*c*–2*e*) MC_2 bonds. This might be written as follows (Scheme 4.1).

Scheme 4.1

Both representations imply transfer of electronic charge from ligand to metal but not vice versa, whereas photoelectron spectroscopic and other studies suggest that overall there is transfer of charge in the reverse direction, a feature that is more easily understood using MO treatments.[25,42,43] These indicate not only that the doubly degenerate π-bonding HOMO of benzene has an appropriate symmetry to transfer charge into two metal *d* AO's (or *pd* hybrid AO's) (Fig. 4.3*a*), but that other filled metal *d* AO's can act as the source of electrons for transfer into the doubly degenerate LUMO of benzene (Fig. 4.3*b*).

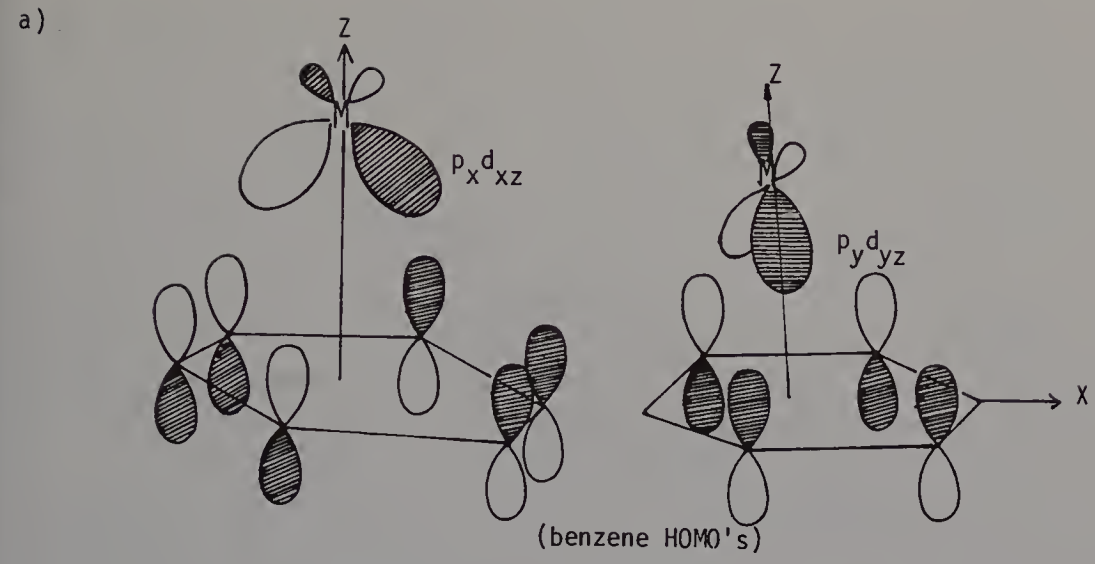


Figure 4.3. Orbitals involved in the metal–carbon bonding in η^6-benzene complexes.

Coordination of benzene to a metal atom like chromium in the examples cited thus entails a shift of electron density from C−C π-bonding orbitals into C−C π-antibonding orbitals, weakening the carbon–carbon bonding. Moreover, although it functions as a six-electron ligand for electron counting purposes, it might be argued that the metal–carbon bonding primarily entails *four* pairs of electrons, those originally in the doubly degenerate HOMO of benzene, and those subsequently using what was originally the doubly degenerate LUMO.

Benzene is therefore in a sense *activated* by coordination. Other ring systems may be *stabilized* by coordination. For example, the complex $(\eta^3\text{-}C_3Ph_3)NiCl(py)_2$ (Fig.

4.1)[29] may be regarded as an example of the stabilization of a cyclopropenyl radical (C_3Ph_3) by coordination. In this case, the filled, fully symmetric π-bonding MO of a trigonal C_3Ph_3 unit can donate electrons to the metal atom, while the pair of degenerate π-antibonding MO's can receive electronic charge from suitable filled metal orbitals, albeit at the expense of C−C bonding in each case. Alternatively, this complex may be regarded as a coordinated form of the cyclopropenium ion, $C_3Ph_3^+$ (Fig. 4.4), stabilized in such a way that it is less susceptible to nucleophilic attack because of the filling of its π-antibonding orbitals, reflected in the C−C bond lengths (1.42 Å;[29] cf. 1.37 Å in $C_3Ph_3^+ ClO_4^-$).[44] In this compound, because three pairs of electrons are involved in the bonding of the metal to the *trihapto* ligand, it would be possible to represent this by three (2*c*–2*e*) Ni−C bonds, though this would exaggerate their strength and imply weaker C−C bonding than actually persists.

The remaining complexes shown in Figures 4.1 and 4.2 can be regarded as stabilized forms of the ring systems C_4H_4, C_5H_5, C_7H_7, and C_8H_8, none of which would have closed shell electronic configurations if they existed in uncoordinated form as ring systems of symmetries D_{nh}, as the orbital energy level diagram in Figure 4.5 illustrates. Note that, whereas both the neutral species D_{4h} C_4H_4 and D_{8h} C_8H_8 would have two unpaired electrons in the HOMOs, and function equally well as sources of or sinks for electronic charge, D_{5h} C_5H_5 and D_{7h} C_7H_7 differ in that the former will be a better acceptor, and the latter a better donor, of electronic charge when coordinating to a metal atom or ion. Coordination effectively stabilizes the aromatic ionic ring systems $C_5H_5^-$ and $C_7H_7^+$.

Ferrocene, $Fe(\eta^5\text{-}C_5H_5)_2$,[36] and related cyclopentadienyl complexes of transition

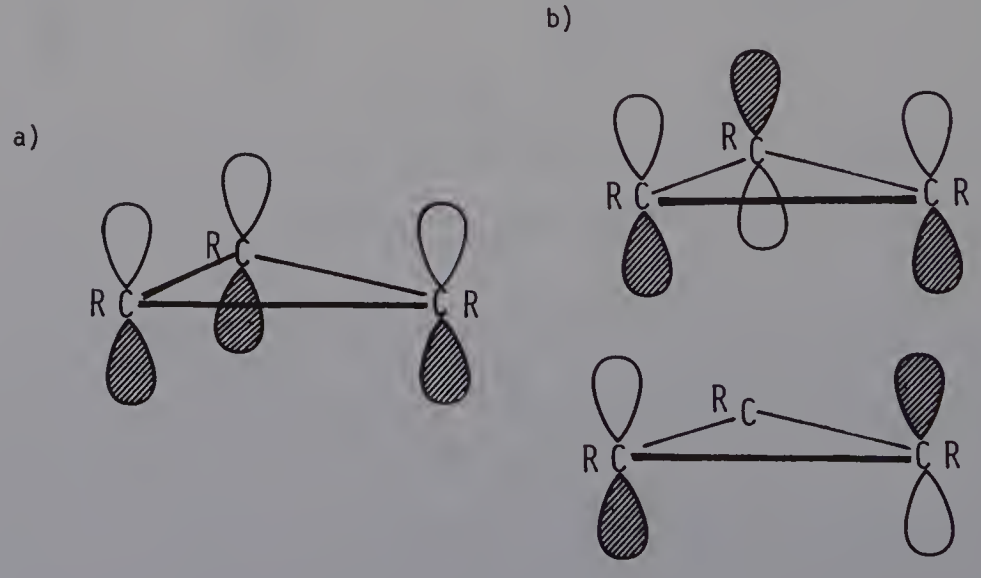


Figure 4.4. The π orbitals of a cyclopropenium cation, $C_3R_3^+$. (*a*) The filled π-bonding MO of the cyclopropenyl cation, $C_3R_3^+$, that can act as a source of electrons for metal–carbon bonding. (*b*) The empty π-bonding MO's of the cyclopropenyl cation, $C_3R_3^+$, that can receive electronic charge from suitable metal *pd* hybrid AO's for metal–carbon bonding.

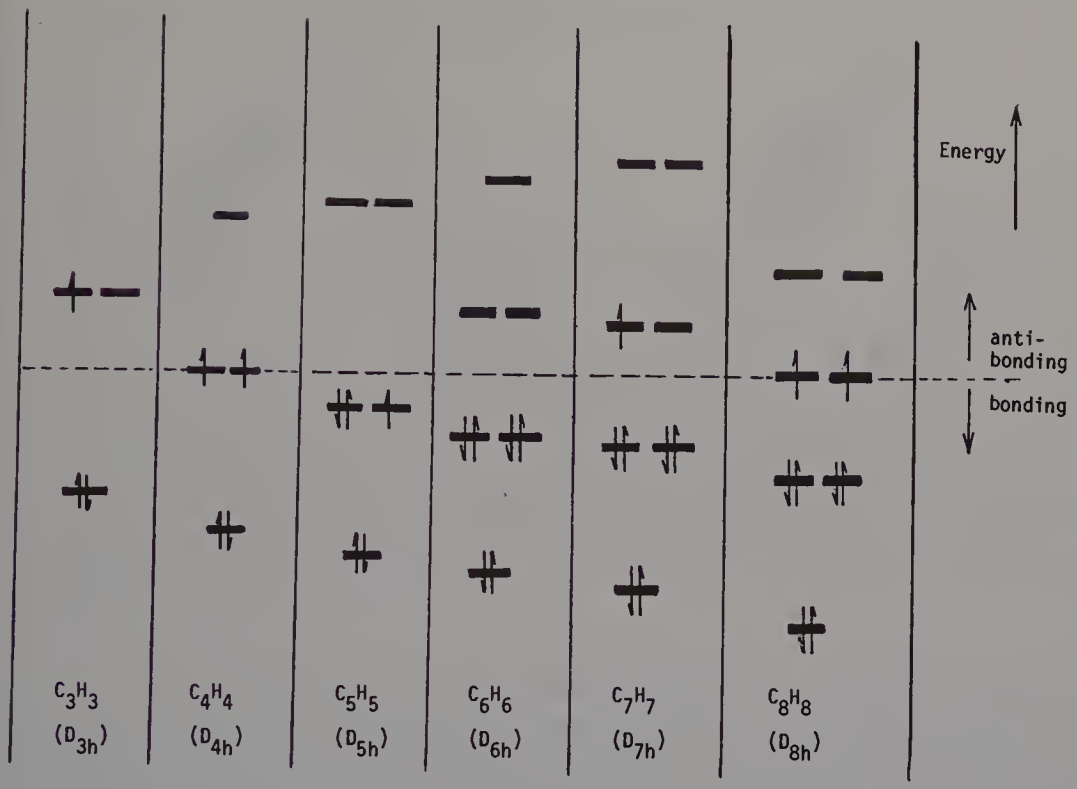


Figure 4.5. Relative energies of the π-bonding and antibonding MO's of C_nH_n-ring systems.

metals in fact are characteristically far more thermally stable, less reactive substances than ionic cyclopentadienides, and have an extensive derivative chemistry that is typically aromatic in that their C−H bonds can undergo such electrophilic substitution reactions as Friedel–Crafts alkylation or acylation, nitration, and so on. Moreover, as a substituent, the ferrocenyl group $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$ (=R) is even more effective than a phenyl substituent in stabilizing carbenium ions, RCH_2^+.[45]

In discussing the scope for the transfer of electronic charge from the C_nH_n ring to the metal atom or vice versa, we have not yet touched on two factors that will have an important bearing on this. These are the overall charge on the complex and the effective electronegativity of the metal residue.[46] For positively charged complexes, transfer of charge from metal to C_nH_n ligand will be less important than from ligand to metal, whereas the reverse will be true for anionic complexes. Again, the effective electronegativity of the metal residue—a function of the metal identity, its oxidation state, and the nature of the ligands it bears—will influence whether on balance it removes charge from the C_nH_n-ring system, rendering it carbocationic and susceptible to nucleophilic attack, or releases charge to it, giving it carbanionic character.

A further feature of the structures of the compounds shown in Figures 4.1 and 4.2 is worthy of comment. This is that the *exo* substituent hydrogen atoms of the C_nH_n ligands lie in the same plane as the carbon atoms only in the case of medium-sized rings (n = 5 or 6). In the case of small rings, as in the cyclopropenium complex,

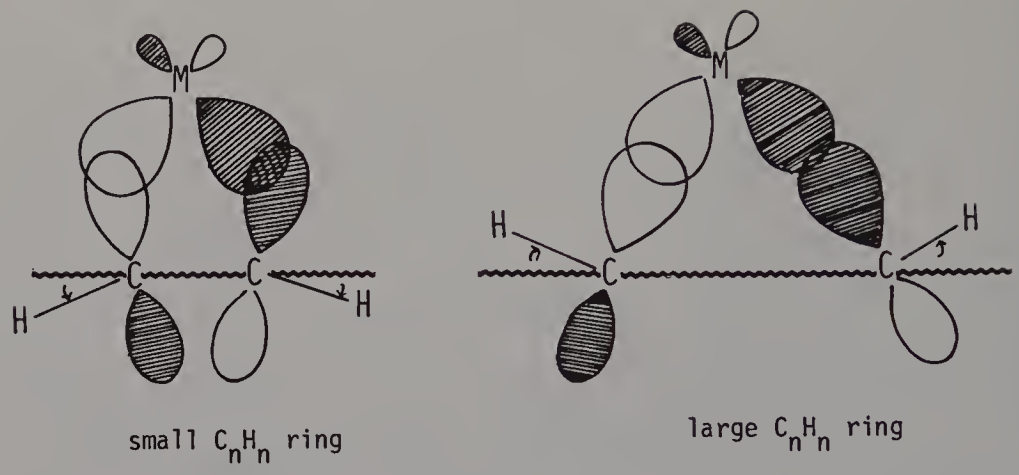


Figure 4.6. Effect of C_nH_n-ring size on *exo* C−H bond orientation in $M(\eta^n\text{-}C_nH_n)$ complexes.

$(\eta^3\text{-}C_3Ph_3)NiCl(py)_2$, the substituent phenyl groups lean *away from* the metal atom (as befits a tetrahedrane-type structure). In complexes of large rings, the substituents typically lean *towards* the metal atom. These distortions from planarity are not due to agostic[47] C---H---M bonding interactions, but reflect the need for the carbon *p* AO's to overlap the metal *pd* hybrid AO's as effectively as possible (Fig. 4.6).

If the compounds shown in Figures 4.1 and 4.2 are regarded as mixed metal–carbon clusters, the pyramidal shapes of their MC_n skeletons will be found to be those appropriate for *nido* systems in which $(n + 1)$ skeletal atoms are formally held together by $(n + 3)$ skeletal bond pairs. (This number includes the n pairs of electrons in the ring carbon–carbon σ bonds as well as the three pairs of electrons in their π-systems).[7,8] For example, in the cyclobutadiene complex $(\eta^4\text{-}C_4H_4)Fe(CO)_3$,[30,31] each CH unit can contribute 3 electrons, and the $Fe(CO)_3$ unit can contribute 2 electrons for skeletal bonding, making a total of seven skeletal bond pairs, and so requiring the structure to be based on the six-vertex deltahedron, the octahedron. For the sandwich compounds, the central metal atom needs 6 electrons to fill the three AO's that are cluster nonbonding. Any remaining electrons supplement those from the ring CH units as skeletal bonding electrons, and are shared between the two MC_n pyramids. Thus, in ferrocene, the d^8 iron atom can contribute 1 electron to each FeC_5 pyramid to supplement the 15 electrons from the five CH units of each ring, giving a total of eight skeletal bond pairs for each half of the molecule.

In the following section, we shall consider some metal–hydrocarbon complexes that are formally *arachno* in type. However, we should not leave this discussion of C_nH_n-ring complexes without noting that though common in transition metal chemistry, they are not unknown in main group chemistry [$MeBe(\eta^5\text{-}C_5H_5)$[48] is an example], though rare because main group metals cannot use filled *d* AO's as sources of electrons to strengthen the metal–carbon bonding.[10]

4.3 COMPLEXES OF ACYCLIC UNSATURATED LIGANDS, C_nH_{n+2}, WITH A METAL ATOM

Figure 4.7 shows the structures of some typical complexes formed by acyclic unsaturated molecules or groups of formulas C_nH_{n+2}.[49–56] They include complexes of molecules capable of stable independent existence (ethylene and 1,3-butadiene) and of species that, if uncomplexed, would be radical species [the allyl radical $HC(CH_2)_2$ and the trimethylenemethane diradical, $C(CH_2)_3$].

Technically, it is possible to assign a pair of electrons to each metal–carbon bond in these complexes and so describe the metal–ligand bonding in classical bonding terms without violating the octet rule for carbon or the 18-electron rule for the transition metal atom involved. (The ethylene complex shown, $[(C_2H_4)PtCl_3]^-$, the anion of Zeise's[49] salt, of historic interest as the first reported metal–hydrocarbon π complex,[50] is actually a 16-electron species, like many platinum complexes.) Indeed, as already noted in Chapter 1 (Fig. 1.14) for the ethylene complex, its depiction as a

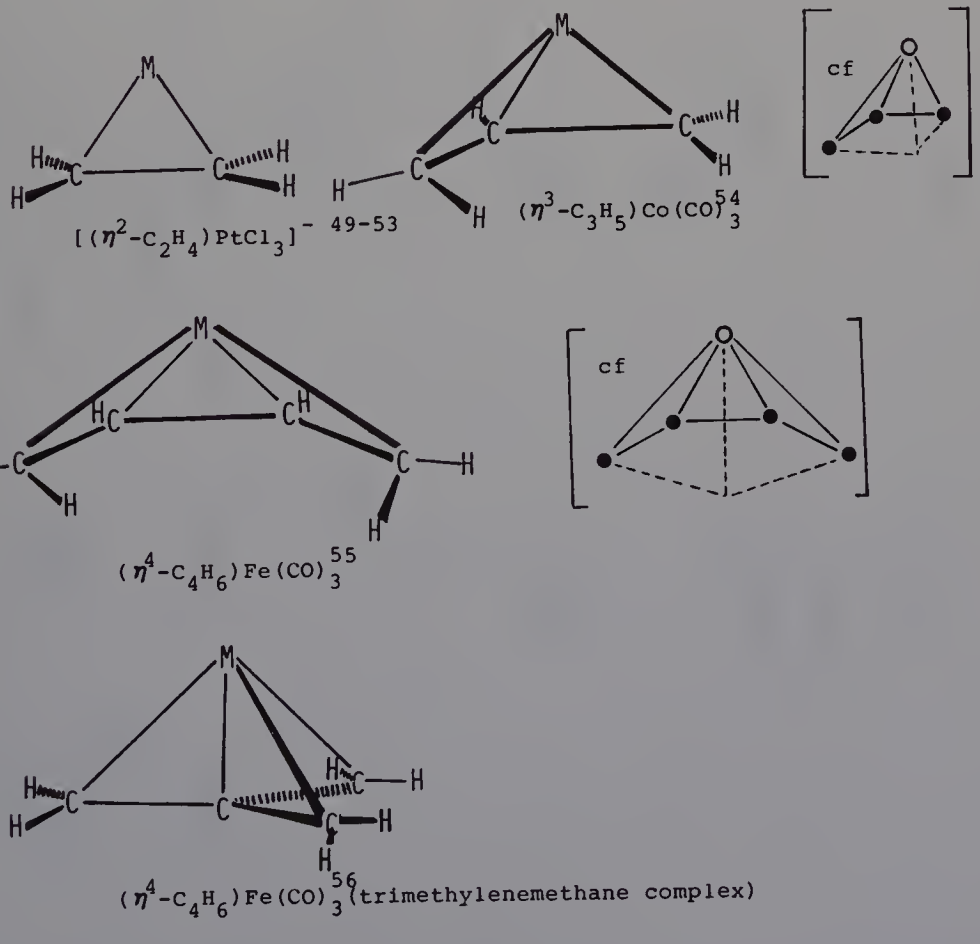


Figure 4.7. Complexes of acyclic unsaturated systems (C_nH_{n+2}).

metallacyclopropane is not without merit,[51–53] and the numbers of electrons such a description involves in metal–ligand and carbon–carbon bonding are not inappropriate for the other systems. Accordingly, we shall not discuss them in detail here, except to indicate (Fig. 4.8) what frontier orbitals the organic ligands can make use of for metal–carbon bonding.[9,11–15] For the allyl ligand (Fig. 4.8*a*), MO's (i) and

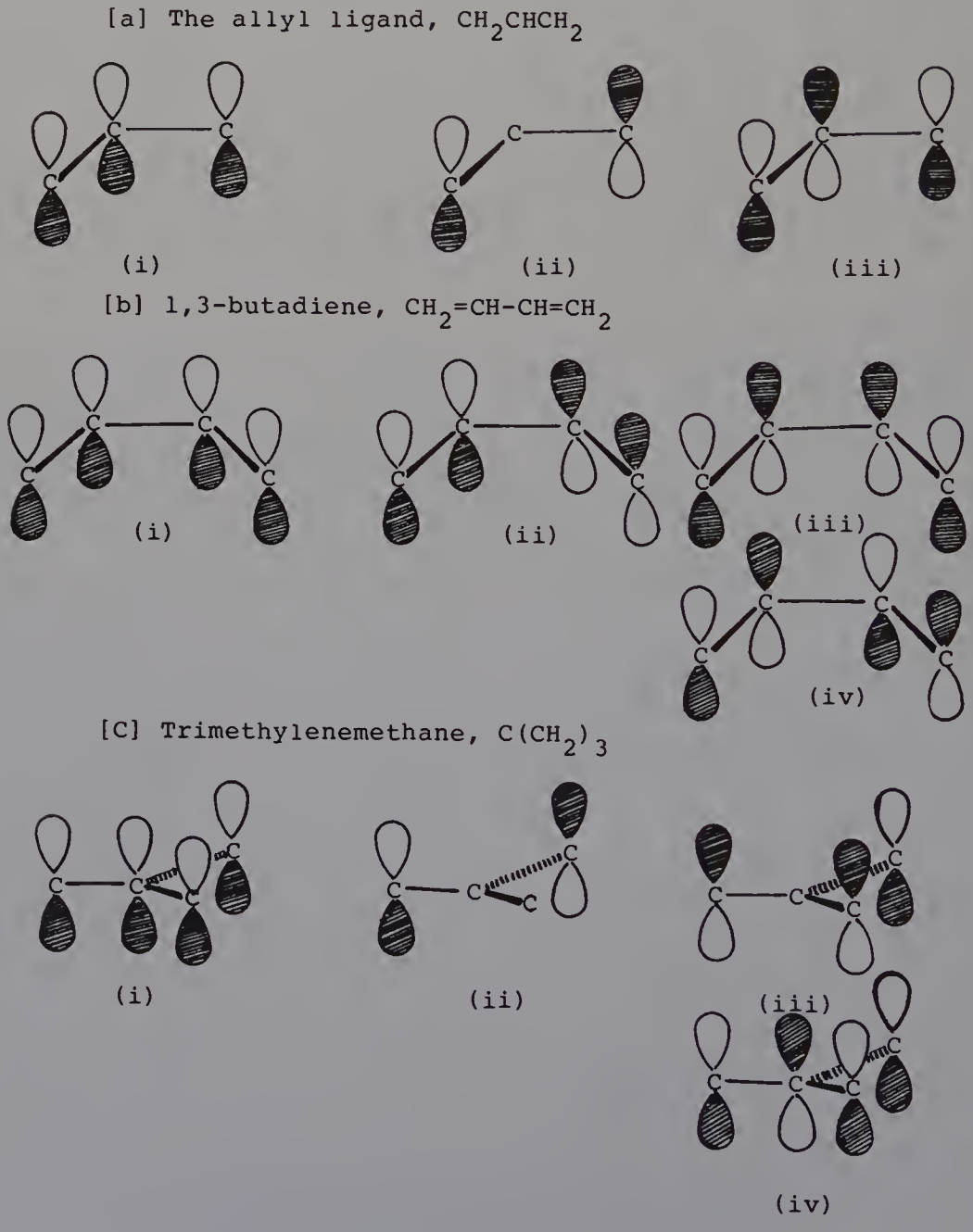


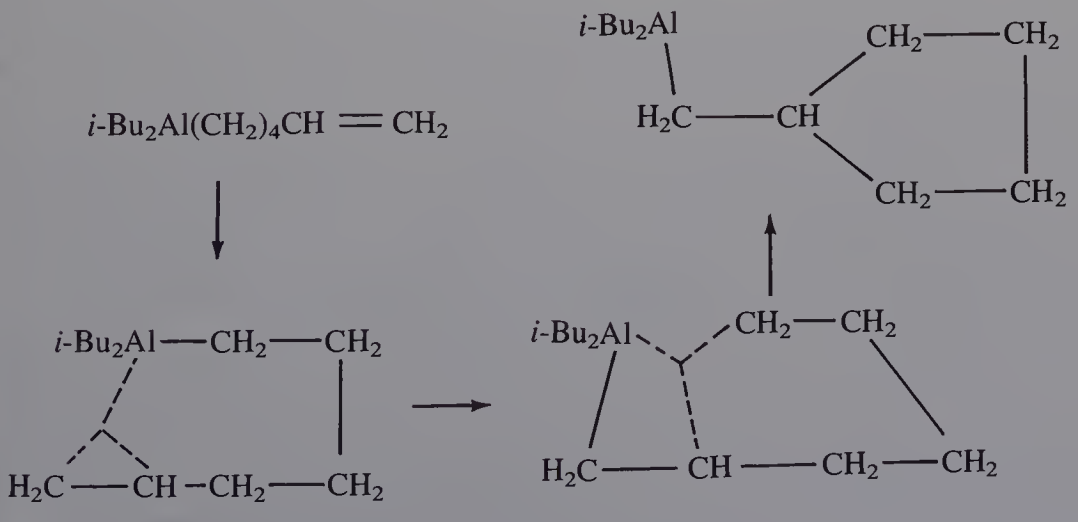
Figure 4.8. Frontier orbitals available for metal–carbon bonding in complexes of acyclic unsaturated systems C_nH_{n+2}.

(ii), particularly the latter, contribute more than (iii).[54] For butadiene (Fig. 4.8*b*), coordination effectively transfers electronic charge from the HOMO (ii) to the LUMO (iii), thereby weakening the terminal C−C bonds and strengthening the central one.[55] For trimethylenemethane (Fig. 4.8*c*),[56] which as an isolated species would have one electron in each of the degenerate pair of orbitals (ii) and (iii), interactions of metal *d* or *pd* hybrid AO's with these and with the filled orbital (i) will primarily account for the metal–ligand bonding, as the antibonding orbital (iv) will be of relatively high energy.

With the exception of the trimethylenemethane complex, it is possible to treat complexes like those shown in Figure 4.7 as mixed metal–carbon clusters of the *arachno* type, formally containing $(n + 4)$ skeletal bond pairs to hold their $(n + 1)$ skeletal atoms together.[7,8]

Again, like C_nH_n-ring complexes, complexes of acyclic ligands C_nH_{n+2} are almost exclusively formed by transition metals in low enough oxidation states to be able to supply filled *d* or *pd* hybrid AO's for metal ⟶ ligand transferal of electronic charge, a most important component of the metal–ligand bonding. Without the capacity to do this, main group metals, or metals from the left-hand side of the transition series in high oxidation states, can function only as weak acceptors of electronic charge from acyclic unsaturated groups. Vibrational and NMR spectroscopic studies on aluminum alkenyls, $i\text{-}Bu_2Al(CH_2)_nCH{=}CH_2$,[57] have shown evidence of intramolecular coordination when *n* is large enough to allow the alkenyl unit to loop around towards the metal, coordination that involves (3*c*–2*e*) AlC_2 bonding and serves as a prelude to the cyclization of the alkenyl substituent that occurs on gentle warming of these systems (Scheme 4.2).[58–60]

Scheme 4.2



4.4 COMPLEXES OF UNSATURATED ORGANIC LIGANDS WITH TWO OR MORE METAL ATOMS: MIXED METAL–CARBON CLUSTERS

In the same way that reactions between alkynes and polyboranes afford mixed boron–carbon clusters (carboranes),[1–6] so reactions between alkynes and polynuclear metal carbonyls (sometimes reactions with mononuclear metal carbonyls) afford compounds that can either be regarded as alkyne complexes of di- or polynuclear metal clusters, or as mixed metal–carbon clusters.[9,16,26,27] Some representative structures are shown in Figure 4.9,[61–69a] which also includes the monocarba pyramidal cluster $Co_3(CO)_9CMe$[62] and two ferracyclopentadienyl species, $Fe_2(CO)_6(CMe)_2(COH)_2$[67] and $Fe_3(CO)_8C_4Ph_4$,[69a] containing more C--C links than were present in the reagents.

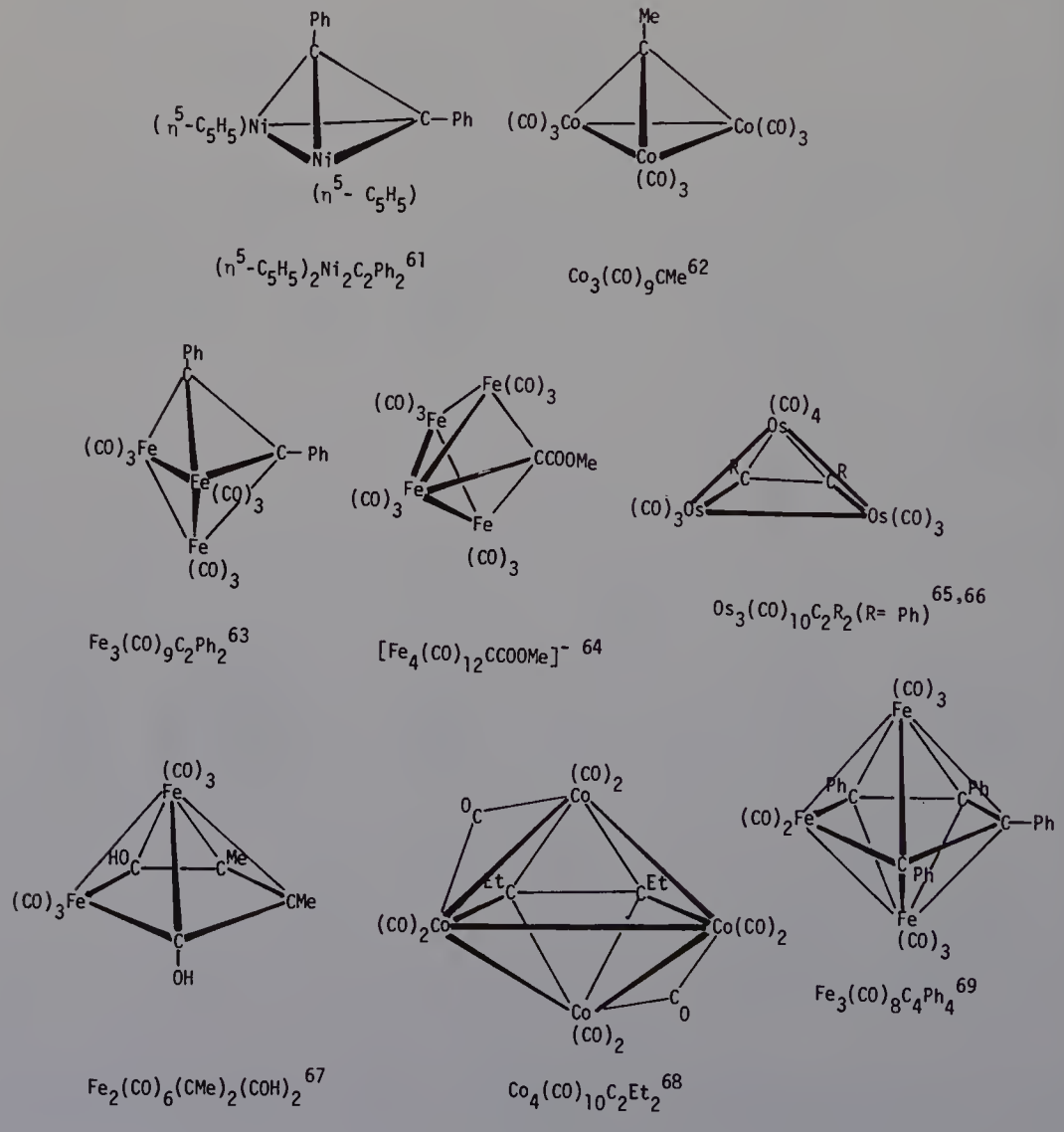


Figure 4.9. Structures of mixed metal–carbon clusters containing two or more metal atoms.

In several of the compounds shown in Figure 4.9, the carbon atoms are four-coordinate, and the numbers of electrons present allow classical ($2c$–$2e$) bonding descriptions to account for their structures. This is indeed the case for the compounds $(\eta^5\text{-}C_5H_5)_2Ni_2C_2Ph_2$[61] and $Co_3(CO)_9CMe$[62] which, together with the cyclopropenium–nickel complex $(C_3Ph_3)NiCl(py)_2$[29] shown in Figure 4.1, can all be regarded as metalla derivatives of that elusive molecule, tetrahedrane, C_4H_4 (recently, the tetra-*t*-butyl derivative of tetrahedrane has been synthesized),[69b] in which one, two, or three CH units have been replaced by isolobal[11–13] metal residues. If all the C−C and Fe−C links in the pentagonal pyramidal skeleton of $Fe_2(CO)_6(CMe)_2(COH)_2$[67] are assigned a pair of electrons, however, then the metal–metal bond in this compound has to be regarded as a dative bond from the apical iron atom to the basal iron atom.

Localized ($2c$–$2e$)-bonding descriptions are clearly inadequate for the compounds $Fe_3(CO)_9C_2Ph_2$,[63] $Co_4(CO)_{10}C_2Et_2$,[68] and $Fe_3(CO)_8C_4Ph_4$,[69a] however, which have trigonal bipyramidal, octahedral, and pentagonal bipyramidal mixed metal–carbon skeletons, respectively, each containing five-coordinate carbon atoms. It is possible to treat the metal–carbon bonding in these clusters in terms of interactions between the frontier orbitals of alkyne residues and metal cluster fragments. Here, it suffices to note the relationship between the compounds in Figure 4.9 and either tetrahedrane (as already noted) or the small *closo* carboranes $C_2B_3H_5$,[70] $C_2B_4H_6$,[70,71] and $C_2B_5H_7$[72] or the *nido* species $C_2B_3H_7$[73] and $C_2B_4H_8$. Electron counts show that the shapes are as expected,[74] so we can assume that the carbon atoms in these clusters are involved in skeletal bonding of the type discussed in Chapter 3.

To underline the structural and bonding relationship between these mixed metal–carbon cluster species and carboranes, we list the formulas of representative species in Table 4.1, classified according to the numbers of skeletal bonding electrons they contain and thus according to their structural type (*closo*, *nido*, or *arachno*).

4.5. METAL CARBIDES

Binary metal carbides, M_xC_y have for a long time been known to be a class of compound that includes a wide range of actual types, differing markedly in their bulk properties, the structural environments of their carbon atoms, and the degree of covalency in their bonding.[16–19,26–28] For example, the hardness and unreactivity of tungsten carbide (WC) and the use of carbon in steel production to increase mechanical strength, can be contrasted with the soft brittle nature and high reactivity of alkali or alkaline earth metal carbides. Their carbon atoms may be present as isolated atoms (formally as anions C^{4-}) or as pairs of atoms (formally as acetylide anions, $C{\equiv}C^{2-}$, as in the "calcium carbide" (CaC_2) that early cyclists used in their lamps). There may even be higher aggregates, such as C_3 units [formally as propadiene anions, $(C{=}C{=}C)^{4-}$].

In practice, highly charged anions such as C^{4-} or even $C_3{}^{4-}$ cannot be expected to exist as such, certainly not in bulk lattices in which they are surrounded by highly polarizing metal cations, so a significant covalent contribution to the bonding must be

TABLE 4.1. Classification of Metal–Hydrocarbon π Complexes, Aromatic Systems, and Various Hydrocarbons as Carborane–Type Mixed Metal–Carbon Clusters[a,b]

Fundamental Polyhedron	b	*Closo* Species ($a=b-1$)	*Nido* Species ($a=b-2$)	*Arachno* Species ($a=b-3$)
Trigonal bipyramid	6	$Fe_3(CO)_9C_2Ph_2$ (63); $[Fe_4(CO)_{12}CR]^-$ (64); $Fe_4(CO)_{12}CCO$ (75)	$Co_3(CO)_9CMe$ (62); $Ni_2(Cp)_2C_2Ph_2$ (61); $NiCl(py)_2C_3Ph_3$ (29) and other η^3-cyclopropenium complexes; C_4H_4 (tetrahedrane)	$Pt(PPh_3)_3C_2H_4$ and other η^2-alkene complexes (51–53); C_3H_6 (cyclopropane)
Octahedron	7	$Co_4(CO)_{10}C_2Et_2$ (68)	$Fe(CO)_2C_4H_4$, $CoCpC_4H_4$ (30,31) and other η^4-cyclobutadiene complexes, $C_5H_5^+$ (the square pyramidal carbocation)	$Co(CO)_3C_3H_5$ (54) and other η^3-allyl complexes; C_4H_6 (bicyclobutane) $C_4H_4^{2-}$ (the cyclobutadiene dianion)
Pentagonal bipyramid	8	$Fe_3(CO)_8C_4Ph_4$ (69)	$Fe_2(CO)_6C_2Me_2C_2(OH)_2$ (67); $Mn(CO)_3C_5H_5$, $BeMeC_5H_5$ and other η^5-cyclopentadienyl complexes $C_6Me_6^{2+}$ (the pentagonal pyramidal carbodication)	$Fe(CO)_3C_4H_6$ (55) and other η^4-butadiene complexes; $C_5H_5^-$ (the cyclopentadienide anion) and other five-membered aromatic ring systems.
Hexagonal bipyramid	9		$Cr(C_6H_6)_2$, $Cr(CO)_3(C_6H_6)$ and other metal- η^6-arene complexes	Benzene and other six-membered aromatic ring systems
D_{2d} Dodecahedron	9			$AlMe_2(\eta^3\text{-}C_5H_5)$; benzvalene
Heptagonal bipyramid	10		$V(CO)_3C_7H_7$ and other η^7-cycloheptatrienyl complexes	$C_7H_7^+$ (the cycloheptatrienyl cation) and related seven-membered, six π-electron aromatic ring complexes

[a] a = number of skeletal atoms; b = number of skeletal bond pairs.
[b] References are in parentheses.

a feature of systems in which they appear to be present. A coordination number of four for a carbide anion C^{4-} would allow it to share a pair of electrons with each of its neighbors, and so form a classically bonded covalent lattice. Zinc blende or wurtzite lattices for such compounds as GeC or SnC obviously allow such a covalent description of the bonding purely in terms of ($2c$–$2e$) metal–carbon bonds. However, most carbides are not like this. The coordination numbers of their carbon atoms generally exceed four, so if their bonding is to be described in covalent terms, some form of multicenter bonding must be invoked.

Discussion in detail of the binary compounds would be inappropriate in this book,

and would be made difficult by the imprecision of much of the structural information. Many metal carbides have structures very similar to that of the bulk metal, with carbon atoms occupying interstitial sites (commonly octahedral holes) in the metal lattice. For these, the most useful treatment of the bonding of the bulk material is in terms of a modification of that of the parent metal, due allowance being made for the fact that each carbon atom can contribute its four valence shell electrons to supplement the metal electrons in the valence band.

For our purpose here, it is more convenient to consider some molecular systems that can be regarded as models for the carbon environments in binary carbides, namely, metal carbonyl carbide clusters in which carbon atoms are incorporated in metal polyhedra, which in turn are surrounded by carbonyl ligands.[20–22] Such compounds, for which few planned syntheses are at present available, have been found in increasing numbers among the products of thermal decomposition of metal carbonyls $M_x(CO)_y$, their "carbidic" carbon atoms originating in the carbonyl ligands.

The structures of some representative examples are shown in Figure 4.10.[23–25,75–80] They include three compounds $[Fe_4(CO)_{13}C,$[75] with a butterfly

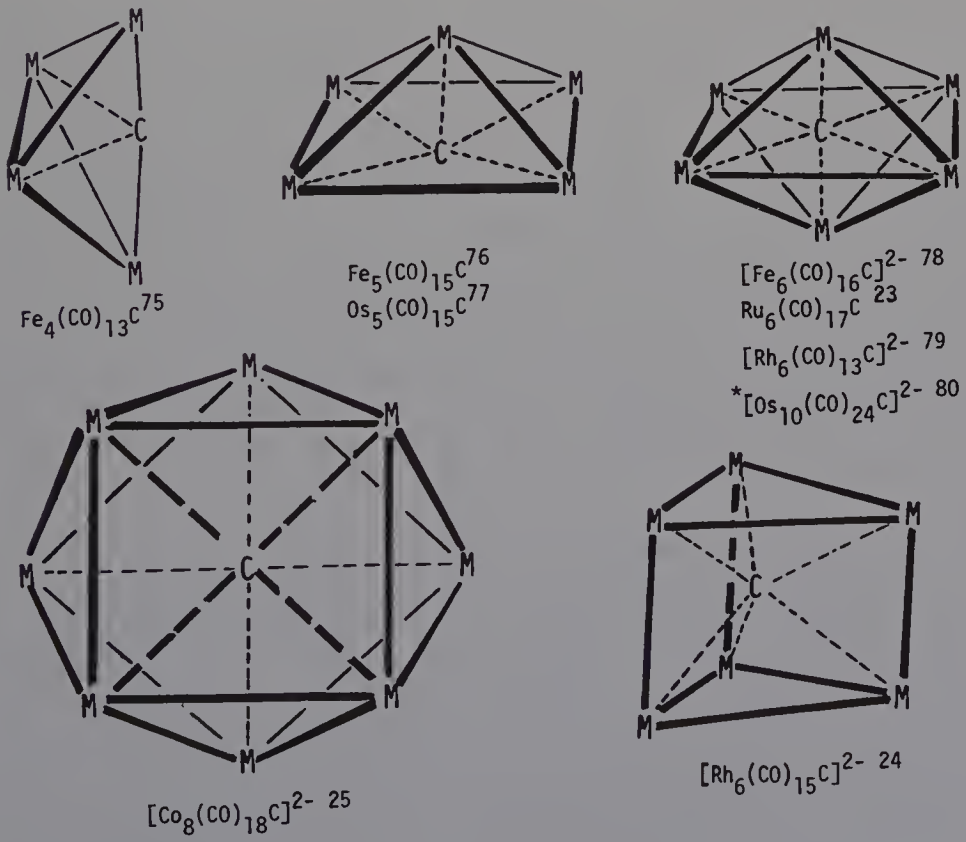


Figure 4.10. Skeletal structures of some metal carbide clusters; * in the osmium cluster in the upper right, 4 of the 10 osmium atoms cap a tetrahedrally related set of faces of the inner Os_6 octahedron that contains the core carbon atom. Each capping Os atom has 3 terminal carbonyl ligands attached. The other Os atoms have 2 terminal carbonyl ligands.

shaped arrangement of its four metal atoms, and $Fe_5(CO)_{15}C$[76] and the isoelectronic $Os_5(CO)_{15}C$,[77] which have square pyramidal M_5 arrangements] in which the carbide carbon atom occupies a relatively exposed position, though clearly bonding to all the metal atoms in the cluster. The complete absence of ligand atoms in more than one half of the coordination sphere makes the carbon atom readily accessible to reagent molecules in each of these compounds, and renders localized ($2c$–$2e$) bonding descriptions very unsatisfactory if not quite impossible in the case of the tetra-iron species.

In the remaining compounds illustrated, the carbide carbon atoms are completely encapsulated by metal atoms which, because they bond to each other as well as to the carbon atom, completely shield it from reagent molecules. In $[Rh_6(CO)_{13}C]^{2-}$,[79] the carbide carbon is accommodated at the center of an octahedron of metal atoms. In $[Rh_6(CO)_{15}C]^{2-}$,[24] the six metal atoms surrounding the core carbon atom form a trigonal prism, while in the cobalt complex anion, $[Co_8(CO)_{18}C]^{2-}$, the eight metal atoms form what was described[25] as a distorted tetragonal antiprism (four of the metal–carbon bonds are significantly shorter than the remaining four, though all are clearly directly bonded to the carbon atom), though it could more appropriately be considered as a dodecahedron.

In considering the bonding in these carbides, it is vital to remember that, in one important respect, they differ from simple coordination complexes ML_n in which *n separate* ligands L surround a central atom M. In such simple complexes, when these ligands L are bound only to that central atom and not to each other, they tend to spread as symmetrically as possible about that central atom, though leaving space for "lone-pair" electrons in the case of typical complexes of main group elements, M. The distribution of the metal atoms in the carbon coordination sphere of $Fe_4(CO)_{13}C$[75] and $Fe_5(CO)_{15}C$[76] (Fig. 4.10) would appear to imply the presence of one or even two stereochemically significant lone pairs of electrons if they were complexes of this type. However, the polyhedral-fragment shapes of their Fe_4 and Fe_5 residues are *not* a consequence of repulsion by lone-pair electrons on the carbide atom (which is susceptible to attack by nucleophiles but not electrophiles),[64,75,81,82] but rather a consequence of the number of electrons available for metal–metal bonding, a number that includes *all four* of the electrons in the carbon atom's valence shell.

This can readily be demonstrated by considering these two compounds as if they were formally derived from anions $[Fe_4(CO)_{13}]^{4-}$ and $[Fe(CO)_{15}]^{4-}$, respectively, by addition of C^{4+}. The appropriate shapes for these anions can be deduced very simply by arguments like those used in Chapter 3 to deduce the shapes of carboranes from their formulas. For example, treating $[Fe_4(CO)_{13}]^{4-}$ as composed of four $Fe(CO)_3$ units (each contributing 2 electrons for skeletal bonding) and an extra carbonyl ligand (contributing two electrons), and taking account of the 4 electrons contributed by the carbide carbon atom and reflected in the $4-$ charge on this anion, we find that altogether 14 electrons, that is, seven pairs, are available for skeletal bonding. With four skeletal atoms, $[Fe_4(CO)_{13}]^{4-}$ can, therefore, be regarded as an *arachno* cluster with a shape based on an octahedron, but with two vacant vertices. Either a butterfly shape or a square arrangement of the metal atoms would be

compatible with this treatment, the former being preferred (compare B_4H_{10} or C_4H_6, bicyclobutane) and the carbide carbon atom is embedded in the open face where the HOMOs of the anion $[Fe_4(CO)_{13}]^{4-}$ would concentrate electronic charge. That this treatment of this compound is realistic is substantiated by the structural data in Figure 4.11, which compares $Fe_4(CO)_{13}C$[75] with a closely related compound, the carboxylate anion $[Fe_4(CO)_{12}CCO_2Me]^-$,[64] into which the carbide (itself prepared by oxidative degradation of the hexa-iron carbonyl carbide $[Fe_6(CO)_{16}C]^{2-}$ can be converted as in Scheme 4.3.[75]

Scheme 4.3

$$[Fe_6(CO)_{16}C]^{2-} \xrightarrow[\text{degradation}]{\text{oxidative}} Fe_4(CO)_{13}C \xrightarrow{CO} Fe_4(CO)_{12}CCO \xrightarrow{MeOH} [Fe_4(CO)_{12}CCOOMe]^-$$

This last compound, treated as a mixed metal–carbon cluster $[Fe_4(CO)_{12}CR]^-$ (R = the one-electron carboxylate ligand) contains six skeletal bond pairs to hold together its five skeletal atoms (one carbon atom and four metal atoms). It is therefore a *closo* cluster, with the expected trigonal bipyramidal shape defined by its skeletal carbon and metal atoms.

Note that both descriptions of the Fe_4 residue, whether as an *arachno* species based on an octahedron, or as a *nido* species based on a trigonal bipyramid, are compatible with the observed butterfly shape. However, the dihedral angle between the wing planes and the M–C–M angles at the core or equatorial carbon atom will differ markedly according to which description is used (a smaller dihedral angle is expected for an *arachno*-type butterfly, for which the M–C–M angle is expected to be about 180°). In Figure 4.11 we show that the metal geometries and M–C–M

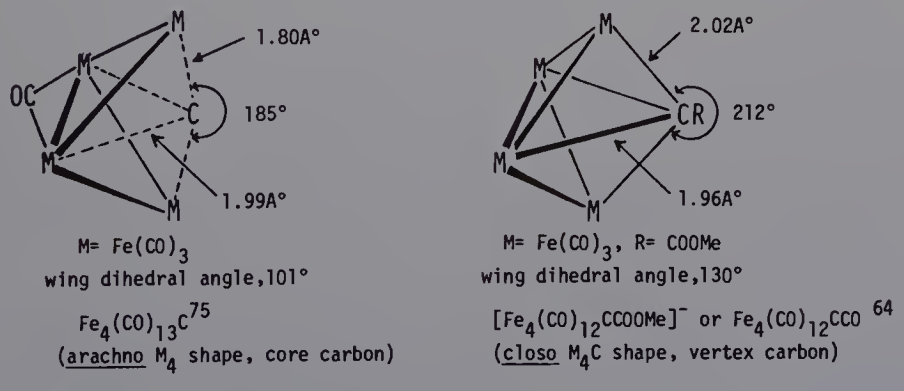


Figure 4.11. A comparison of the skeletal Fe_4C geometries of the compounds. $Fe_4(CO)_{13}C$ and $Fe_4(CO)_{12}CCOOMe$.

angles in $Fe_4(CO)_{13}C$ and $Fe_4(CO)_{12}CCO_2Me$ differ in precisely the manner that is appropriate for the description used.

The intermediate $Fe_4(CO)_{12}CCO$, through which $Fe_4(CO)_{13}C$ can be converted into $[Fe_4(CO)_{12}CCO_2Me]^-$, is also a *closo* species, of particular interest in revealing the capacity of a carbon atom to bond simultaneously to the *exo* carbonyl ligand [effectively by a (2*c*–4*e*) double bond] and to all four of the iron atoms of the cluster.

The ^{13}C NMR resonances due to the core carbon atoms in $Fe_4(CO)_{13}C$ and the other metal carbonyl carbides shown in Figure 4.10 tend to lie well downfield. As such core carbons serve as the sites at which carbonyl ligands can coordinate, they probably should more realistically be regarded as sequestered electron-deficient carbonium ions rather than as carbanionic carbides.

If the square pyramidal metal carbonyl carbides $Fe_5(CO)_{15}C$[76] and $Os_5(CO)_{15}C$[77] are treated in a similar manner to $Fe_4(CO)_{13}C$, that is, as clusters in which all four of the core carbon atom's valence shell electrons are used for skeletal bonding, then they are seen to have the expected *nido* shapes of systems with five skeletal atoms (the metal atoms) and seven skeletal bond pairs. By contrast, if these carbide carbon atoms had occupied polyhedral vertex sites, with a lone pair of electrons occupying an *exo*-oriented hybrid orbital, then the number of skeletal bond pairs would have been reduced by one, and the five metal atoms *and* the carbide carbon atom would have needed to be accommodated in some way on a trigonal bipyramidal skeleton. Clearly, the assumption that all four valence shell electrons from the carbon atom are involved in the skeletal bonding is vindicated.

Turning to the octahedral hexanuclear-metal clusters shown in Figure 4.10—$Ru_6(CO)_{17}C$,[19] $[Fe_6(CO)_{16}C]^{2-}$,[78] and $[Rh_6(CO)_{13}C]^{2-}$ [79]—we find that all of them formally contain seven skeletal bond pairs, as appropriate for their *closo* structures, assuming that all four valence shell electrons of the carbide carbon atoms are used for skeletal bonding, an assumption clearly justified by the completely enclosed sites they occupy. The skeletal bonding orbitals for such species (Fig. 4.12) are very similar to those already discussed in Chapter 3 in connection with 1,6-$C_2B_4H_6$ (Fig. 3.8),[83] although the higher symmetry (O_h as opposed to D_{4h}) of these homonuclear metal species increases the degeneracy of the seven skeletal bonding MO's, which in tensor surface harmonic terminology would be classed as of type *S* (nondegenerate, A_{1g}), *P* (triply degenerate, T_{1u}), and *D* (triply degenerate, T_{2g}).[84] The core carbon orbitals, therefore, have the appropriate symmetries to stabilize the fully symmetric (A_{1g}) combination of inward-pointing orbitals (carbon 2*s*) and the T_{1u} set of orbitals that perform a π-bonding role around each of the three M_4 squares (carbon $2p_x$, $2p_y$, and $2p_z$), as illustrated in Figure 4.12. The skeletal bonding T_{2g} MO's, however, have the wrong lobal characteristics to be stabilized by the core carbon atom, which cannot use the *d* AO's (d_{xy}, d_{yz} and d_{xz}) that would have the correct symmetries.

As it happens, the octahedral arrangement of six metal atoms about a core carbon atom, the commonest type of coordination known for core carbon atoms in metal carbonyl carbide chemistry, is capable of rationalization relatively simply in terms of localized bonds. If the core carbon atom is regarded as sp^3 hybridized, and the sp^3 hybrid AO's point toward the centers of four of the eight faces of the M_6 octahedron,

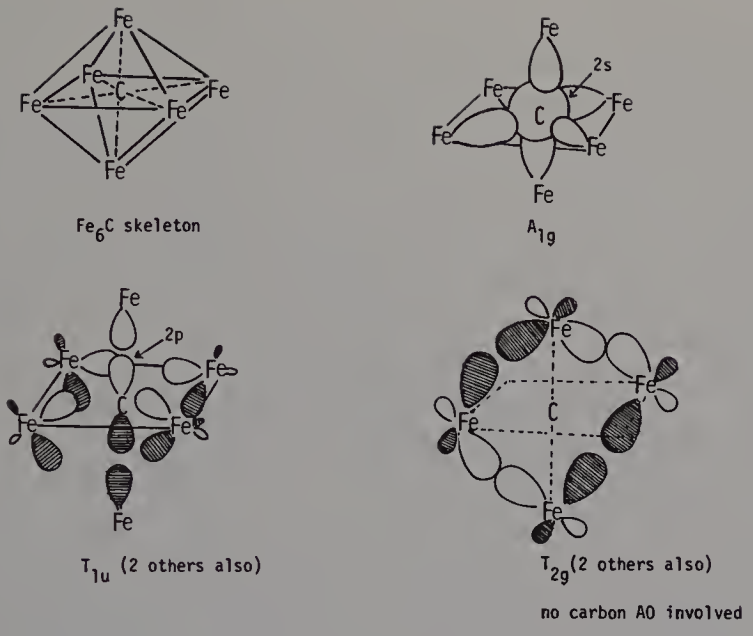


Figure 4.12. Interactions of the carbon 2*s* and 2*p* AO's with the $Fe_6 A_{1g}$ and T_{1u} MO's of the cluster $[Fe_6(CO)_{16}C]^{2-}$.

where they could overlap with a suitable AO from each metal atom, then this would allow the metal–carbon bonding to be described by four (4*c*–2*e*) CM_3 bonds *inside* the octahedron. Resonance between the only two possible orientations of these four, four-center bonds, would need to be invoked, but otherwise such a bonding description is well suited to the symmetry of the system. Moreover, since such four-center bonding would have the effect of conferring a metal–metal bonding role on up to half of the electron density involved, it is nicely consistent with the picture obtained from the MO treatment. In this localized (4*c*–2*e*) treatment of the metal–carbon bonding, incidentally, each metal atom would need to participate in two such bonds, as illustrated in Figure 4.13 (which for the sake of simplicity shows only half of an octahedron).

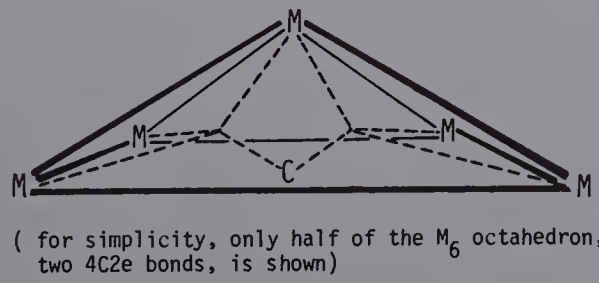


Figure 4.13. Localized (4*c*–2*e*) bonds of the type that can be used to describe the bonding of core carbon atoms in the M_6 octahedron. For simplicity, only half of the M_6 octahedron, containing two (4*c*–2*e*) bonds, is shown.

The trigonal prismatic cluster $[Rh_6(CO)_{15}C]^{2-}$,[24] shown in Figure 4.10 differs from the carbonyl carbide clusters already discussed in that it has a structure in which the metal–metal bonds can be represented satisfactorily as (2*c*–2*e*) bonds. Its trigonal prismatic shape evidently uses the available nine skeletal bond pairs more effectively than would an *arachno*-type fragment of a D_{2d} dodecahedron. As before, the metal–carbon bonding can either be described in terms of stabilization of four of the skeletal bonding MO's by the carbon 2*s* and 2*p* AO's (Fig. 4.14), or by the various possible ways of allowing two (2*c*–2*e*) carbon–rhodium bonds and two (3*c*–2*e*) rhodium–carbon–rhodium bonds [or three (2*c*–2*e*) C—Rh bonds and one (4*c*–2*e*) CRh_3 bond] to resonate around the trigonal prismatic carbon coordination sphere.

The largest polyhedron of metal atoms shown to enclose a core carbon atom in Figure 4.10, the Co_8 polyhedron in the complex anion $[Co_8(CO)_{18}C]^{2-}$,[25] is

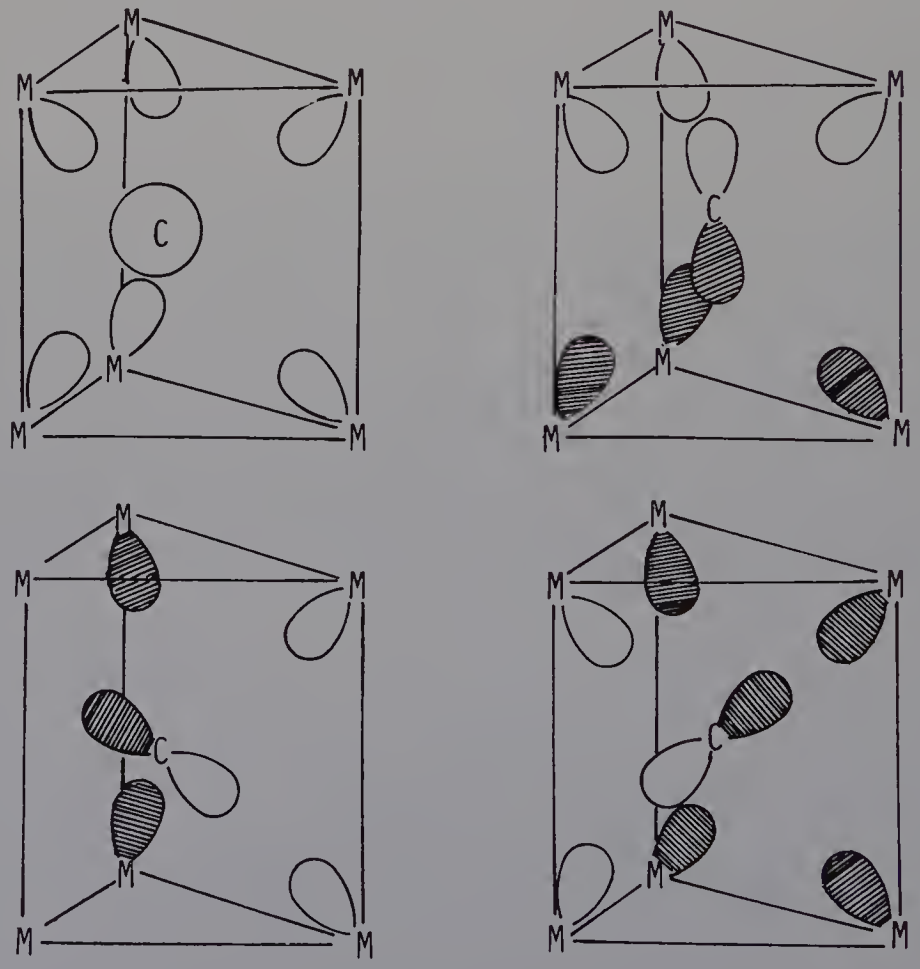


Figure 4.14. Schematic representation of the types of M_6 skeletal bonding MO of $[Rh_6(CO)_{15}C]^{2-}$ that can be stabilized by the core carbon AO's. Metal AO's are shown monolobal for simplicity.

essentially the *closo* D_{2d} dodecahedron expected for a system of eight skeletal atoms held together by nine skeletal bond pairs. Again, both MO and localized bond treatments of the metal–carbon bonding are possible. In the former, four of the skeletal bonding MO's (the *s* and *p* types) are stabilized by interaction with the carbon 2*s* and 2*p* AO's. In the latter, since there are eight atoms in the carbon coordination sphere to be accounted for (though not all equidistant), four (3*c*–2*e*) CCo_2 bonds resonating between the 18 Co--Co polyhedral edges [or four (4*c*–2*e*) CCo_3 bonds resonating between the 12 Co_3 polyhedral faces] might be used, though such descriptions hardly convey a clear picture of the metal–carbon bonding.

So far in this discussion we have confined our attention to clusters whose shapes were illustrated in Figure 4.10. These are just a selection of the metal carbonyl carbide species that have been subjected to x-ray crystallographic study. In Table 4.2 we list the formulas and reported carbon atom environments of a wider range of compounds that contain carbon atoms encapsulated within metal polyhedra. The prevalence of structures in which carbon atoms occupy core positions of octahedral or trigonal prismatic polyhedra can probably be accounted for by using radius ratio arguments—the larger the polyhedron, the less likely it is that the carbon atom can maintain bonding contact with all of its neighbors. The hole in a metal icosahedron, for example, is big enough to accommodate an atom virtually the same size as those forming the icosahedron. Radius ratio arguments also explain why core atoms are not found in carborane polyhedra, the holes in which are too small to accommodate most atoms.

Although, in these metal carbonyl carbides, the core carbon atom, as we have seen, can stabilize only four of the metal skeletal bonding MO's, this nevertheless confers much greater stability on these clusters than their counterparts with no core atom, and hints at the strengthening effect that interstitial carbon atoms can have on metals. For example, whereas rhodium carbonyl clusters are usually degraded under high pressures of carbon monoxide and hydrogen, those incorporating a core carbon atom like $[Rh_6(CO)_{15}C]^{2-}$,[24] {or indeed incorporating other main group atoms, as in $[Rh_9(CO)_{21}P]^{2-}$,[85] $[Rh_{10}(CO)_{22}P]^{3-}$,[86] or $[Rh_{10}(CO)_{22}As]^{3-}$ [87]} resist such degradation. Encapsulated carbon atoms can stabilize paramagnetic clusters such as $[Co_6(CO)_{14}C]^{-}$,[88] $[Co_{13}(CO)_{24}C_2]^{4-}$,[89] and $[Rh_{12}(CO)_{23}C_2]^{3-}$,[90] while the tetranuclear osmium cluster, $[Os_{10}(CO)_{24}C]^{2-}$, with an octahedral Os_6 arrangement about the central carbon atom, resists degradation by carbon monoxide even at 250 °C and 1500-atm. pressure, conditions that usually generate low nuclearity species.[91]

An increasing number of metal carbonyl clusters containing two "carbide" carbon atoms embedded in the cluster is being discovered and structurally characterized, two of which, $[Co_{13}(CO)_{24}C_2]^{4-}$ [89] and $[Rh_{12}(CO)_{23}C_2]^{3-}$,[90] were just cited. Such compounds fall into two categories: species in which the carbon atoms separately occupy distinct sites, far enough apart to suggest that there is negligible carbon–carbon bonding; and species that are best regarded as acetylides, in which the carbon atoms, separated typically by a distance rather longer than a normal carbon–carbon triple bond distance (1.21 Å), nevertheless are clearly bonded strongly to each other. Such C_2 units necessarily require larger cavities in the metal polyhedron than do individual carbon atoms, so typically are found in higher

TABLE 4.2. Formulas and Hypercarbon Environments of Some Representative Metal Carbonyl Carbide Clusters

Coordination Number	Coordination Atoms	Shape	Examples[a]
4	Fe_4	Butterfly	$Fe_4(CO)_{13}C$ (75)
5	Fe_5, Os_5	Square pyramidal	$Fe_5(CO)_{15}C$ (76); $Os_5(CO)_{15}C$ (77)
5	Os_5	Capped square pyramidal	$Os_6(CO)_{16}C_2Me_2C$ (92); $[Os_6(CO)_{16}C]^{2-}$; $Os_6(CO)_{17}C$ (93)
6	Ru_6	Octahedral	$Ru_6(CO)_{17}C$ (23)
6	Fe_6, Ru_6	Octahedral	$[Fe_6(CO)_{16}C]^{2-}$; $[Ru_6(CO)_{16}C]^{2-}$ (94,95)
6	Co_6, Rh_6	Octahedral	$[Co_6(CO)_{14}C]^{-}$ (88); $[Rh_6(CO)_{13}C]^{2-}$ (79)
6	Fe_5M	Octahedral	$[Fe_5M(CO)_{17}C]^{2-}$ (M=Cr,Mo,W) (22,96,97)
6	Fe_5M	Octahedral	$[Fe_5M(CO)_{16}C]^{-}$ (M=Rh,Ir) (22,96)
6	Fe_5M	Octahedral	$[Fe_5M(CO)_{15}C]^{2-}$; $Fe_5M(CO)_{16}C$ (M=Ni,Pd,Pt) (22,96)
6	Fe_5M	Octahedral	$[Fe_5Cu(CO)_{14}(NCMe)C]^{-}$ (22,96)
6	Fe_4M_2	Octahedral	$[Fe_4Mo_2(CO)_{18}C]^{2-}$; $[Fe_4Ni_2(CO)_{14}C]^{2-}$ (22,96)
6	Re_6	Capped octahedral	$[Re_7(CO)_{21}C]^{3-}$ (98)
6	Os_6, Re_6	Bicapped octahedral	$Os_8(CO)_{21}C$ (91); $[Re_8(CO)_{24}C]^{2-}$ (98)
6	Os_6	Tetracapped octahedral	$[Os_{10}(CO)_{24}C]^{2-}$ (80,91,93)
6	Co_6, Rh_6	Trigonal prism	$[M_6(CO)_{15}C]^{2-}$ (M=Co,Rh) (21,22,89)
6	Co_6	Trigonal prism	$Co_6(CO_{12}S_2C)$ (100)
6	Co_2Rh_4	Trigonal prism	$[Co_2Rh_4(CO)_{15}C]^{2-}$ (99)
6	Co_6	Trigonal prism	$[Co_{13}(CO)_{24}C_2]^{4-}$ (89,101,102)
6	Rh_6	Trigonal prism	$[Rh_{12}(CO)_{23}C_2]^{3-}$ (90)
6	Os_6	Trigonal prism	$[Os_{11}(CO)_{27}C]^{2-}$ (91)
6	Rh_6	Capped trigonal prism	$Rh_8(CO)_{19}C$ (22,25,99)
6	Rh_6	Capped trigonal prism	$Rh_6Cu_2(CO)_{15}(NCMe)_2C$ (22,103)
8	Co_8	Dodecahedron	$[Co_8(CO)_{18}C]^{2-}$ (21,25)
8	Ni_8	Tetragonal antiprism	$[Ni_8(CO)_{16}C]^{2-}$ (104)
8	Ni_8	Capped square antiprism	$[Ni_9(CO)_{17}C]^{2-}$ (104)
8	Ni_8	Tetracapped square antiprism	$[Ni_9Co_3(CO)_{20}C]^{3-}$ (104)

[a]References are in parentheses.

nuclearity metal cluster polyhedra. Representative examples are included in Table 4.2.[92–104]

4.6. CONCLUSIONS

In this chapter and the previous one we have surveyed the circumstances in which carbon atoms can participate in cluster formation by forming polyhedral aggregates with metal and/or boron atoms, or by incorporation within metal polyhedra. The compounds considered have included coordination complexes in which coordinatively unsaturated metal residues interact with the π-bonding electrons of unsaturated organic ligands, either activating or stabilizing them. They have also included species in which carbyne units, CR, bond simultaneously to as many as five metal and/or boron atoms, and species in which bare carbon atoms are accommodated in octahedral, trigonal prismatic, or dodecahedral holes in metal polyhedra. Such systems are members of the wider family of cluster compounds that have seen striking developments over the past decade or so, and are of special importance both as models for the type of fragmentation that small organic molecules can undergo when interacting with metal surfaces, and as potential catalyst systems in their own right. Although it is beyond the scope of this book to illustrate and survey further the many other fascinating facets of cluster chemistry that recent work has opened up, it is hoped that this brief discussion will have shown what structural and bonding possibilities are available to carbon atoms in cluster systems when electrons are in relatively short supply. They also further demonstrate the increasing significance of hypercarbon containing systems in chemistry.

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chapter 5

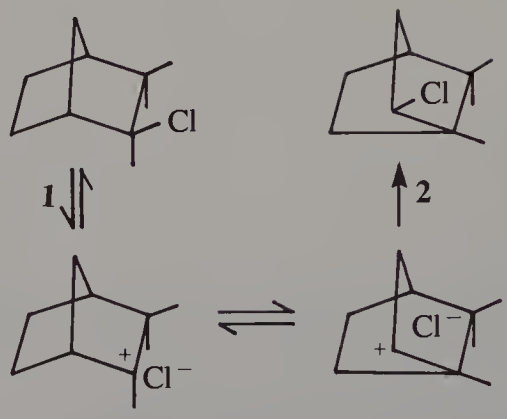
HYPERCOORDINATE CARBOCATIONS

5.1. GENERAL CONCEPT OF CARBOCATIONS: CARBENIUM VERSUS CARBONIUM IONS

At the turn of the century, the pioneering work by Norris, Kehrmann, Gomberg, Baeyer, and others on triarylcarbenium ions, Ar_3C^+, first generated interest in positively charged carbon compounds.[1] It was at the time assumed that these ions generated the color in triarylmethyl systems noted for their significance in certain dyestuffs. However, the idea that carbocations might be intermediates in the course of organic reactions that start from nonionic reactants and lead to nonionic covalent products laid dormant for nearly another quarter of a century.

It was Meerwein and Van Emster[2] who, in 1922, while studying the kinetics of the rearrangement of camphene hydrochloride, **1**, to isobornyl chloride, **2**, noticed that the reaction rate increased in a general way with the dielectric constant of the solvent. Further, he found that metallic chlorides such as $SbCl_5$, $SnCl_4$, $FeCl_3$, $AlCl_3$, and $SbCl_3$ (but not BCl_3 or $SiCl_4$), as well as dry HCl (all of which promote the ionization of triphenylmethyl chloride by the formation of ionized complexes), also considerably accelerate the rearrangement of camphene hydrochloride. Meerwein concluded that the conversion of camphene hydrochloride to isobornyl chloride actually does not proceed by way of migration of the chlorine *atom*, but by a rearrangement of a cationic intermediate. Thus, the modern concept of carbocation intermediates was born.

With the exception of the early isolation of the highly stabilized triarylmethyl cation salts, carbocation chemistry[1,3–5] grew to maturity through kinetic,



stereochemical, and product studies of a wide variety of reactions, especially unimolecular nucleophilic substitutions and eliminations. Besides Meerwein, leading investigators like Ingold, Hughes, Whitmore, Bartlett, Nenitzescu, Winstein, and others have made fundamental contributions to the development of modern carbocation theory and the concept of electron-deficient cationic intermediates.[3] Direct observation of stable, long-lived carbocations, generally in highly acidic (superacid) solvent systems, became possible only in the early 1960s.[4,5] By observing them as long-lived species, it became increasingly apparent that carbocations were of broader scope and more widely involved in organic reactions than had previously been recognized. This necessitated a general definition. Such a definition was offered by Olah,[6] which recognized that carbocations, the positive ions of carbon compounds (named in accordance to the related anions called carbanions) may be considered to belong to two distinct, limiting classes.

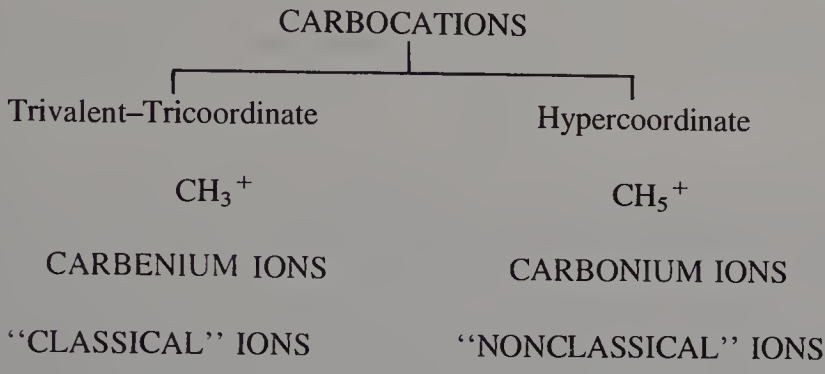
5.1.1. Trivalent–Tricoordinate (Classical) Carbenium Ions

This is the class of carbocations that contain an sp^2-hybridized electron-deficient carbocation center, which tends to be planar in the absence of constraining skeletal rigidity or steric interference. The carbenium carbon contains six valence electrons and the structure of the carbocation can always be adequately described using only two-center, two-electron bonds [(2*c*–2*e*) bonds; Lewis valence bond structures]. The methyl cation or methenium ion (CH_3^+) may be considered the parent of the trivalent carbocations. The trivalent carbocations are also referred to as classical ions.

5.1.2. Hypercoordinate (Nonclassical) Carbonium Ions

This second class of carbocations contains one or more hypercoordinate carbon atoms. These hypercarbons are normally coordinated to five or more atoms within reasonable bonding distance. Hypercoordinate or nonclassical carbocations cannot be described by (2*c*–2*e*) single bonds alone, but necessitate the involvement of three- (or multi-) center, two-electron bonds [e.g., (3*c*–2*e*) bonds]. Each hypercarbon in the cation is always associated with eight electrons, although the ion, overall, is electron

deficient. The methonium ion (CH_5^+) may be considered the parent of the hypercoordinate carbocations.

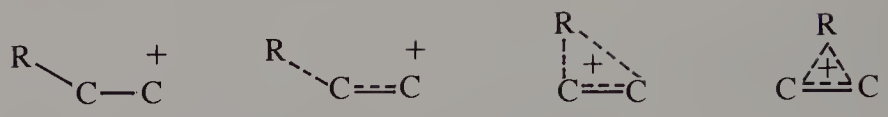


In the English chemical literature, a long period of common usage named the trivalent planar ions of the CH_3^+ type (the only ions known initially) as carbonium ions. If the name is considered analogous to other onium ions (ammonium, sulfonium, phosphonium ions, etc.), then it should relate to the higher coordination state carbocations, that is, the nonclassical carbocations. The German and French literature have frequently used the term "carbenium ion" for the trigonal cations and if we consider these ions as protonated carbenes, the nomenclature is indeed correct and is in accord with IUPAC rules.[7a] The IUPAC Organic Chemistry Division recently reviewed the nomenclature for physical organic chemistry[7b] and recommended the general use of the term "carbocation" for naming all positive ions of carbon and also accepted the differentiation of trivalent carbenium ions from hypercoordinate carbonium ions.

The two classes of carbocations are not mutually exclusive but represent the limits of a spectrum of carbocations with various types and degrees of charge delocalization. The interaction of neighboring groups with the vacant *p*-orbital of a carbenium ion center can contribute to ion stability. This may involve the interaction of unshared electron pairs (*n* donors), bent σ bonds (as in cyclopropylcarbenium ions), π-electron systems (direct conjugative or allylic stabilization) as well as C−C and C−H bond interactions.

The interaction with proximal groups and bonds leads to a continuum of several possible kinds and degrees of delocalization. These (see the following illustration) range from one extreme, conjugation or hyperconjugation, where there is little change in the cation geometry, to partially bridged structures, in which there is significant but unequal bonding to a second atom, to the other extreme where strong symmetrical bridging occurs. Gradations of cation structure and properties are thus expected, although the extreme cases—trivalent (classical) and hypercoordinate (nonclassical) cations—are recognized as limiting.

For many years, a lively controversy centered over the actual existence of nonclassical carbocations.[8,9] The focus of argument was whether nonclassical cations, such as the norbornyl cation, are *bona fide* delocalized bridged intermediates



Open trivalent | **Hyperconjugation, but no bridging** | **Unsymmetrical bridging** | **Symmetrical bridging**

or merely transition states of rapidly equilibrating carbenium ions. Considerable experimental and theoretical effort has been directed towards resolving this problem and unequivocal experimental evidence, notably from solution and solid state ^{13}C NMR spectroscopy and ESCA has been obtained supporting the nonclassical carbocation structures that are now recognized as hypercoordinate ions (see the following section). In the context of our present discussion, only these ions will be reviewed.

5.2. METHODS OF GENERATING HYPERCOORDINATE CARBOCATIONS

The methods employed to generate trivalent classical carbocations work equally well in the preparation of nonclassical carbocations. The most commonly employed superacid systems are FSO_3H, $FSO_3H{:}SbF_5$, $HF{:}SbF_5$, or SbF_5 although other superacids have also been used. The most convenient low-nucleophilic solvent systems that are frequently used are SO_2, SO_2ClF, and SO_2F_2. To be able to study liquid ionic solutions at very low temperatures (about -160 °C) by NMR spectroscopy, Freons such as $CHCl_2F$ or CH_2F_2 may be used as cosolvents to decrease the viscosity of the solution.

$$R{-}X \xrightarrow[\substack{SO_2ClF \text{ or } SO_2 \\ \text{or } SO_2F_2}]{\text{superacid}} R^+Y^- \quad [Y^- = FSO_3^- \text{ or } SbF_5X^- \text{ or } SbF_5\,(FSO_3)^- \text{ or } SbF_6^-]$$

The success of preparing carbocations in superacids generally depends on the technique employed. For most of the stable systems, Olah's original method[10] of combining the precooled progenitor dissolved in an appropriate solvent system along with the superacid using a simple vortex stirrer to mix the components generally works adequately. However, care must be taken to avoid moisture and local heating. Low temperatures (e.g., -78 °C, using acetone/dry ice; or -120 °C using liquid N_2/ethanol slush) are most commonly employed to suppress side reactions such as dimerizations and oligomerizations.

More efficient mixing methods for the generation of reactive carbocations have been developed, most notably by Ahlberg and co-worker[11,12] and Saunders et al.[13] The former group describes an ion generation apparatus consisting of a Schlenk tube

attached to an NMR tube in which the carbocation is prepared in a low temperature unit.

Saunders' method involves the codeposition of streams (molecular beams) of the starting reagents from the gas phase on a surface cooled to liquid nitrogen temperature to produce stable solutions of carbocations.[13,14] Myhre and Yannoni[15] used it to generate carbocations in an SbF_5 matrix at a very low temperature for solid state ^{13}C NMR spectroscopic studies.

5.3. METHODS USED TO STUDY HYPERCOORDINATE CARBOCATIONS

Various spectroscopic techniques have been applied to the characterization of carbocations as stable ions in solution and in the solid state. The techniques that have found most application in the study of hypercoordinate carbocations are those that are capable of distinguishing cations undergoing rapid degenerate rearrangements from stable delocalized species. In recent years, theoretical studies have become particularly useful in the study of hypercoordinate carbocations whose energies can be calculated as a function of molecular geometries.

5.3.1. Nuclear Magnetic Resonance Spectroscopy in Solution

One of the most powerful tool in the study of carbocations is nuclear magnetic resonance (NMR) spectroscopy. This method yields direct information about the cation's structure through chemical shift values, coupling constants, and the temperature dependence of line shapes.

Early observations of stable carbocations in solution relied heavily upon ^1H NMR spectroscopy. Subsequently, ^{13}C NMR spectroscopy has proved to be an even more useful technique.[5] ^{13}C NMR permits the direct observation of the cationic center and the observed chemical shifts and coupling constants can be correlated to the cation geometry and hybridization.

Degenerate rearrangements of carbocations, if they are fast enough, result in temperature-dependent NMR spectra. At slow exchange rates, the signals of the exchanging nuclei show up as separate absorptions. If the exchange rate is gradually increased by raising the temperature, the signals first broaden and eventually coalesce. A further increase of the exchange rate with increasing temperatures results in a sharpening of the broad coalesced signals (Fig. 5.1).

The equations in Figure 5.1*c* show that the larger the shift difference (ν_{AB}) between the exchanging signals, the larger the rate constant, k, needed to get coalescence at a specific temperature. Thus, since chemical shift differences in ^{13}C NMR spectra are usually much larger (in Hertz) than in ^1H NMR spectra, ^{13}C NMR spectroscopy permits the quantitative study of faster processes than can be investigated by ^1H NMR spectroscopy.

With high sensitivity, high resolution superconducting NMR spectrometers, rate

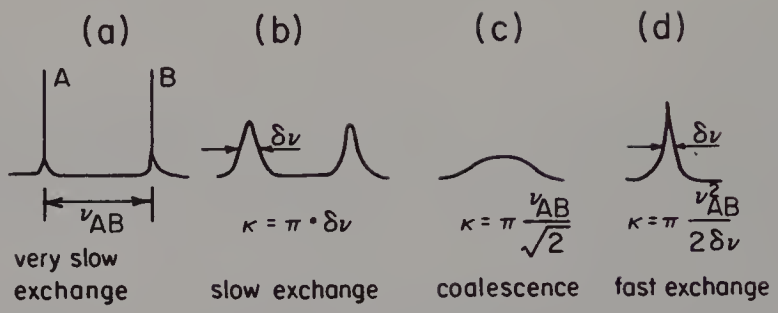


Figure 5.1. Results in the NMR spectrum of exchange of two equally populated sites at different rates. The rate constants (k) for the exchange at the conditions (b), (c) and (d) could be approximately estimated using the shown formulas and corrected values of $\delta\nu$.

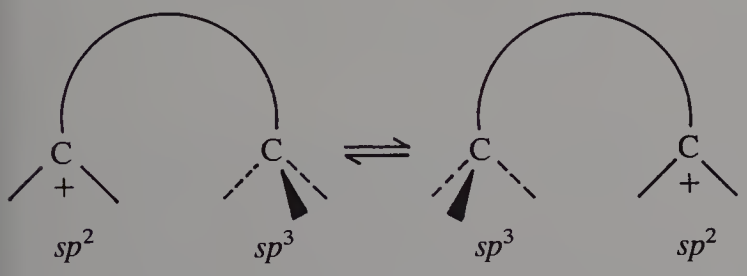
constants of degenerate rearrangement of the order of 10^7 s^{-1} may be determined. This corresponds to a process with a free energy of activation of $\leqslant 3.3$ kcal mol^{-1} at -160 °C.[16]

Very slow exchange can be detected and the rate measured by the transfer of spin saturation technique, a tool that can be useful in the elucidation of reaction mechanisms causing exchange. One of the signals participating in very slow exchange is saturated by an external rf field while the rest of the spectrum is observed. If exchange of the spin-saturated nuclei takes place at a rate comparable to that of the nuclear-spin relaxation time (T_1), then transfer of the spin saturation by the degenerate reaction will partially saturate the other exchanging nuclei. From the degree of transferred spin saturation and measured T_1, the rate of exchange can be evaluated. This technique was devised by Forsen and Hoffmann[17,18] using ^{1}H NMR spectroscopy and has found use in the study of carbocations. The method has some limitations with ^{1}H NMR spectra due to the small shift differences and large couplings between the protons. However, the method has recently been applied using ^{13}C NMR spectroscopy (proton decoupled) to complex carbocation rearrangements.[19]

The tricoordinate carbons in carbenium ions typically exhibit ^{13}C chemical shift values in the range 330–340-ppm deshielded from TMS[5] and the presence of substituents capable of delocalizing charge moves the resonance to a somewhat higher field. In contrast, the hypercoordinate carbons in nonclassical carbonium ions are more highly shielded and their chemical shift values are found at a much higher field. Typically, the highly coordinated carbons in the nonclassical cations so far observed are between $+30$ and -30 ppm from TMS (in many cases to a higher field than the corresponding sp^3 carbons in their neutral precursors). Thus, the ranges of the relevant ^{13}C NMR chemical shift values of the trivalent carbenium ions and the hypercoordinate carbonium ions are mutually exclusive and the substantial differences between the chemical shift values of the trigonal and the hypercoordinate carbons usually permit their differentiation.

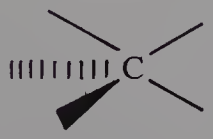
If a nucleus exchanges its environment at a sufficiently fast rate, a spectrum with averaged NMR parameters, for example, shifts and coupling constants, is obtained.

The difference between the chemical shift value of the hypercarbons in a static nonclassical carbocation and the relevant ^{13}C chemical shift values of equilibrating classical forms allows their structural differentiation. In the NMR spectrum of a rapidly equilibrating classical cation the observed chemical shift must be the linear average of the shift of an sp^2 carbenium carbon center (about 330 ppm) and a neutral (sp^3) carbon center (about 30 ppm). The average chemical shift (about 180 ppm) is still a highly deshielded chemical shift value compared to those in ions containing hypercarbon atoms.



Equilibrating trivalent carbocationic centers

$\delta^{13}C \sim 330$ $\delta^{13}C \sim 30$ $\delta^{13}C \sim 30$ $\delta^{13}C \sim 330$ Average $\delta^{13}C \sim 180$



Hypercoordinate Carbocation

$\delta^{13}C \simeq -30$ to $+30$

5.3.2. ^{13}C NMR Chemical Shift Additivity

An empirical criterion based on additivity of ^{13}C NMR chemical shifts for distinguishing classical trivalent from nonclassical hypercoordinate carbocations has been developed.[20] This technique involves comparing the sums of the chemical shift values of carbocations with their respective hydrocarbon precursors. Trivalent carbocations generally yield ^{13}C chemical shift values that when totaled give a numerical value at least 350 ppm greater than the totals for the corresponding neutral hydrocarbons. This difference can be partly rationalized by the hybridization change from sp^3 to sp^2 and to the deshielding influence of the unit positive charge.

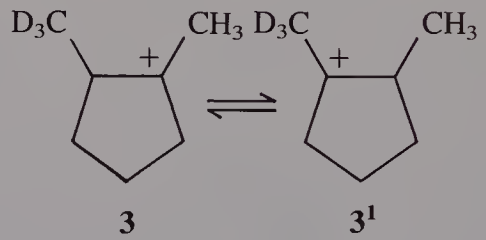
The hypercoordinate (nonclassical) carbocations have penta- and hexacoordinated carbons and the sum totals of the chemical shift values of such ions, relative to their neutral hydrocarbons, are much smaller. The difference is generally < 200 ppm.

5.3.3. Isotopic Perturbation Studies

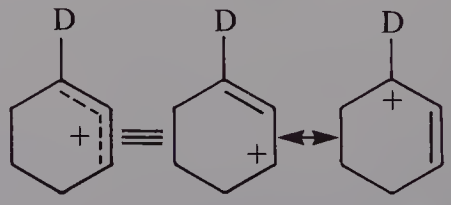
The deuterium isotopic perturbation technique developed by Saunders et al.[21a,22] is capable of providing a convenient means to differentiate between rapidly

equilibrating classical trivalent cations and nonclassical carbocations containing hypercarbons.

Saunders and Vogel discovered, in 1971,[21a,22b] that by asymmetrically introducing deuterium into some carbocations that were known to undergo degenerate, very rapid, and reversible rearrangement processes, large splittings were produced in their NMR spectra. Although the ions were interconverting extremely rapidly and still gave averaged spectra, the presence of the isotope made the energies of the two interconverting species slightly different and thus the equilibrium constant between them was no longer unity. Each ion, therefore, spent a little more time on one side of the equilibrium barrier than on the other side, as a function of the temperature. The weighted-average peaks of the two carbon atoms that were interchanging by the rearrangement process thus no longer coincided. In the case of classical equilibrating cations (see **3** and **3′**), splitting values in the ^{13}C NMR spectrum of over 100 ppm were observed as a result of perturbation by deuterium.[23]



3 **3¹**



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However, when deuterium was introduced into single minimum, nonequilibrating species[24] such as the cyclohexenyl cation, **4**, (an allylic cation with allylic resonance) no large splittings were observed. Unlike the behavior of the equilibrating systems, there were no observable changes in the spectra of **4** with temperature. In fact, the isotope-induced changes in the spectrum were not very different from changes that occur in any simple molecule upon introducing deuterium, and were roughly only 2% of the effects detected in the equilibrating systems.

These observations led to the method of observing changes in NMR spectra produced by asymmetric introduction of isotopes (isotopic perturbation) as a means of distinguishing between systems involving equilibrating species passing rapidly over a low energy barrier, from molecules a with single energy minimum, intermediate between the presumed equilibrating structures. Application of this method for individual hypercoordinate carbocations will be discussed later. This method also allows accurate determination of equilibrium isotope effects.

5.3.4. Solid State ^{13}C NMR at Low Temperatures

The use of magic-angle spinning and cross polarization techniques has enabled high resolution ^{13}C NMR spectra to be obtained in the solid state. Yannoni and Myhre obtained solid state NMR spectra of frozen carbocation solutions at very low temperatures,[15,25] as low as 5 K. At such low temperatures, facile rearrangements and most molecular motions are suppressed, which in turn simplifies the interpretation of the spectral data. This technique should be able to distinguish readily between a rapidly equilibrating pair of two classical cations and a static symmetrically bridged species. Indeed, this method has recently been employed to establish the σ-bridged nature of the 2-norbornyl cation.[25]

5.3.5. Tool of Increasing Electron Demand

The nature of electronic effects in cationic reactions has been probed by application of the Gassman–Fentiman tool of increasing electron demand.[26] An aryl substituted cationic center can be made more electron demanding, that is, electrophilic, by introduction of electron-withdrawing substituents onto the aryl ring.

When a cationic center becomes sufficiently electrophilic, it may draw on electrons from neighboring π and σ bonds and thus delocalize the positive charge. The onset of participation of π and σ bonds can be detected as a departure from linearity in a Hammett type plot as the electron-withdrawing ability of the aryl substituent increases.

In stable ion studies, ^{13}C NMR chemical shifts are generally used as a structural probe reflecting the charge density at the cation center. In closely related homologous cations other factors that may affect chemical shift may be assumed constant.

The tool of increasing electron demand has proved useful in detecting the onset of π or σ delocalization under stable-ion conditions in a number of carbocationic systems. It is, however, a coarse technique to probe nonclassical ions since the aryl group can still delocalize charge into its π-aromatic system even with strongly electron-withdrawing substituents. Only in cases where neighboring σ bonds can effectively compete with the aryl ring in stabilizing the cationic center may significant deviations from linearity be observed in the Hammet-type plots. Furthermore, the "tool" is obviously not selective in differentiating between π and σ participation.

5.3.6. Electron Spectroscopy for Chemical Analysis (ESCA)

X-ray photoelectron spectroscopy measures the energy distribution of the electrons emitted from a compound on irradiation with x rays.[27] The electron binding energy (E_b), is a function of the chemical environment of the atom. In particular, the atomic charge on carbon can be directly correlated to the carbon 1*s* electron binding energy.[28] The cationic center of a classical carbocation, for example, *t*-butyl cation has a carbon 1*s* E_b approximately 4-eV higher than a neutral sp^3 carbon atom.[28] Electron deficiencies of different degrees in different carbocations give different

carbon core electron 1*s* binding energy differences, that is, the delocalization of charge from a cationic center lowers the carbon 1*s* binding energy.

In principle, ESCA is the most definitive technique applied to differentiate between nonclassical carbocations and equilibrating classical species. The time scale of the measured ionization process is of the order of 10^{-16} s so that definite species are characterized regardless of inherently slower intra- and intermolecular exchange reactions, for example, hydride shifts, Wagner–Meerwein rearrangements, proton exchange, and so on.

5.3.7. Low Temperature Solution Calorimetry

In a series of investigations, Arnett and co-workers[29,30] have determined heats of ionization (ΔH_i) of secondary and tertiary chlorides and alcohols in SbF_5/SO_2ClF solutions, respectively, at low temperatures. They have also measured heats of isomerizations of secondary to tertiary carbocations in superacid media. These measured thermochemical data have been extremely useful in determining the intrinsic thermodynamic stabilities of tertiary and secondary carbocations.

5.3.8. Quantum Mechanical Calculations

One of the main aims of quantum mechanical methods is the calculation of energies of molecules as a function of their geometries. This requires the generation of potential energy hypersurfaces. If these surfaces can be calculated with sufficient accuracy they may be employed to predict equilibrium geometries of molecules, relative energies of isomers, the rates of their interconversions, and other properties. Carbocations are ideally suited for calculations since relative energies of well-defined structural isomers are not easily determined experimentally. It should always be kept in mind that theoretical calculations refer to isolated ion structures in the gas phase.

Over the years, several computational methods have been developed. The variational theory can be used either without using experimental data other than the fundamental constants (i.e., *ab initio* methods) or by using empirical data to reduce the amount of numerical work (i.e., semiempirical data methods). There are various levels of sophistication in both *ab initio* and semiempirical methods. In the ab initio methods, various kinds of basis sets can be employed, while in the semiempirical methods, different choices of empirical parameters and parametric functions exist. The reader is referred to reviews on the subject.[3a,21b]

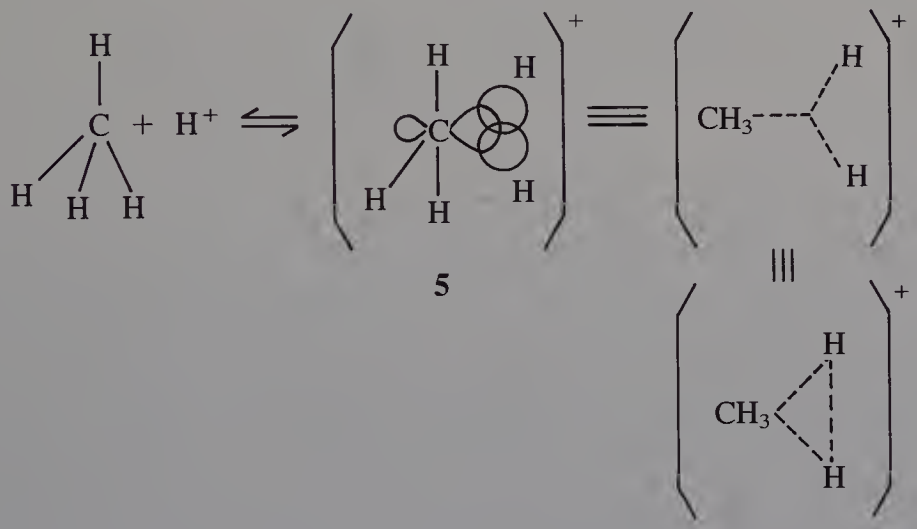
5.4. LONG-LIVED HYPERCOORDINATE (NONCLASSICAL) CARBOCATIONS

5.4.1. Alkonium Ions Incorporating Bridging Hydrogens (Protonated Alkanes, $C_nH_{2n+3}^+$)

The pioneering work of Meerwein, Ingold, and Whitmore[2,3] demonstrated that trivalent alkyl cations ($C_nH_{2n+1}^+$) play an important role in the acid catalyzed

transformations of hydrocarbons as well as various electrophilic and Friedel–Crafts type reactions. These trivalent alkyl cations are formed by the ionization of precursors (*n* bases) containing nonbonded electron pairs such as alkyl halides, alcohols, thiols, and so on, or by protonation of olefins.

Over 40 years later it was found that protonated alkanes ($C_nH_{2n+3}^+$) also play a significant role in many alkane reactions. Saturated hydrocarbons can be protonated to alkonium ions of which the methonium ion (CH_5^+), **5**, may be considered the parent. The formation of these pentacoordinate carbocations involves the conversion of (2*c*–2e) CH bonds into (3*c*–2*e*) CH_2 bonds. (As described, the triangular dotted lines depict in a simplified way the electron pair occupying the bonding orbitals of three atoms, that is, the three-centered, two-electron bond. The junction of the dotted lines does not represent an additional atom).



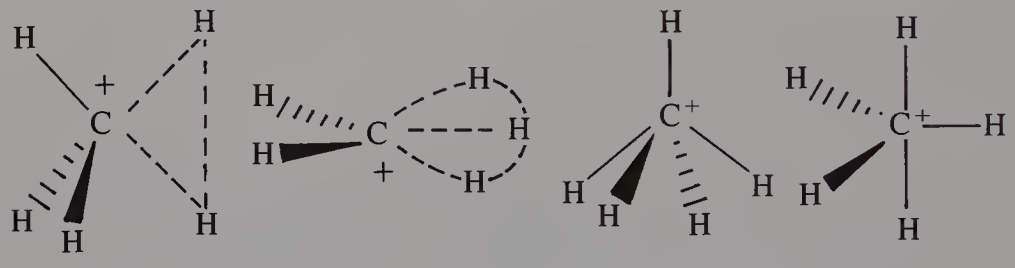
5

5.4.1.1. The Methonium Ion (CH_5^+). The existence of the methonium ion (CH_5^+), **5**, was first indicated by mass spectrometric studies[31a] of methane at relatively high source pressures as resulting from the molecule-ion reaction between a neutral CH_4 molecule and a proton. Some of the chemistry of methane and the homologous alkanes, for example, hydrogen–deuterium exchange and varied electrophilic substitutions in superacidic media indicated that alkonium ions were involved in their condensed state chemistry. Isotope exchange and collisional association in the reactions of CH_3^+ and its deuterated analogs with H_2, HD, and D_2 have also been studied mass spectrometrically using the variable temperature selected ion flow method.[31b] The energy of dissociation of CH_5^+ to CH_3^+ and H_2 is known experimentally to be 40 kcal mol^{-1} [31d] and calculated as 34.5 kcal mol^{-1} by *ab initio* MO theory (MP3/6.31G* + ZPE).[31d]

Direct spectroscopic observation of CH_5^+, **5**, in the condensed state is difficult as the concentration of the ion, even in superacidic media, under any condition is extremely low. However, when matrices of superacids such as FSO_3H/SbF_5 or HF/SbF_5 saturated with methane were studied by ESCA[32] at −180 °C the observed ESCA shift, although differing by less than 1 eV from that of methane was considered

to be due to CH_5^+ (neutral methane has practically no solubility in the superacids at the low temperature of the experiment and at the high vacuum applied, that is, 10^{-9} torr, neutral methane would be pumped out of the system in any event). The relatively low 1*s* carbon binding energy in CH_5^+ is in good accord with theoretical calculations,[33] indicating that the positive charge is spread over the hydrogen atoms leaving the five-coordinate carbon with relatively little positive charge.

Of the possible structures for the methonium ion, **5**, for example, D_{3h}, C_{4v}, C_s, or C_{2v} symmetries, Olah, Klopman, and Schlosberg[33] expressed a preference for the C_s front side protonated configuration.



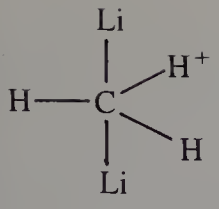
C_s C_{2v} C_{4v} D_{3h}

Preference for this form was based on consideration of the observed chemistry of methane in superacids, hydrogen–deuterium exchange, and polycondensation reactions, which reflect the ease with which CH_5^+ cleaves into CH_3^+ and H_2, as well as self-consistent field (SCF) calculations.[33] More extensive theoretical methods including *ab initio* calculations[31d,34] utilizing an "all geometry" parameter search, also favor the C_s symmetry. This structure is about 3.7 kcal mol^{-1} more stable than the structures of C_{4v} symmetry and about 11.7 kcal mol^{-1} more stable than the trigonal bipyramidal D_{3h} configuration. Interconversion of stereoisomeric forms is obviously possible by a pseudorotation process. Muetterties suggested[34e] that stereoisomerization processes of this type, in pentacoordinated compounds, be termed "polytopal rearrangements." However, it is preferable to call intramolecular carbonium ion rearrangements "bond to bond" rearrangements since these are not limited to equivalent bonds in the case of the higher homologs of CH_5^+.

Recently, the shapes of several lithiated analogs of CH_5^+, **5**, such as structures **6** and **7** have been calculated by *ab initio* methods by Schleyer and co-workers.[35,36] $CH_3Li_2^+$ and CLi_5^+ have been observed by mass spectrometry.[37]

Quantum mechanical calculations have also been performed on diprotonated methane (CH_6^{2+}) **8**,[38] and a C_{2v} structure with two stabilizing (3*c*–2*e*) interactions is found to lie at a minimum on the potential energy surface. Similar calculations have been carried out for CLi_6^{2+}, **9**, for which an octahedral structure is preferred.[35]

5.4.1.2. The Ethonium Ion ($C_2H_7^+$). The next higher alkonium ion, the ethonium ion (protonated ethane) $C_2H_7^+$, **10** or **10′**, is analogous to its parent CH_5^+ ion. Protonation of ethane can take place either at a C–H bond or the C–C bond and interconversion of the resulting ions would be a facile process. Gas phase experimental studies by Hiroaka and Kebarle[31c] have shown the existence of isomeric



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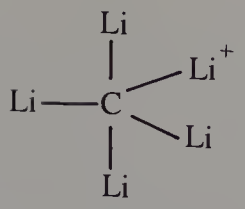

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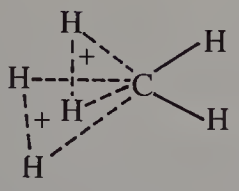

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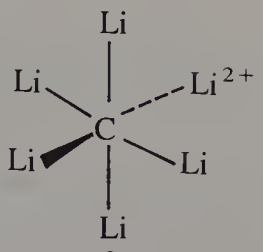
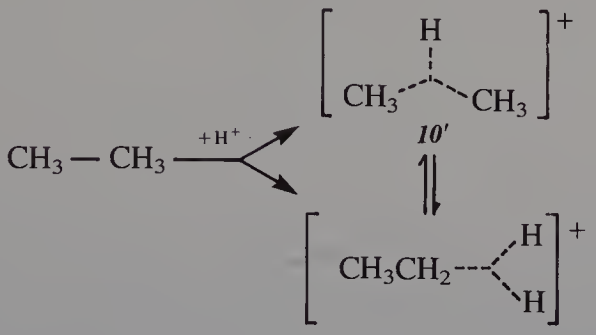


9

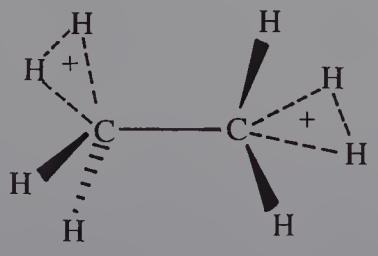
$C_2H_7^+$ cations with an energy difference of 7–8 kcal mol^{-1}. Based on high level *ab initio* theory,[31d] the C–C protonated form **10′** is preferred over the C–H protonated form **10** by about 18.4 kcal mol^{-1}.



10

Such a protonation process would be consistent with the observed H–D exchange in labeled systems as well as the formation of methane as a by-product in the protolytic cleavage of ethane in superacids.[33]

The structure of the diprotonated ethane dication, $C_2H_8^{2+}$, **11**, has been considered theoretically[38a] and the preferred structure incorporates two pentacoordinate carbons and an unprotonated C–C bond.



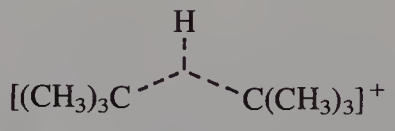
11

5.4.1.3. Higher Alkonium Ions. The higher homologous alkonium ions, for example, $C_3H_9^+$ and $C_4H_{11}^+$, and so on, have been observed in the gas phase by high pressure mass spectrometry.[31] In solution, the higher hydrocarbons show an increasing tendency to form C–H–C three-center, two-electron bonds on protonation as evidenced by the increasing tendency to form products rationalized by subsequent C–C bond cleavage.

The acid induced H–D exchange of isobutane, **12**, in deuterosulfuric acid was studied by Otvos and co-workers.[39] All nine methyl hydrogens are readily exchanged, but not the methine hydrogen. The mechanism for this observation must involve the initial formation of the trivalent *t*-butyl cation, **13**, probably in an oxidative ionization step. The *t*-butyl cation, **13**, might then undergo reversible deprotonation—protonation involving isobutylene, **14**, accounting for the exchange of the methyl hydrogens with the deuterosulfuric acid.

$$(CH_3)_3CH \longrightarrow (CH_3)_3C^+ \xrightarrow{-H^+} (CH_3)_2C{=}CH_2 \xrightarrow{+D^+} (CH_3)_2\overset{+}{C}{-}CH_2D \quad \text{etc.}$$

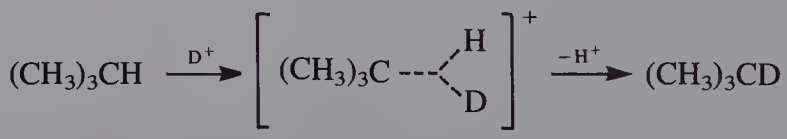
12 **13** **14**



15

The *t*-butyl cation, **13**, reforms isobutane by hydride abstraction from isobutane involving the tertiary C–H bond only, through intermediate structure **15**, and thus no methine hydrogens would exchange with the deuterosulfuric acid.

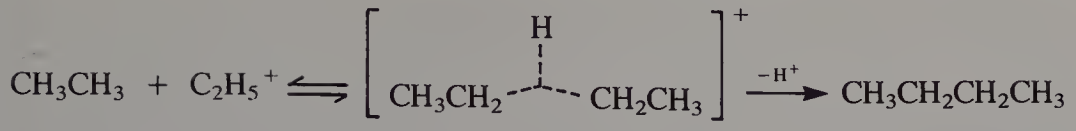
In contrast, Olah et al.[40] showed that in superacidic media, for example, FSO_3D/SbF_5 or DF/SbF_5, and at low temperatures, only the methine hydrogen is exchanged (with the acid) indicating that no deprotonation–reprotonation equilibria involving species such as **13** and **14** are involved in the strong superacid medium. In fact, the latter reaction necessarily proceeds through the intermediary of protonated isobutane, **16**.



16

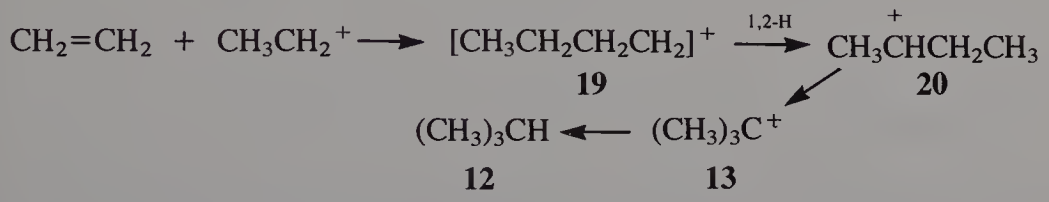
Clear evidence for a C–C protonated $C_4H_{11}^+$ ion, **17** (which would resemble **15**), has been obtained by Siskin and co-workers.[41] while studying the HF/TaF_5 catalyzed ethylation of excess ethane with ethylene in a flow system. *n*-Butane was obtained as the only product; no isobutane was detected. This remarkable result can be explained by C–H bond ethylation of ethane by the ethyl cation thus producing the hypercoordinate carbocation intermediate, **17**, which subsequently, by proton elimination, yields *n*-butane, **18**.

The use of a flow system that limits the contact of the product, *n*-butane, **18**, with the acid catalyst is essential. Prolonged contact causes isomerization of *n*-butane to isobutane to occur (see Chapter 7).



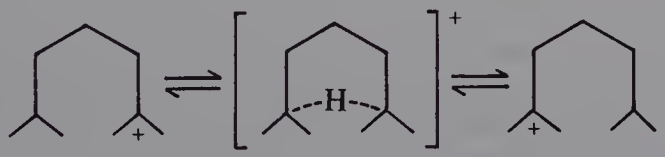
17 18

If the reaction instead involved initial ethylation of ethylene giving the trivalent 1-butyl cation, **19**, as an intermediate, then rearrangement via 1,2-hydrogen shifts would inevitably produce the 2-butyl cation, **20**, which in turn would isomerize into the *t*-butyl cation, **13**, and ultimately produce isobutane, **12**.



19 20 12 13

5.4.1.4. Hydrogen-Bridged Cycloalkonium Ions. The early studies of Prelog et al.[42] and Cope et al.[43] clearly established that medium sized cycloalkyl rings, for example, C_8 to C_{11}, undergo transannular hydride shifts in reactions involving electrophilic intermediates. Saunders and co-workers[44] have examined the 2,6-dimethylheptyl cation, **21**, and even at the lowest temperature studied (about -100 °C) the ion exhibits a single average peak for the four methyl groups implying the ease 1,5-hydride shifts occurring with an activation energy barrier of 5 kcal mol^{-1} or less. Alternatively, the ion could have a symmetrical hydrogen-bridged ground-state structure such as **22**.



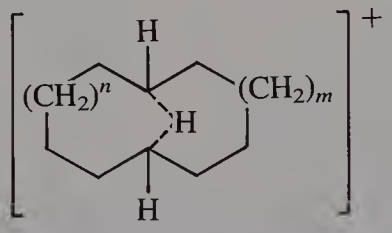
21 22

Sorensen and co-workers[45] showed that at -100 °C the cyclodecyl cation, **23**, exists as a static 1,6- or 1,5-hydrogen-bridged structure, **24c** or **24e**. Similar behavior[46] was observed for the 1,6-dimethyl analog, **25**. The bridging hydrogen in ion **24c** is observed at an unusually high field, that is, $\delta^1H = -6.85$.

The stable hydrogen-bridged cycloalkyl cations, **24a**, **24b**, and **24d** with 8, 9, and 11 membered rings have subsequently been observed.[47] The bridging hydrogen was found to be increasingly more shielded in the ^1H NMR spectra as the ring size became greater. This trend indicates increased negative charge on the bridged hydrogen and conversely increased positive charge on the terminal hydrogens as the distance of separation between the bridged carbons is increased. The ^1H NMR chemical shifts of the terminal and bridging hydrogens of various hydrogen-bridged carbocations are shown in Table 5.1.

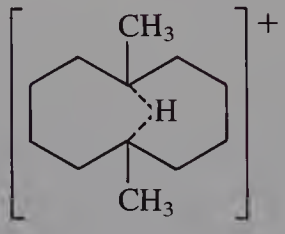
TABLE 5.1. δ^1H in Hydrogen-Bridged Carbocations

Cation Structure	H———C------H------C———H		
24a	+7.9	−7.7	+7.9
24b	+6.8	−6.6	+6.8
24c	+6.8	−6.85	+6.8
24d	+6.3	−6.0	+6.3
25	—	−3.9	—



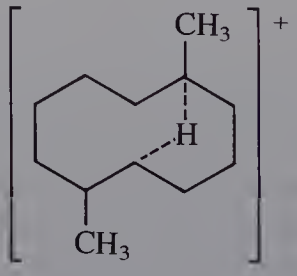
a $m = 0, n = 0$
b $m = 1, n = 0$
c $m = 1, n = 1$
d $m = 2, n = 1$ or $m = 3, n = 0$
e $m = 2, n = 0$

24



25

Sorensen and co-workers obtained evidence[48] for 1,5-μ-hydrogen bridging between secondary and tertiary carbon sites in a number of substituted cyclooctyl cations. The μ-1,5-bridged 1,5-dimethylcyclodecyl cation, **25a**, was obtained[49a] and studied as a distinct stable species.

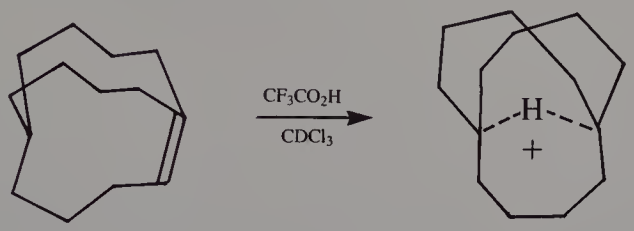


25a

Application of Saunder's isotopic perturbation technique[24] to ion **25** confirmed the bridged structure. With one trideuteromethyl group, an isotopic splitting of only 0.5

ppm is observed in the ^{13}C resonance of bridged carbon and this clearly supports the assigned hydrogen-bridged structure containing hypercoordinate carbon atoms.

Furthermore, McMurry and Hodge were successful[49b] in preparing an unique μ-hydrido bridged cation, **26**, in *in,out*-bicyclo[4.4.4]tetradecane. The intriguing hydrogen-bridged propellane cation **26** was obtained by protonating the bridgehead olefin in trifluoroacetic acid solution. The ion, **26**, was found remarkably stable in trifluoroacetic acid solution even at room temperature.

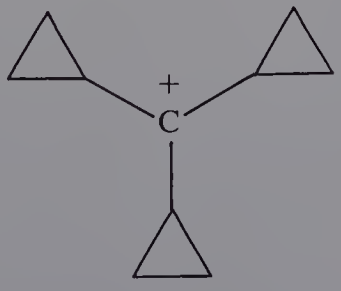


26

5.4.2. Hypercoordinate (Nonclassical) Carbocations Containing (3c–2e) CCC Bonds

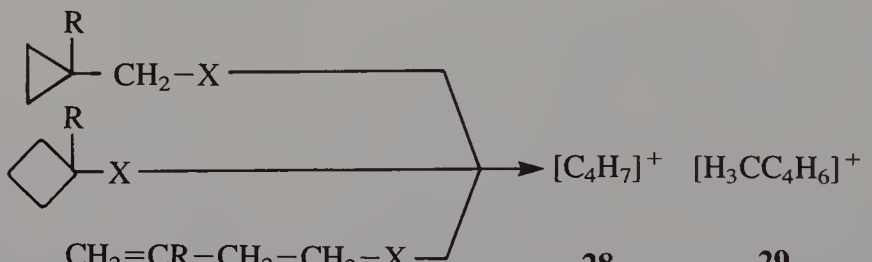
5.4.2.1. Cyclopropylmethyl and Cyclobutyl Cations. The ease of interconversion of cyclopropylmethyl cations to cyclobutyl cations and homoallylic cations under both solvolytic and stable ion conditions has long been recognized.[3a,5,8a,50,51] Wide ranging studies[52–54] showed that the cyclopropyl group is equal to or better than a phenyl group in stabilizing an adjacent carbocationic center. The direct observation of cyclopropylmethyl cations provides a clear example of positive charge delocalization into a saturated πσ-hydrocarbon system.

The first cyclopropylmethyl cation to be directly observed was the tricyclopropylmethyl cation, **27**, and the subsequent study of a variety of cyclopropylmethyl cations[3a,55–57] led to the conclusion that the tertiary cations are static and, in the absence of constraining skeletal rigidity, adopt a bisected geometry rather than an eclipsed one (making the α substituents on the carbenium center nonequivalent) with positive charge delocalized into the cyclopropane ring.[58,59] The majority of the secondary cyclopropylmethyl cations, however, undergo degenerate equilibria.[60–62]



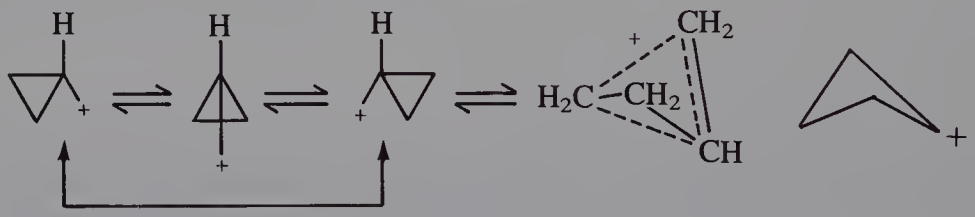
27

In contrast to the "classical" secondary and tertiary systems, primary cyclopropylmethyl cations are delocalized and the nonclassical nature of both the parent cyclopropylmethyl cation, **28**, and the 1-methylcyclopropylmethyl cation, **29**, is now firmly established.[63–69] The ion, **28**, can be generated from alkenyl, cyclobutyl, and cyclopropylmethyl precursors under stable ion conditions. Even at the lowest temperatures studied by NMR spectroscopy, that is, −155 °C, the ion, **28**, gives rise to a spectrum indicating a structure of threefold symmetry or a set of rapidly interconverting structures with average threefold symmetry.[63]



28 (R=H) **29** (R=CH_3)

It was suggested that the temperature dependence of the chemical shifts in the ^{13}C spectrum of structure **28** was due to an equilibrium between two or more energetically similar structural isomers of $C_4H_7^+$ that interconvert rapidly, even at −155 °C. Using chemical shift arguments, the major contributing isomer was assigned to the nonclassical bicyclobutonium structure, **31**.[64a]

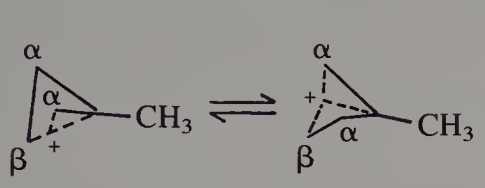


30 **31** **32**

Saunders and Siehl[69a] subsequently reported a small, temperature dependent equilibrium isotope effect in deuterated derivatives of **28** and this lends support to the conclusion that $C_4H_7^+$ may best be represented by **31** in equilibrium with another isomer, perhaps **30** and/or **32**. A similar conclusion has also been reached by Roberts and co-workers.[69b] Arguments strongly favoring **31** as the predominant structure were also derived from ^{11}B–^{13}C chemical shift relationships (see Chapter 6).[64b,64c]

At −80 °C the 1-methylcyclopropylmethyl cation ($CH_3C_4H_6^+$), **29**, also exhibits an NMR spectrum indicative of an ion of pseudo threefold symmetry[63,65,66] involving structures **33** and **34**. However, at lower temperatures the rapid equilibration involving C−C bond migration can be slowed enough to reveal a nonclassical species of twofold symmetry.[67,68] The extreme high field shift of the β-methylene carbon, $\delta^{13}C = -2.81$, is direct evidence for the presence of a pentacoordinate hypercarbon and confirms structure **35** (or the symmetrically bridged

structure **36**). Additional support for the bridged structure comes from deuterium isotope perturbation studies.[69c,69d]



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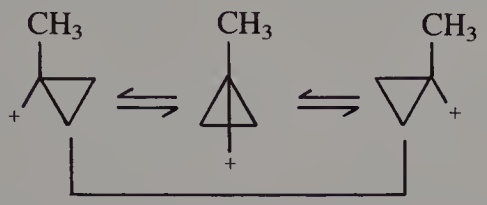

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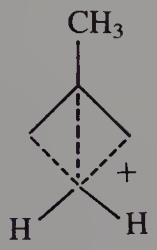

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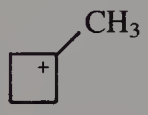
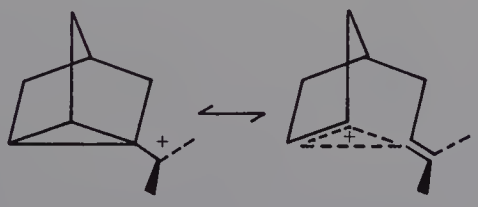


34

The correspondence in the spectroscopic properties of **29** with those of **28** suggests that the parent ion, **28**, also can best be presented in the same way. The 1-ethyl and 1-propyl analogs of **29** are similarly nonclassical but rearrange irreversibly upon warming to cycloalkyl cations.[68]

Schmitz and Sorensen[70] have prepared the nortricyclylmethyl cation, **37**, a static primary cyclopropylmethyl cation. The ^{1}H and ^{13}C NMR spectroscopic studies of **37** indicate that the system has features of both a bridged 2-norbornyl cation as well as a bisected cyclopropylmethyl structure.



a **b**

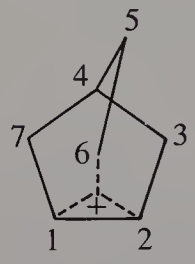
37

The ^{13}C chemical shift and C−H coupling constant analysis of **37** with respect to other secondary and tertiary systems seem to indicate that **37** is best represented as a structure somewhere between **37a** and **37b**. Molecular orbital calculations[71] as well as $^{13}C/^{11}B$ comparisons (see Chapter 6)[64b,64c] support such a proposal.

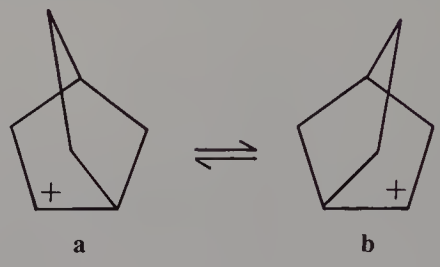
5.4.2.2. The 2-Norbornyl Cation. The 2-norbornyl cation, **38**, holds a unique position in the history of organic chemistry through the important role it has played in understanding ionic rearrangements and the bonding theory of carbocations. Ever

since Winstein's earliest solvolytic investigations in 1949[72] the 2-norbornyl cation has been at the center of the so-called nonclassical ion controversy. No other system has been studied so extensively by all available physical and chemical methods.

The norbornyl ion controversy[9,73–77] centered on the question of whether the ion had the static bridged nonclassical structure, **39**, containing pentacoordinated hypercarbons or whether its structure was better depicted as a rapidly equilibrating pair of trivalent classical ions, **40a** and **40b**.



39



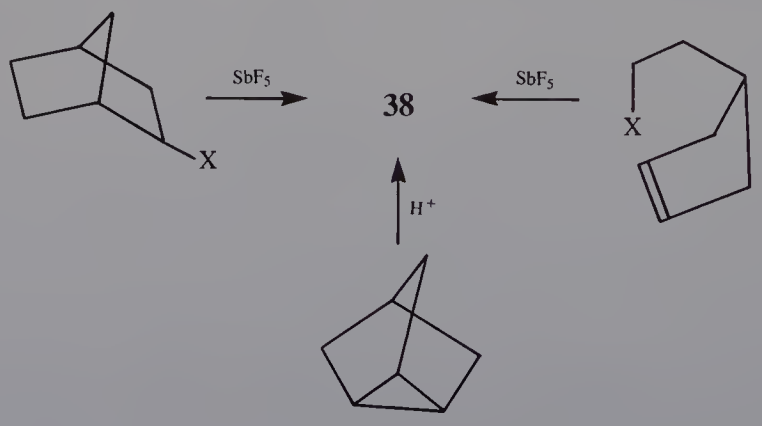
a **b**

40

The nonclassical ion dispute has been instrumental in the development of important methods in physical organic chemistry and critical evaluation of the limits of their applicability.

The methods that were worked out in the early 1960s to generate and observe stable carbocations in low nucleophilicity solutions[5] were successfully applied to the direct observation of the 2-norbornyl cation, **38**. Preparation of the ion by the "σ route" from 2-norbornyl halides, by the π route from cyclopentenylethyl halides and by protonation of nortricyclene all led to the same 2-norbornyl cation.

The method of choice for the preparation of the 2-norbornyl cation (giving the best resolved NMR spectra) is from *exo*-2-fluoronorbornane in SbF_5/SO_2 or SO_2ClF solutions.



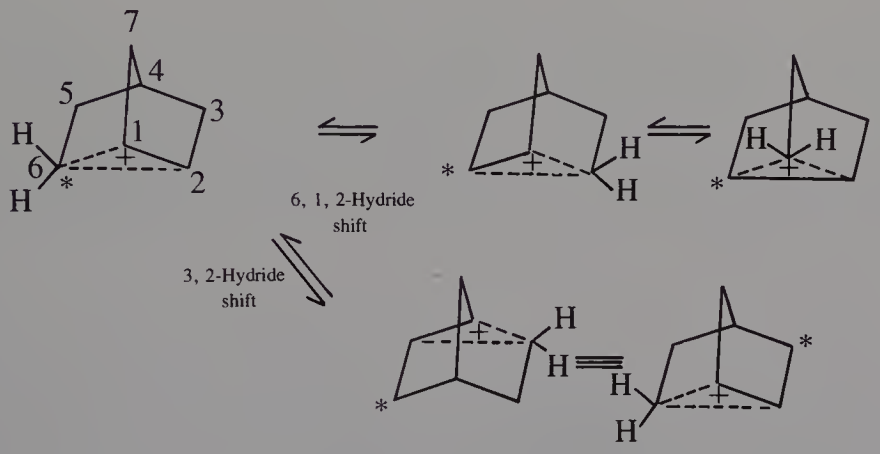
In a joint effort, Olah, Saunders, and Schleyer first investigated the 60 MHz ^1H NMR spectrum of the 2-norbornyl cation in the early 1960s.[78] Subsequently, Olah et al.[79,80] in the early 1970s carried out detailed 100 MHz ^1H and 25 MHz ^{13}C NMR spectroscopic studies at successively lower temperatures. From the detailed ^1H NMR

investigations at various temperatures (room temperature to $-154\,^{\circ}C$) the barriers for the 2,3-hydrogen shift, as well as the 6,1,2-hydrogen shift, were determined by line shape analysis and found to be 10.8 ± 0.6 kcal mol^{-1} and 5.9 ± 0.2 kcal mol^{-1}, respectively [Scheme 5.1].[79]

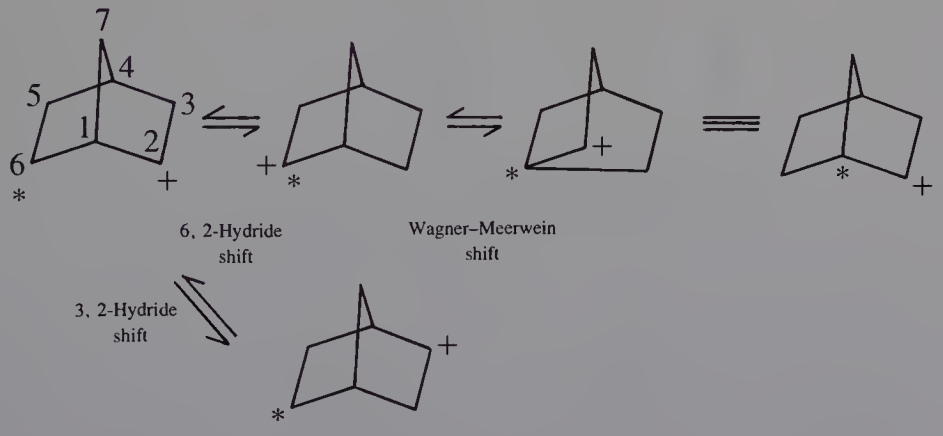
Scheme 5.1

Degenerate Shifts in the 2-Norbornyl Cation (*, one of the carbons is labelled for clarity):

Nonclassical Ion Formulation



Classical Ion Formulation



In the 1980s ^{1}H and ^{13}C NMR spectra of the 2-norbornyl cation at substantially higher fields, that is, 395 MHz ^{1}H and 50 MHz ^{13}C, have been obtained at similar low temperatures.[81] The 395 MHz ^{1}H NMR spectrum of structure **38** is fully resolved compared to that previously reported at 100 MHz,[79] Figure 5.2.

At $-100\,^{\circ}C$ the 2-norbornyl cation, **38**, in the SbF_5–SO_2ClF–SO_2F_2 solvent system shows three peaks at δ4.92 (four protons), 2.82 (one proton), and 1.93 (six

protons) indicating that the 2,3-hydrogen shift is fully frozen, whereas 6,1,2-hydrogen and Wagner–Meerwein shifts (if any) remain rapid on the NMR time scale.

A lowering of the temperature to −158 °C results in significant changes in the spectrum. The peak at δ4.92 develops into two peaks at δ6.75 and 3.17 with a ratio of 2:2. The high field peak broadens and splits into two peaks at δ2.13 and 1.37 in the ratio 4:2. The peak at δ2.82 remains unchanged. One other significant aspect of the high field study[81] is the observed proton signal linewidths at 395 MHz. The ≃60Hz linewidth observed at −158 °C is rather small as compared to the one obtained earlier[79] at 100 MHz (≃30 Hz) at −154 °C. If the linewidth were due to any slow exchange process still occuring at such low temperatures, the line should have broadened 15.6 times at 395 MHz compared to the width observed at 100 MHz. The observation of comparably narrow linewidths at 395 MHz indicates that either the 6,1,2-hydrogen shift and the Wagner–Meerwein shift (if any) are completely absent and the 2-norbornyl cation has the symmetrically bridged structure, **39**, or the 6,1,2-hydrogen shift is absent and the Wagner–Meerwein shift remains rapid on the NMR time scale and involves a very shallow activation energy barrier (≤3 kcal mol^{-1}).

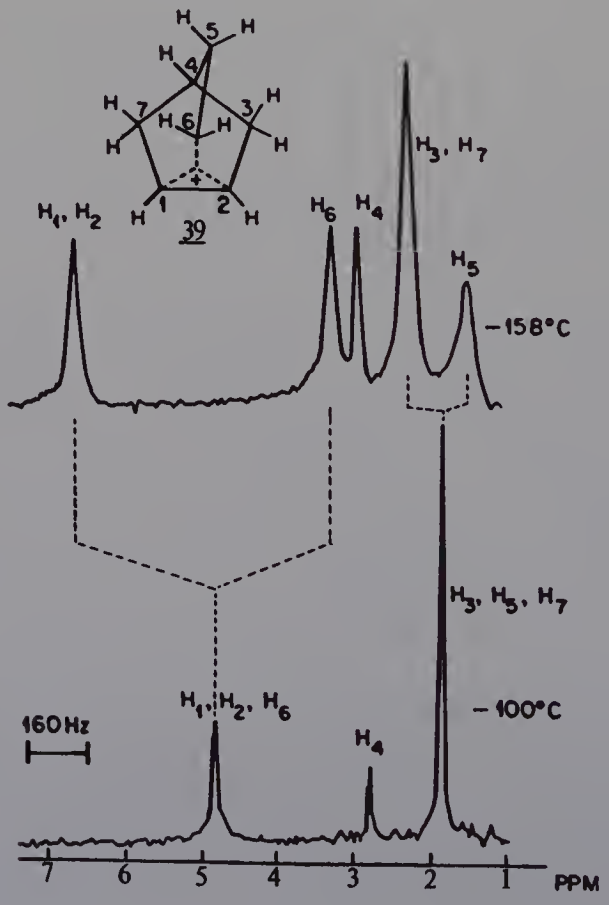


Figure 5.2. 395 MHz ^1H NMR spectra of 2-norbornyl cation in SbF_5–SO_2ClF–SO_2F_2 solution.

The second possibility raises the question as to the nature of the ion if it is still undergoing equilibration. It has been pointed out[9g] that if such a process occurs it must be exclusively between unsymmetrically bridged ions, **41**, equilibrating through the intermediacy of the symmetrically bridged species, **39**.

41

The 50 MHz ^{13}C NMR spectrum of the 2-norbornyl cation, **38**, was obtained in a mixed solvent system, $SbF_5/SO_2ClF–SO_2F_2$, at -159 °C.[81] In order to obtain a well-resolved ^{13}C NMR spectrum, the cation was generated from 15% ^{13}C enriched *exo*-2-chloronorbornane (one ^{13}C label present per molecule). The ionization at -78 °C led to the 2-norbornyl cation, wherein the ^{13}C label is distributed evenly over all

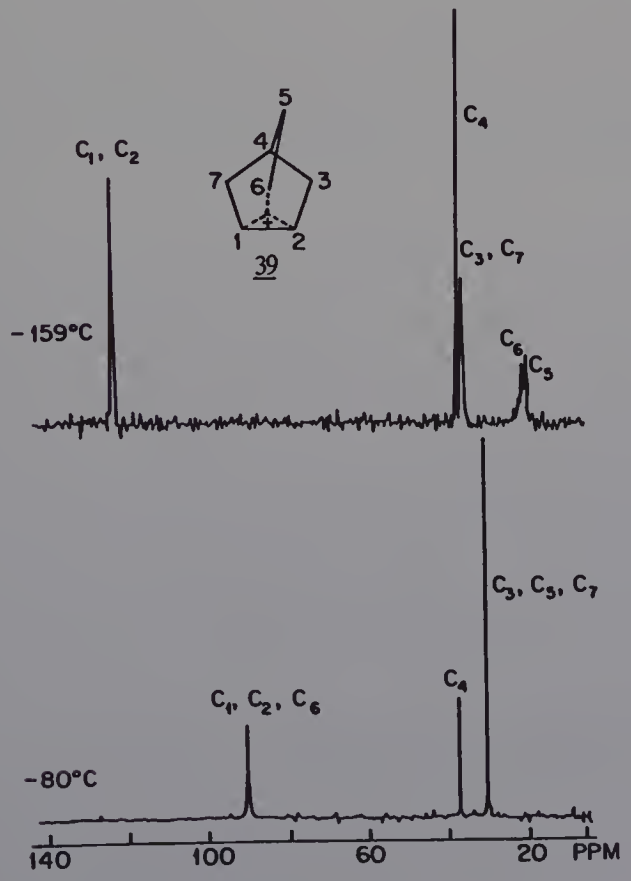


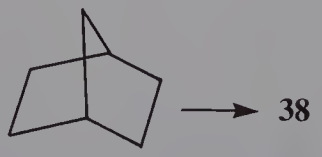
Figure 5.3. 50 MHz ^{13}C NMR spectra of the 2-norbornyl cation in $SbF_5–SO_2ClF–SO_2F_2$ solution.

seven carbons as a result of slow 2,3-hydrogen and fast 6,1,2-hydrogen and Wagner–Meerwein rearrangements.

At −80 °C, the 50 MHz ^{13}C NMR spectrum of the cation (Fig. 5.3) shows three absorptions at δ91.7 (quintet, J_{C-H} = 55.1 Hz), 37.7 (doublet, J_{C-H} = 153.1 Hz), and 30.8 (triplet, J_{C-H} = 139.1 Hz), indicating that the 2,3-hydrogen shift is slow and the 6,1,2-hydrogen and Wagner–Meerwein shifts are still fast on the NMR time scale.

Cooling the solution further results in broadening and slow merging into the base line of the peaks at δ91.7 and 30.8, but the peak at δ37.7 remains relatively sharp. At −159 °C, the peaks at δ91.7 and 30.8 separate into two sets of two peaks at δ124.5 (doublet, J_{C-H} = 187.7 Hz), 21.2 (triplet, J_{C-H} = 147.1 Hz), and 36.3 (triplet, J_{C-H} = 131.2 Hz), 20.4 (triplet, J_{C-H} = 153.2 Hz), respectively. The observed ^{13}C NMR spectral data at −159 °C complement well the 395 MHz ^{1}H NMR data at −158 °C. The observation of the C-1 and C-2 carbons at δ124.5 and the C-6 carbon at δ21.2 clearly supports the bridged structure for the ion. Five (or higher) coordinate carbons generally show shielded (upfield) ^{13}C NMR shifts[20] (similar ^{11}B NMR shifts are observed for borons in isoelectronic polyboranes).[64b,64c]

Applying the additivity of the chemical shift analysis[20] to the 2-norbornyl cation also supports the nonclassical bridged nature of the ion. The chemical shift difference of 168.0 ppm between 2-norbornyl cation, **38**, and its parent hydrocarbon norbornane is characteristic of the < 200 ppm difference observed between a nonclassical ion and its parent hydrocarbon. In contrast, an ordinary classical trivalent carbocation such as the cyclopentyl cation, **42**, reveals a chemical shift difference of > 360 ppm (between the ion and the parent hydrocarbon, cyclopentane). This is consistent with the 350 ppm difference characteristic of classical carbocations and their precursor hydrocarbons.



38

$\Delta\Sigma\delta$ = 168

$\Delta\Sigma\delta$ = 360 **42**

Yannoni, Macho and Myhre[82] obtained magic-angle cross polarization ^{13}C NMR spectra of the ^{13}C enriched 2-norbornyl cation in an SbF_5 solid matrix at −196 °C. The solid state chemical shifts correlate well with the solution data except for the lack of resolution in the methylene region. Subsequently, they[83a] have been successful in obtaining the ^{13}C NMR spectrum in the solid state at −268 °C (5° K) (see Fig. 5.4) which is a remarkable achievement!

A fortuitous combination of large isotropic chemical shifts and small chemical shift anisotropies permitted them to obtain reasonable resolution of the positively charged resonance without the need for magic-angle spinning (MAS). Comparison with their previous MAS spectra[82] at −196 °C shows that the nonspinning spectra reflect a slowing of the 6,2,1-hydride shift. No changes were observed in the

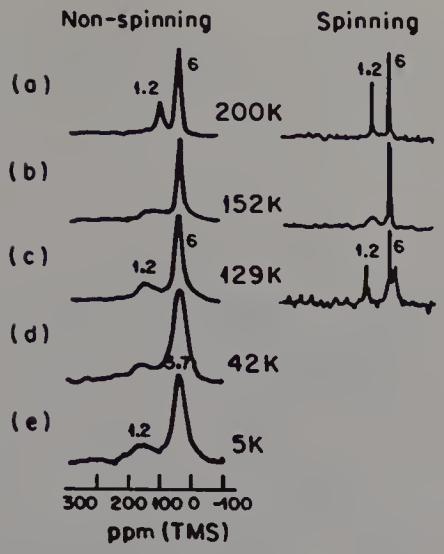


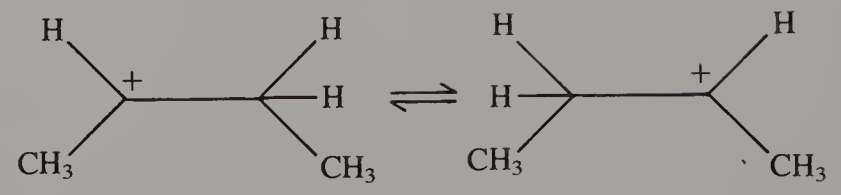
Figure 5.4. Solid state ^{13}C NMR spectra of the 2-norbornyl cation.[83a]

positively charged carbon resonance at 124.5 between -173 and -268 °C. The authors, therefore, concluded[83a] that if such a hypothetical 1,2-Wagner–Meerwein shift were still occurring, it should be rapid and an upper limit for the barrier for such a process, involving limiting structures such as **40** can be estimated to be no greater than 0.2 kcal mol^{-1}. This equals the energy of a vibrational transition. Dewar and Merz[83b] suggested the possibility of low energy carbon tunneling between unsymmetrically delocalized nonclassical ions such as **41** based on MINDO/3 calculations.

These results are the most definitive spectroscopic evidence, besides the ESCA studies for the symmetrically (or very close to symmetrical) bridged structure of the 2-norbornyl cation, **39**.

In other equilibrating systems, where classical carbenium ions are preferred, this has been clearly demonstrated by similar low temperature solid state NMR studies. For example, Yannoni and Myhre[83,84] have succeeded in freezing the degenerate hydrogen shift in the cyclopentyl cation, **42**, in the solid state at -203 °C (the ion undergoes rapid 1,2-hydride shifts in solution at -150 °C). They obtained chemical shift values of δ320, 71.0, and 28.0 (for the ^{+}C center, and the two types of methylenes, respectively), which indicate the regular trivalent classical nature of the ion and are in good agreement with estimated shift values in solution based on the observed average chemical shift data.

The method[84] has also been successfully applied to other equilibrating cations such as 2-butyl, 2,3-dimethyl-2-butyl, and 2,2,3-trimethyl-2-butyl cations, **20**, **43**, and **44**, respectively. These systems undergo rapid degenerate equilibration in solution even at -160 °C.[3c] However, in the solid state the species, **42**, **43**, and **44** were observed as static trivalent cations at even higher temperatures, that is, -130 °C.



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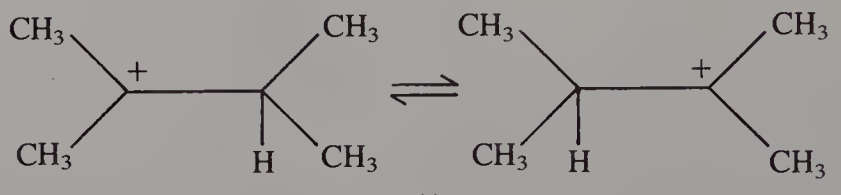

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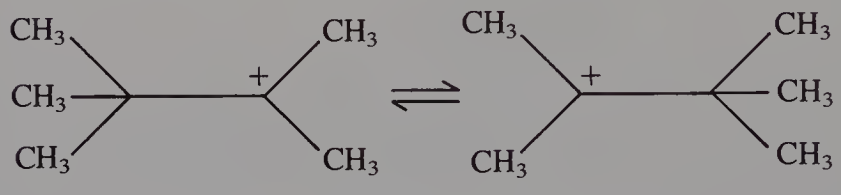
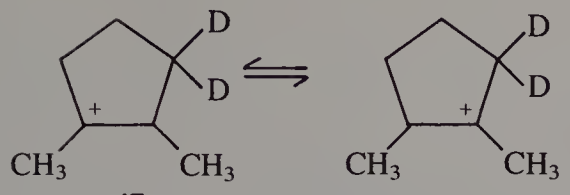


44

These results further demonstrate the ability of very low temperature solid state NMR methods to differentiate rapidly equilibrating classical ion systems from nonclassical bridged systems, even when the equilibration barrier involved is much less than 3 kcal mol^{-1}.

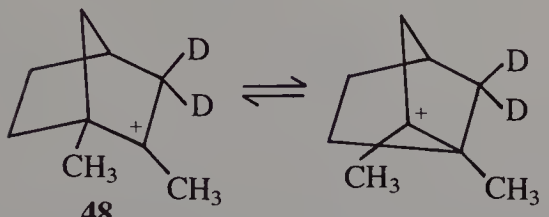
As mentioned in Section 5.3.3, the method of observing changes in NMR spectra produced by asymmetric introduction of isotopes (isotopic perturbation) as a means of distinguishing between dynamic molecules (involving rapidly equilibrating species passing over a low barrier) and static molecules (with a single energy minimum, intermediate between the presumed equilibrating structures) was developed by Saunders and co-workers.[21–24] Applying this method to the 2-norbornyl cation further supports the static bridged form, **39**.[85]

In the ^{13}C NMR spectrum of the 2-norbornyl cation, even at low temperatures, besides Wagner–Meerwein rearrangement, the 6,1,2-hydride shift has a barrier of only 5.9 kcal mol^{-1} and this results in a certain amount of line broadening of the lowest field signal observed. Even in the ion with no deuterium, the downfield signal at 124.5 (C-2 and C-6 cyclopropanelike carbons) is found to be 2-ppm wide. Nevertheless, no additional isotopic splitting or broadening was observed with either 2-monodeutero or 3,3-dideutero cations, **45** and **46**, and, therefore, the isotopic splitting can be no more than 2 ppm. This is true even if a slow 6,2-hydride shift converts part of the latter ions to a symmetrical 5,5-dideutero system that lacks an equilibrium isotope effect. This result, when compared with the significantly larger splitting observed[23] for deuterated dimethylcyclopentyl and dimethylnorbornyl cations, **47** and **48** (known to be equilibrating ions) is in accordance with the nonclassical nature of the 2-norbornyl cation. A similar conclusion was reached[86] based on a high-temperature deuterium isotopic perturbation effect in the 2-norbornyl cation.



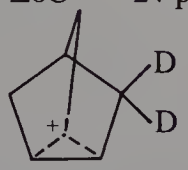
47

$\Delta\delta C = 104$ ppm



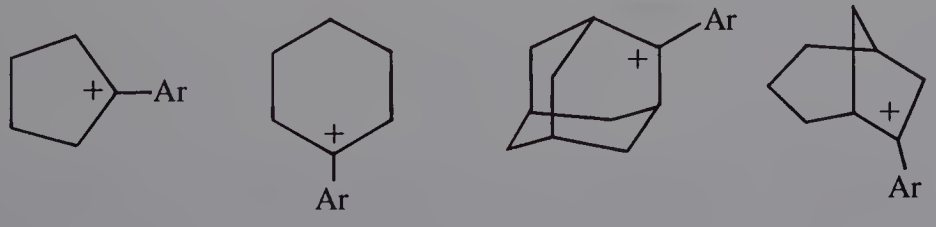
48

$\Delta\delta C = 24$ ppm



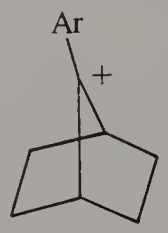
$\Delta\delta C < 2$ ppm

Farnum and Olah's groups have extended the so-called Gassman–Fentiman tool of increasing electron demand coupled with ^{1}H and ^{13}C NMR spectroscopy as the structural probe under stable ion conditions to show the onset of π, $\pi\sigma$, and σ delocalization in a variety of carbocationic systems.[26,87–95] The ^{13}C NMR chemical shifts of the cationic carbon of a series of regular trivalent cations such as arylcyclopentyl, **49**; arylcyclohexyl, **50**; 2-aryl-2-adamantyl, **51**; 6-aryl-6-bicyclo[3.2.1]octyl, **52**, and 7-aryl-7-norbornyl, **53** cations (typical classical cations) correlate linearly with the observed cationic chemical shifts of substituted cumyl cations, **54**, over a range of substituents [from the most electron-releasing groups, e.g., *p*-OCH_3, to the most electron-withdrawing 3,5-$(CF_3)_2$ groups].[92–95]



49 **50** **51** **52**

However, systems such as the 2-aryl-2-norbornyl cation, **55**, show deviations from linearity in such chemical shift plots when electron-withdrawing substituents are involved (Fig. 5.5). This is indicative of the onset of nonclassical σ delocalization fully supporting the nonclassical nature of the parent secondary cation. Although it has been argued[95] that the observed deviations from linearity could be caused by other factors such as π polarization, this was subsequently shown to be highly improbable.[26]



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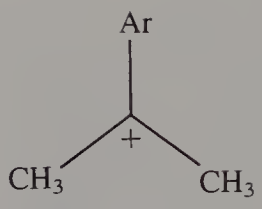

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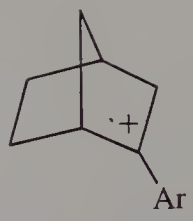

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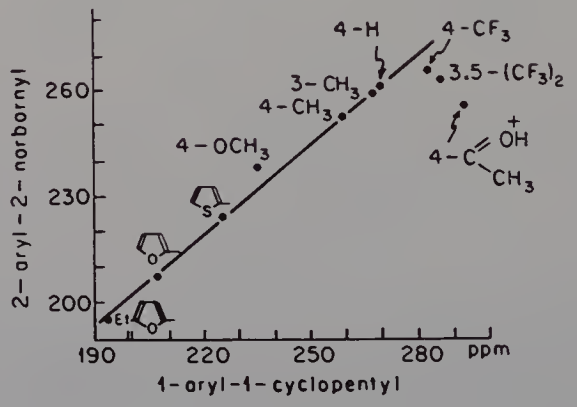
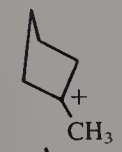
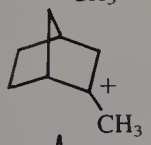


Figure 5.5. Plot of the ^{13}C NMR chemical shifts of cationic center of 2-aryl-2-norbornyl cations versus those of model 1-aryl-1-cyclopentyl cations.

As mentioned earlier, since in electron spectroscopy the time scale of the various ionization processes is of the order of 10^{-16} s, definite ionic species are characterized, regardless of their possible intra- and intermolecular interactions (e.g., Wagner–Meerwein rearrangements, hydride shifts, etc.) even at rates equaling or exceeding those of vibrational transitions. Thus, electron spectroscopy can give an unequivocal answer to the long-debated question of the "classical" or "nonclassical" nature of the norbornyl cation, regardless of the rate of any possible equilibration processes.

An ESCA study by Olah et al.[80] succeeded in observing the ESCA spectrum of the 2-norbornyl cation and compared it with those of the "related" 2-methyl-2-norbornyl cation, **56**, and other trivalent carbenium ions such as the cyclopentyl, 1-methyl-1-cyclopentyl and *t*-butyl cations (**41**, **57**, and **13**). The 1*s* electron spectrum of the 2-norbornyl cation shows no high binding energy carbenium center and a maximum separation of < 1.5 eV is observed between the two equivalent "cyclopropyl" type carbons to which bridging occurs from the other carbon atoms (including the pentacoordinate bridging hypercarbon). In contrast, the 2-methyl-2-norbornyl cation, **56**, shows a high binding energy carbenium carbon center, deshielded with the ΔE_b of 3.7 eV from the other carbon atoms. Typical ESCA shift differences are summarized in Table 5.2.

TABLE 5.2. Binding Energy Differences of Carbocation Centers from Neighboring Carbon Atoms $\Delta E_b{}^+{}_{C-C}$

Ion	$\Delta E_b{}^+{}_{C-C}$	Approx. Relationship C^+:C Intensity
$(CH_3)_3{}^+C$	3.9 ± 0.2	1:3
	4.2 ± 0.2	1:5
	3.7 ± 0.2	1:7
	4.3 ± 0.5	1:4
	1.5 ± 0.2	2:5

Recently, Grunthaner reexamined the ESCA spectrum of the 2-norbornyl cation on a higher resolution x-ray photoelectron spectrometer using highly efficient vacuum techniques.[96] The spectrum closely matches the previously published spectra.[80] Furthermore, the reported ESCA spectral results are consistent with the theoretical considerations of Goetz et al.[97] which compare the classical and nonclassical 2-norbornyl structures at the STO-3G and STO-4.31G levels. Using these parameters Clark et al.[98] were able to carry out a detailed interpretation of the experimental ESCA data for the core-hole state spectra at SCF STO-4.31G level and calculated equivalent cores at STO-3G level. Agreement between experimentally obtained spectra and those calculated for the nonclassical cation are good and dramatically different from those that would be anticipated for the classical cation (Fig. 5.6). Whereas Kramer[74] and Dewar[83b] argued that peak ratio of the ESCA spectrum to be closer to 1:6 than 2:5, integration by curve resolution is ambiguous. Further any inevitable carbon impurity (including still unionized precursor) enhances the main peak area. Thus peak area intensity is less significant. The important aspect of the ESCA study is the magnitude of the binding energy difference.

Direct experimental evidence for the unusual stability of the 2-norbornyl cation arises from the low temperature solution calorimetric studies of Arnett et al.[99] In a series of investigations they determined[99] the heats of ionization (ΔH_i) of secondary and tertiary chlorides in SbF_5/SO_2ClF and subsequently[30] alcohols in FSO_3H:SbF_5/SO_2ClF solutions.

It was found that the difference between the heats of ionization of 2-methyl-2-*exo*-norbornyl chloride and 2-*exo*-norbornyl chloride in SbF_5/SO_2ClF solution is 7.4 kcal mol^{-1} while the difference between the corresponding alcohols

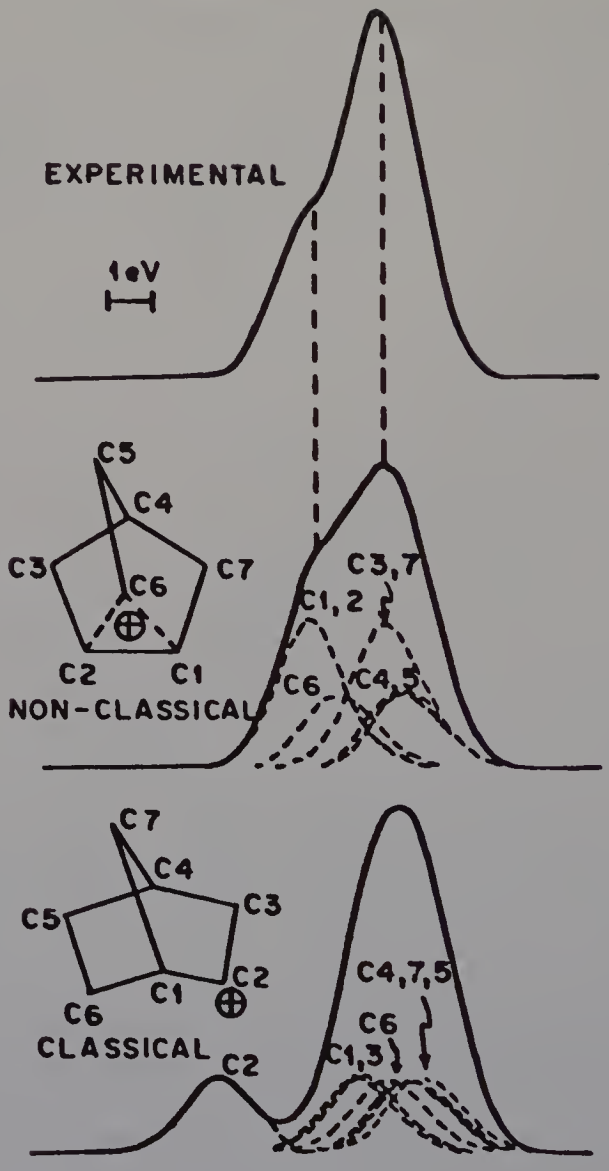


Figure 5.6. Carbon 1*s* core-hole state spectra of the 2-norbornyl cation and simulated spectra for classical and nonclassical ions according to Clark et al.[98]

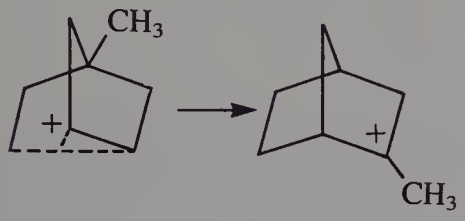
$$R{-}Cl + SbF_5 \xrightarrow{\Delta H_i} R^+SbF_5Cl^+$$

$$R{-}OH + FSO_3H{:}SbF_5 \xrightarrow{\Delta H_i} R^+SbF_5(FSO_3)^- + H_3O^+$$

was only 2.5 kcal mol^{-1}. This indicates that the heats of ionization value (ΔH_i) seem to largely depend on the nature of the starting precursors (initial state effects). However, the observed differences are remarkably small if the 2-methyl derivatives gave classical tertiary cations and the nonalkylated derivatives gave classical secondary cations. Usually, tertiary cations are 10–15 kcal mol^{-1} more stable than the corresponding trivalent secondary cations.

Thus, in the case of the 2-norbornyl cation, there seems to be at least an unaccounted 7.5 kcal mol^{-1} "extra" stability. The "extra" stability can be easily rationalized if the cation has the nonclassical structure, **39**.

Further compelling evidence indicating additional stabilization of the 2-norbornyl cation comes from Arnett's measured heats of isomerization of secondary cations to tertiary cations.[99] The measured heat of isomerization of the 4-methyl-2-norbornyl cation, **58**, to the 2-methyl-2-norbornyl cation, **56**, is -6.1 kcal mol^{-1}. In contrast, the related isomerization of the 2-butyl cation, **20**, to the *t*-butyl cation, **13**, involves a difference of -14.2 kcal mol^{-1}.



58 **56**

$\Delta H_{\text{isomerization}} = -6.6$ kcal mol^{-1}

20 **13**

$\Delta H_{\text{isomerization}} = -14.2$ kcal mol^{-1}

If the latter value is taken as characteristic for the isomerization of classical secondary to classical tertiary cations, one must conclude that the secondary cation, **58**, has an extra stabilization of at least 7.6 kcal/mole.[99] Farcasiu[100] has questioned these conclusions, arguing that Arnett et al.[99] neglected to account for the extra stabilization due to bridgehead methyl substitution in ion **58** as indicated by his molecular force field calculations. Schleyer and Chandrasekhar[101] have subsequently shown, based on MINDO/3 calculations, that such effects are very small.

Even correcting for the bridgehead methyl effect, there is still 6 ± 1 kcal mol^{-1} extra stabilization in the 2-norbornyl cation for which no reasonable explanation, other than bridging (i.e., structure **39**) has been suggested.

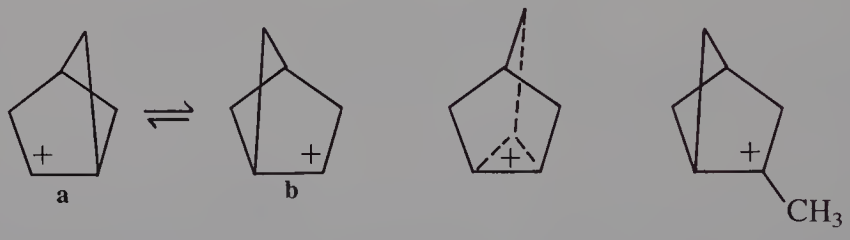
Gas-phase mass spectrometric studies[102,103a] also indicate exceptional stability of the 2-norbornyl cation relative to other potentially related secondary cations. A study by Kebarle and co-workers[103b] also suggests that the 2-norbornyl cation is more stable than the *t*-butyl cation in the gas phase (based on hydride transfer equilibria from their respective hydrocarbons).

Theoretical quantum mechanical calculations[104–109] have been performed on the 2-norbornyl cation at various levels. These calculations reveal a significant preference for the delocalized nonclassical structure. High-level calculations, including electron correlations with a double zeta plus polarization basis set, indicated[108–109] that the only minimum on the 2-norbornyl cation potential energy surface is the symmetrically bridged structure. The nonclassical symmetrically

bridged 2-norbornyl cation, **39**, was calculated to be 24.8 kcal mol^{-1} more stable than the isopropyl cation, **59** (based on the hydride transfer reaction). The structure with "classical" 2-norbornyl-like geometry, **40**, did not correspond to a potential energy minimum on the potential energy surface. The extra stabilization of the nonclassical 2-norbornyl cation, **39**, over the classical alternative, **40**, was roughly estimated to be 12–15 kcal mol^{-1} at this high level of ab initio theory.[108]

5.4.2.3. The 2-Bicyclo[2.1.1]hexyl Cation. Another bicyclic cation that is a close relative of the 2-norbornyl cation is the 2-bicyclo[2.1.1]hexyl cation, **60**. Although initially conflicting conclusions were reached based on ^1H and ^{13}C NMR studies, the ion is now agreed to be significantly σ bridged in nature.

The bicyclo[2.1.1]hexyl cation, **60**, was first observed by Seybold, Vogel, Saunders, and Wiberg in superacid media.[110] Based upon the observed ^1H NMR chemical shift data they suggested a static nonclassical symmetrically bridged ion, **61**, as the most probable structure since they could not freeze out any degenerate equilibria, that is, there was no evidence for the equilibrating pair, structures **60a** and **60b**. Similar conclusions were drawn from solvolytic studies.[111]

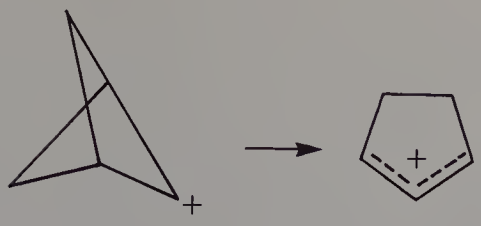


60 **61** **62**

In a subsequent ^{13}C NMR study Olah, Liang, and Jindal[112] concluded that there is little bridging and they favored the rapidly equilibrating ion, that is, **60a** and **60b**. The ^1H NMR spectrum of the ion in SbF_5/SO_2ClF showed three resonances at δ^1H 8.32 (two protons), 3.70 (six protons), and 2.95 (one proton). There was no significant line broadening down to −140 °C. The ^{13}C NMR spectrum of the ion shows three resonances at $\delta^{13}C$ 157.8 (doublet, J_{C-H} = 184.5 Hz; C-1 and C-2), 49.1 (triplet, J_{C-H} = 156.9 Hz; C-3, C-5, and C-6), and 43.4 (doublet, J_{C-H} = 164.6 Hz; C-4). Above −90 °C the ion irreversibly rearranges to the cyclohexenyl cation **4**.[113]

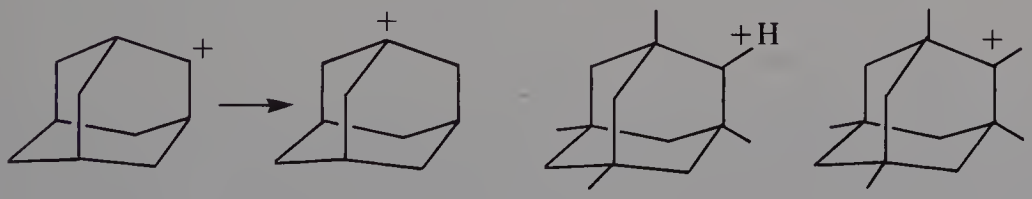
Nevertheless, a recent study by Saunders et al.[114] involving deuterium labeling at the exchanging sites indicates that there is significant bridging in the ion. Sorensen and Schmitz[115] showed that the free energy difference between the secondary cation, **60**, and the tertiary cation, **62**, is 7–9.8 kcal mol^{-1} compared to 5.5 for the 2-norbornyl and 11.4 for the cyclopentyl cations. The intermediate value observed for the bicyclo[2.1.1] system substantiates the intermediate (partially bridged) nature of the secondary cation.

Attempts to prepare[116]the analogous bicyclopentyl cation, **63**, from the 2-bicyclopentyl derivatives were unsuccessful and gave only the rearranged cyclopentenyl cation, **64**.[113]



63 64

5.4.2.4. The 1,3,5,7-Tetramethyl-2-adamantyl Cation. The nature of the 2-adamantyl cation, **65**, has been difficult to study since it undergoes facile rearrangement to the more stable 1-adamantyl cation, **66**.[5] This difficulty was circumvented by Lenoir et al.[117] by blocking all four bridgehead positions with methyl groups in a study that involved 1,3,5,7-tetramethyl- and 1,2,3,5,7-pentamethyl-2-adamantyl cations, **67** and **68**.

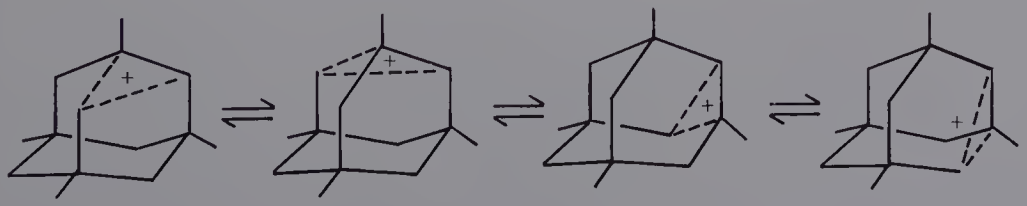


65 66 67 68

The ^{1}H NMR spectrum of **67** in superacid had the right number of peaks to fit the symmetry of a static 2-adamantyl cation but the chemical shift value of the CH proton at the presumed carbocation center C-2 was only δ5.1. This is 8 ppm to higher field than expected for a typical static secondary carbenium ion such as the isopropyl cation, **59**.[5]

Since the symmetry of the spectrum was incompatible with either a static bridged 2-adamantyl cation, **69**, or a static tertiary protoadamantyl cation, **70**, two mechanisms were postulated involving sets of the cations from **69** or **70** undergoing rapid degenerate rearrangements at −47 °C (Schemes 5.2 and 5.3).

Scheme 5.2



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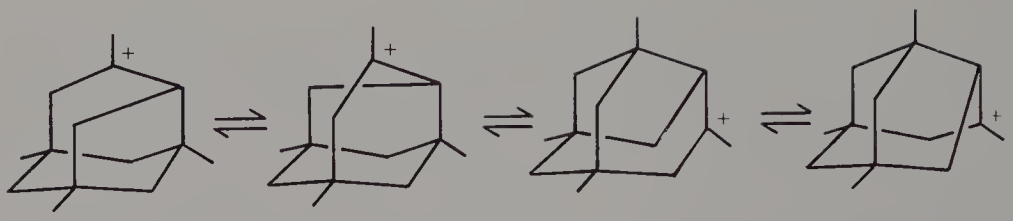
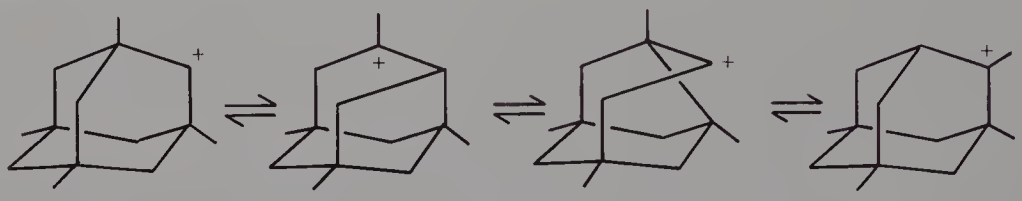
Scheme 5.3



70

Scheme 5.4

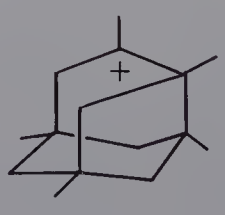


67 **72** **71**

Apart from one of these degenerate rearrangements, **67** also underwent a nondegenerate rearrangement to the more stable tertiary 2-adamantyl cation, **71**, with a half-life of about 1 hr at −47 °C. The kinetics of this rearrangement, which involves protoadamantyl cations as intermediates (Scheme 5.4) was advantageously studied in the tertiary 2-adamantyl system, **68**, where it is degenerate. Line shape analysis for the degenerate rearrangement of structure **68** gave $E_a = 12.1 \pm 0.4$ kcal mol^{-1} in accord with molecular mechanics calculations.

Since it was difficult to make an exclusive choice between bridged (involving **69**) and unbridged (involving **70**) mechanisms for the degenerate rearrangement and the average structure of **67** on the basis of the ^{1}H NMR data alone, further evidence were derived from a solvolytic study, and the mechanism involving **69** became the preferred explanation for the behavior of **67** in superacid.

Criticism of these conclusions by Farcasiu[118,119] led Schleyer et al.[20] to study **67** and **68** by ^{13}C NMR spectroscopy under stable ion conditions. The spectra of **68** confirmed its classical carbenium ion structure at low temperatures. At 30 °C an average of the C-1, C-2, and C-3 signals and the signals of the CH_3 groups attached to these positions were observed due to the degenerate rearrangement involving the protoadamantyl cation, **73**.

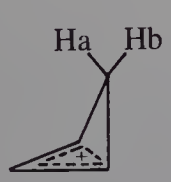


73

A totally different spectrum was obtained for the presumed ion, **67**; the C-2 ^{13}C resonance was located at δ 92.3. This value was more than 200 ppm to higher field than the position expected for a static classical cation. Since a static structure like **67** was clearly incompatible with the observed spectrum, a chemical shift estimate was made for the protoadamantyl cation, **70**. However, the discrepancy between the estimated and observed values was too large to explain the behavior of the 1,3,5,7-tetramethyl-2-adamantyl cation with properties of an equilibrating set of ions such as **70**, even with the partial contribution of **67**. This left the set of equilibrating nonclassical bridged ions, **69**, as the only possible structure for the cation (Scheme 5.2).

5.4.2.5. Bishomocyclopropenium Cations. The concept of homoaromaticity[9c,120–123] was advanced by Winstein[9c] in 1960 and homoaromatic overlap was studied first in 6π-Hückeloid systems such as the homotropylium cation. Several 2π-electron homoaromatic systems have been discovered subsequently, including the homocyclopropenium cation ($C_4H_5^+$), **74**.[124]

The magnitude of any homoaromatic stabilization is expected to decrease with increasing interruption by methylene groups of the otherwise conjugated π framework in neutral molecules. However, in an ionic species there is additional incentive for charge delocalization. Two of the most widely studied bishomoaromatic cations are the 7-norbornenyl and 7-norbornadienyl cations, **75**, and **76**.[125–128]



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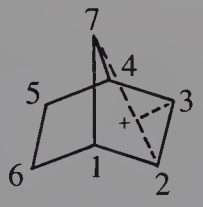

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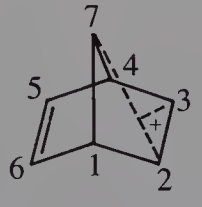
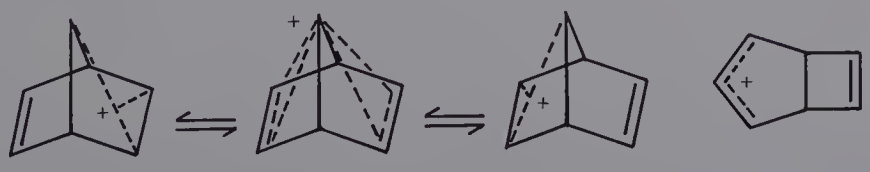


76

The ^{13}C NMR spectrum of the cation, **75**, shows substantial shielding of both the C-7 cationic and vinylic carbon chemical shifts at δ34.0 and 125.8, respectively:[125] A similar shielding phenomenon is observed for the ion **76**.

Interestingly, ion **76** undergoes several degenerate rearrangements. In search of a bridge flipping rearrangement in **76** through the intermediate, **77**, Winstein and co-workers observed the ^1H NMR spectrum of structure **76** in FSO_3H.[127–129]

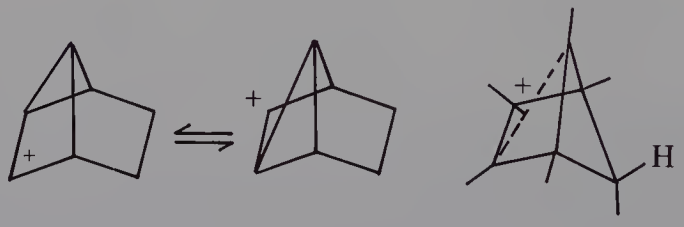


76 **77** **78**

At −77 °C the signals from protons bonded to carbons C-7, C-1, C-6, C-5, and C-4 showed broadening but the other protons, at C-2 and C-3 did not. The mechanism for the rearrangement of the protons was elucidated using several deuterium labeled precursors.

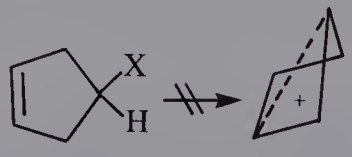
A ring contraction–ring expansion mechanism was proposed[130] for the five carbon scrambling involving the intermediacy of the bicyclo[3.2.0]heptadienyl cation, **78**. The mechanism was also independently confirmed[130] by using labeled *cis* and *trans* bicycloheptadienyl precursors. The barrier for this five carbon rearrangement at −40 °C has been found to be $\Delta G^{\ddagger} = 16.7$ kcal mol^{-1}. Ion **76** also undergoes a bridge flipping type of rearrangement that is slower and results in C-2 and C-3 becoming equivalent to C-5 and C-6. This second rearrangement requires about 3 kcal mol^{-1} more activation than the five carbon rearrangement. Thus a combination of both processes allows all seven carbons in **76** to become scrambled.

Several studies, including the application of the tool of increasing electron demand,[59a,60,128] best describe the ion **75** as a nonclassical symmetrical bridged 2π-bishomocyclopropenium cation as opposed to a rapidly equilibrating pair of cyclopropylmethyl cations, for example, **79**. The observed unusually large $^{13}C-^{1}H$ coupling constants at the C-7 position of **75** and **76** (i.e., 218.9 and 216.4 Hz, respectively) demonstrate the higher coordination of the carbocationic carbon. Several studies[131–135] on the hexamethylbicyclo[2.1.1]hexenyl cation have shown that the ion is best represented as a bishomoaromatic species, **80**, analogous to structures **75** and **76**.



79 **80**

The extent of bishomoaromatic delocalization as expected, is critically dependent upon the structural geometry. Attempts to prepare the parent bishomoaromatic 4-cyclopentenyl cation, **81**, from 4-halocyclopentene were unsuccessful.[136–137] The allylic cyclopentenyl cation, **64**, was formed instead.

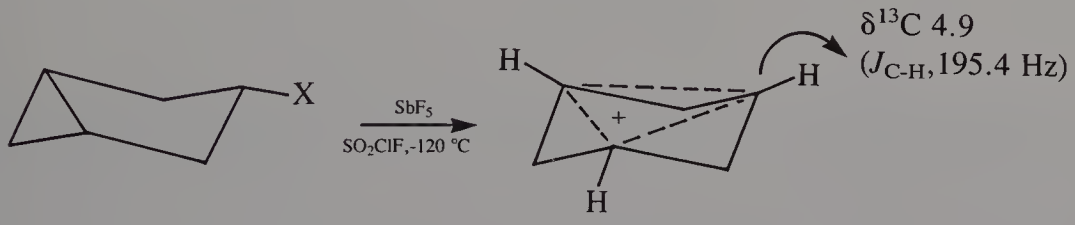


X = Cl, Br **81**

The inability to form bishomoaromatic ions from cyclopentenyl derivatives is primarily due to steric reasons. The planar cyclopentene skeleton has to bend into an unfavorable "chair" conformation to achieve any significant overlap between the

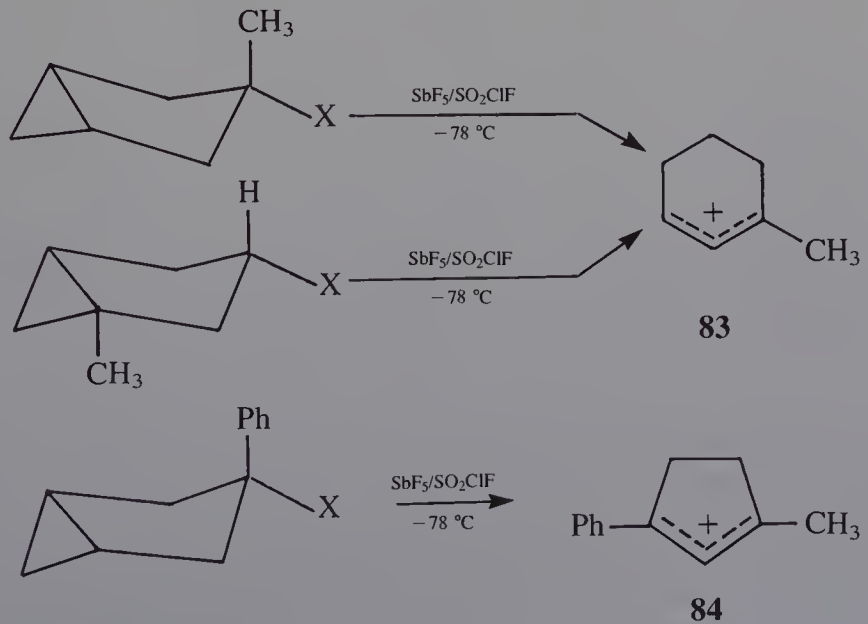
empty p orbital and the π p lobe of the olefinic bond. Such conformations, however, exist in the cations, **75** and **76**.

5.4.2.6. Trishomocyclopropenium Cations. The trishomocyclopropenium ion, **82**, was first proposed by Winstein and co-workers[138] as an intermediate in the solvolysis of *cis*-bicyclo[3.1.0]hexyl tosylate and extensive efforts were directed towards its generation under stable ion conditions. The cation, **82**, was first prepared by Masamune et al.[139] by the ionization of *cis*-3-chlorobicyclo[3.1.0]hexane in superacid media and it has since been generated from the corresponding alcohol.[137] The NMR spectra of structure **82** are consistent with an ion of C_3 symmetry. The three equivalent C−H groups are found at high field in the ^{13}C NMR spectrum in accordance with their hypercoordinate environments.



82

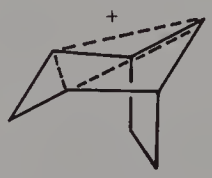
Attempts to prepare methyl and phenyl substituted trishomocyclopropenium cations by the ionization of various *cis*-bicyclo[3.1.0]hexyl alcohols and halides have been unsuccessful and have led instead to rearranged cyclohexenyl and cyclopentenyl cations, **83** and **84**. Jørgenson's theoretical calculations[140] on the $C_7H_{11}^+$ potential energy surface have shown that the delocalized methyltrishomocyclopropenium cation is less stable than the corresponding classical tertiary ions.



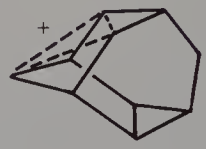
83

84

Two analogs of **82**, the ions, **85**[141] and **86**,[142] with additional "scaffolding," which favors stability, have been reported and both resemble the parent ion in their spectroscopic properties. The cation, **86**, was originally prepared by Coates and Kirkpatrick[143] and has been extensively studied by solvolytic methods. The dramatic enhancement of solvolysis rates and the analysis of remote and proximal effects on the kinetics of ionization of 9-pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonyl derivatives strongly support the nonclassical nature of the cation, **86**.[144,145]



85



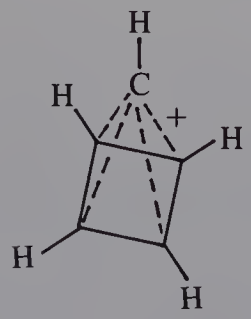
86

Application of Saunders isotopic perturbation technique,[85] the tool of increasing electron demand,[91] and chemical shift additivity[20] also confirm the nonclassical nature of ion **86**.

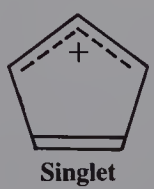
5.5 HYPERCOORDINATE (NONCLASSICAL) PYRAMIDAL CARBOCATIONS

5.5.1. $(CH)_5^+$-Type Cations

The close relationship between carbocations and polyboranes led Williams[146] to suggest the square pyramidal structure, **87**, for the $(CH)_5^+$ cation based upon the isoelectronic square pyramidal structure of pentaborane (see Chapter 6). Stohrer and Hoffman[147] subsequently reached the same conclusion using extended Hückel MO calculations.

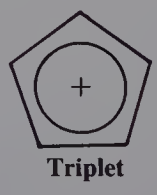


87



Singlet

88



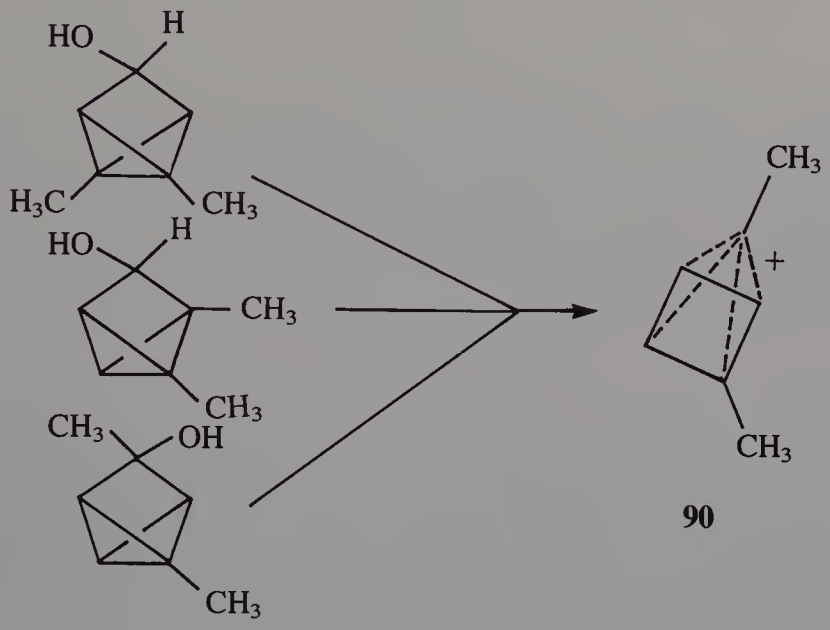
Triplet

89

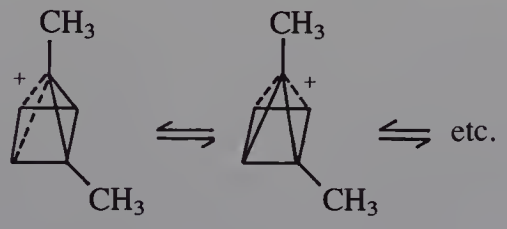
The cation, **87**, can be viewed[147] as a square cyclobutadiene moiety capped by a CH^+ group (see Chapter 1). Several calculations of the structure of $(CH)_5^+$, at more sophisticated levels have appeared.[148] MINDO/3 calculations[149] indicated that the pyramidal cation, **87**, is less stable by 14.4 kcal mol^{-1} than the isomeric singlet cyclopentadienyl cation, **88**. The triplet ion, **89**, was calculated to be more stable than the singlet ion, **85**, but only by 1.6 kcal mol^{-1}. The triplet ion, **89**, has been

prepared[150] by molecular beam codeposition of 1-bromocyclopentadiene with SbF_5 at 78° K, and was characterized by ESR spectroscopy.

Although the parent square pyramidal ion, $(CH)_5^+$, has not yet been reported, the dimethyl derivative, **90**, has been prepared by Masamune and co-workers[151] under stable ion conditions and characterized by ^1H and ^{13}C NMR spectroscopy. Starting with three different precursors (two with adjacent methyl groups and one with nonadjacent methyl groups) a single ion was obtained to which the pyramidal structure, **90**, has been assigned.



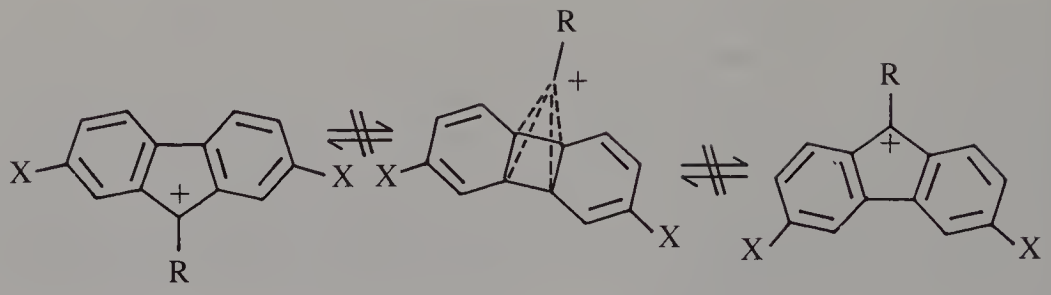
90



91

The alternative singlet structure (analogous to structure **88**), was incompatible with the spectroscopic data. The highly shielded C-5 apical carbon ^{13}C chemical shift (δ-23.0) supports the structure **90** with a symmetrically centered $C-CH_3$ group rather than a set of rapidly equilibrating structures such as **91**. The quenching of ion **90** at low temperatures yields mixtures of cyclopentenes.[151]

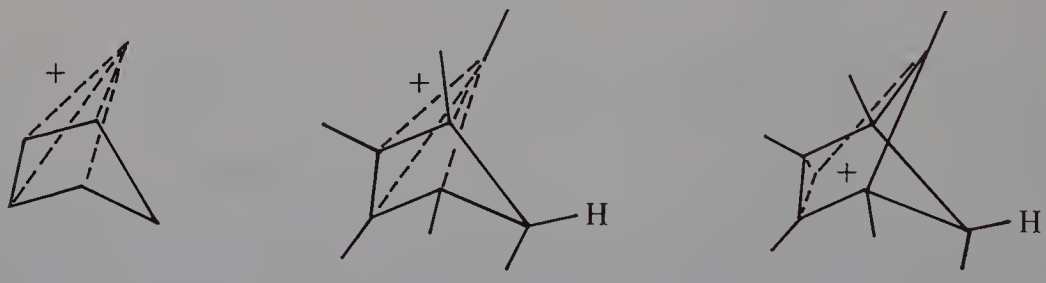
Attempts have been made to observe[149] the potential interconversion of fluorenyl cations such as structures **92–93**. Such intramolecular interconversion (**92** $\rightleftharpoons$ **93**) through the capped pyramidal ion, **94**, was not observed. MINDO/3 calculations[149] on the isomeric structures of cyclopentadienyl, indenyl, and fluorenyl cations indicated strongly decreasing relative stabilities of pyramidal forms due to benzannulation.



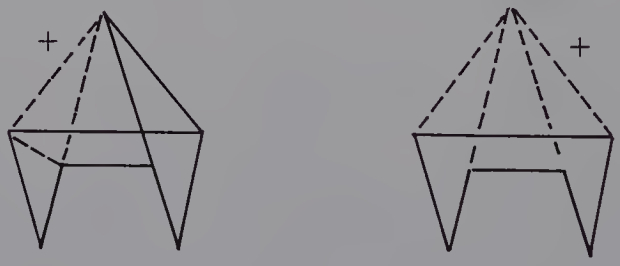
92 **94** **93**

Insertion of a methylene group into the four-membered ring yields the homoderivative, **95**. A number of studies on the hexamethylbicyclo[2.1.1]hexenyl cation[131–135] have shown that the ion is best represented as the bishomocyclopropenyl cation, **80**, rather than the pyramidal ion, **96**.

The trishomocyclopropenyl cation derivative, **97**, has been investigated by both solvolytic and stable ion studies.[151,152]



95 **96** **80**

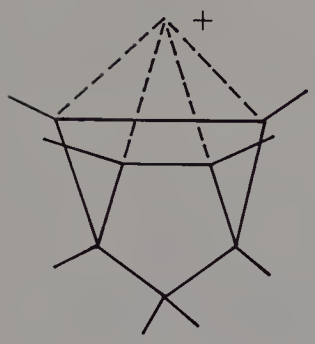


97 **98**

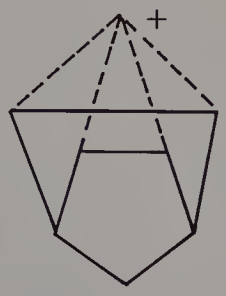
The ^{1}H and ^{13}C NMR data could be best explained with the intermediacy of the bishomopyramidal ion, **98**. Although no conclusive distinction could be made between a rapidly equilibrating system, **97**, and **98**, the structure **98** was preferred based on related MINDO/2 calculations.[153]

Two other substituted bishomo-$(CH)_5^+$ cations that have been investigated in superacid media are the octamethylated ion, **99**, and its parent, **100**.[151c]

The observed[151c,154] ^{13}C NMR data of both ions are consistent with the highly symmetrical structures, **99** and **100**, but the data could also be explained by degenerate rapidly equilibrating systems of lesser symmetry. Recently,



99



100

rearrangements involving $C_8H_8F^+$ cations, **101**, have been studied.[154e] Hart and Willer determined[154f] the apical $^{13}C-H$ coupling constant of the ion, **99**, (J_{C-H} = 220 Hz), which is consistent with the single pyramidal structure, **99**, with close to *sp*-hydridization of the apical carbon atom. Surprisingly, the bishomoaromatic 7-norbornenyl cation, **75**, has nearly an identical $^{13}C-^{1}H$ coupling constant as the ion, **99**, at the C-7 carbon.[125]

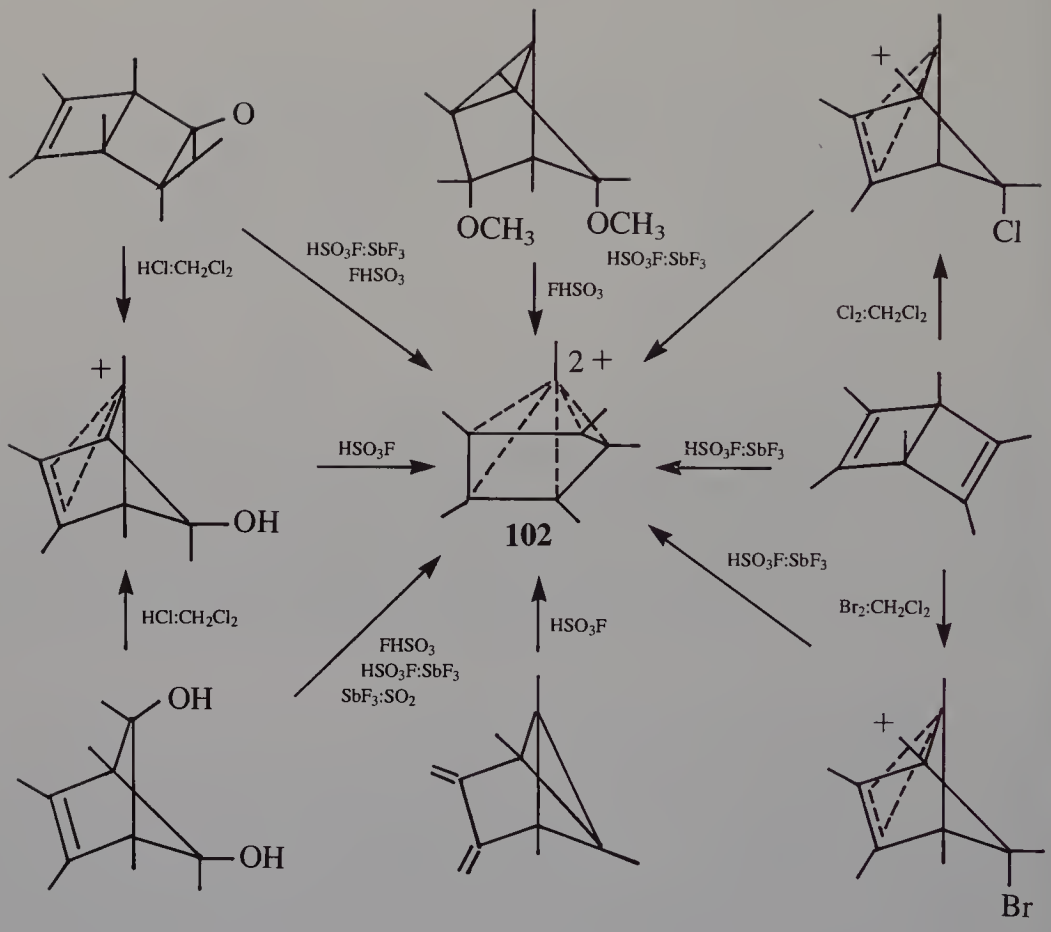
5.5.2. $(CH)_6^{2+}$ Type Dications

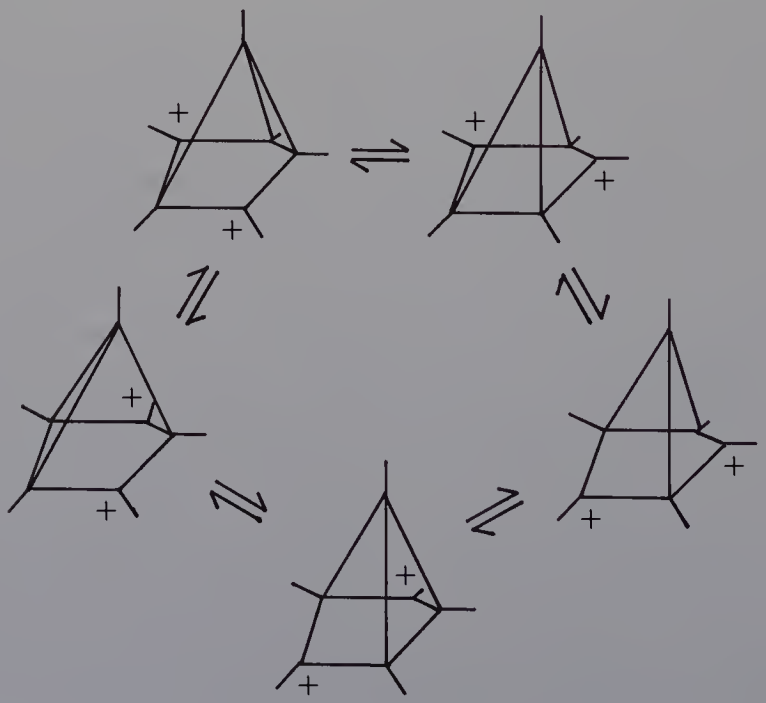
The first known representative of the $(CH)_6^{2+}$ pyramidal type dications was the hexamethyl derivative, **102**.[155–157] This unique dication was prepared by Hogeveen and Kwant from a variety of precursors in superacid media at low temperatures.[155]

Both the ^{1}H and ^{13}C NMR spectra of structure **102** indicate fivefold symmetry, even at low temperatures, for example, -150 °C, with no significant line broadening. This leaves only two alternatives for the structure of the dication: the nonclassical structure, **102**, or a set of rapidly equilibrating degenerate dications, **103**, with an activation energy for the exchange, of < 5 kcal/mole.[157]

The observed chemical shift of the carbon atoms of the five-membered ring is δ ^{13}C 126.3, whereas the calculated average of a classical equilibrating ion, **103**, would be δ ^{13}C 166.1 based upon model systems.[155–157] Moreover, the extreme high field shift of the apical carbon atom (δ ^{13}C 2.0) cannot be explained in terms of equilibrating classical structures and clearly supports a high coordinate environment of the carbon at this center. The dication, **102**, shows no UV absorption above nm,[155] which is consistent with ab initio calculations of the electronic structure of the dication. The rates of deuterium exchange, the rate of carbonylation, and the thermal stability provide strong evidence for the nonclassical nature of the ion, **102**. Furthermore, definite evidence for the pyramidal bridged nature of structure **102** comes from isotopic perturbation studies.[158] Very little isotopic perturbation on the basal carbon signal is observed in the ^{13}C NMR spectrum of the dication $[C_6(CH_3)_4(CD_3)_2^{2+}]$. This indicates that the ion must be symmetrically bridged. Other supporting evidence comes from a comparison of the ^{13}C and ^{11}B NMR chemical shifts of the isoelectronic borane, B_6H_{10} (see Chapter 6).[64b,64c]

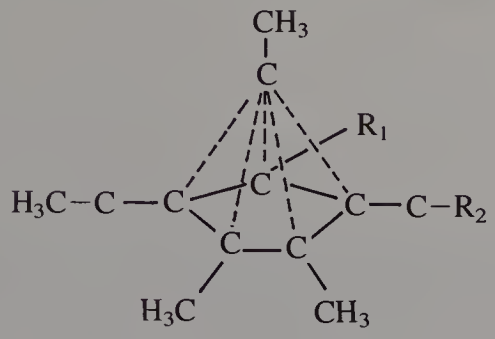
Hogeveen, Heldeweg and co-workers[159,160] also prepared the ethyl and isopropyl


O
OCH3
OCH3
Cl
HCl:CH2Cl2
HSO3F:SbF3
FHSO3
FHSO3
HSO3F:SbF3
Cl2:CH2Cl2
2 +
HSO3F
HSO3F:SbF3
OH
102
HSO3F:SbF3
HCl:CH2Cl2
Br2:CH2Cl2
FHSO3
HSO3F:SbF3
SbF3:SO2
HSO3F
OH
OH
Br



103

derivatives of these pyramidal dications, **102–107**, and their bridged structures have been confirmed by ^{1}H and ^{13}C NMR spectra and quenching studies.



104, $R^1 = CH_3$, $R^2 = C_2H_5$
105, $R^1 = CH_3$, $R^2 = i\text{-}C_3H_7$
106, $R^1 = R^2 = C_2H_5$
107, $R^1 = R^2 = i\text{-}C_3H_7$

5.6. CONCLUSIONS

In this chapter we discussed the structural (spectroscopic) and chemical evidence for a variety of carbocations containing hypercoordinated carbon atoms involved in two-electron, three-center (or multicenter) bonding. Our intention was to show the reader that hypercoordinated carbocations are well-defined chemical entities and constitute one of the important classes of hypercarbon compounds. Although the structures of "nonclassical" carbocations were for a long time in the center of a highly debated controversy, following their direct spectroscopic characterization this is now generally recognized to be resolved. These studies also led to the realization that the nonclassical ions fill a logical sequence of hypercarbon containing compounds that happen to contain only carbon and hydrogen atoms.

It is also significant to note that nearly all carbocations have known counterparts in polyborane compounds that are isoelectronic and isostructural. Chapter 6 discusses these boron compounds along with the analogy of their ^{11}B NMR chemical shifts with the corresponding ^{13}C NMR chemical shifts of carbocations. The role of hypercarbon reaction intermediates is discussed in Chapter 7. Again by necessity our treatment is selective to illustrate major types and systems that show the significant role hypercarbon species play in chemistry.

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chapter 6

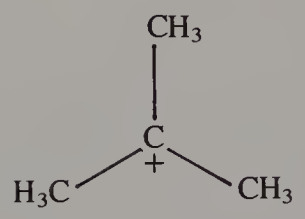
CARBOCATION, BORANE, AND POLYBORANE ANALOGS

6.1. INTRODUCTION

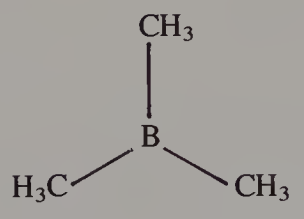
Boron and carbon are consecutive first-row elements. Thus a neutral tetravalent carbon is isoelectronic with a tetravalent boron anion (or borane–Lewis base adduct). Similarly, trivalent carbocations are isoelectronic with the corresponding neutral trivalent boron compounds.

The structural similarity of trivalent boranes and trivalent carbocations was first experimentally established by their vibrational spectra. The infrared (IR) and Raman spectra of $(CH_3)_3C^+$, **1**, in SO_2ClF solution were studied in 1971 by Olah et al.[1] and the vibrational frequencies, the number of lines, and the activity of those lines, was correlated with the spectrum of $(CH_3)_3B$, **2**. The similarity between the skeletal modes of vibration in $(CH_3)_3B$, **2**, and $(CH_3)_3C^+$, **1**, provided unambiguous evidence that the two species possessed analogous structures and bonding, that is, the carbon skeleton in $(CH_3)_3C^+$, **1**, is planar with C_{3v} symmetry. The IR spectrum of CH_3^+, **3**, in the gas phase was obtained by Oka and co-workers[2] in 1985. Analysis of the IR bands strongly suggests the planar structure with D_{3h} symmetry in agreement with theory.[3] The expected similar planar structure for the isoelectronic boron analog, BH_3, **4**, is based on IR analysis.[4]

In 1971, based on the square pyramidal structure of pentaborane, **5**, Williams[5] proposed a similar square pyramidal structure for $C_5H_5^+$, **6**. Subsequent support for the $C_5H_5^+$ structure came from extended Hückel MO calculations by Hoffman and Stohrer[6] in 1972.



1



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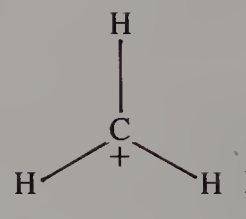

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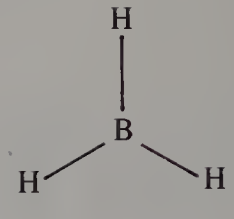

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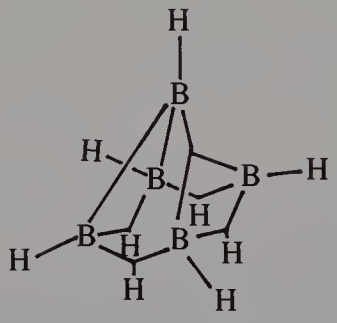

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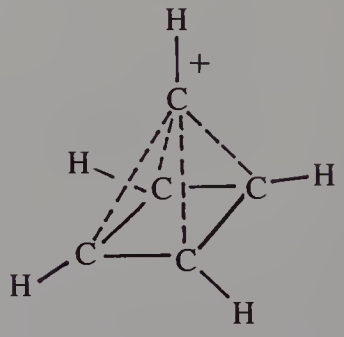
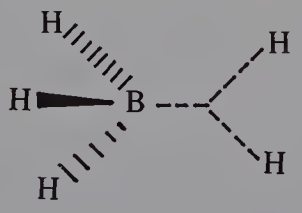


6

Extending similar carbocation–borane analogies from trigonal to pentacoordinate species, Olah suggested in 1972 that the carbon analog of BH_5, **7** (pentahydrido boron) is the parent hypercoordinate carbocation CH_5^+, **8**.



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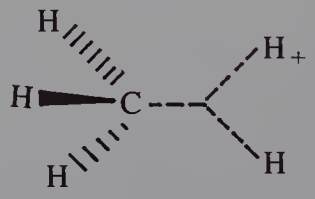


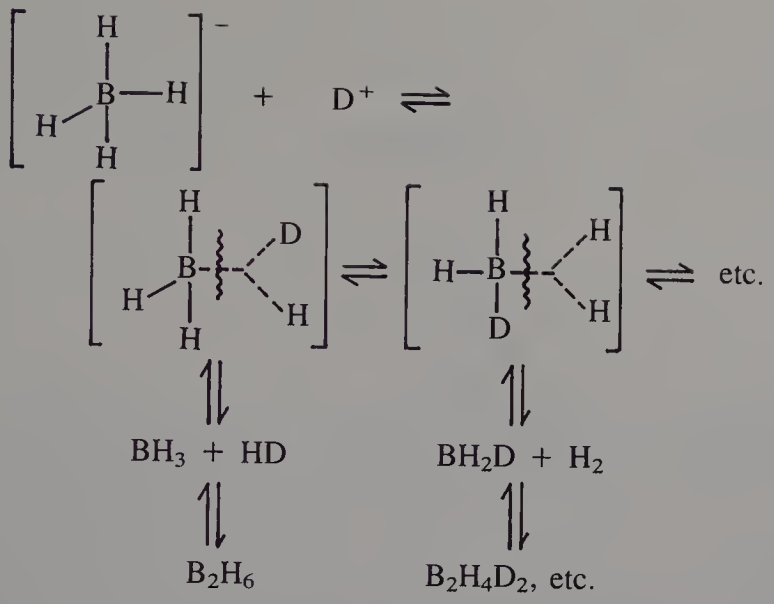
8

Messmer and Jolly,[7] while studying the aqueous protolysis of sodium borohydride in D_2O, observed that besides HD as the primary product, some H_2 (about 4%) was also formed. This observation indicated the possibility that the attack of deuterium is not colinear on the hydrogens of BH_4 but can involve one of the B−H bonds itself, permitting subsequent scrambling in BH_4D prior to cleavage into HD and BH_3 (Scheme 6.1).

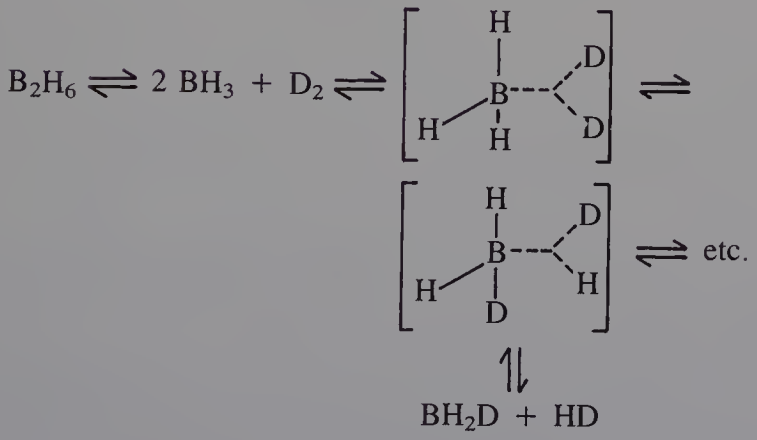
The reversibility of the $BH_3 + H_2$ reaction is also evident by the work of Pitzer and co-workers[8] who were able to prepare B_2D_6 by treating B_2H_6 with D_2. The only reasonable mechanism one can envisage for the exchange seems to be the direct insertion of BH_3 into D_2 followed by polytopal bond to bond rearrangement (Scheme 6.2).[9,10]

Olah et al.[10] studied the protolysis (deuterolysis) of the borohydride anion in

Scheme 6.1



Scheme 6.2

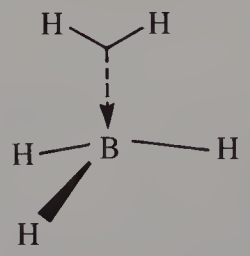


anhydrous strong acids and found extensive hydrogen–deuterium exchange. When excess sodium borohydride is treated with 100% DF (in a bomb), H_2 and HD (as well as a trace of D_2) are formed (as analyzed by mass spectrometry) showing that extensive H−D scrambling occurs with the intermediacy of BH_4D followed by bond to bond rearrangement. Similar exchange was also observed when sodium borodeuteride was treated with H_2SO_4.

It should be pointed out that similar hydrogen–deuterium exchange has been observed in the case of CH_4 with deuterated superacids or CD_4 with protio superacids thus implicating the involvement of CH_5^+ isotopomers.[10]

Olah et al.[10] in their CNDO/2 calculations on BH_5 found the C_s symmetry

preferred, as is the case with CH_5^+. More detailed *ab initio* MO calculations by Lipscomb and co-workers,[11] as well as by Collins et al.,[12] and by Hoheisel and Kutzelnigg[13] showed BH_5 to be a metastable species with C_s symmetry with identifiable BH_3 and H_2 subunits, that is, a weak interaction between BH_3 and H_2 (structure **9**).



9

In solution chemistry, of course, additional solvation effects can affect the stability of BH_5.

The analogy of carbocations and boranes is very apparent in the ability of CH fragments to replace BH_2 groups[14,15] in polyboranes leading to carboranes. Each of the compounds listed in Scheme 6.3 has a pyramidal skeleton, wherein CH groups systematically replace BH_2 units in the clusters. The nature of bonding in such polyboranes and carboranes is well understood and the existence of this complete series of isoelectronic and isostructural compounds clearly reinforces the idea that carbon atoms incorporated in a polyborane framework can participate in multicenter (cluster) bonding (also see Chapter 3) in an exactly analogous manner as boron atoms.

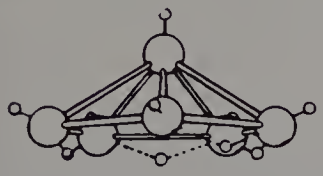
Scheme 6.3 shows the first complete set of isoelectronic and isostructural polyboranes and carboranes discovered in the 1950s through the 1970s. They are B_6H_{10}, **10**,[16] CB_5H_9, **11**,[14] $C_2B_4H_8$, **12**,[15] $C_3B_3H_7$, **13**,[17] $C_4B_2H_6$, **14**,[18] and $C_5BH_5I^+$, **15**.[19]

Each of the compounds (in Scheme 6.3) **10–15** subscribes[20] to the *nido*-borane formulation and the structure of the unknown carbodication, $C_6H_6^{2+}$, **16**, is a natural extension of this sequence.

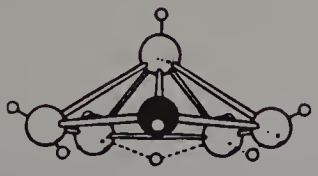
Indeed, the permethylated derivative of structure **16** has been prepared by Hogeveen and Kwant[21] and the nonclassical pyramidal structure $Me_6C_6^{2+}$, **17**, was deduced from its ^1H and ^{13}C NMR spectroscopic data. The sequence in Scheme 6.3 represents the first complete series of isoelectronic and isostructural compounds within the polyborane–carborane–carbocation continuum. The dication **17** can be depicted in several different ways. It can be represented as one of five possible cannonical (3*c*–2*e*) resonance forms. Hereafter when a (3*c*–2*e*) depiction is shown it is understood that it is only one of the possible cannonical (3*c*–2*e*) forms.

Each of the different "types" of nonclassical carbocations thus far discovered has one or more potential isoelectronic and isostructural polyborane counterparts. The NMR chemical shift values of the skeletal ^{11}B and ^{13}C atoms of these boron–carbon analogs show clear parallels demonstrating that the carbon atoms in nonclassical carbocation frameworks participate in multicenter bonding exactly as do boron atoms in the analogous polyboranes.

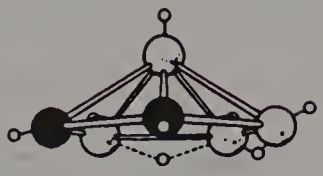
Scheme 6.3



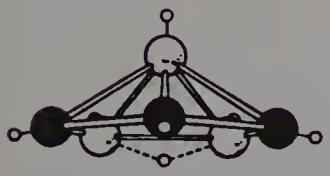
B_6H_{10}, **10**



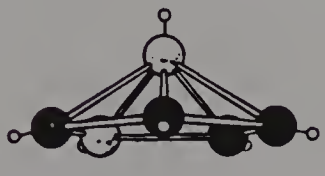
CB_5H_9, **11**



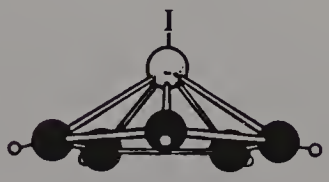
$C_2B_4H_8$, **12**



$C_3B_3H_7$, **13**

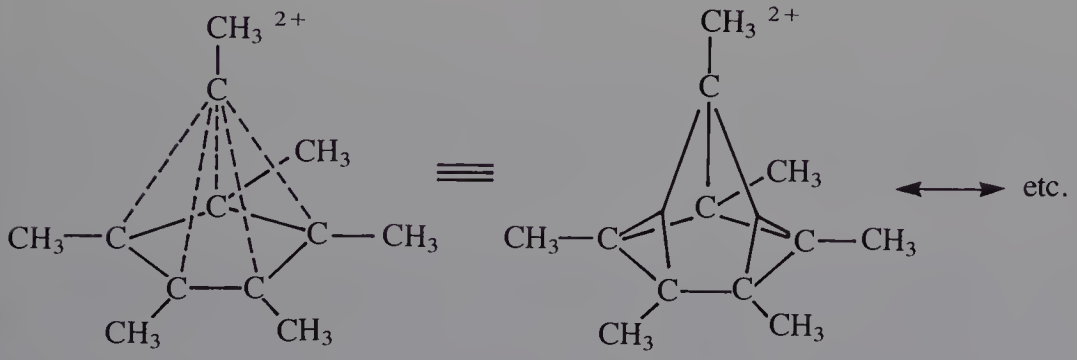


$C_4B_2H_6$, **14**



$C_5BH_5I^+$, **15**

$C_6H_6^{2+}$, **16**



17

6.2. NMR SPECTROSCOPIC COMPARISON OF ANALOGOUS CARBOCATIONS AND POLYBORANES[22]

6.2.1. Trigonal Carbocations and Trigonal Boranes

As mentioned previously, a trivalent carbon atom bearing a single positive charge is isoelectronic with a neutral boron atom. The close relationship between the ^{11}B NMR chemical shifts of the boron atoms in boron compounds and the ^{13}C NMR chemical

shifts of the corresponding trigonal carbocations was first shown by Nöth and Wrackmeyer,[23] and Spielvogel and Purser.[24] The general correlation is shown in Equation (6.1).

$$\delta^{11}B_{(BF_3:OEt_2)} = 0.4\ \delta^{13}C_{(TMS)} - 46 \qquad (6.1)$$

In Equation 6.1, the $\delta^{11}B$ is the chemical shift of the ^{11}B nucleus in parts per million with respect to the BF_3:OEt_2 absorption while $\delta^{13}C$ is the chemical shift of the cationic carbon of the corresponding carbocation with respect to tetramethylsilane (TMS) signal.

Compounds involving alkyl, halogen, oxygen, or hydrogen substituents correspond well to Equation (6.1) while compounds with phenyl, cyclopropyl, or olefinic groups, which may conjugate with the cationic carbon and boron centers to differing degrees, deviate from Equation 6.1.

6.2.2. Tetrahedral Hydrocarbons and Tetrahedral Borate Anions

Equation 6.1 is restricted to the comparison of neutral electron-deficient boron compounds and sp^2 carbocations. However, if the ^{11}B chemical shifts of electron precise tetracoordinate borate anions are compared with the ^{13}C chemical shifts of their neutral carbon analogs, they fall close to a similar line.

A general equation (Equation 6.2) has been derived by incorporating both electron-deficient trigonal and electron-precise tetrahedral ^{11}B and ^{13}C values in the analysis (see Fig. 6.1 for the combined correlation).

$$\delta^{11}B_{(BF_3:OEt_2)} = 0.33\ \delta^{13}C_{(TMS)} - 30 \qquad (6.2)$$

Equations 6.1 and 6.2 have been derived empirically. They are in good agreement with most of the available data spanning some 600 ppm on the ^{13}C chemical shift scale. Clearly the same factors that determine the chemical shifts of the boron nuclei also govern the chemical shifts of the carbon nuclei.

6.2.3. Hypercoordinate (Nonclassical) Carbocations and Polyboranes

All polyboranes are electron deficient and many of their structures are well known by x-ray crystallography. They all contain many hypercoordinate boron atoms (hyperborons). In Chapter 5 we discussed the structures of many carbocations that contained hypercoordinated carbon atoms (hypercarbons). In this section we systematically compare the ^{11}B NMR chemical shifts of polyboranes with the ^{13}C NMR chemical shifts of the corresponding isolelectronic nonclassical carbocations. Table 6.1 lists the six pairs of isostructural and isoelectronic nonclassical carbocations and polyboranes that would be ideal to make NMR chemical shift comparisons.

The terms *nido*, *arachno*, and *hypho* have been borrowed from polyborane literature[20] and reflect the number of skeletal electron pairs ($n + 2$, $n + 3$, and $n + 4$, respectively) in the skeletons of the various families of compounds. However, in

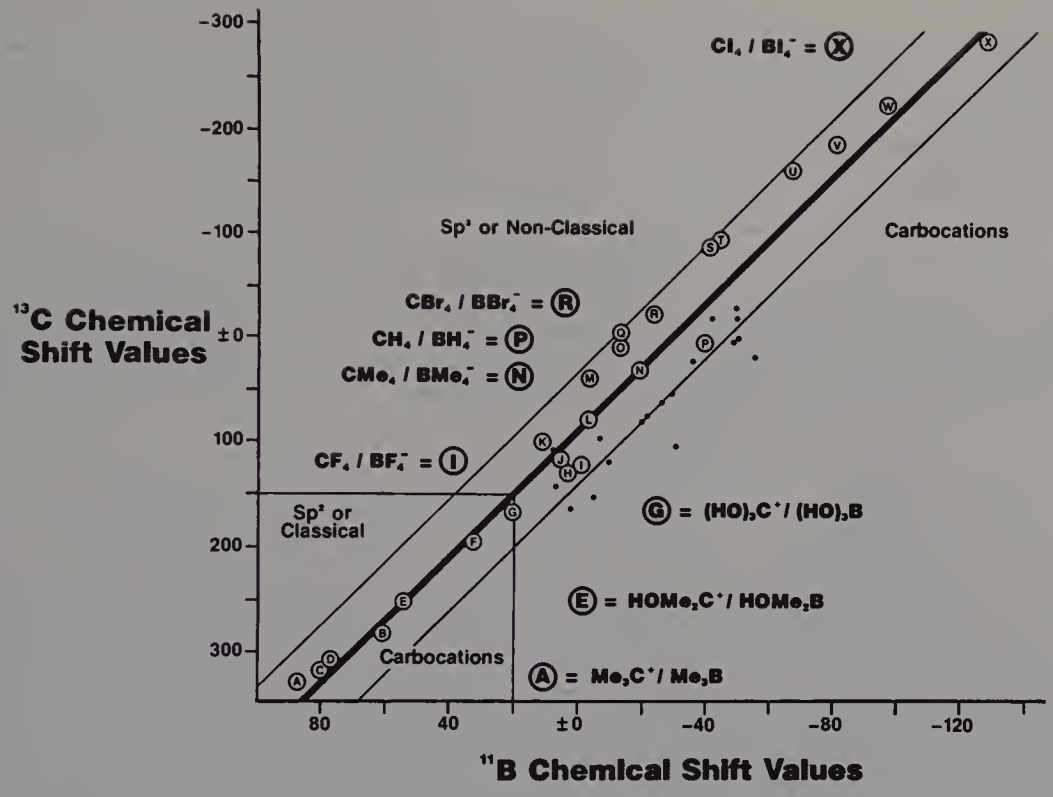


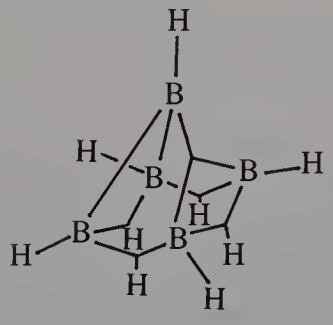
Figure 6.1. Combined correlation of trigonal carbocations and tetrahedral hydrocarbons with their boron analogs (only representative examples are shown).

TABLE 6.1. Candidates for Comparison between Polyboranes and Nonclassical Carbocations

Available Carbocation	"Ideal Pairs"	Available Polyborane
	Nido	
1, 2-$Me_2C_5H_3^+$	$\xleftarrow{-2\,H\ +2\,Me}$ $C_5H_5^+/B_5H_5^{4-}$ $\xrightarrow[+4\,H^+]{+2\,Me,\ -2\,H}$	1, 2-$Me_2B_5H_7$
$Me_6C_6^{2+}$	$\xleftarrow{-6\,H\ +6\,Me}$ $C_6H_6^{2+}/B_6H_6^{4-}$ $\xrightarrow[+4\,H^+]{}$	B_6H_{10}
	Arachno	
$R_3C_3H_4^+$	$\xleftarrow{+3\,R,\ -3\,H}$ $C_3H_7^+/B_3H_7^{2-}$ $\xrightarrow[+H^+]{}$	$[B_3H_8^-] \sim B_3H_7$:L
2-Norbornyl		
$C_4H_7^+$	$\longleftarrow$ $C_4H_7^+/B_4H_7^{3-}$ $\xrightarrow[+2\,H^+]{}$	$B_4H_9^-$
Cyclopropropylcarbinyl		
	Hypho	
$R_6C_3H_3^+$	$\xleftarrow{+6\,R,\ -6\,H}$ $C_3H_9^+/B_3H_9^{2-}$ $\longrightarrow$	BH_2:L fragment of B_3H_7:L
Trishomocyclopropenium		
$R_4C_5H_5^+$	$\xleftarrow{+4\,R,\ -4\,H}$ $C_5H_9^+/B_5H_9^{4-}$ $\xrightarrow[+2\,H^+]{}$	$[B_5H_{11}^{2-}]$ B_5H_9:L_2

none of the cases in Table 6.1 are the "ideal" compounds available to make rigorous comparisons. On the other hand, suitable derivatives are available that differ from the ideal cases by the presence or absence of alkyl groups and bridge hydrogens. The effects of these factors on the ^{11}B and ^{13}C NMR chemical shifts can roughly be estimated permitting more legitimate comparisons to be made.[22]

6.2.3.1. Square Pyramidal $Me_2C_5H_3^+$ and Pentaborane (*nido*-B_5H_9). Following the synthesis of $Me_2C_5H_3^+$ in 1972 by Masamune et al.,[25] it was noted that the ^{13}C NMR spectrum was consistent in every detail with the pyramidal structure, **18**, previously predicted by Williams[5] based upon the structure of the isoelectronic boron hydride, *nido*-B_5H_9, **5**.



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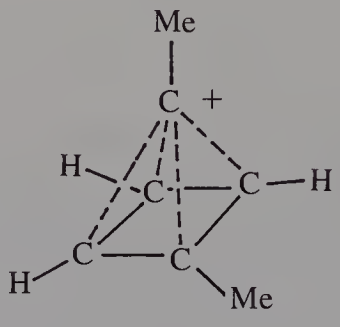
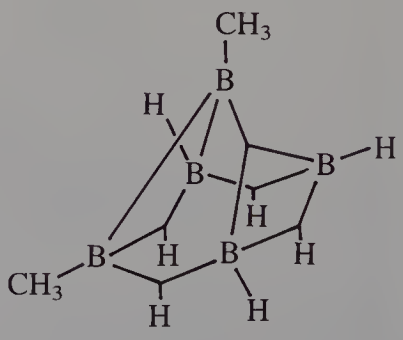


18



19

Among the various polyboranes, the boron atoms with the maximum number of adjacent boron atoms (highest coordination site) typically exhibit ^{11}B chemical shift values at the highest field.[26] In the ^{11}B NMR spectrum of structure **5** the apical boron atom is upfield by 40 ppm when compared to those of the basal atoms; likewise, in the ^{13}C NMR spectrum of the cation, **18**, the apical carbon is found shielded by about 100 ppm from the chemical shifts of basal atoms. The preparation and NMR data of *nido*-1,2-$Me_2B_5H_7$, **19**, an almost exact isoelectronic analog of **18**, have been reported.[27] In the NMR spectrum of structure **19**, the ^{11}B chemical shifts of the five skeletal boron atoms parallel the ^{13}C chemical shifts of the corresponding carbon atoms in structure **18**. The chemical shifts are compared in Figure 6.2 (the locations of the relevant ^{11}B and ^{13}C resonances are compared with the general correlation line of Fig. 6.1).

In constructing Figure 6.2, the approximate chemical shift influence of the removal of bridge hydrogens in polyboranes has been estimated[24] to be about 10–15 ppm per neighboring bridge hydrogen and the estimated correction for this change, that is, making structure **19** more like structure **18**, causes the chemical shift values of the basal borons in **19** to move away from the "line" generated in Figure 6.1. In general, it has been found that the points of intersection of the ^{13}C and ^{11}B chemical shift values, after correction for bridge hydrogen and/or alkyl group removal, tend to be slightly "off" in the direction of higher ^{11}B values or slightly lower ^{13}C chemical shift values.

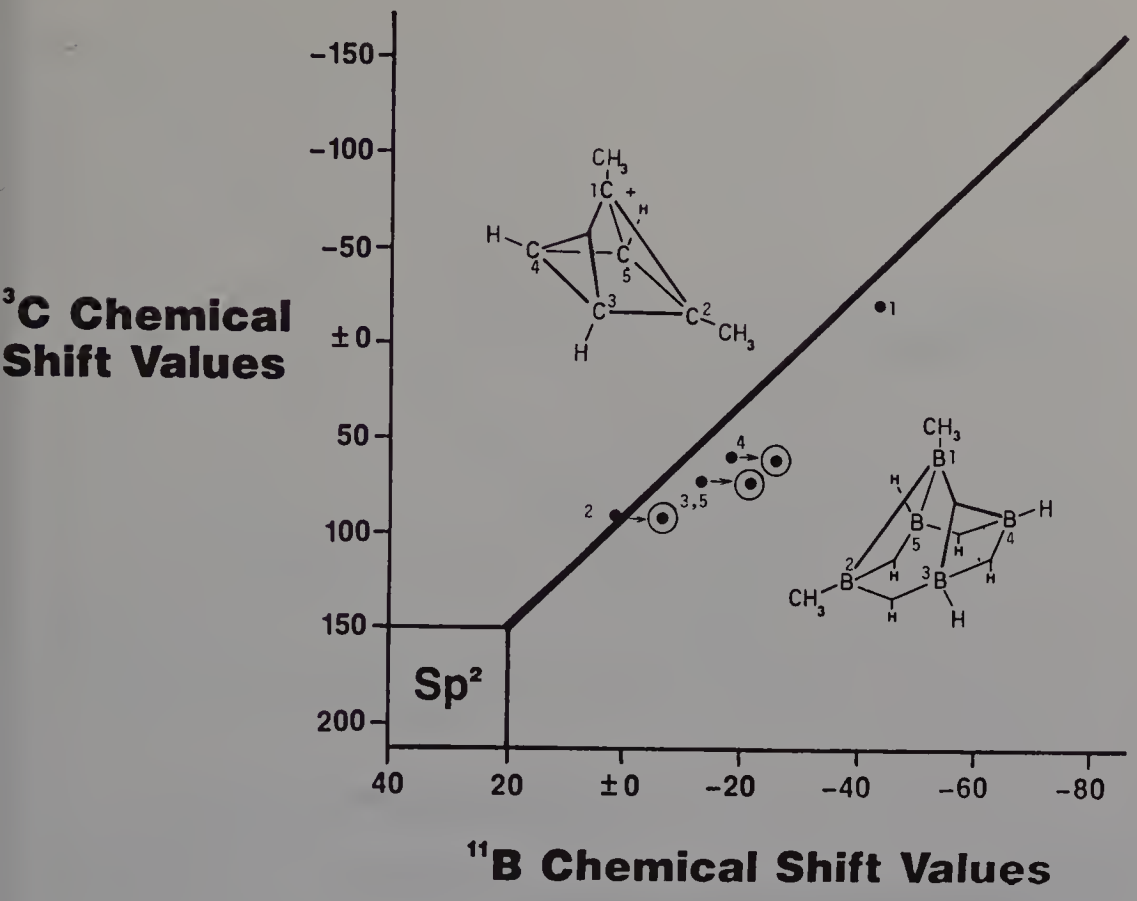


Figure 6.2. Comparison of $1,2\text{-}(CH_3)_2C_5H_3^+$ and $1,2\text{-}(CH_3)_2B_5H_7$. • raw data; ⊙ corrected data for bridge hydrogen removal.

6.2.3.2. $Me_6C_6^{2+}$ and *nido*-B_6H_{10}. Structure **16**, $C_6H_6^{2+}$, would be isoelectronic with *nido*-B_6H_{10}, **10**. Its fully methylated derivative, $Me_6C_6^{2+}$, **17**, has been synthesized and spectroscopically characterized.[21]

In Figure 6.3 are shown the correlation of the ^{11}B chemical shift values for B_6H_{10}, **10**, with the ^{13}C chemical shift values for $Me_6C_6^{2+}$, **17**. When an alkyl group replaces a hydrogen substituent, the chemical shift of a ^{11}B nucleus moves down field (8–15 ppm) and the minor effects of methyl substitution (removal) and bridge hydrogen removal may be qualitatively taken into account as indicated in Figure 6.3.

6.2.3.3. 2-Norbornyl and Related Cations and *Arachno*-B_3H_7:L. The nonclassical nature of the 2-norbornyl cation, **20**, was first proposed by Winstein and Trifan[28a] in 1949 and has since been verified by numerous experimental studies (see Chapter 5). There are several known cations of the bicyclo[2.2.1]heptyl type, for example, **21** and **22**, and all may be regarded as trialkyl derivatives of protonated cyclopropane, $C_3H_7^+$, **23**, with variations in the hydrocarbon "scaffolding" that supports and surrounds the cationic center.

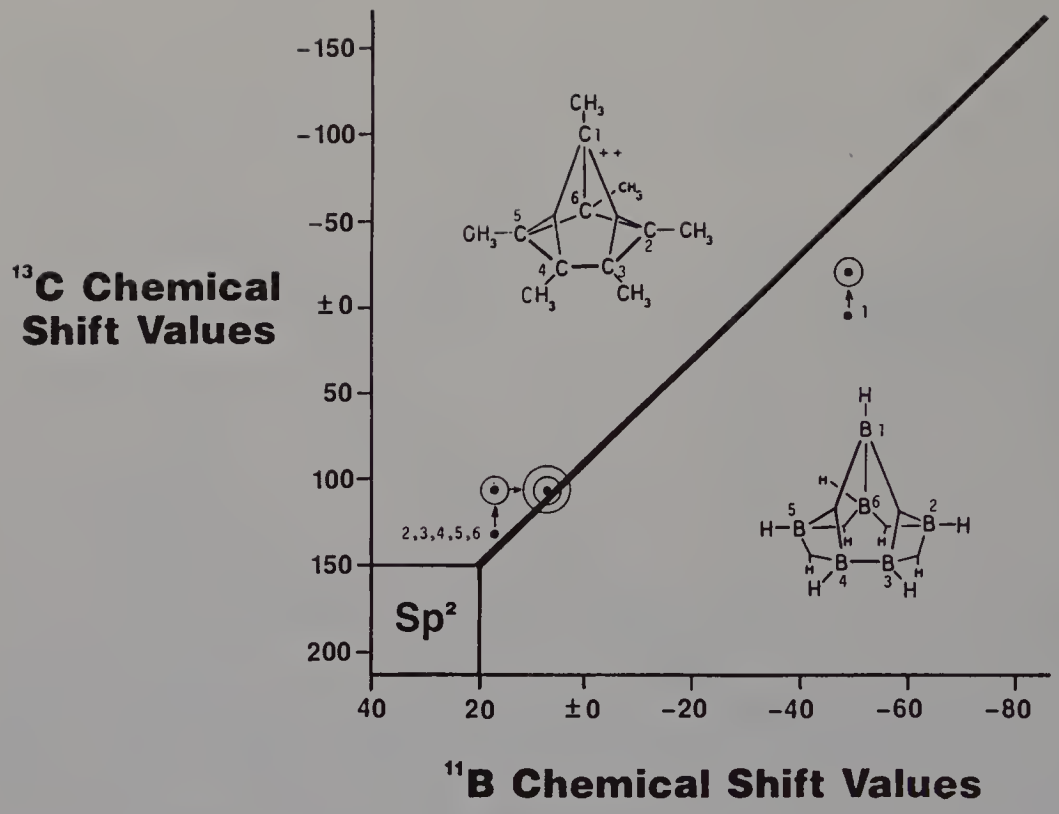
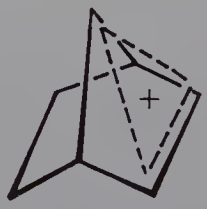


Figure 6.3. Comparison of $(CH_3)_6C_6^{2+}$ and B_6H_{10}. • raw data; ⊙ corrected data for alkyl group removal; and, ◎ corrected data for alkyl group and bridge hydrogen removal.

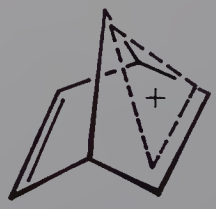
2-Norbornyl

20



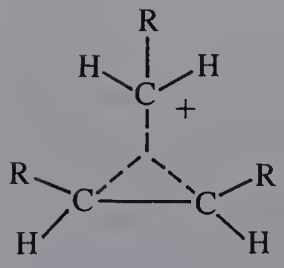
7-Norbornenyl

21



7-Norbornadienyl

22



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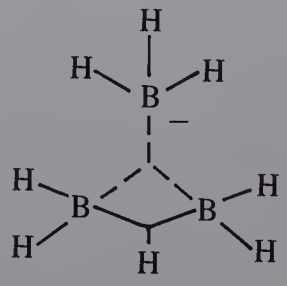

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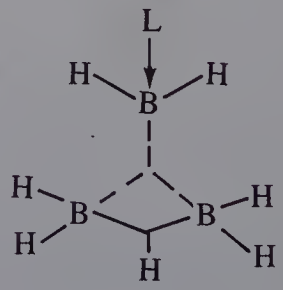


25

The cyclopropane-like face of the 2-norbornyl cation, **20**, is notionally isoelectronic and isoskeletal with a trialkyl derivative of $B_3H_8^-$, **24**. The anion, **24**, however, is fluxional in solution with all protons exchanging rapidly on the NMR time scale.[26b] There are several Lewis base adducts of B_3H_7[29] (B_3H_7:L is isoelectronic with the less prevalent tautomer of $B_3H_8^-$), which are not fluxional, however, and have the symmetrical structure **25**. Therefore, **20** and **25** are compared in Figure 6.4.

In otherwise identical environments, boron atoms with phosphorus ligands exhibit chemical shift values that are coincidentally very similar to those of the "same" borons wherein hydride ligands, H^-, replace the phosphorus ligands, L. This is not true with other electron-pair donors such as ethers and amines. For this reason, the ^{11}B NMR data of phosphorus containing compounds such as B_3H_7:L were selected where L equals PF_2Cl, PF_2Br, and PF_2NMe_2. Their ^{11}B NMR spectra consist of high field triplets ($\delta\ ^{11}B = -50 \pm 10$ ppm, relative area one) and low field triplets ($\delta\ ^{11}B = -12 \pm 5$ ppm, relative area two). Figure 6.4 shows the correlation of the ^{13}C chemical shifts of structure **20** and the ^{11}B chemical shifts of structure **25**. Again, the effect of alkylation and the removal of bridge hydrogens were qualitatively taken into account in constructing Figure 6.4.

As discussed in Chapter 5, if the 2-norbornyl cation was actually a set of

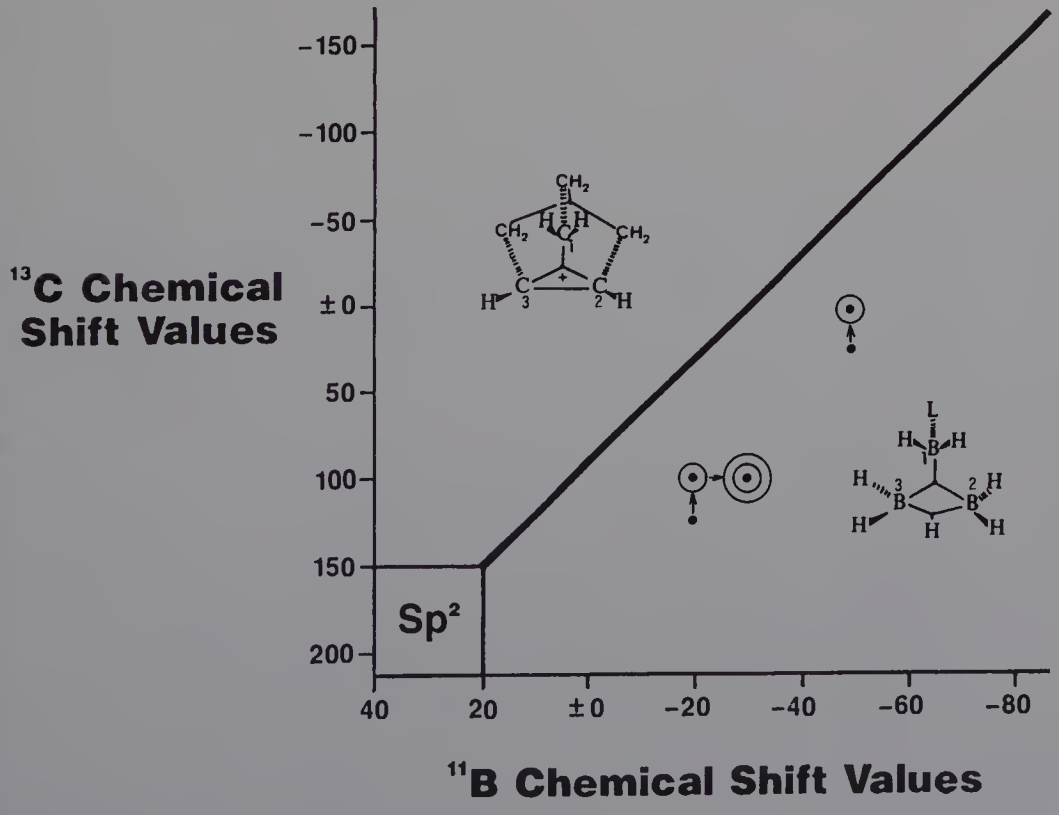
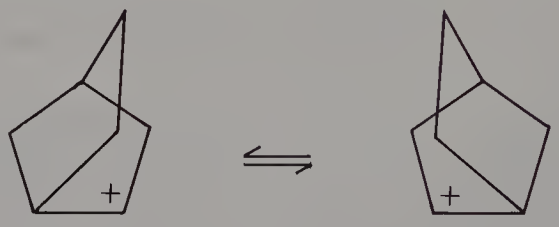


Figure 6.4. 2-Norbornyl cation and B_3H_7:L. • raw data; ⊙ corrected data for alkyl group removal; and ◎ corrected data for alkyl group and bridge hydrogen removal.

equilibrating classical carbenium ions, **20a** $\rightleftharpoons$ **20b**, the ^{13}C chemical shifts of C-2 and C-3 would be the average of a highly deshielded carbocationic center at 320 ppm and an sp^3 center at 60 ppm. In the latter case, the ^{13}C chemical shift values would be much further removed from the main correlation line in Figure 6.4.



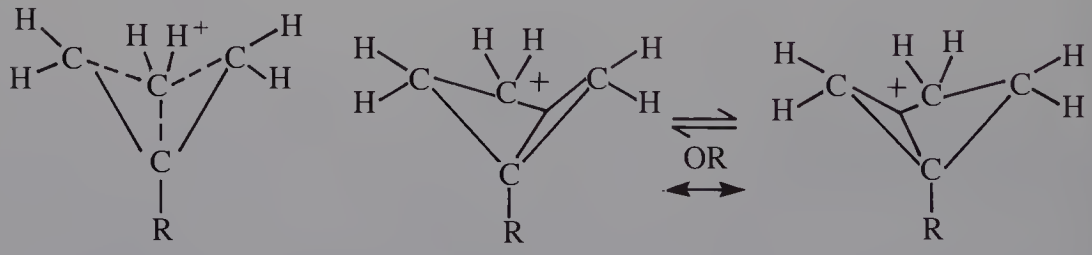
a **b**

20

6.2.3.4. Cyclopropylcarbinyl Cation $C_4H_7^+$ and *Arachno*-$B_4H_9^-$. There are difficulties in comparing the parent compounds, $C_4H_7^+$, **26**, and $B_4H_9^-$, **27**, as the former is fluxional (rapidly averaging all methylenes) at the lowest temperatures studied.[30a] However, the ^{13}C NMR spectrum of 1-Me$C_4H_6^+$, **28**, a derivative of $C_4H_7^+$, **26**, shows[30b] two nonequivalent types of methylene carbons at low temperatures (δ ^{13}C 72.7 and -2.8 from TMS), which may be attributed to the preferred symmetrical nonclassical structure **29**, or, much less likely, to a rapid equilibrium between the unsymmetrical structures **30a** $\rightleftharpoons$ **30b**.

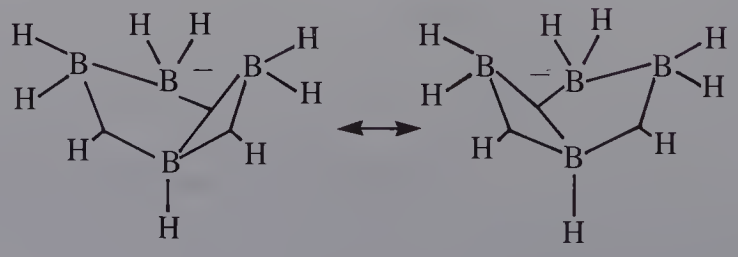
$C_4H_7^+$ $B_4H_9^-$ $1-MeC_4H_6^+$

26 **27** **28**



29 **30**

R = H or CH_3



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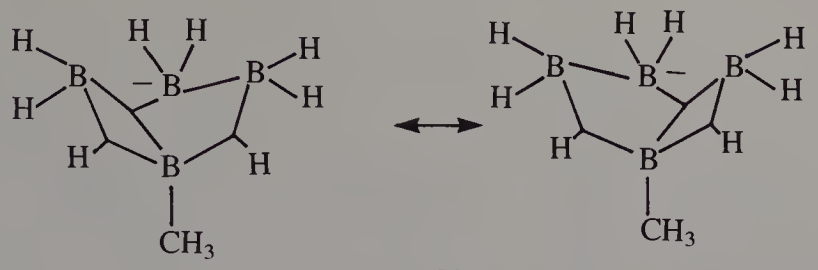


32

The resonance forms, **30a** ⟷ **30b**, are analogous to those that have been proposed for the parent anion ($B_4H_9^-$), **31** (isoelectronic with $C_4H_7^+$, **26**[31]).

In the methylated polyborane anion ($MeB_4H_8^-$), **32**,[32] the NMR absorption of the atom bearing the methyl substituent is found at a lower field, as expected, compared to the corresponding boron atoms in structure **31**. The chemical shift agreement between structures **32** (after correcting for bridge hydrogen removal) is quite good (Fig. 6.5).

In contrast, the ^{13}C NMR spectrum of the parent cyclopropylcarbinyl (or cyclobutyl or bicyclobutyl) cation, **26**, (see Chapter 5), as it is fluxional on the NMR time scale even at temperatures down to -155 °C,[30b] is less easily interpreted. At low

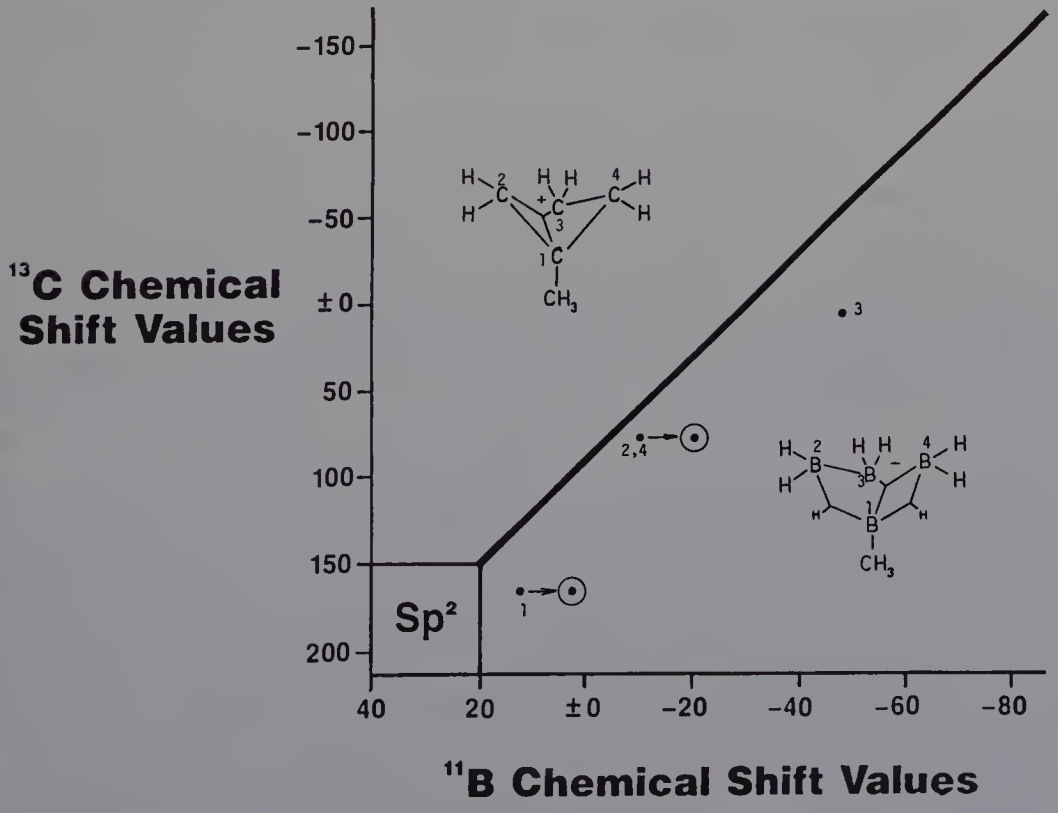


Figure 6.5. Comparison of 1-$CH_3C_4H_6^+$ and 1-$CH_3B_4H_8^-$ • raw data and ⊙ corrected data for bridge hydrogen removal.

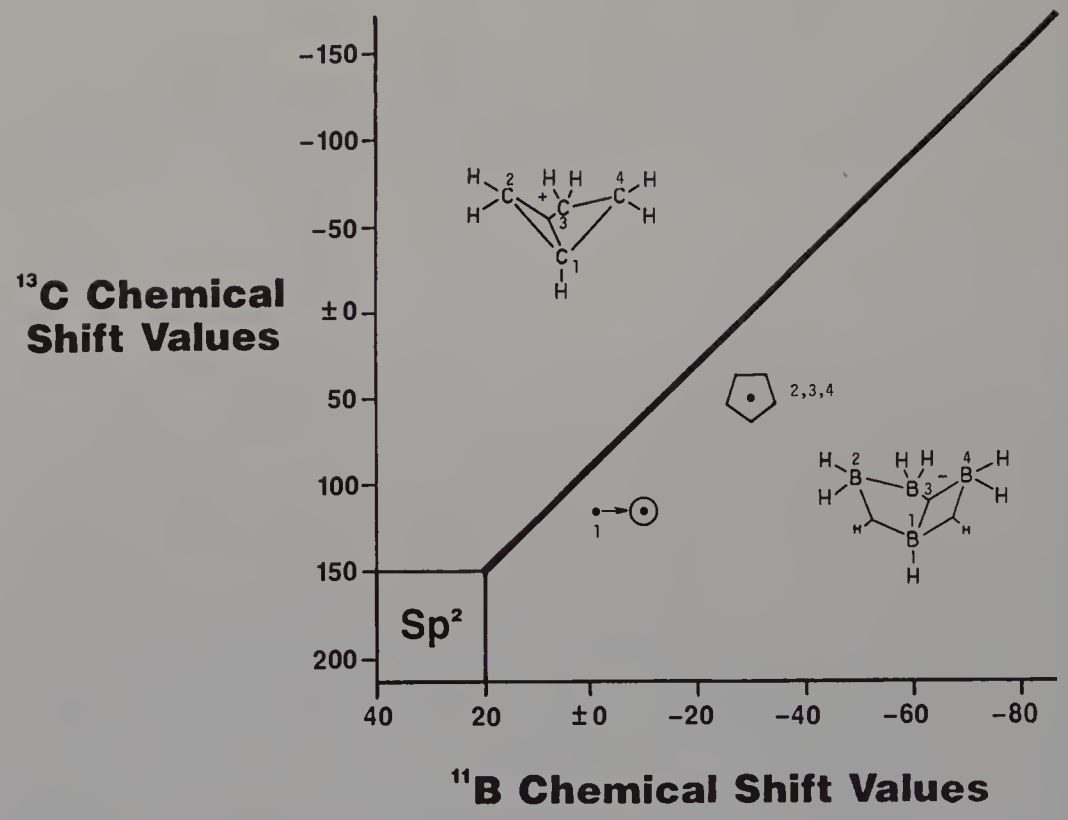


Figure 6.6. Comparison of $C_4H_7^+$ and $B_4H_9^-$. • raw data; ⊙ corrected data for bridge hydrogen removal; and ⊙ averaged data corrected for bridge hydrogen removal.

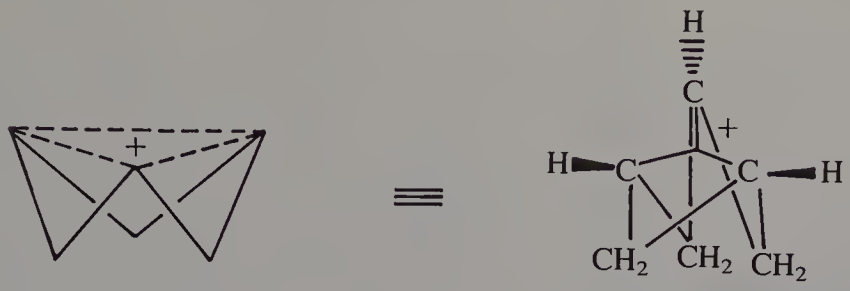
temperatures, the ^{13}C NMR spectrum of the cation consists of a CH resonance ($\delta\ ^{13}C = 115$ from TMS) and an average CH_2 resonance at a higher field ($\delta\ ^{13}C = 47$). The NMR chemical shifts of $C_4H_7^+$, **26**, and $B_4H_9^-$, **27** are compared in Figure 6.6.

In contrast, hydride migration in $B_4H_9^-$, **27**, has been frozen on the NMR time scale at −45 °C revealing three discrete boron absorptions.

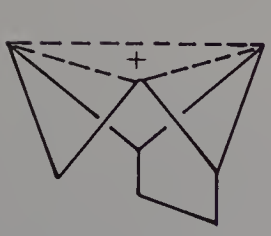
As the x-ray crystal structure of a Lewis base adduct, that is, B_4H_8:L, is known[33] and since its NMR spectrum is almost identical to those of $B_4H_9^-$, **27**, and $MeB_4H_8^-$, **32**, it may be assumed that structures **27** and **32** are also similar.

6.2.3.5. Trishomocyclopropenium Cations and the BH_2:L Fragment of *Arachno*-B_3H_7:L. Following the earlier predictions of Winstein and co-workers in 1959,[34a,34b] the trishomocyclopropenium cation, **33**, was prepared and characterized.[35] Two other more highly constrained polycyclic derivatives, **34** and **35**, have also been reported (see Chapter 5).[36,37] For the purposes of the present analysis, compounds **33**, **34**, and **35**, may notionally be regarded as hexaalkyl derivatives, **36**, of a hypothetical $C_3H_9^+$, **37**.

Among the boron hydrides, no stable species related to $B_3H_9^{2-}$ which would be an exact boron analog of the cation, **36**, has yet been reported. One candidate, a



33



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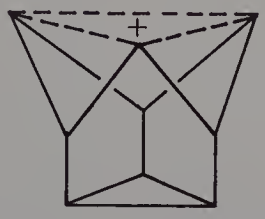

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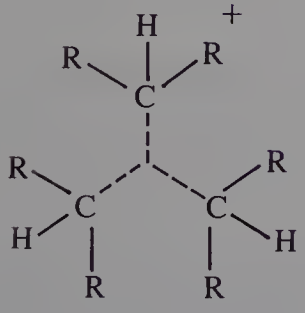

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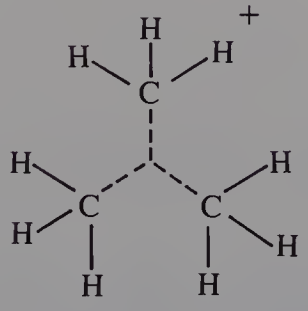
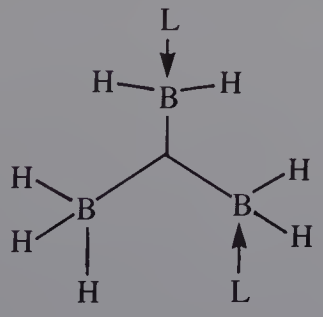


37

hypho-di-Lewis base adduct of B_3H_7, has been proposed as an intermediate[29] in the Lewis base exchange involving *arachno*-B_3H_7:L, but the intermediate **38**, has not been isolated.



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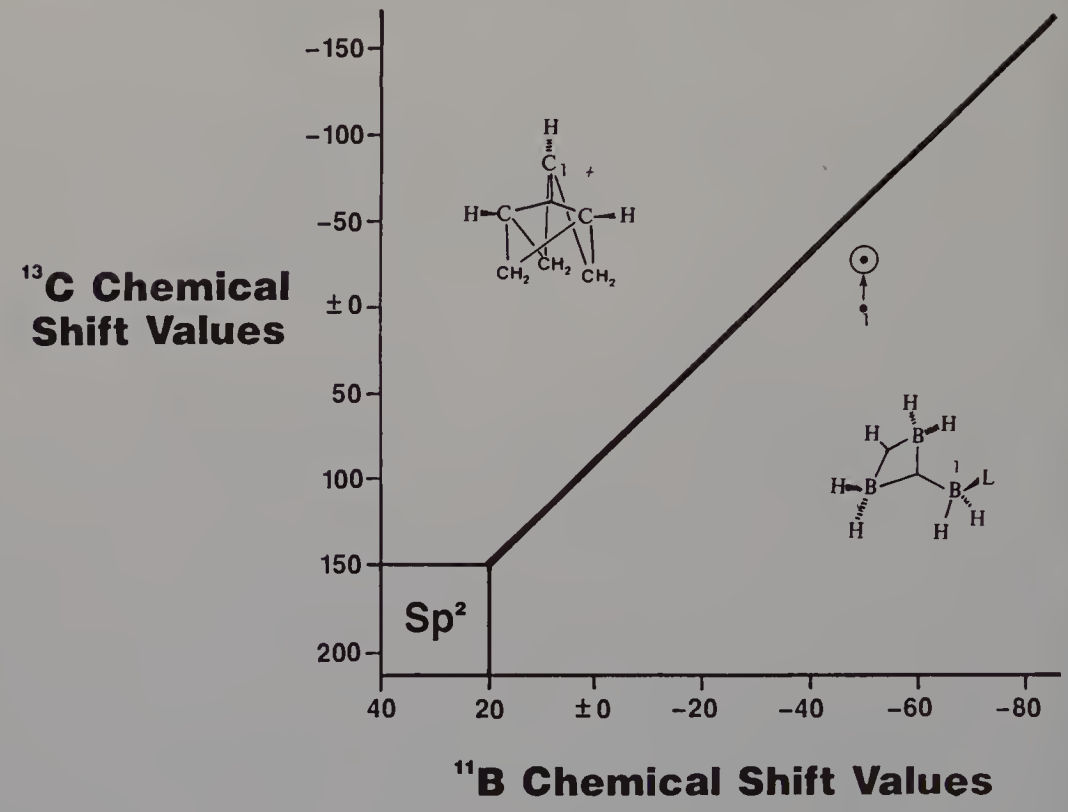


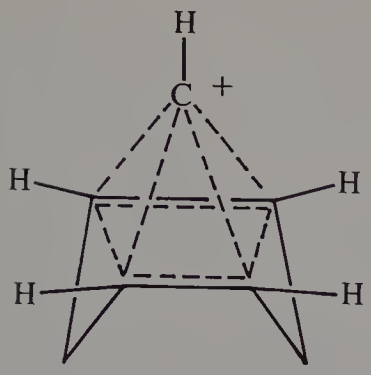
Figure 6.7. Comparison of trishomocyclopropenium ion and the BH_2:L group of L:B_3H_7. • raw data and ⊙ corrected data for bridge hydrogen removal.

The boron atom to which the Lewis base is coordinated in B_3H_7:L is isoelectronic with each of the boron atoms in the B_3H_7:L_2, **38**, or the unknown $B_3H_9^{2-}$ anion, **38**. Lacking a better model, the best available analog for each of the three equivalent carbon centers in structures **33** to **37** is the five-coordinate boron atom in B_3H_7:L, **25** (see Fig. 6.7 for the chemical shift plot).

6.2.3.6. Bishomo–Square Pyramidal $C_5H_9^+$ Type Cations and *Hypho*-B_5H_9:L_2. The bishomo-square pyramidal carbocation ($C_7H_9^+$), **39**,[38] and each of the more highly strained methano-bridged species, **40**[39] and **41**,[40] may be regarded as alkylated derivatives of the unknown parent cation ($C_5H_9^+$), **42**. In each of these cations the apical carbon resonates at substantially higher field than the other carbon atoms in the framework, consistent with its hypercoordinate environment.

Attempting to select polyboranes that would be isoelectronic with **42** can be perilous. The species $B_5H_{11}^{2-}$, **43**, would be "partially" isoelectronic with $C_5H_9^+$, **42**, but **43** is unknown. Several di-Lewis base adducts of B_5H_9, B_5H_9:L_2, **44**, are known and **44** would be isoelectronic with **43**.

The x-ray crystal structure of $B_5H_9(PMe_3)_2$, **44**, reveals the presence of one apical and one basal ligand.[41]



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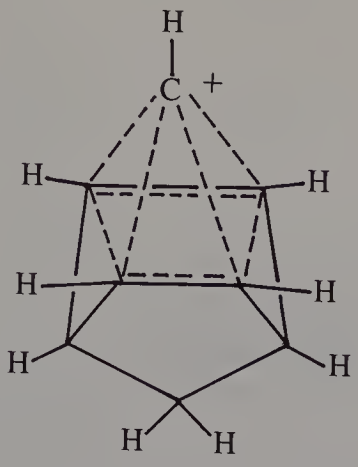

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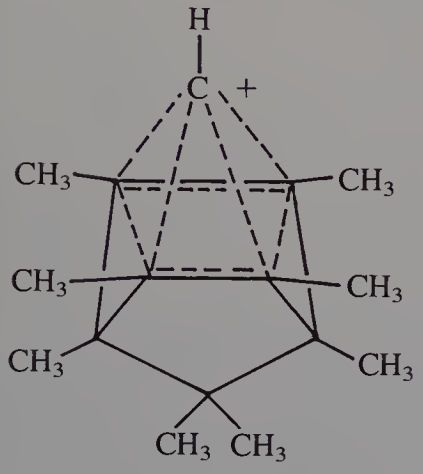

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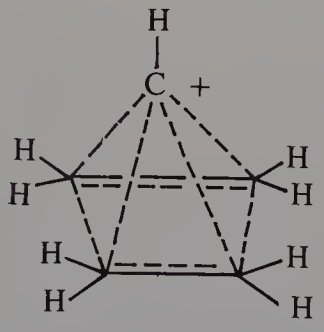

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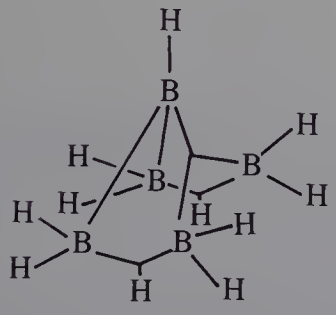

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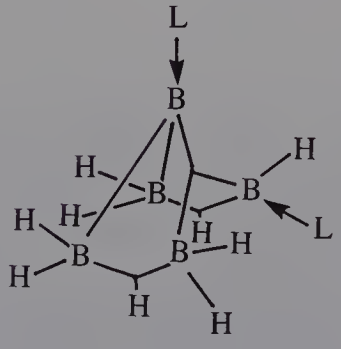


44

The ^{11}B NMR spectrum of **44** reflects some equilibration between the basal hydrogens[41,42] but all of the basal resonances fall within the range of $-25+7$ ppm. Figure 6.8 shows the correlation of the ^{13}C chemical shifts in **40** and the ^{11}B chemical shifts in **44**.

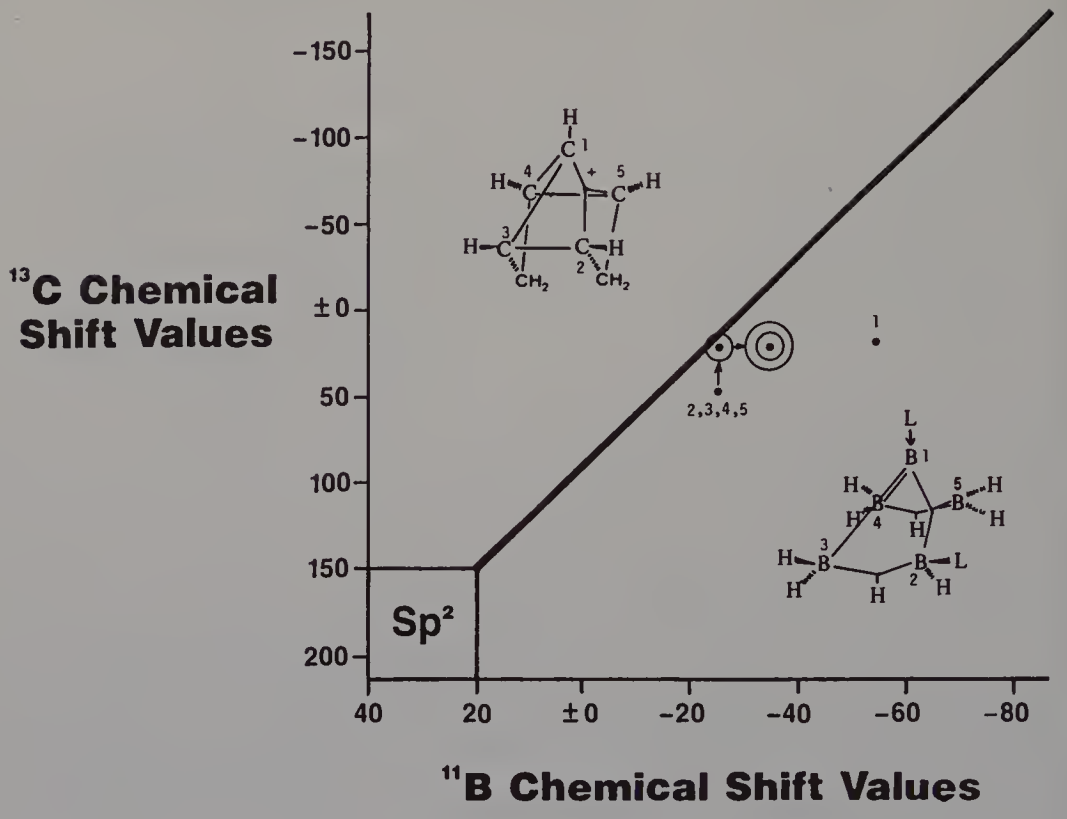
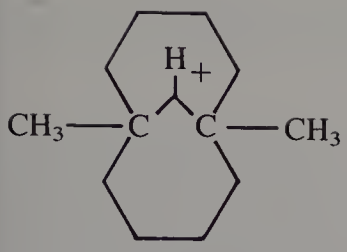


Figure 6.8. Comparison of an analog of $C_5H_9^+$ and $B_5H_9(:L)_2$. • raw data; ⊙ corrected data for bridge hydrogen removal; and ◎ corrected data for alkyl group and bridge hydrogen removal.

The correlations in Figure 6.8 are not overly impressive. Certainly the presence of nonclassical hypercarbons is revealed by their high field chemical shift values and both points are fairly close to the main line of Figure 6.1, but **42** and **44** would not seem to be quite as isoelectronic as the other pairs listed in Table 6.1

6.2.3.7. Hydrogen-Bridged $C_2H_7^+$ Type Cations and *Arachno*-$B_2H_7^-$ Derivatives. The discussion in the previous sections centered on carbocations containing CCC (3*c*–2*e*) bonds and were compared to polyborane analogs containing BBB (3*c*–2*e*) bonds. Sorensen and co-worker[43] and McMurry and Hodge[44] have reported a number of polycyclic carbocations that incorporate C−H−C (3*c*–2*e*) bonds which may be compared to isoelectronic polyborane anions possessing bridged hydrogens, that is, B−H−B (3*c*–2*e*) bonding as shown in Figure 6.9. The bridging carbons of **45** and **46** and boron or structure **47** (the compound may as well be **48**)[45] are in excellent agreement.



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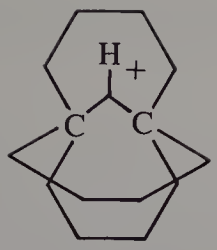

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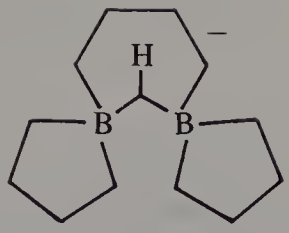

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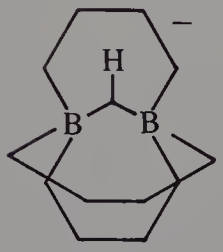

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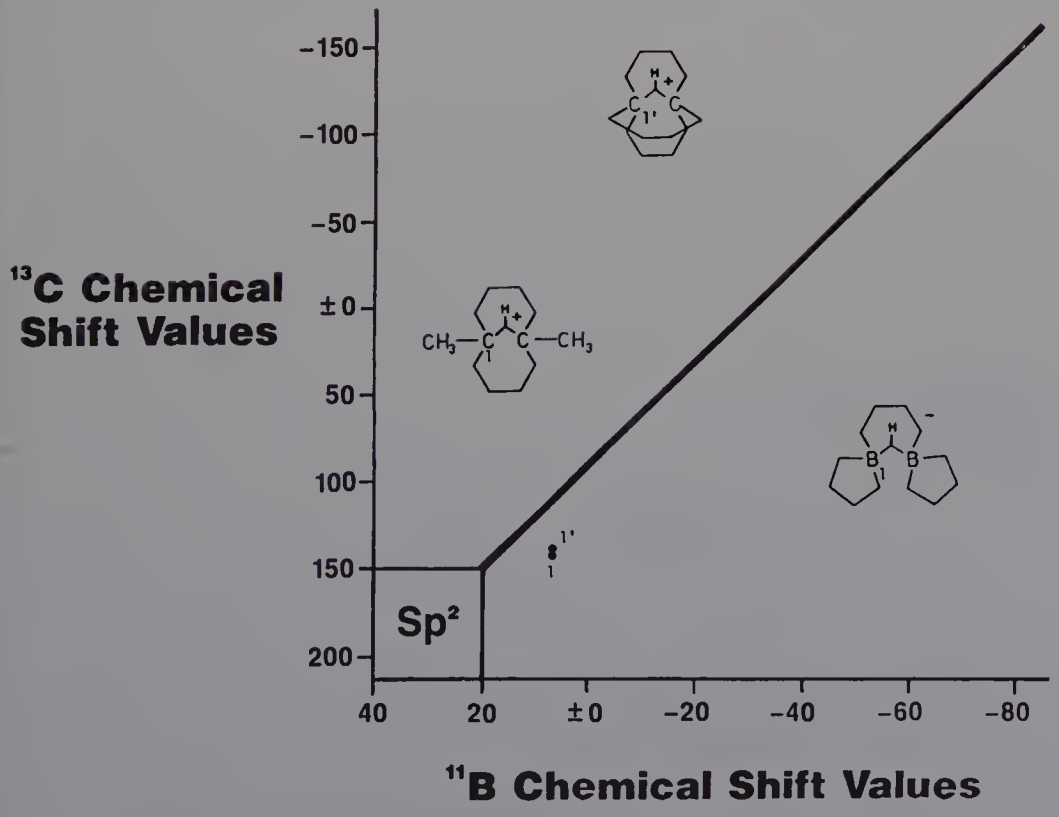

Figure 6.9. Comparisons of hexaalkyl derivatives of $C_2H_7^+$ and $B_2H_7^-$. • raw data.

6.3. CORRELATION OF CLASSICAL AND NONCLASSICAL CARBOCATIONS WITH CORRESPONDING BORON COMPOUNDS

With the exception of the trishomocyclopropenium ions, **33** (Fig. 6.7) and perhaps the bishomo-square pyramidal cations, **39** and **41** of Figure 6.8, each of the nonclassical carbocations discussed has a fairly precise isoelectronic and isostructural polyborane analog. In each of the nonclassical carbocations described, the hypercarbon atoms within the critical cluster of each compound exhibit ^{13}C chemical shifts that closely parallel the ^{11}B chemical shifts in isoelectronic and isostructural polyboranes.

The correlation of the ^{11}B and ^{13}C chemical shifts in the various nonclassical carbocations and the ^{11}B chemical shifts of their isoelectronic boron compounds discussed in Sections 6.2.3.1. to 6.2.3.7 have been added on to the correlation line of Figure 6.1 as solid black dots. It can be seen that the solid black dots roughly follow the same relationships that exist between the ^{13}C chemical shifts within hydrocarbon derivatives (see circles H to X in Fig. 6.1) and classical carbocations (see circles A to G in Fig. 6.1).

If the electron precise compounds (circles H to X) are ignored and *only* the two types of electron-deficient compounds are compared, then a substantially better correlation is obtained (i.e., the compounds, circles A to G) and the hypercarbon

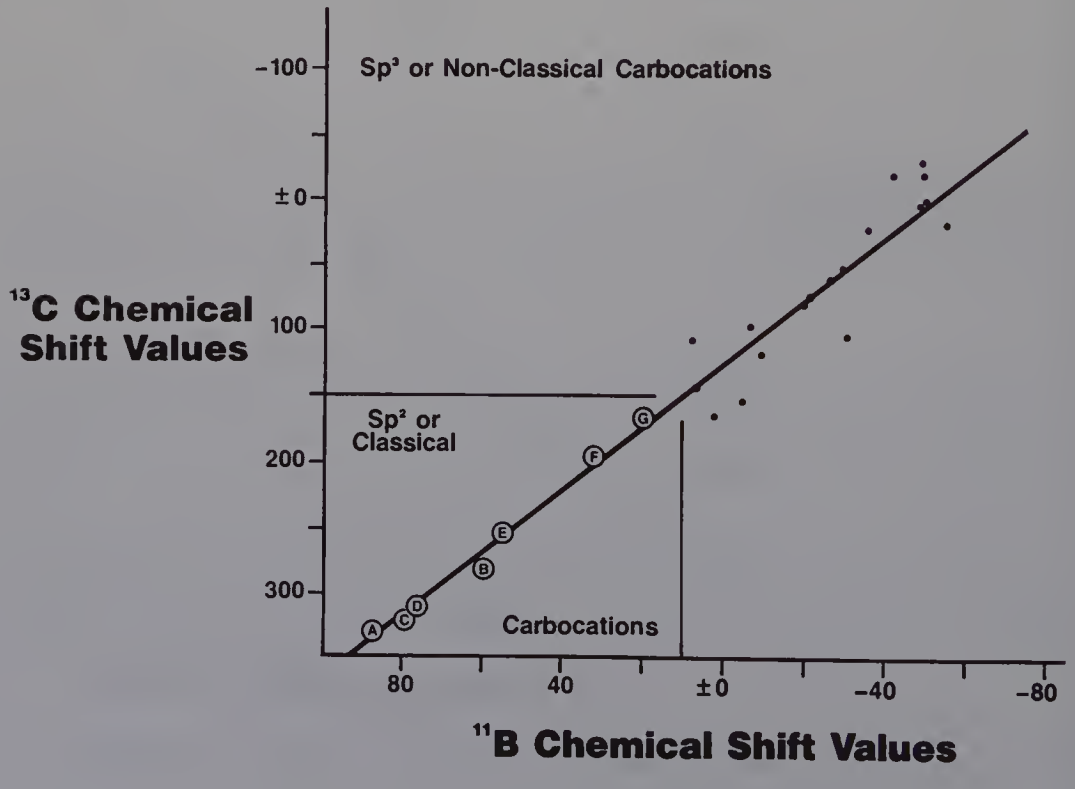

Figure 6.10. Correlation of electron deficient classical and nonclassical carbocations versus their boron analogs.

compounds represented by the solid black dots in Figure 6.1. These points that are reproduced in Figure 6.10 show an excellent linear relationship.

6.4. CONCLUSIONS

With the exception of bishomo-square pyramidal type cations ($C_5H_9^+$) and trishomocyclopropenium ions, each of the nonclassical carbocations has isoelectronic and isostructural polyborane analogs for comparison. In each of the carbocations described, the carbon atoms within the critical cluster of each compound exhibit ^{13}C NMR chemical shifts that parallel the ^{11}B NMR chemical shifts in the isoelectronic and isostructural polyboranes. Moreover, the correlation of ^{11}B to ^{13}C NMR shifts in these compounds closely follows the *same* relationship that exists between the ^{13}C chemical shifts in classical carbocations and the ^{11}B chemical shifts in the corresponding tricoordinate boron compounds. Furthermore, the combined chemical shift correlation (Fig. 6.10) of only the electron-deficient classical as well as nonclassical carbocations with isoelectronic boron analogs shows a much closer relationship of even greater utility for future investigations. The nonclassical carbocations and polyboranes have similar structures and both types involve (3*c*–2*e*) bonds.

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chapter 7

HYPERCARBON REACTION-INTERMEDIATES

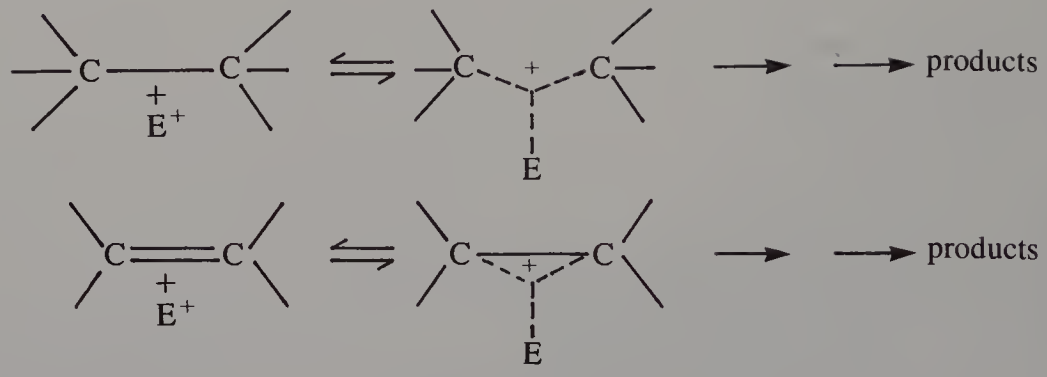
7.1. INTRODUCTION

In the previous chapters, we discussed systems that contained hypercoordinated carbon atoms in their most stable ground state. There are also many organic and organometallic reactions and rearrangements that proceed via short-lived intermediates or transition states containing higher coordinate carbon atoms even though the reactants and products contain only conventionally coordinated carbon atoms. In many rearrangements, intermediates involving hypercoordinate carbon atoms may be readily accessible and hence provide suitable reaction paths through which rearrangement occurs with great facility. We are using the terms "intermediate" and "transition state" somewhat ambiguously, referring to either high-lying, short-lived intermediates (i.e., energy minimum) or related transition states (energy maximum) on the energy profile.

The involvement of intermediates and transition states containing higher coordinate carbon has been proposed in both electrophilic reactions involving electron-deficient systems such as carbocations, heterocations, carbenes, nitrenes, silylenes, coordinatively unsaturated metal compounds, and so on, and nucleophilic S_N2 reactions. Whereas in electrophilic reactions, the five coordinate carbocation centers are associated with eight electrons and thus can be in intermediates (albeit high-lying), the S_N2 reactions represent ten electron cases and therefore are only transition states.

When an electrophile approaches a substrate molecule it preferentially interacts with the electron rich sections of the molecule, primarily the *n*-donor [nonbonded

Scheme 7.1

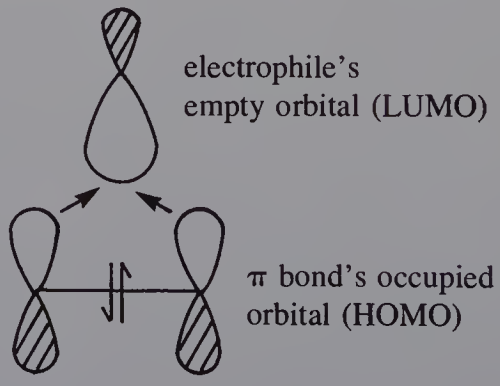


electron-pair donor, i.e., O, N, X (X = Cl, Br, I), etc.], and π-donor sites. In the absence of *n*- and π-donor sites, electrophiles will interact with σ bonds. The initial interaction between an electrophile and either a σ or π bond is considered to be a three-center types (Scheme 7.1), which subsequently rearrange or fragment to yield the products.

When the interaction is intermolecular, condensation (dimerization, polymerization) or redistribution products may be formed. An intramolecular reaction may give rise to rearrangement of the hydrocarbon skeleton (isomerization) or group migrations.

The facile reaction of an electrophile with a π bond can be rationalized by frontier-orbital theory.[1a] The high-lying HOMO of the π bond reacts with the low-lying LUMO of the electrophile in a concerted fashion leading to a three-center interaction (symmetry allowed) as shown in Scheme 7.2 for ethylene.

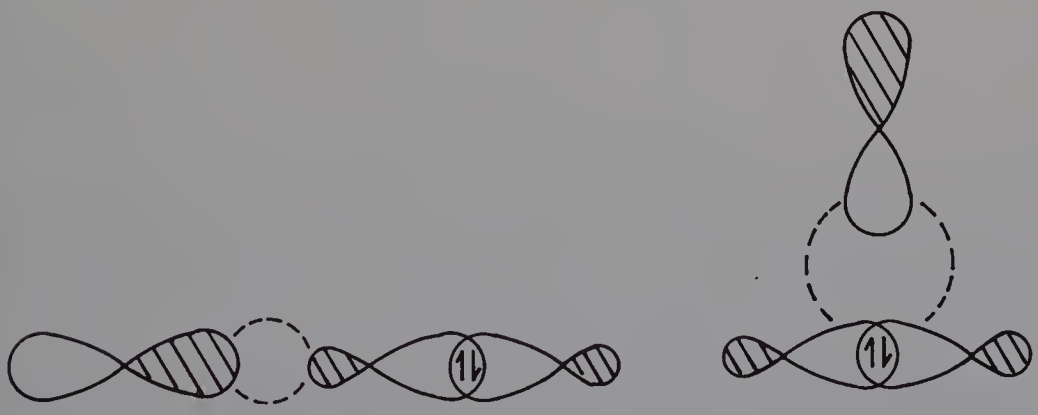
Scheme 7.2



On the other hand, σ bonds of alkanes are far less reactive and this is largely due to the unavailability of lone pairs and of empty orbitals. Carbon and hydrogen atoms that make up alkanes both belong to a small group of elements having the same number of valence electrons as valence orbitals. The strong bonding between carbon–hydrogen

and carbon–carbon (dissociation energy, 80–110 kcal mol^{-1}) results in low-lying σ-bonding orbitals (HOMOs) and high-lying unoccupied antibonding σ* levels (LUMOs) neither of which are easily accessible to attacking reagents (electrophiles or nucleophiles). The low polarity as well as polarizability of the C−H and C −C bonds is also a factor that contributes to the relatively unreactive nature of alkanes. Furthermore, the tetrahedral nature of a saturated carbon atom also places steric inhibition on the attacking reagents. An incoming reagent towards an alkane σ bond can interact in three ways (a) being an electron donor to the σ* orbital, (b) abstracting σ electrons from C−H and C−C bonds, and (c) doing both electron donation to σ orbital and electron abstraction of σ orbital at once. The first possibility appears to be the least successful in the case of alkanes since they do not react with nucleophiles. However, with proper substituents (with good leaving group ability) the reaction does occur with inversion of configuration—the general S_N2 reaction. The second approach (b) is adopted by a variety of electrophilic reagents such as carbocations, heterocations, Brønsted, and Lewis acids. The reaction can be depicted with the LUMO of the electrophile interacting with the HOMO of the alkane (Scheme 7.3). Symmetry allowed both back- and front-side attack is possible.

Scheme 7.3



(*a*) Back-side attack (inversion)

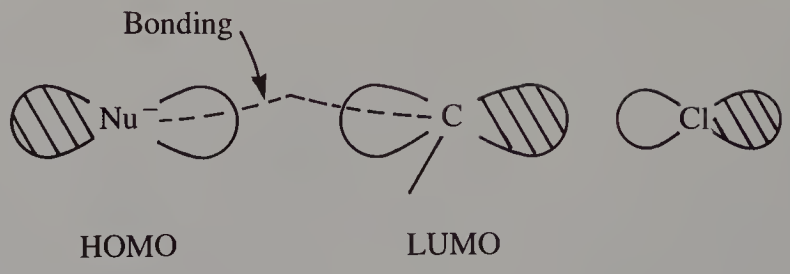
(*b*) Front-side attack (retention)

A much better overlap is provided by the direct attack on the covalent bond thus favoring front-side attack. Depending on the heterogeneity of the molecular orbital (HOMO) one may envisage various possible cases, from a central attack on the covalent bond all the way to a back-side attack. The latter rarely occurs in electrophilic reactions of saturated carbon atoms.

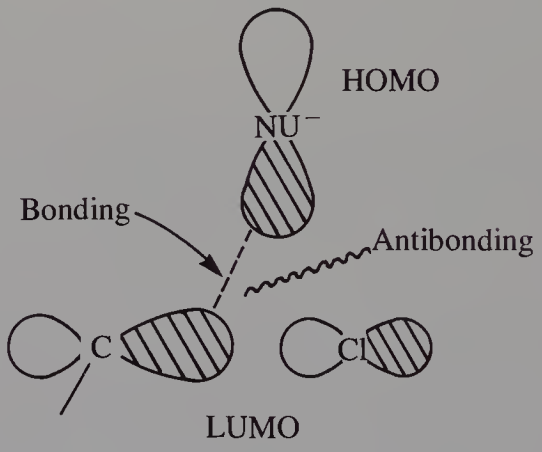
The third approach, path (c), seems to be the most successful one adopted by carbenes, free radicals, metal surfaces, and low valent metal complexes.

In nucleophilic reactions at saturated carbon atoms such as S_N2 reactions [path (a)], inversion of configuration occurs. Again, this can be easily rationalized by a simple frontier-orbital approach (Scheme 7.4).

Scheme 7.4



(*a*) Inversion of configuration



(*b*) Retention of configuration

The overlap between the HOMO of the nucleophile and the LUMO of the alkane derivative is bonding when the nucleophile approaches from the rear, but both bonding and antibonding when approached from the front. The former (***Scheme*** 7.4*a*) is clearly preferred over the latter (***Scheme*** 7.4*b*).

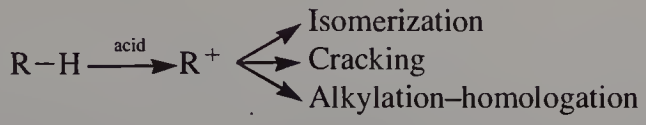
In this chapter, we shall successively review reactions of electrophiles, coordinatively unsaturated metal compounds, carbenes, nitrenes, silylenes, and so on, with C−C and C−H σ bonds. Discussion of some electrophilic reactions of π-donor systems is also included along with S_N2 reactions. The emphasis in all these discussions will be centered on the involvement of hypercarbon intermediates (or transition states) in the reactions.

7.2. REACTIONS OF ELECTROPHILES WITH C−H and C−C SINGLE BONDS

7.2.1. Acid Catalyzed Reactions and Rearrangements of Alkanes, Cycloalkanes, and Related Compounds

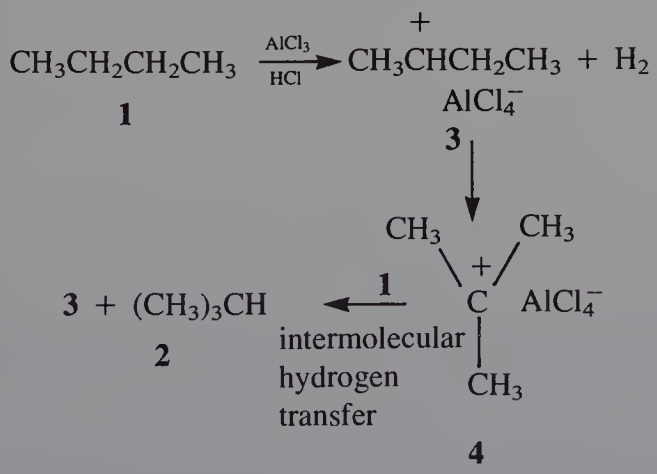
7.2.1.1. Carbon–Hydrogen and Carbon–Carbon Bond Protolysis. The fundamental step in acid-catalyzed hydrocarbon conversions, as first recognized in a

general way by Whitmore,[1b] is the formation of intermediate carbocations. Although all studies involving isomerization, cracking, and alkylation reactions of alkanes (and cycloalkanes) with alkenes under acidic conditions agree that trivalent carbocations (carbenium ions) are the key intermediates,[2] the mode of their formation from the neutral hydrocarbon and the detailed path of the reactions remained for many years unexplained.



As early as 1946, Bloch, Pines, and Schmerling observed[3] that *n*-butane, **1**, would isomerize to isobutane, **2** (Scheme 7.5), under the influence of pure aluminum chloride only in the presence of HCl. An initial protolytic ionization step was proposed as evidenced by the formation of minor amounts of hydrogen in the early stages of the reaction. The *sec*-butyl cation, **3**, thus formed, rapidly isomerizes to the *t*-butyl cation, **4**, which then intermolecularly abstracts hydride from *n*-butane, **1**, to form isobutane, **2**, and regenerate **3** according to the general Bartlett,[4b] Nenitzescu,[4c] and Schemerling[4a] concept of hydride transfer. The more detailed nature of the initial protolytic ionization and of alkyl(hydride) shifts, however, was not clear.

Scheme 7.5

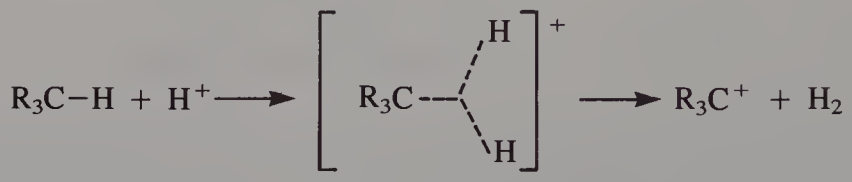


The first direct evidence for the protonation of alkanes under highly acidic (superacid) conditions was independently reported by Olah and Lukas[5a] as well as Hogeveen and co-workers.[5b,c] Protolytic reactions of hydrocarbons in superacid media were interpreted by Olah[6] as an indication of the general electrophilic reactivity of covalent C–H and C–C single bonds of alkanes and cycloalkanes. The reactivity is due to the donor ability of the σ-bond electron pairs via a two-electron, three-center bond formation. The transition state for protolytic ionization of hydrocarbons was presumed to be linear.[5b,c] It was later suggested[5,6] that such

two-electron, three-center interactions in carbocations generally tend to be non-linear (even in sterically crowded cases) in nature. (Similar to transition states proposed for front-side S_E2 reactions,[6] also see Chapter 1).

$$R_3C{-}H + H^+ \longrightarrow [R_3C{---}H{---}H]^+ \longrightarrow R_3C^+ + H_2$$

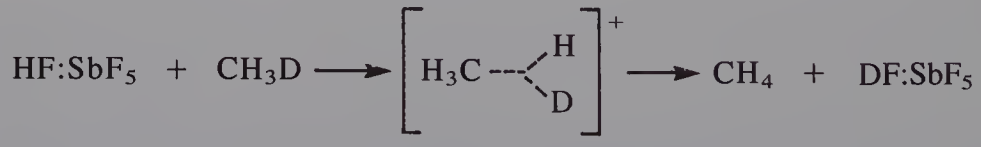
Linear



Nonlinear

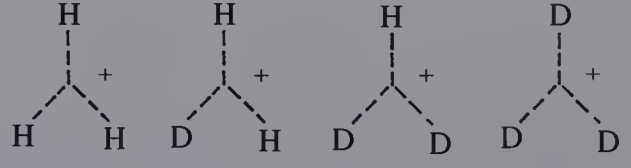
Evidence for this mode of protolytic attack was obtained from deuterium–hydrogen exchange studies.[7] Monodeuteromethane was reported to undergo H−D exchange in $HF{-}SbF_5$ via hypercoordinate isotopic methonium ions (Scheme 7.6) without any detectable side reactions (also see Chapter 5). Exchange involving protolytic ionization via $CH_3^+ + HD$ is improbable in the case of methane, because of the unfavorable, highly energetic nature of the primary methyl cation. However, in higher homologous alkanes protolytic ionization takes place with ease.

Scheme 7.6



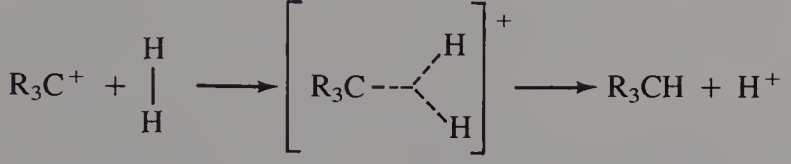
d_{12}-Neopentane, when treated with Magic Acid ($FSO_3H{:}SbF_5$), was also reported to undergo H−D exchange before cleavage, again implicating a hypercoordinate carbocation.

Based on the demonstration of H−D exchange of molecular hydrogen (and deuterium) in superacid solutions, it was suggested[7] that this reaction also goes through trigonal isotopic H_3^+ ions. The structure of H_3^+ and its isotopomers is reinforced by theoretical calculations and IR studies.[8]



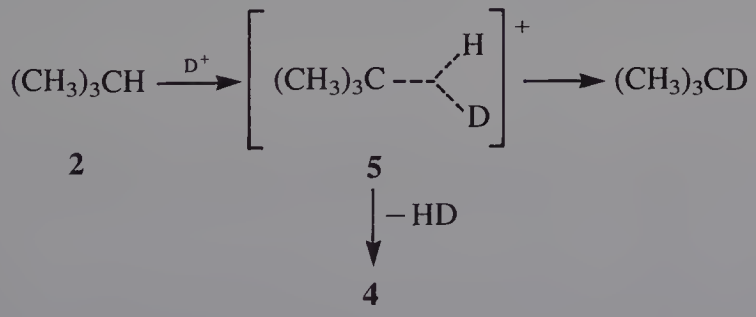
The reverse reaction of protolytic ionization of hydrocarbons to carbenium ions, that is, the reaction of carbenium ions with molecular hydrogen[9,10] (Scheme 7.7), can be considered as alkylation of H_2 by the electrophilic carbenium ion through a pentacoordinate carbonium ion. Indeed Hogeveen and Bickel have experimentally reduced stable alkyl cations in superacids to hydrocarbons with molecular hydrogen.[9]

Scheme 7.7



Further evidence for the pentacoordinate carbonium ion mechanism of alkane protolysis was obtained in the H–D exchange reaction observed with isobutane, **2** (Scheme 7.8). When isobutane, **2**, is treated with deuterated superacids (DSO_3F:SbF_5 or DF:SbF_5) at low temperature (−78 °C) and atmospheric pressure, the initial hydrogen–deuterium exchange is observed only at the tertiary carbon. Ionization yields only the deuterium-free *t*-butyl cation, **4**, and HD.[11] Isobutane, recovered from the reaction mixture at low temperatures shows only methine hydrogen–deuterium exchange. This result is best explained by implicating the pentacoordinate carbonium ion, **5**, as the intermediate in the reaction.

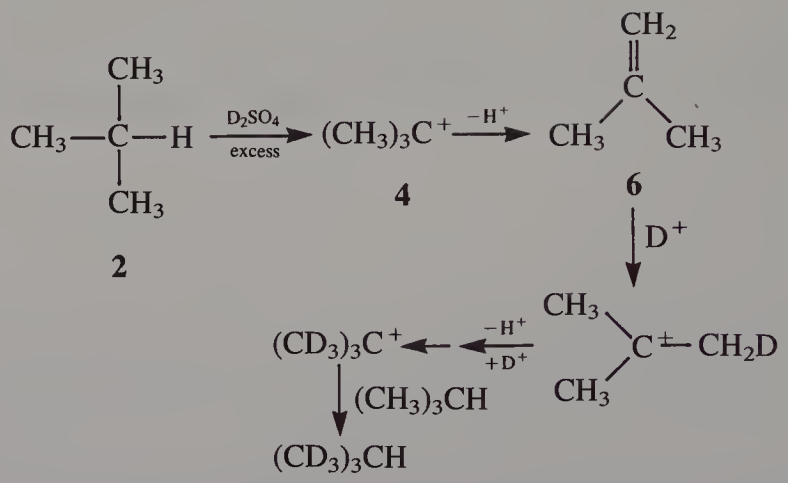
Scheme 7.8



As mentioned earlier in Chapter 5, the H–D exchange in isobutane in superacid media is fundamentally different from the H–D exchange observed by Otvos et al.,[12] in weaker acids such as D_2SO_4, who found the eventual exchange of all the nine methyl hydrogens with deuterium. However, no exchange of the methine hydrogen was observed (Scheme 7.9).

Otvos suggested[12] that under these reaction conditions a small amount of *t*-butyl cation, **4**, is formed in an oxidative step that subsequently deprotonates to form isobutylene, **6**. The reversible protonation (deuteration) of **6** is responsible for the

Scheme 7.9



observed H−D exchange on the methyl hydrogens, whereas tertiary hydrogen is involved in intermolecular hydride transfer from unlabeled isobutane (at the CH position). Under superacidic conditions, where no olefin formation occurs, the reversible isobutylene protonation cannot be involved in the exchange reaction. A kinetic study of hydrogen–deuterium exchange in deuteroisobutane[13] has shown that the exchange of the tertiary hydrogen is appreciably faster than the hydride abstraction by C−H protolysis.

One of the main difficulties in understanding the carbocationic nature of acid-catalyzed transformations of alkanes via the hydride abstraction mechanism was that a stoichiometric amount of hydrogen gas evolution was never observed from the reaction mixtures, although even in the early work of Nentizescu[4c] H_2 gas was detected in measurable amounts. For this reason, an alternative mechanism was proposed: the direct hydride abstraction by the Lewis acid (Scheme 7.10).[14]

Scheme 7.10

$$RH + 2SbF_5 \longrightarrow R^+SbF_6^- + SbF_3 + HF$$

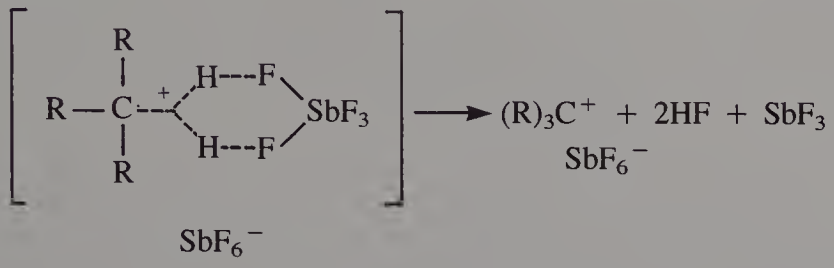
However, it has been pointed out[11] that if SbF_5 abstracted H^- an SbF_5H^- ion would be formed involving an Sb−H bond, which is extremely weak compared to the strong C−H bond being broken. Thermodynamic calculations[15] also show that the direct oxidation of alkanes by SbF_5 is not feasible. Hydrogen is generally assumed to be partially consumed in the reduction of one of the superacid components.

$$2\,HSO_3F + H_2 \longrightarrow SO_2 + H_3O^+ + HF + SO_3F^- \quad \Delta H = -33 \text{ kcal mol}^{-1}$$
$$SbF_5 + H_2 \longrightarrow SbF_3 + 2HF \quad \Delta H = -49 \text{ kcal mol}^{-1}$$

The direct reduction of SbF_5 in the absence of hydrocarbon by molecular hydrogen necessitates, however, more forcing conditions (50 atm, high temperature), which

suggests that the protolytic ionization of alkanes proceeds probably via solvation of the pentacoordinate carbocation by SbF_5 and concurrent ionization–reduction (Scheme 7.11).[11]

Scheme 7.11

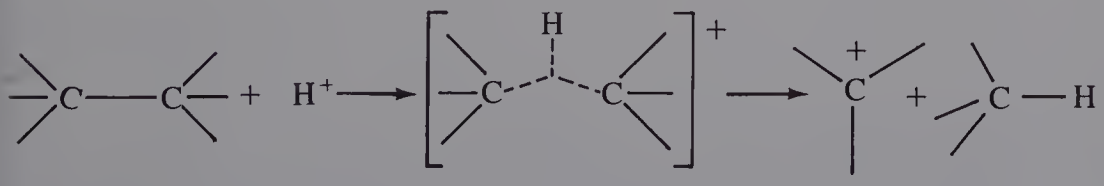


In studies involving solid acid catalyzed hydrocarbon cracking reactions using HZSM-5 zeolite, Haag and Dessau[16] were able to account nearly quantitatively for H_2 formed in the protolysis ionization step of the reaction. This is a consequence of the solid acid zeolite catalyst which is not easily reduced by the hydrogen gas evolved.

It must also be pointed out, however, that initiation of acid catalyzed alkane transformations under oxidative conditions (chemical or electrochemical) can also involve radical cations or radical paths leading to the initial carbenium ions. In the context of our present discussion we shall not elaborate on this interesting chemistry further and limit our treatment to purely protolytic reactions.

Under strongly acidic conditions C–H bond protolysis is not the only pathway by which hydrocarbons are heterolytically cleaved. Carbon–carbon bonds can also be cleaved by protolysis[17,18] involving pentacoordinate intermediates (Scheme 7.12).

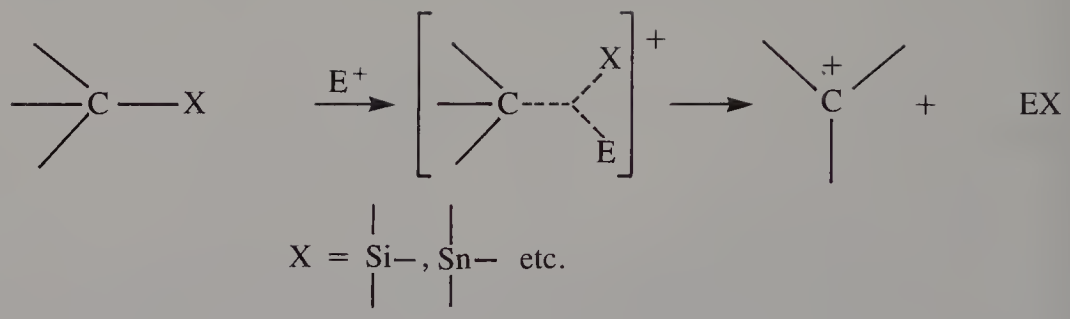
Scheme 7.12



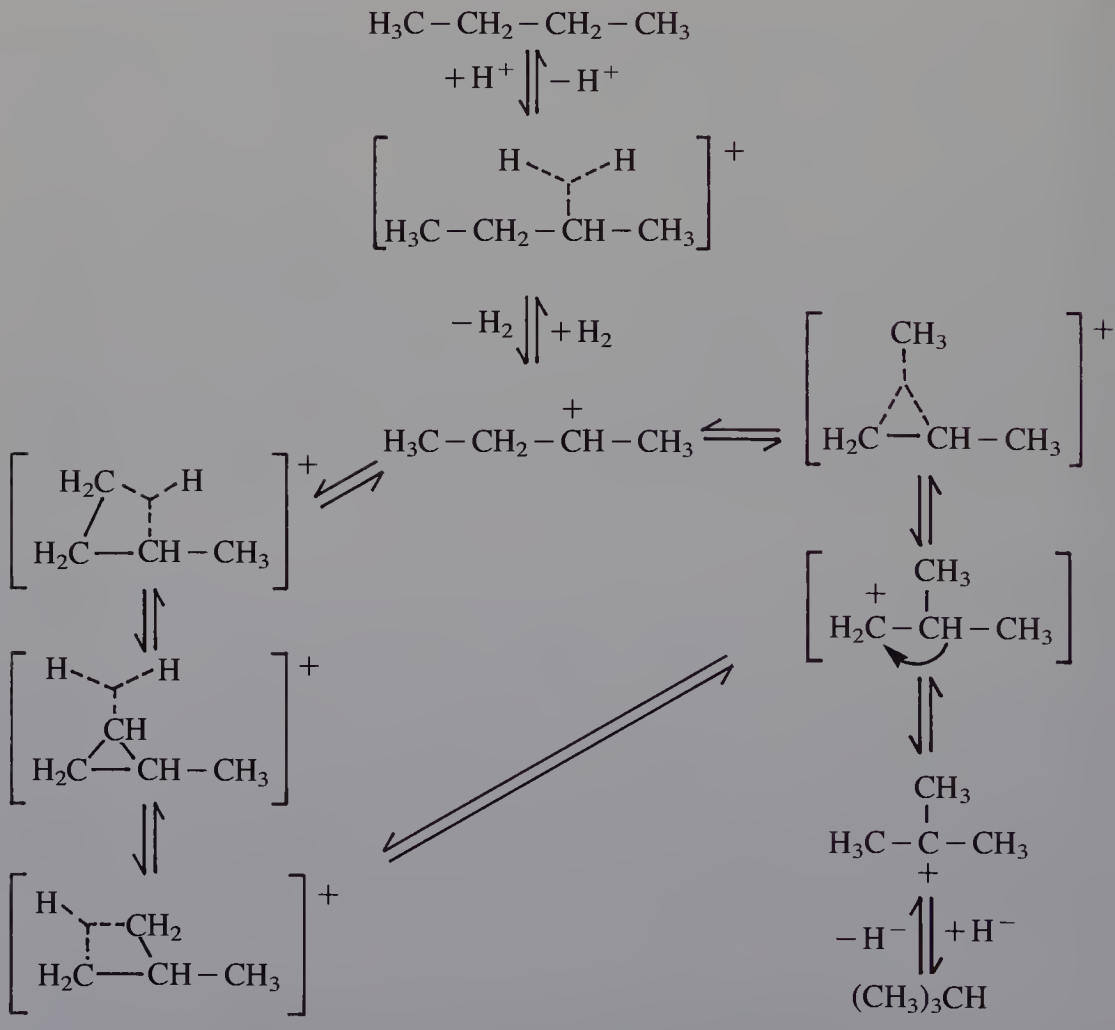
Similarly, many carbon–heteroatom bonds are also cleaved[6,19] under strong acid catalysis involving pentacoordinate carbon intermediates (Scheme 7.13).

7.2.1.2. Isomerization and Rearrangement. The isomerization of *n*-butane, **1**, to isobutane, **2**, is of substantial importance because of a variety of useful products that can be obtained from **2** (isobutylene, *t*-butyl alcohol, methyl *t*-butyl ether, and *t*-butyl hydroperoxide).[20] A number of methods involving solution as well as solid

Scheme 7.13



Scheme 7.14

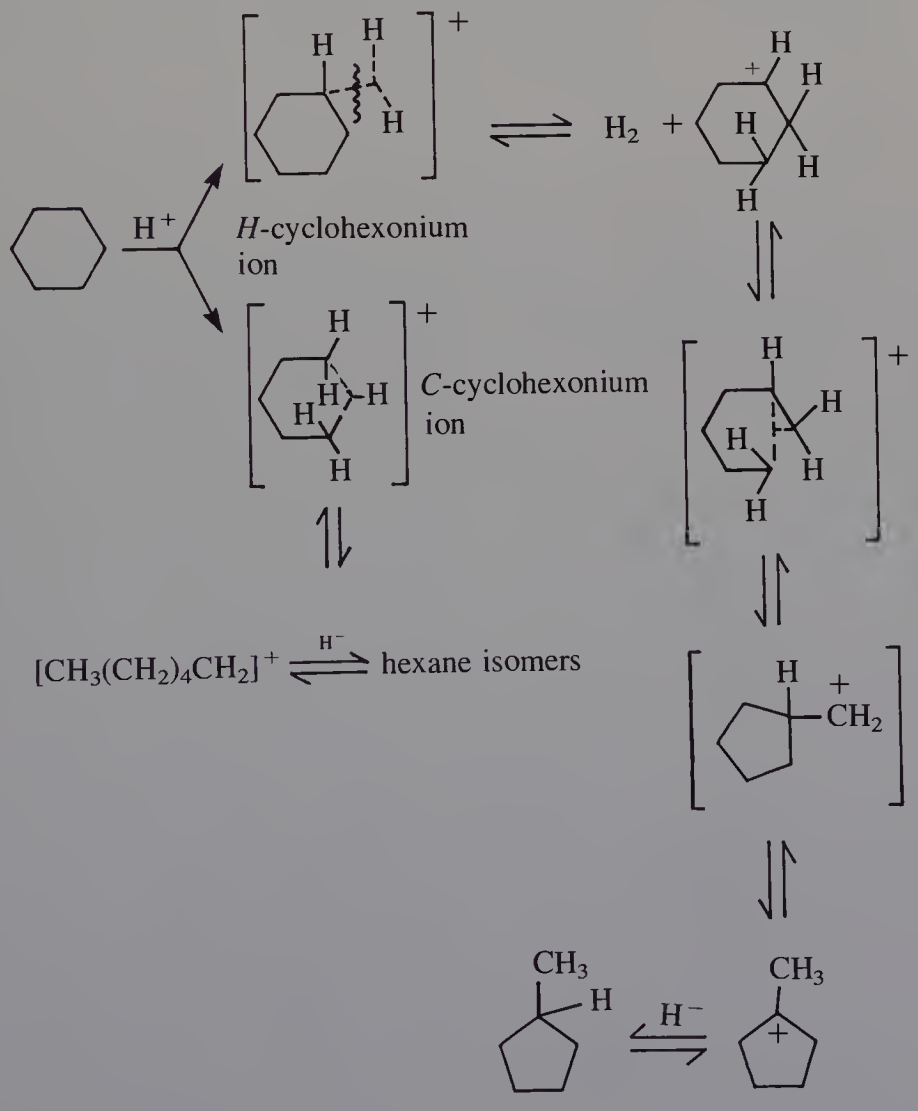


acid catalysts[21] have been developed to achieve isomerization of *n*-butane as well as other linear higher alkanes to branched isomers.

The electron donor character of C–H and C–C single bonds that leads to pentacoordinated carbonium ions explains the detailed mechanism of acid catalyzed isomerization of *n*-butane, **1**, as shown in Scheme 7.14 supplementing the overall carbocationic mechanism already mentioned (Scheme 7.5). Carbon–carbon bond protolysis, however, can also take place giving methane, ethane, and propane.

Related alkanes such as pentanes, hexanes, and heptanes isomerize by similar pathways with increasing tendency towards cracking (i.e., C–C bond cleavage).

Scheme 7.15

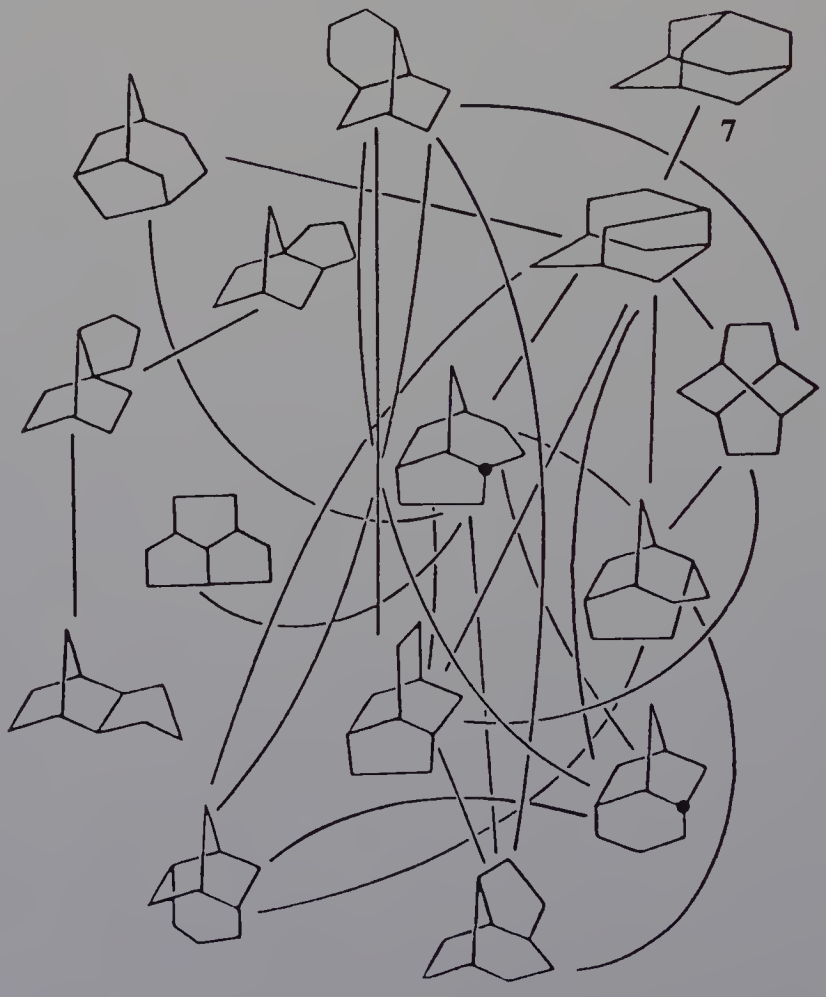


Cycloalkanes also undergo related acid-catalyzed rearrangements. Again higher coordinate carbocations play a key role in the mechanism as shown in the cyclohexane $\rightleftharpoons$ methylcyclopentane rearrangement.[6]

Whereas the cyclohexane–methylcyclopentane isomerization involves initial formation of the cyclohexyl (methylcyclopentyl) cation (i.e., via protolysis of a C–H bond) it should be mentioned that in the acid-catalyzed isomerization of cyclohexane up to 10% hexanes are also formed and this is indicative of C–C bond protolysis (Scheme 7.15).

The isomerization of practically any tricyclic C_{10} hydrocarbons under strongly acidic conditions gives the unusually stable cage hydrocarbon adamantane **7** (Scheme 7.16). The first such isomerization was reported by Schleyer in 1957.[22a] The formation of adamantane from a variety of C_{10} precursors involves a series of hydride and alkyl shifts through the intermediacy of hypercoordinate carbocations.[22b]

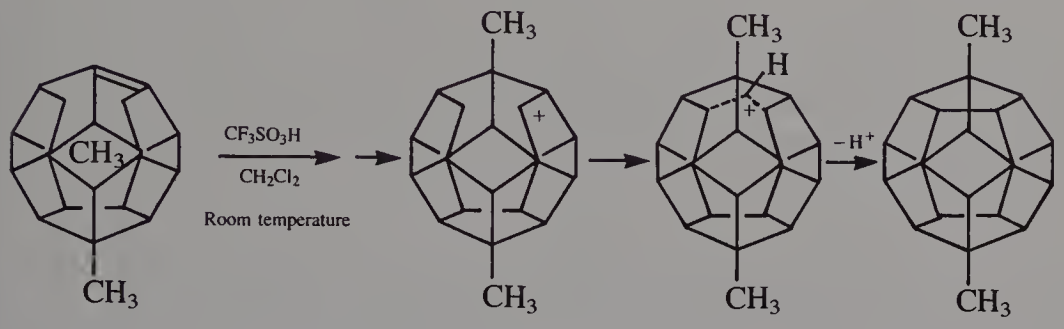
Scheme 7.16



Rearrangement Map of C_{10} Hydrocarbons to Adamantane

The superacid catalyzed formation of the stable "Platonic" type hydrocarbon, 1,16-dimethyldodecahedrane, **8**, by Paquette and Balogh[23] also involves the intermediacy of hypercoordinated carbocations such as **9** (Scheme 7.17).

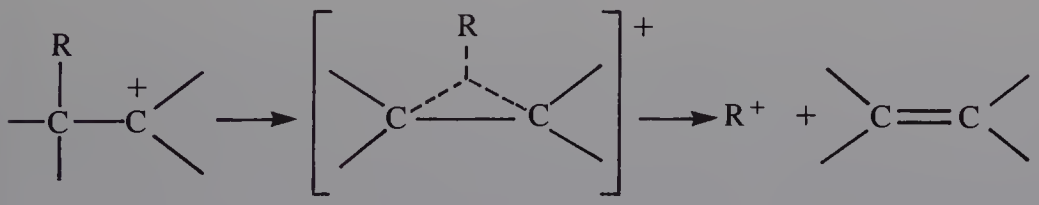
Scheme 7.17



9 **8**

The reduction in molecular weight (cracking) of various fractions of crude oil is an important process in petroleum chemistry.[2b,24] *Acid catalyzed cracking*, besides the already discussed direct protonation of C–C bonds (Scheme 7.12), can also involve trivalent carbocations that undergo β-scission through the intermediacy of hypercoordinated carbocations (Scheme 7.18).

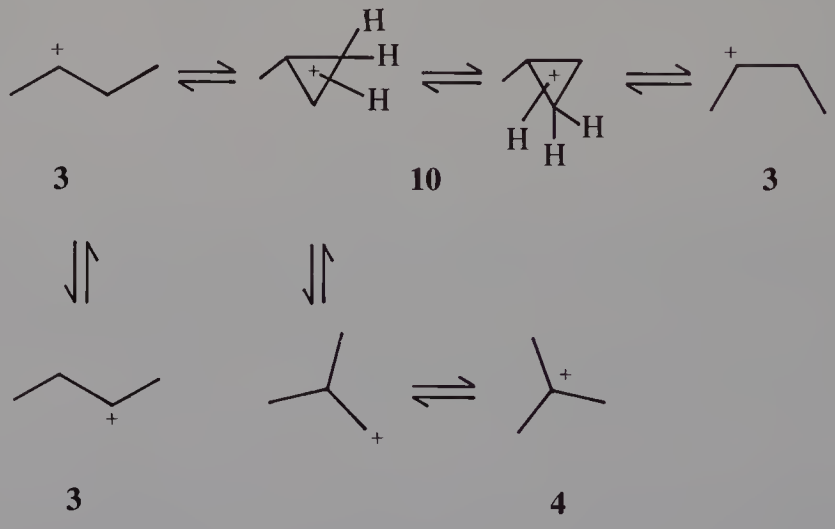
Scheme 7.18



Neighboring group migrations to electron-deficient carbon centers is well recognized.[25] The well-known Wagner–Meerwein rearrangement,[26] pinacol rearrangement,[27] and diazomethane insertion involve migration of an alkyl group to an electron-deficient carbon center. These are some of the representative reactions involving hypercarbon intermediates (or transition states).

Fast Wagner–Meerwein rearrangements and degenerate 1,2-hydride shifts have been extensively investigated under superacid conditions to probe the nature of intermediate carbocations. The 2-butyl cation, **3**, has been prepared from 2-chlorobutane in SbF_5/SO_2ClF at -100 °C in a vacuum line by Saunders and Hagen[28] with very little contamination from the *t*-butyl cation, **4**. Even at -110 °C, only two signals from 2,3, and 1,4 protons are observed in the ^1H NMR spectrum of **3**

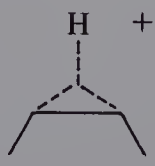
(at δ^1H 6.7 and 3.2, respectively). This is consistent with the 2-butyl cation undergoing a very rapid 1,2-hydride shift ($\Delta G^{\ddagger}$ 6 $\approx$ kcal mol^{-1}). Warming the sample from -110 to -40 °C first causes line broadening and then coalescence of the two peaks, revealing a rearrangement process making all protons equal on the ^{1}H NMR time scale (indicating the formation of **4**). Line shape analysis gave an activation barrier of 7.5 kcal mol^{-1} for the process. This low barrier is not compatible with a mechanism involving primary cations as suggested for the corresponding rearrangement of the isopropyl cation (a secondary cation). It appears necessary to invoke hypercoordinate protonated methylcyclopropanes, **10**, as intermediates. The barrier for the irreversible rearrangement to **4** was measured to be about 18 kcal mol^{-1}, indicating that this rearrangement probably involves primary cationic structures as intermediates.



3 **10** **3**

3 **4**

An early ^{13}C NMR INDOR spectrum[29] of **3** also showed a single peak from the two central carbon atoms in reasonable agreement with values calculated from model equilibrating ions. It was, therefore, concluded that **3** is a classical equilibrating ion rather than being bridged as in **11**. The bridged ion, **11**, was involved only as a high-lying unpopulated intermediate or transition state.



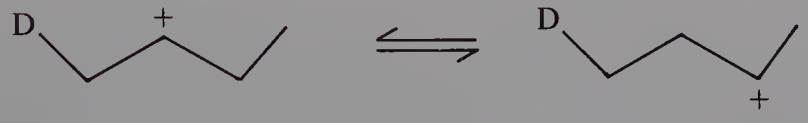
11

In a comprehensive ^{13}C NMR spectroscopic study of alkyl cations, Olah and Donovan[30] applied the constancy of ^{13}C methyl substituent effects to the study of equilibrating cations and their rearrangements. They calculated the chemical shifts of the 2-butyl cation, **3**, from both the isopropyl cation and *t*-amyl cation using methyl group substituent effects and reached practically the same result in both cases. The

observed chemical shifts deviate from the calculated ones by 9.2 and 19.8 ppm for the equilibrating methyl and carbocation carbons, respectively. Therefore, involvement of a hydrogen-bridged intermediate, **11**, was suggested. A static hydrogen-bridged 2-butyl cation was excluded by the observation of two quartets in the fully ^{1}H-coupled ^{13}C NMR spectrum (one with an average $^{13}C-^{1}H$ coupling of only 66.7 Hz). Comparison with bridged halonium ions indicates that equilibrating hydrogen-bridged ions have more shielded carbons (C-2, C-3) than are observed experimentally for the 2-butyl cation. Therefore, it was suggested that the open-chain 2-butyl cation is of similar thermodynamic stability as the hydrogen-bridged structure **11** and that these intermediates in equilibrium may contribute to the observed average ^{13}C shifts. However, the percentage of different structures could not be calculated owing to lack of accurate models to estimate ^{13}C chemical shifts of hydrogen-bridged structures.

In a study of rates of degenerate 1,2-shifts in tertiary carbocations, Saunders and Kates[31] used high-field (67.9 MHz) ^{13}C NMR line broadening in the fast-exchange limit. The 2-butyl cation showed no broadening at -140 °C. Assuming the hypothetical "frozen out" chemical shift difference between C-2 and C-3 to be 277 ppm, an upper limit for $\Delta G^{\ddagger}$ was calculated to be 2.4 kcal mol^{-1} at this temperature.

Application of the isotopic perturbation technique by Saunders et al.[32] to the 2-butyl cation **3d** showed it to be a mixture of equilibrating open-chain ions since a large splitting of the ^{13}C resonance (C-2, C-3) was obtained upon deuterium substitution.[33]

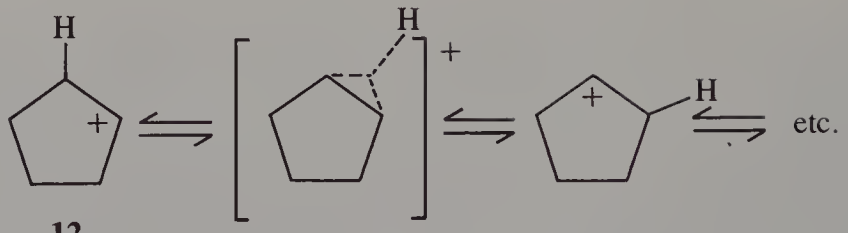


3d

The cross-polarization, magic-angle spinning method has been applied by Yannoni and Myhre[34] to structure **3** in the solid state at very low temperatures using ^{13}C NMR spectroscopy. In the initial study, no convincing evidence for a frozen out 2-butyl cation was obtained even at -190 °C. However, they were able to freeze out the equilibration of the 2-butyl ion, **3**, at -223 °C.[35] It behaves like a normal secondary trivalent carbocation.

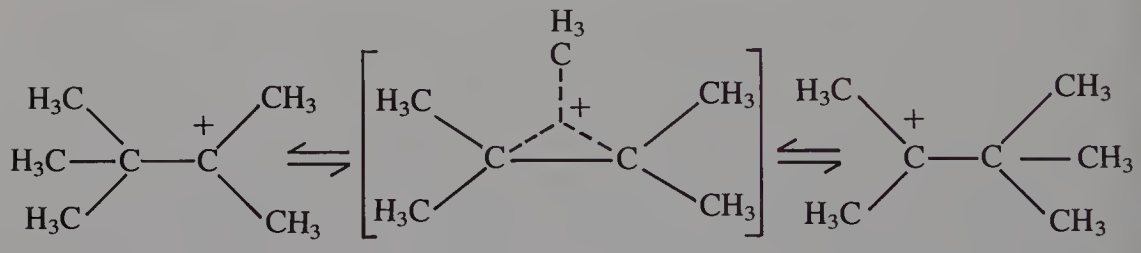
The cyclopentyl cation, **12**, shows a single peak in the ^{1}H NMR spectrum of $\delta^{1}H$ 4.75 even at -150 °C.[36] In the ^{13}C NMR spectrum,[37] a 10-line multiplet centered around 99.0 ppm with $J_{C-H} = 28.5$ Hz was observed. This is in excellent agreement with values calculated for simple alkyl cations and cyclopentane and supports the complete hydrogen equilibration by rapid 1,2-shifts (involving a hypercoordinate intermediate or transition state).

Furthermore, Yannoni and co-workers[35] succeeded in freezing out the degenerate hydride shift in structure **12** in the solid state at -203 °C. The observed ^{13}C chemical shifts at δ320.0, 71.0, and 28.0 indicate the regular trivalent nature of the ion and are in good agreement with the estimated shifts in solution based on the average shift data.

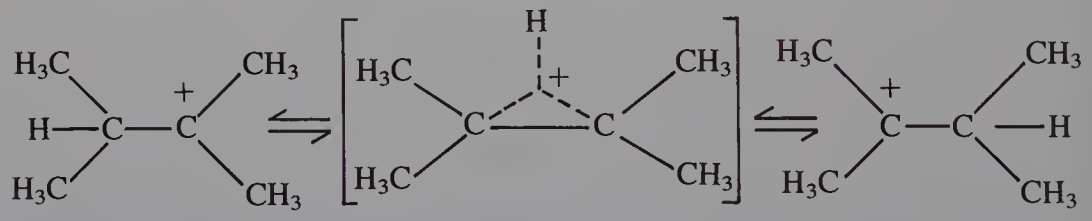


12

The 2,2,3-trimethyl-2-butyl cation, **13** (triptly cation), consists of a single proton signal at δ^1H 2.90 for all the methyl groups.[36] This indicates that all five methyl groups undergo rapid interchange through 1,2-methyl shifts (fast Wagner–Meerwein shifts). The chemical shift of the singlet is similar to that of 2,3-dimethyl-2-butyl cation, **14**, another equilibrating ion that undergoes rapid 1,2-hydride shifts.[36]

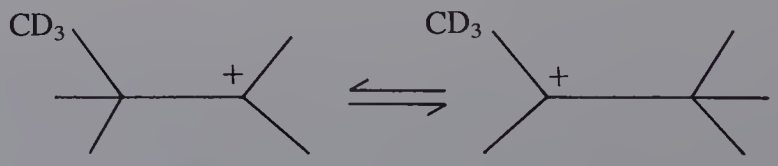


13 13



14 14

The ^{13}C NMR spectroscopic data of the average cationic center in **13** and **14** were found to be at δ ^{13}C 205 and 197 ($J_{C-H} \approx 65$ Hz), respectively, indicating their regular trivalent carbenium nature. From studies of methyl substituent effects, Olah and Donovan[30] reached the same conclusions and these are supported by laser Raman and ESCA studies.[38,39] Saunders and Vogel[40] have introduced deuteriums into a methyl group of **13** and thereby perturbed the statistical distribution of the otherwise degenerate methyl groups and split the singlet into a doublet. The CD_3 group prefers to be attached to the tertiary carbon, **15**.

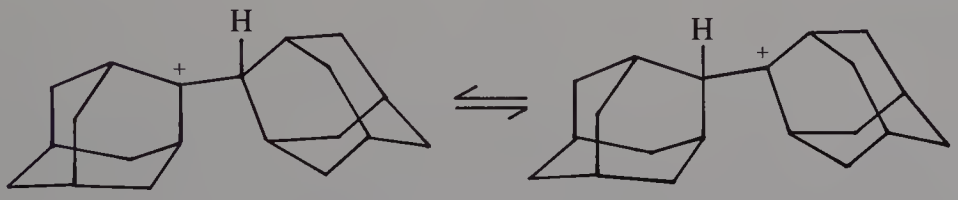


15 16

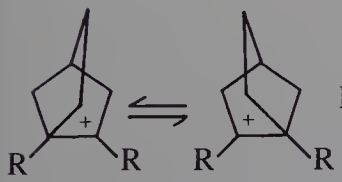
Saunders and Kates have been successful[31] in measuring the rates of degenerate 1,2-hydride and 1,2-methide shifts of simple tertiary alkyl cations employing high-field (67.9 MHz) ^{13}C NMR spectroscopy. From line broadening in the fast-exchange limit, the free energies of activation ($\Delta G^{\ddagger}$) were determined to be 3.5 $\pm$ 0.1 kcal mol^{-1} at -136 °C for **13** and 3.1 $\pm$ 0.1 kcal mol^{-1} at -138 °C for **14**. The rapid equilibrium in cations **13** and **14** have been frozen out in the solid state at -165 and -160 °C, respectively, by Yannoni, and co-workers.[35]

Many more cyclic and polycyclic equilibrating carbocations have been reported.[21] Some representative examples are the following (Scheme 7.19). All these systems again involve hypercoordinate high-lying intermediates or transition states.

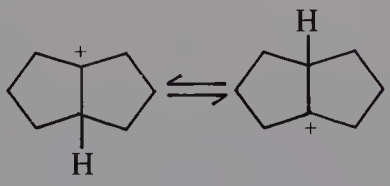
Scheme 7.19



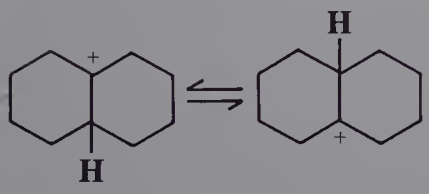
17

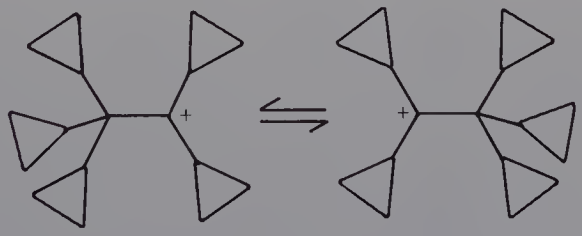


R = CH_3, C_6H_5 and so on



18 **19**



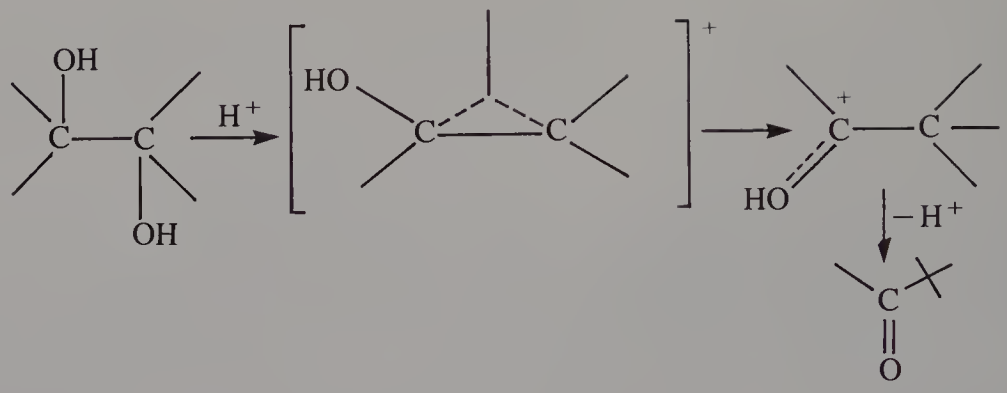


20 **21**

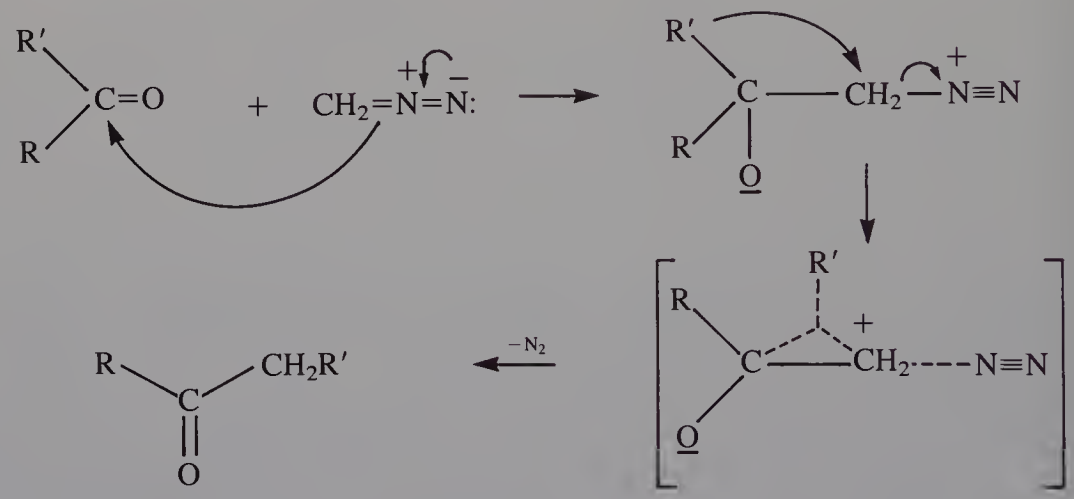
In the pinacol–pinacolone rearrangement[27] of 1,2-diols as depicted in Scheme 7.20, the carbon atom of the migrating group becomes pentacoordinated during the course of the rearrangement.

The diazomethane insertion into ketones and aldehydes to provide their homologs[41] also involves migration of an alkyl group to an electron-deficient carbon center of a zwitterion through a five-coordinate carbocation. The mechanism is depicted in Scheme 7.21.

Scheme 7.20



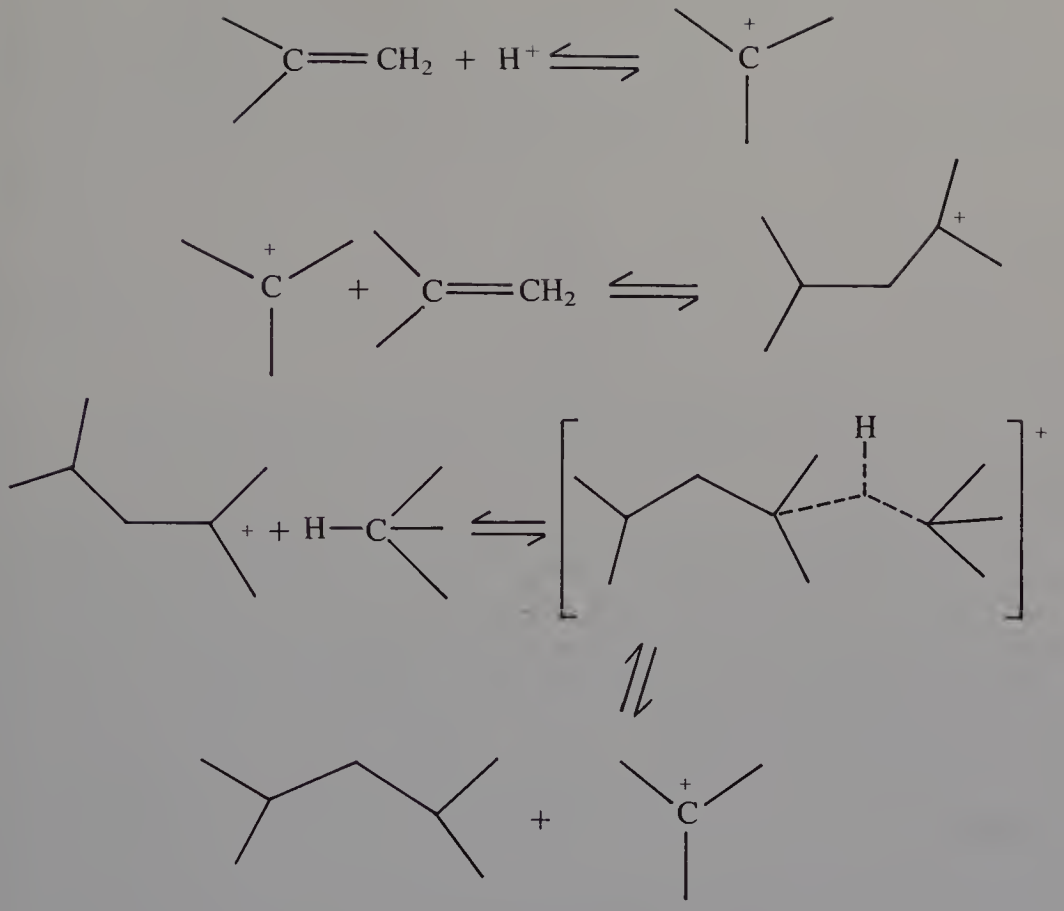
Scheme 7.21



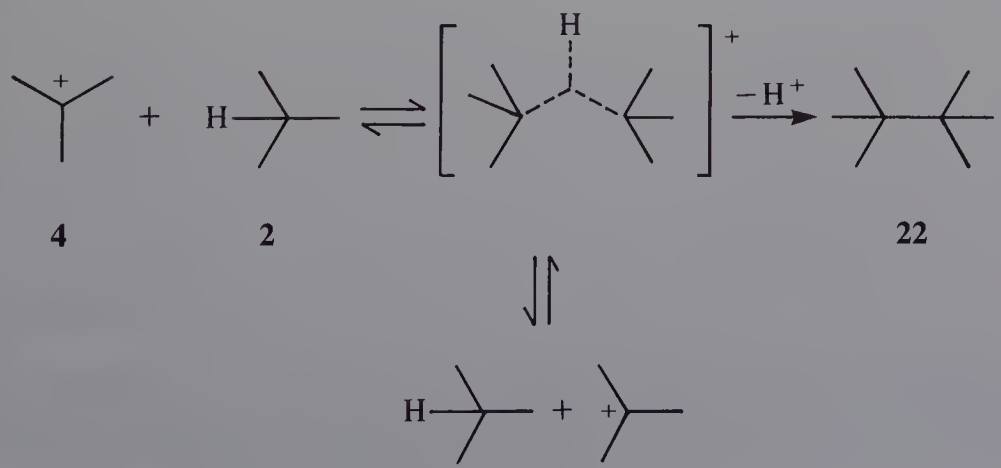
7.2.1.3. Alkylation. Conventional acid catalyzed alkylation of isoalkanes by olefins, from a mechanistic point of view, must be considered as the alkylation of the olefin by the carbenium ion formed by the protonation of the olefin. The resulting carbocation then abstracts hydride from the isoalkane to give the alkylation product and generates a new alkyl cation that propagates the reaction. The well-recognized acid catalyzed isobutane–isobutylene reaction (Ipatieff alkylation) involves a pentacoordinated intermediate in the hydride transfer reaction resulting in the branched C_8 hydrocarbon while regenerating the *t*-butyl cation (Scheme 7.22).

Direct σ alkylation of isobutane, **2**, by the *t*-butyl cation, **4**, would yield 2,2,3,3-tetramethylbutane.[17] In fact, small amounts of 2,2,3,3-tetramethylbutane, **22**, were observed in such a reaction under stable ion conditions indicating the involvement of five-coordinated transition state (or high-lying intermediate), Scheme 7.23. The hydride transfer reaction cannot have an entirely linear transition state despite the highly crowded nature of the tertiary–tertiary system. Furthermore, *t*-butylation of adamantane to 1-*t*-butyladamantane, **23**, has also been achieved,[42]

Scheme 7.22

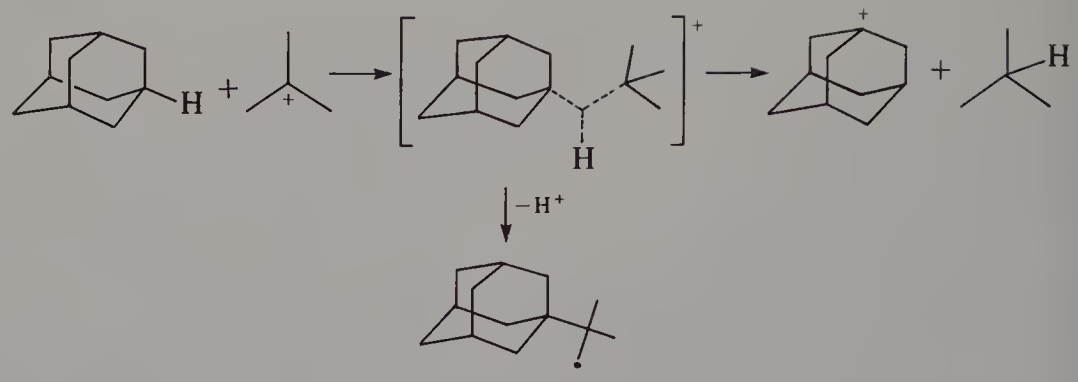


Scheme 7.23



4 **2** **22**

Scheme 7.24

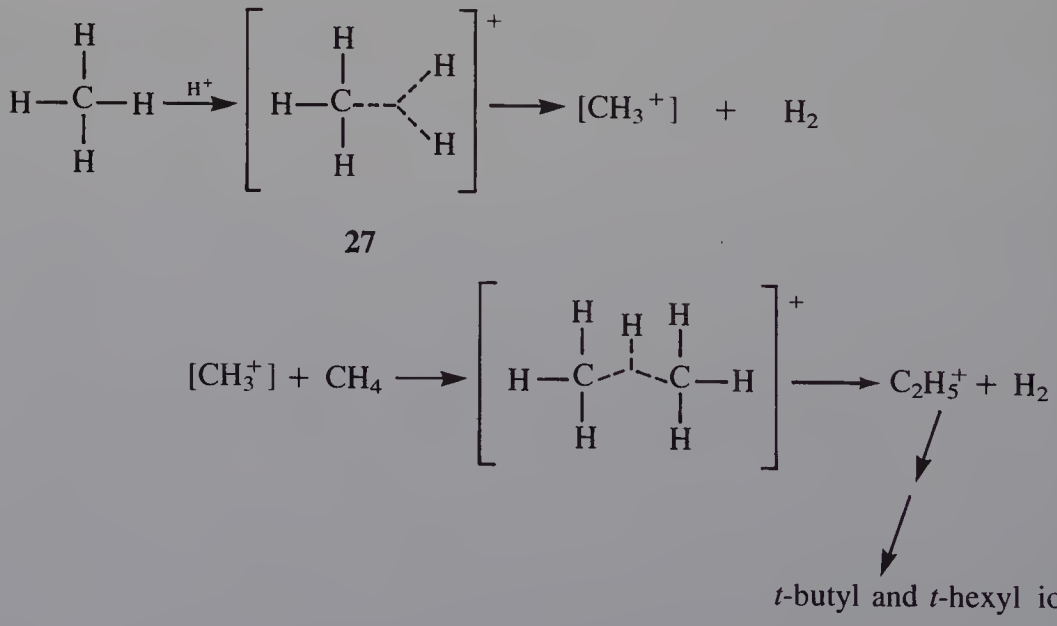


23

and this again involves a highly congested tertiary–tertiary pentacoordinate species (Scheme 7.24).

The protolytic condensation of methane in highly acidic Magic Acid solution at −60 °C is evidenced by the formation of higher alkyl cations such as *t*-butyl and *t*-hexyl cations again involving methonium, ethonium, and higher alkonium ions (Scheme 7.25). To make the reaction thermodynamically feasible, however, the hydrogen produced must be oxidatively removed from the reaction (by the acid system or some other oxidants).

Scheme 7.25



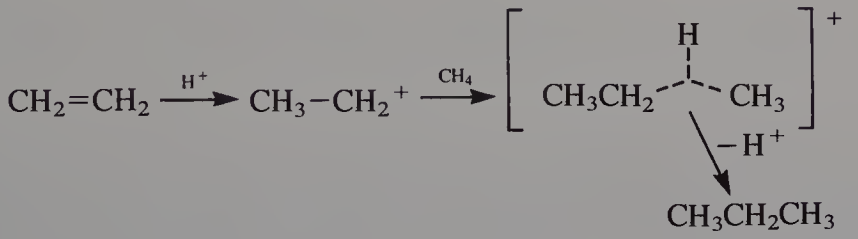
27

t-butyl and *t*-hexyl ions

Alkylation of methane, ethane, propane, and *n*-butane by the ethyl cation generated by protonation of ethylene in superacid media has been studied by Siskin,[43] Sommer et al.,[44] and Olah et al.[45] The difficulty lies in generating a very energetic

primary carbenium ion in a controlled way in the presence of excess methane and at the same time avoiding oligocondensation of ethylene itself. Siskin carried out the reaction of a methane–ethylene (86:14) gas mixture in a flow system through a 10:1 HF:TaF_5 solution under pressure with vigorous mixing. Among the reaction products recovered 60% of C_3 was found (propane and propylene), Scheme 7.26. Propylene is formed when propane (a substantially better hydride donor) reacts with the ethyl cation.

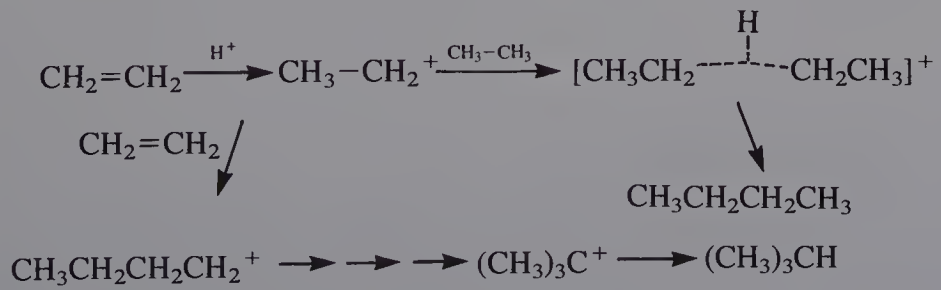
Scheme 7.26



Propane as a degradation product of oligomerized ethylene (polymerized ethylene) was ruled out because ethylene alone under the same conditions does not give any propane. Under similar conditions, but under hydrogen pressure, polyethylene is quantitatively depolymerized to form C_3 to C_6 alkanes, 85% of which are isobutane and isopentane. These results further substantiate the direct alkane-alkylation reaction and the intermediacy of the pentacoordinate carbonium ion.

Siskin[43] found that when ethylene was allowed to react with ethane in a flow system, *n*-butane was obtained as the sole product (Scheme 7.27) indicating that the ethyl cation is alkylating the primary C–H bond through a five-coordinate carbonium ion.

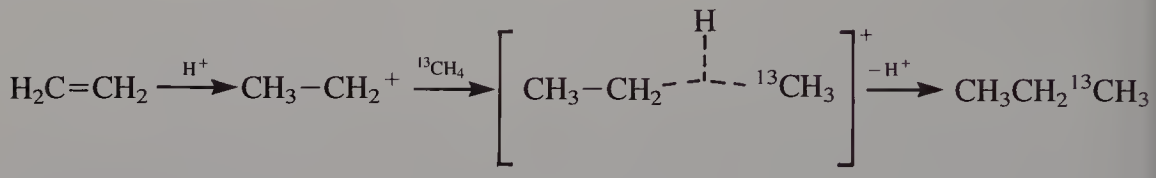
Scheme 7.27



If the ethyl cation would have reacted with excess ethylene, primary 1-butyl cation would have been formed, which inevitably would have rearranged to the more stable 2-butyl and subsequently *t*-butyl cations giving isobutane as the end product.

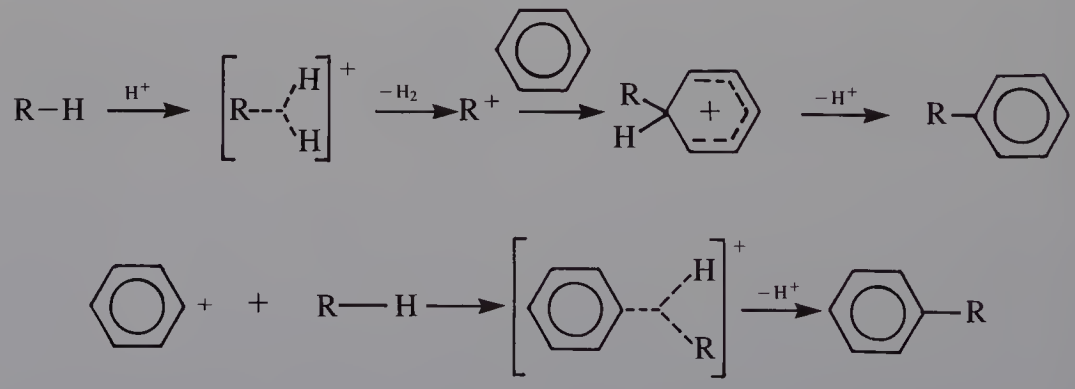
The direct ethylation of methane with ethylene has also been investigated[45] using ^{13}C-labeled methane (99.9 ^{13}C) over solid superacid catalysts such as TaF_5:AlF_3, TaF_5, and SbF_5:graphite. The results show a high selectivity in monolabeled propane, $CH_3CH_2{}^{13}CH_3$, which can only arise from direct electrophilic attack of the ethyl cation on methane via a pentacoordinate carbonium ion (Scheme 7.28).

Scheme 7.28



The superacid catalyzed alkylation of benzene with alkanes was also achieved. Alkyl cation formation for the required electrophilic attack again involves protolytic ionization of alkanes via five-coordinate carbocations. Sperenza and co-workers,[46] on the other hand, have shown that phenyl cations generated in the gas phase readily insert into the C–H bonds of simple alkanes to provide corresponding alkylated aromatics (Scheme 7.29).

Scheme 7.29



7.2.2. Nitration and Nitrosation

Electrophilic nitration and nitrosation of aromatics are fundamental synthetic reactions and well understood in terms of mechanism.[21] On the other hand, similar nitration and nitrosation of alkanes were only studied in the 1970s and 1980s.

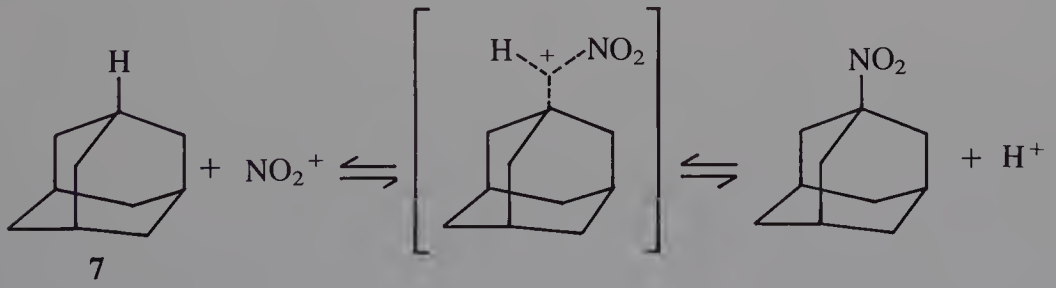
Nitronium ion salts with counter ions such as PF_6^-, SbF_6^-, and BF_4^- are very powerful nitrating agents[47] and are even capable of reacting with saturated aliphatic compounds. Nitration of alkanes, cycloalkanes, and polycyclic alkanes has been

TABLE 7.1. Nitration and Nitrolysis of Alkanes and Cycloalkanes with $NO_2^+PF_6^+$

Hydrocarbon	Nitroalkane Products and Their Mole Ratio
Methane	CH_3NO_2
Ethane	$CH_3NO_2 > CH_3CH_2NO_2$, 2.9:1
Propane	$CH_3NO_2 > CH_3CH_2NO_2 > 2\text{-}NO_2C_3H_7 > 1\text{-}NO_2C_3H_7$, 2.8:1:0.5:0.1
Isobutane	$t\text{-}NO_2C_4H_9 > CH_3NO_2$, 3:1
n-butane	$CH_3NO_2 > CH_3CH_2NO_2 > 2\text{-}NO_2C_4H_9 > 1\text{-}NO_2C_4H_9$, 5:4:1.5:1
Neopentane	$CH_3NO_2 > t\text{-}C_4H_9NO_2$, 3.3:1
Cyclohexane	Nitrocyclohexane
Adamantane	1-Nitroadamantane > 2-nitroadamantane, 17.5:1

carried out in CH_2Cl_2-tetramethylenesulfone solution to obtain aliphatic nitro compounds.[48] The nitration occurred on both C–C and C–H σ bonds involving two-electron, three-center bonded five-coordinated carbocations. The results are summarized in Table 7.1. The reaction is depicted in the case of adamantane **7**, a cage polycycloalkane (Scheme 7.30).

Scheme 7.30



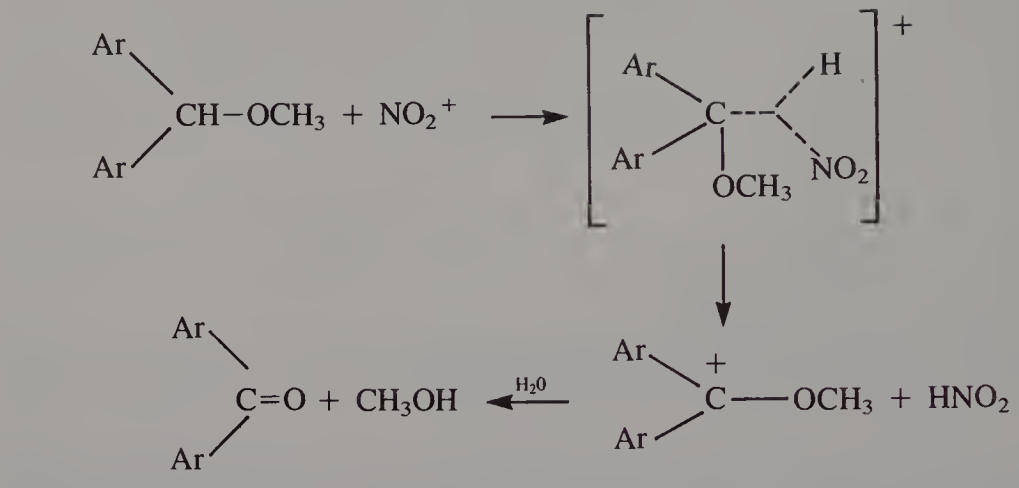
7

1-Fluoroadamantane and 1-adamantanol are by-products of the reaction indicating that the pentacoordinate carbocation can also cleave to the 1-adamantyl cation (hydride abstraction). These results also show the nonlinear nature of the ionic intermediate.

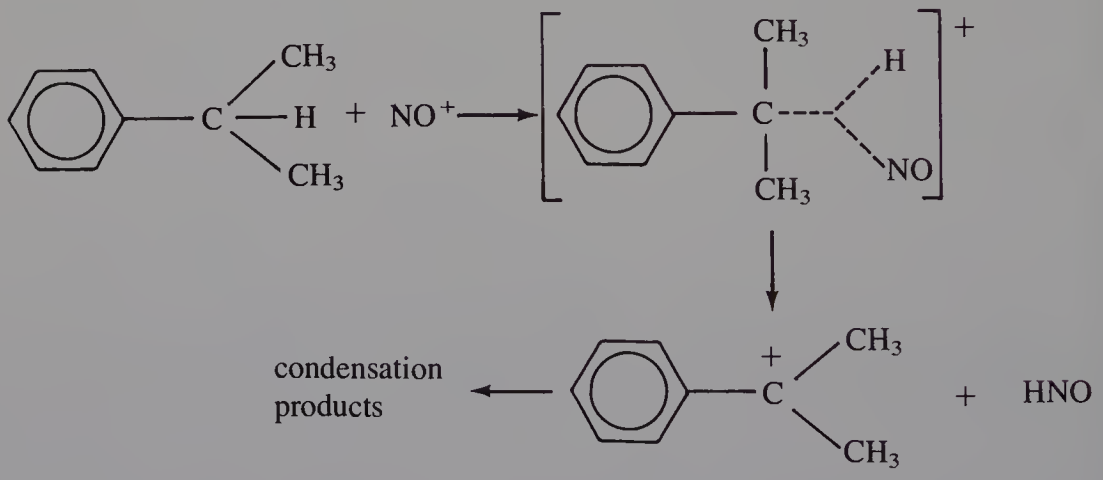
Nitronium ion is also capable of acting as an oxidizing agent[49] effecting hydride abstraction from a variety of functionalized alkanes. The oxidation of diaryl methyl ethers is best illustrated involving pentacoordinated carbocations (Scheme 7.31).

The nitrosonium ion (NO^+), the electrophilic species formed in nitrous acid media, is also an excellent hydride abstracting agent. Cumene reacts with NO^+ to give various condensation products that involve intermediate formation of the cumyl cation.[50] The formation of the cumyl cation again involves a pentacoordinated carbocation (Scheme 7.32). In fact, the NO^+ ion is advantageously used to prepare stabilized carbocations such as tropylium, benzhydryl, and trityl cations.[51]

Scheme 7.31



Scheme 7.32



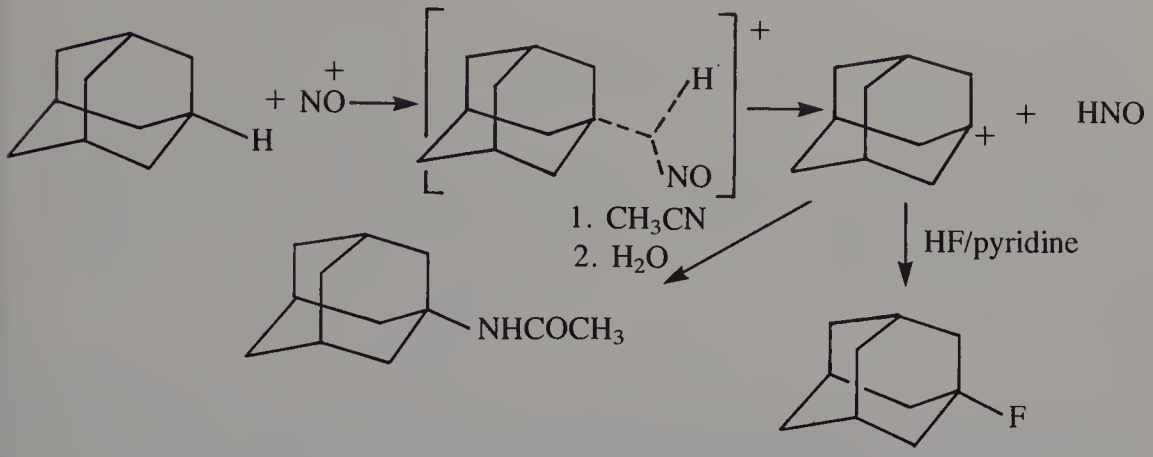
The hydride abstracting ability of (NO^+) has been employed to carry out a variety of organic transformations such as the Ritter reaction,[49] ionic fluorination,[49] and so on (Scheme 7.33).

7.2.3. Halogenation

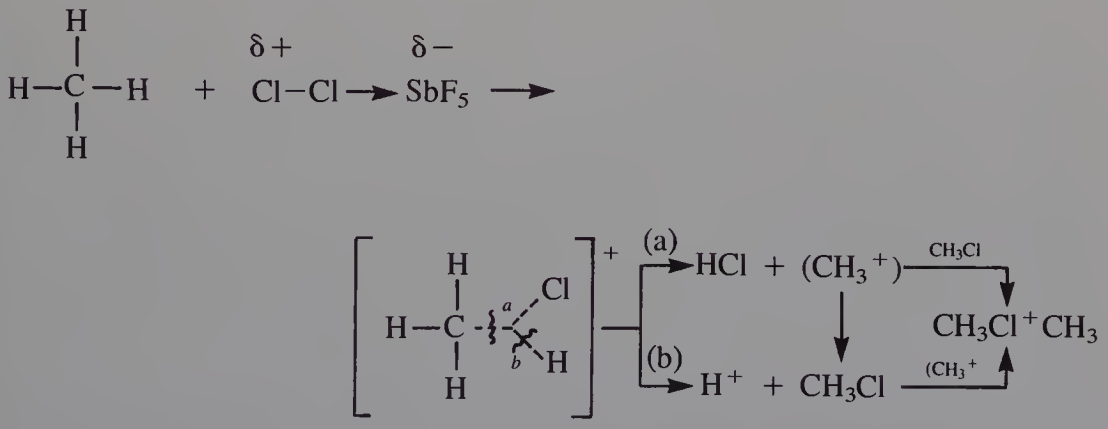
The halogenation of saturated aliphatic hydrocarbons is usually achieved by free radical processes.[52] Ionic halogenation of alkanes has also been reported under superacid catalysis. Chlorination and chlorolysis of alkanes have been carried out[53] using Cl_2 in the presence of SbF_5, Al_2Cl_6, and $AgSbF_6$ catalysts. As a representative, the reaction of methane with Cl_2:SbF_5 is depicted in Scheme 7.34, and pentacoordinated carbocations are implicated as reaction intermediates.

Selective ionic chlorination of methane to methyl chloride has been achieved in the gas phase over solid acid catalysts.[54]

Scheme 7.33



Scheme 7.34

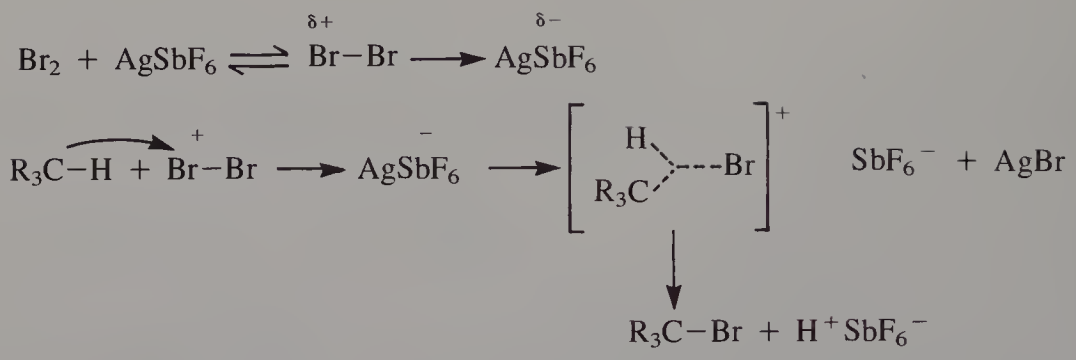


Electrophilic bromination of alkanes has been carried out[55] with Br_2 in solution in the presence of silver hexafluoroantimonate (Scheme 7.35) or over solid acid catalysts in the gas phase.

When using heterogeneous solid catalysts, even at relatively modest temperatures, competing free radical halogenations cannot be excluded. The borderline between heterolytic and homolytic reactions in heterogeneous catalytic systems may be less pronounced than previously realized.

Even electrophilic fluorination of alkanes is possible. Fluoroxytrifluoromethane and F_2 have been used to fluorinate tertiary centers in steroids and adamantanes by Barton and co-workers.[56] The strong influence of electron-withdrawing substituents on the substrates to the reaction rate as well as reaction selectivity in the presence of radical inhibitors seems to suggest the electrophilic nature of the reaction involving polarized, but not cationic fluorine species. The possibility of fluorine cation formation has been refuted.[57] Gal and Rozen[58] carried out direct electrophilic

Scheme 7.35



fluorination of hydrocarbons in the presence of chloroform. Fluorine appears to be strongly polarized in chloroform (due to hydrogen bonding with the acidic proton of chloroform). However, so far no fluorine-containing onium species is known in solution chemistry (i.e., fluoronium ions).

7.2.4. Oxyfunctionalization

Conversion of alkanes in a controlled way into their oxygenated derivatives is of substantial significance. Nature achieves this by enzymatic activation. The specific reaction that occurs in nature is hydroxylation of hydrocarbons. Cytochrome P-450[59] reduces molecular oxygen to an equivalent of water and an equivalent of oxo fragment that is capable of oxidizing the hydrocarbon substrate. The reaction is shown to occur by free radical processes.[59,60] Another system that is frequently used for hydroxylating alkanes is Fenton's reagent,[61] Fe^{2+} and aqueous H_2O_2, known since 1897. This also operates via free radical chain processes. There are numerous oxidizing systems that in most part involve free radical processes.

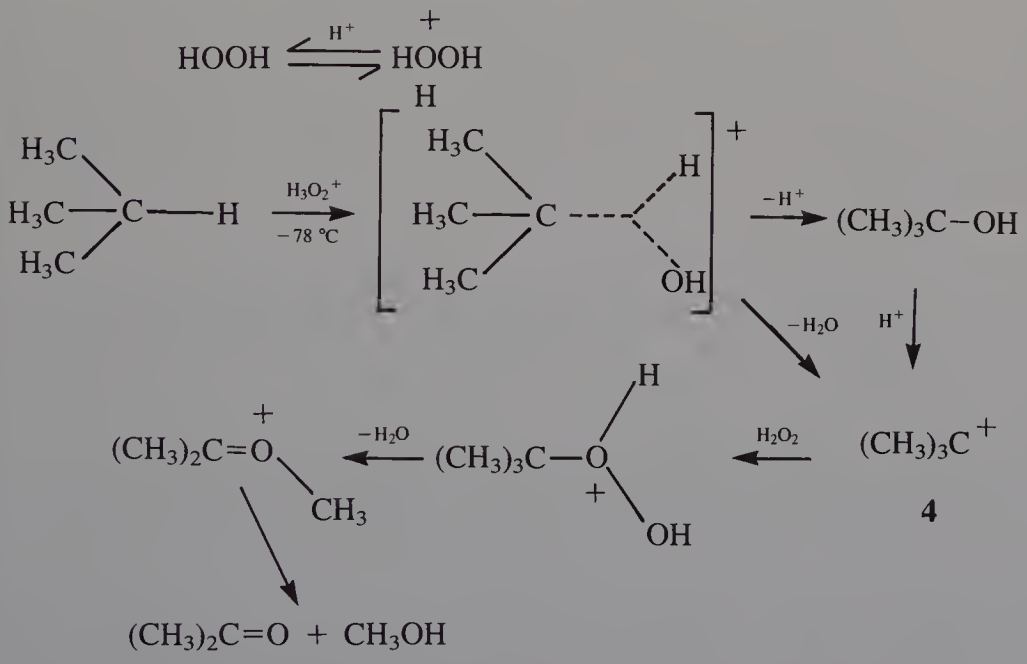
The discovery and development of superacidic systems and weakly nucleophilic solvents such as HSO_3F:SbF_5:SO_2, HSO_3F:SbF_5:SO_2ClF, and HF:SbF_5:SO_2ClF has enabled the preparation and study of a variety of carbocations.[21] In connection with these studies, it was also found that electrophilic oxygenation of alkanes with ozone (O_3) and hydrogen peroxide (H_2O_2) takes place readily in the presence of superacids under typical electrophilic conditions.[62] The reactions giving oxyfunctionalized products of alkanes can be explained in terms of initial electrophilic attack by protonated ozone, that is (^+O_3H) or the hydroperoxonium ion, $H_3O_2^+$, respectively, on the σ bonds of alkanes via pentacoordinated carbonium ions.

7.2.4.1. Oxygenation with Hydrogen Peroxide. Hydrogen peroxide (H_2O_2) in superacid media is protonated to hydroperoxonium ion ($H_3O_2^+$). Christe et al.[63] reported the characterization and isolation of several peroxonium salts. The ^{17}O NMR spectrum of $H_3O_2^+$ has also been obtained.[64] The hydroperoxonium ion may be considered as an incipient OH^+ ion capable of electrophilic hydroxylation of single (σ) bonds in alkanes, and thus be able to effect reactions similar to such

previously described electrophilic reactions as protolysis, alkylation, chlorination (chlorolysis), and nitration (nitrolysis).

The reaction of branched-chain alkanes with hydrogen peroxide in Magic Acid–SO_2ClF solution has been carried out with various ratios of alkane and hydrogen peroxide, at different temperatures.[65] As neither hydrogen peroxide nor Magic Acid–SO_2ClF alone led to any reaction under the conditions employed, the reaction must be considered to proceed via electrophilic hydroxylation. Protonated hydrogen peroxide inserts into the C–H bond of the alkane. A typical reaction path is as depicted (Scheme 7.36) for isobutane.

Scheme 7.36

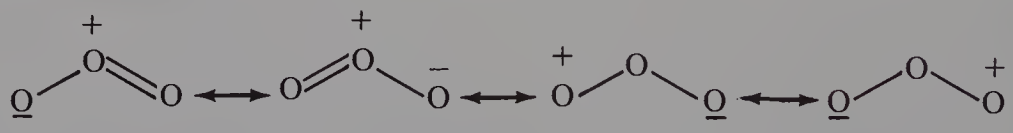


The reaction proceeds via a pentacoordinate hydroxycarbonium ion transition state, which cleaves to either *t*-butyl alcohol or the *t*-butyl cation. Since 1 mol of isobutane requires 2 mol of hydrogen peroxide to complete the reaction, one can conclude that the intermediate alcohol or carbocation reacts with excess hydrogen peroxide, giving *t*-butyl hydroperoxide. The superacid-induced rearrangement and cleavage of the hydroperoxide results in very rapid formation of the dimethylmethylcarboxonium ion, which upon hydrolysis gives acetone and methyl alcohol.

When the reaction was carried out at room temperature, by passing isobutane into a solution of Magic Acid and excess hydrogen peroxide, the formation of methyl alcohol, methyl acetate, and some dimethylmethylcarboxonium ion together with dimeric acetone peroxide was observed. These results clearly show that the products can be rationalized as those arising from hydrolysis of the carboxonium ion and from Baeyer–Villiger oxidation of acetone.

Under the same reaction conditions as employed for branched-chain alkanes, straight-chain alkanes such as ethane, propane, butane, and even methane gave related oxygenation products.[65] Methane, when reacted with hydrogen peroxide–Magic Acid above 0 °C, gave mainly methyl alcohol. A similar result was obtained with hydrogen peroxide–HSO_3F at 60 °C. Ethane with hydrogen peroxide–Magic Acid at −40 °C gave ethyl alcohol as well as some methyl alcohol. The reaction of propane with hydrogen peroxide takes place more easily than that of methane or ethane and yields isopropyl alcohol as the initial oxidation product. On raising the temperature, isopropyl alcohol gave acetone, which underwent further oxidation with hydrogen peroxide, giving dimeric acetone peroxide, methyl acetate, methyl alcohol, and acetic acid.

7.2.4.2. Oxygenation with Ozone. Ozone can be depicted as the resonance hybrid of cannonical structures **24a–24d**[66] and this might explain why ozone reacts as a 1,3 dipole, an electrophile, or nucleophile. The electrophilic nature of ozone has been recognized in its reactions towards alkenes, alkynes, arenes, amines, sulfides, phosphines, and so on.[67–71] Reactions of ozone as a nucleophile, however, are less well documented.[72]



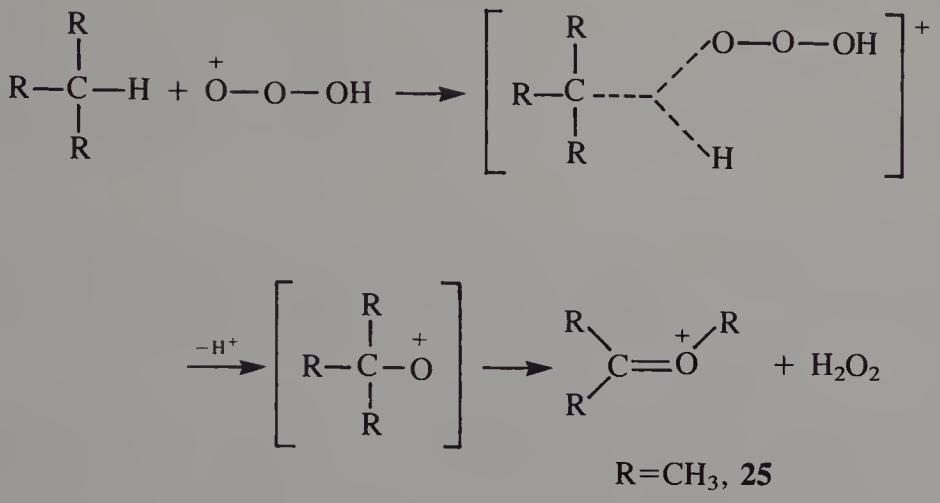
24 **a** **b** **c** **d**

When a stream of oxygen containing 1–5% ozone was passed through a solution of isobutane in HSO_3F:SbF_5:SO_2ClF solution held at −78 °C, the colorless solution immediately turned brown. ^1H and ^{13}C NMR spectra of the resultant solution were consistent with formation of the dimethylmethylcarboxonium ion, **25** (Scheme 7.37) in 45% yield.[73] Similar treatment of isopentane, 2,3-dimethylbutane, and 2,2,3-trimethylbutane resulted in formation of related carboxonium ions as the major products.

For the reaction of ozone with alkanes under superacid conditions, two mechanistic pathways may be considered. The first possible pathway is the formation of an alkylcarbenium ion via protolysis of the alkane prior to quenching of the ion by ozone, as shown in Scheme 7.38a. Alkylcarbenium ions may also be generated via initial oxidation of the alkane to an alcohol followed by protonation and ionization (Scheme 7.38b). There have already been a number of reports of ozone reacting with alkanes to give alcohols and ketones.[74–76] In both cases, intermediary alkylcarbenium ions would then undergo nucleophilic attack by ozone as described earlier.

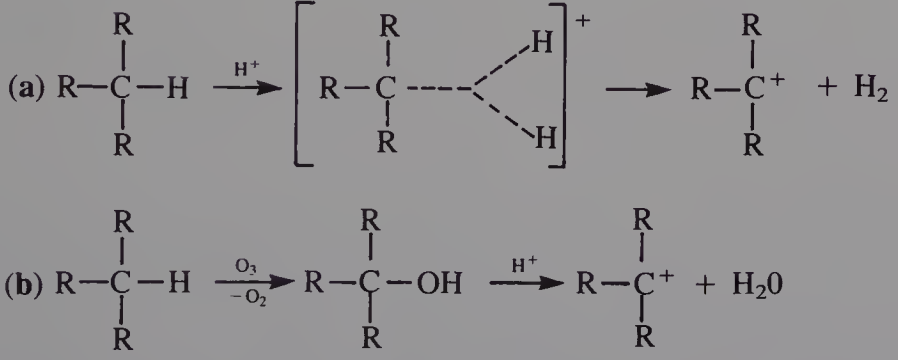
Since the relative rate of formation of dimethylmethylcarboxonium ion from isobutane is considerably faster than that of the *t*-butyl cation from isobutane in the absence of ozone under the same conditions,[73] it is highly likely that protonated ozone inserts into the C−H bond of the alkane (Scheme 7.37) to form a

Scheme 7.37



R=CH_3, **25**

Scheme 7.38



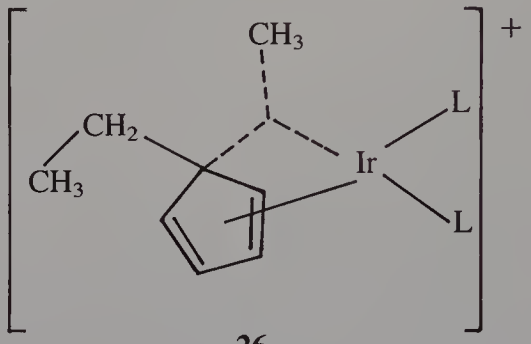
pentacoordinated peroxonium ion that decomposes to a very reactive *t*-alkyloxenium ion that undergoes Baeyer–Villiger oxidation.

7.2.5. Reactions of Coordinatively Unsaturated Metal Compounds and Fragments with C–C and C–H σ Bonds

Metals can attain a more stable electronic configuration by accepting electrons from *n*-donor and π-donor systems. As discussed in Chapter 2, a variety of compounds such as alkyllithiums, aluminum, beryllium, magnesium, and other related systems form stable alkyl bridged species where the metal draws upon the electrons in σ bonds in the alkyl substituent to attain electronic stability.

In the complexes of transition metals, where the metal is coordinatively unsaturated (i.e., it has access to less than 18 electrons in its coordination shell) the metal becomes electron deficient. In the absence of better *n*- and π-donor systems, such coordinatively unsaturated metals can draw electrons from neighboring σ bonds to satisfy the electron deficiency of the metal. In fact, many such stable C–H σ bond

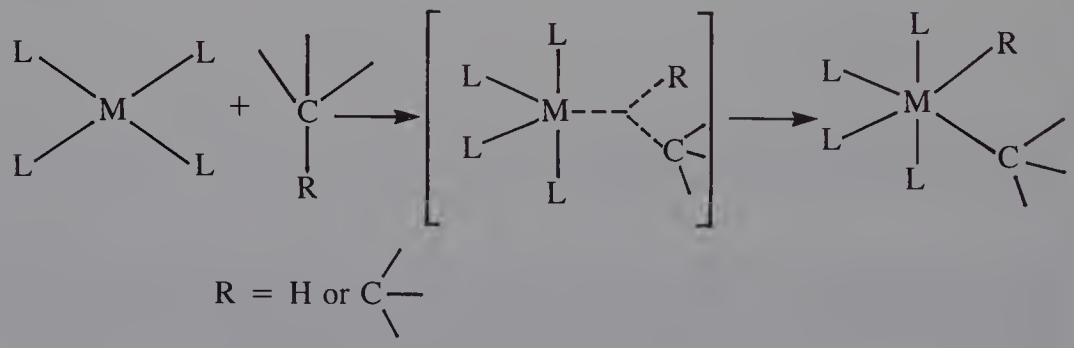
inserted complexes containing hypercoordinated carbons are known (also see Chapter 2).[77] There is even a reported example wherein one could envisage a C−C σ bond inserted complex.[78] The crystal structure of the complex Ir $[C_5H_4(CH_3)(CH_2CH_3)]L_2^+$, **26**, shows that the carbon–carbon bond between quaternary carbon and the *endo* methyl group appears to be well within the sum of the van der Waals radii from the metal and thus interactions between them may exist.



26

We shall subsequently review pertinent examples of reactions that involve alkane activation by metals. The initial step in the reactions of metals with alkanes involves either a C−H or C−C bond insertion (Scheme 7.39). The C−H bond insertions are more common than C−C bond insertions. The latter appear to be more common in the case of strained σ bonds as well as in the case of free metal ions.

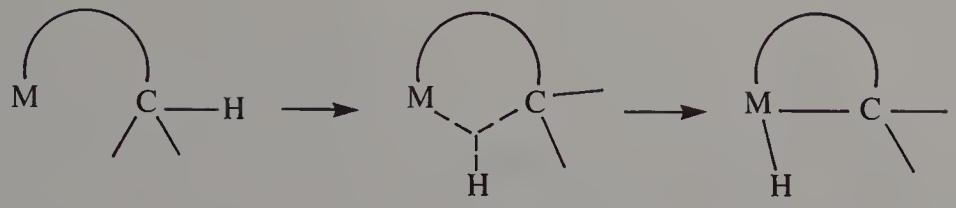
Scheme 7.39



7.2.5.1. Carbon–Hydrogen Bond Insertions. In the early 1960s the activation of alkanes by metal systems was realized from the related development of oxidative–addition reactions[79] in which low valent metal complexes inserted into carbon–heteroatom, silicon–hydrogen, and hydrogen–hydrogen bonds. The direct oxidative–addition of metals into C−H bonds was found in the cyclometallation reaction (Scheme 7.40).[80]

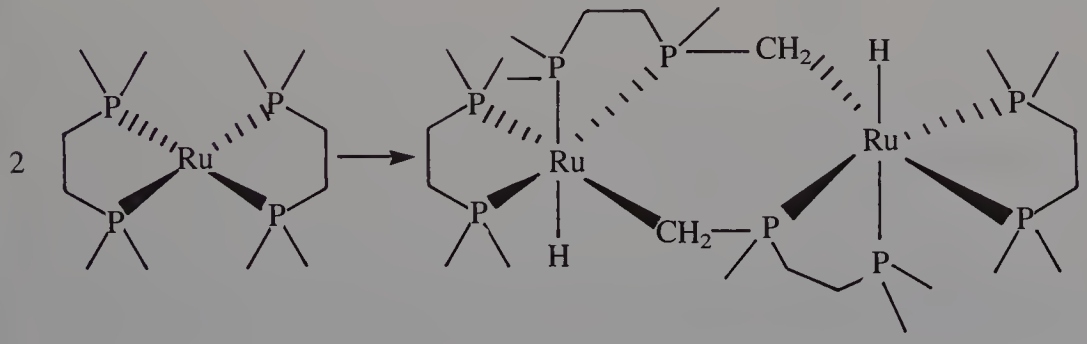
The first clear example of cyclometallations of sp^3 C−H bonds was shown in the case of the ruthenium complex, $Ru(dmpe)_2$.[81] This complex was found to spontaneously cyclometallate the C−H σ bond of the methyl group on the

Scheme 7.40



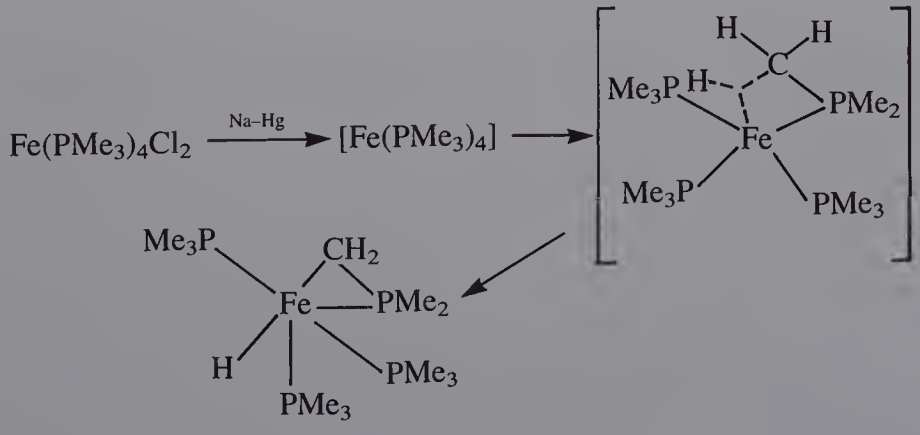
phosphorous through a pentacoordinated hypercarbon intermediate to provide an interesting dimer (Scheme 7.41).[81b] The same complex also reacts with the aromatic C–H bond of the naphthalene.[81]

Scheme 7.41



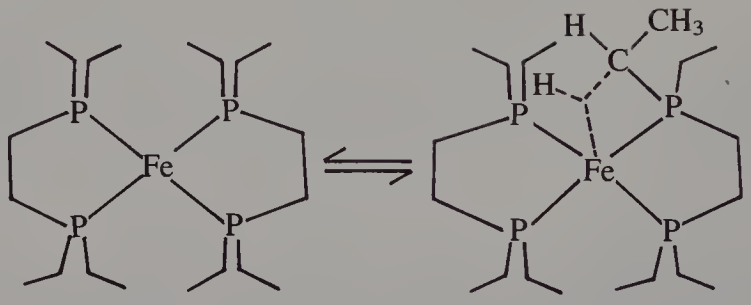
Similarly Rathke and Muetterties have shown[82] the intramolecular insertion of coordinatively unsaturated iron(0)phosphine complex (Scheme 7.42).

Scheme 7.42



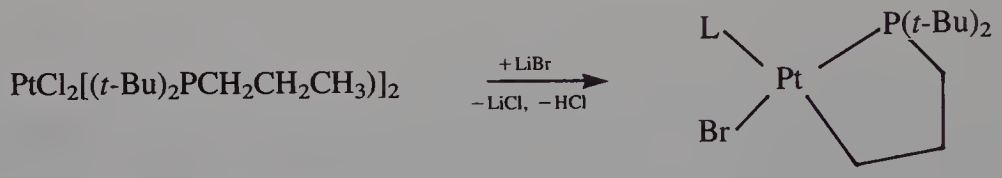
A reversible intramolecular oxidative–addition/reductive elimination has been reported by Baker and Field (Scheme 7.43).[83]

Scheme 7.43



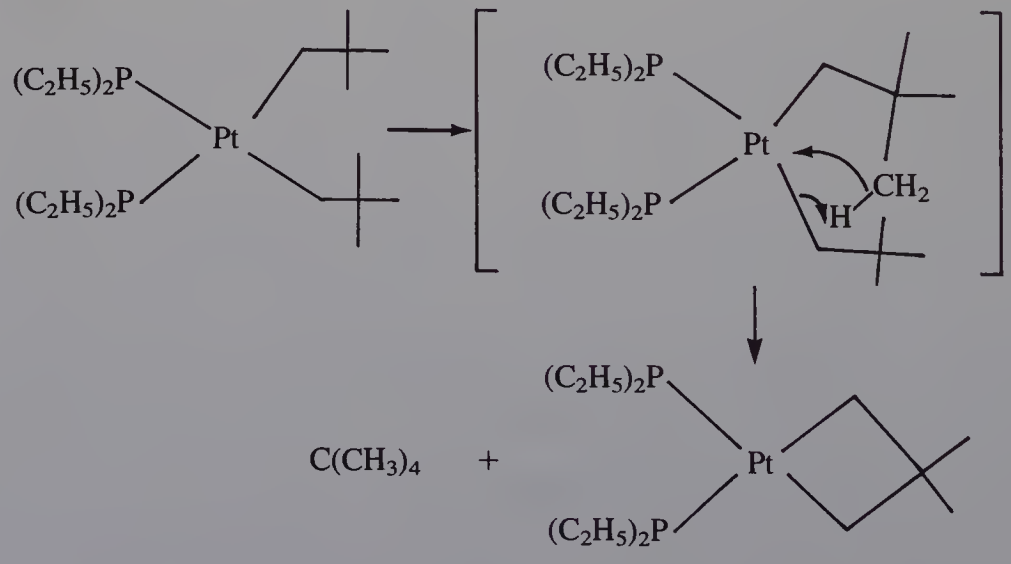
Strong steric effects (steric congestion) has been found to accelerate cyclometallation reactions as shown by the example in Scheme 7.44.[84]

Scheme 7.44



Whitsides and co-workers[85] found that a bisneopentyl complex of Pt decomposes irreversibly to a platina–cyclobutane with loss of neopentane (Scheme 7.45).

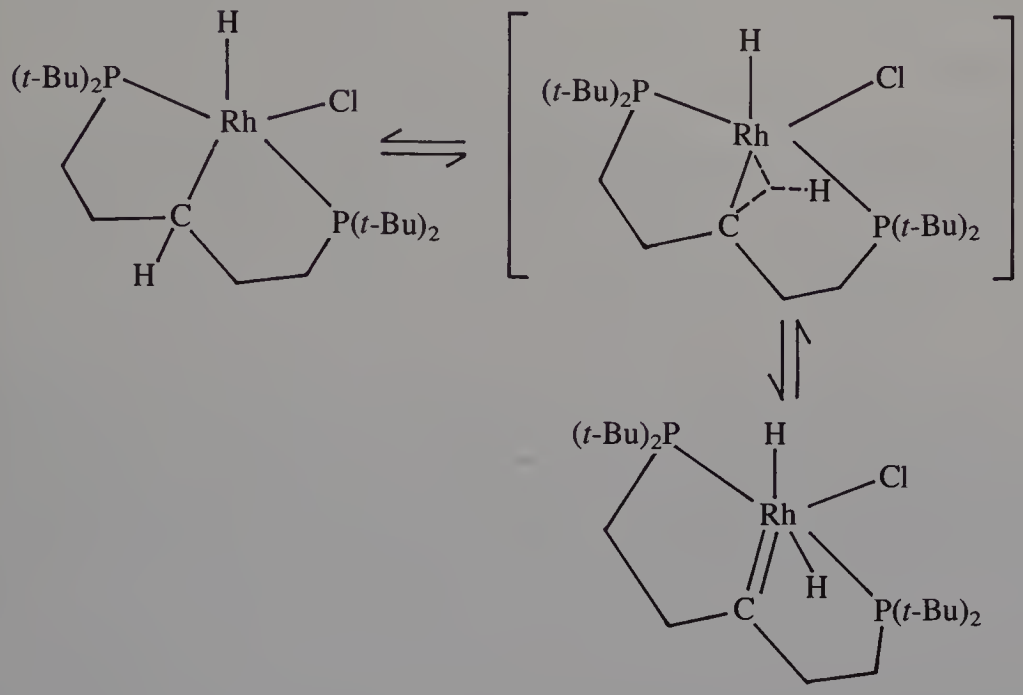
Scheme 7.45



Cyclometallation in a rhodium complex has been used to form an unusual alkylidene complex in the conformationally restricted backbone of certain

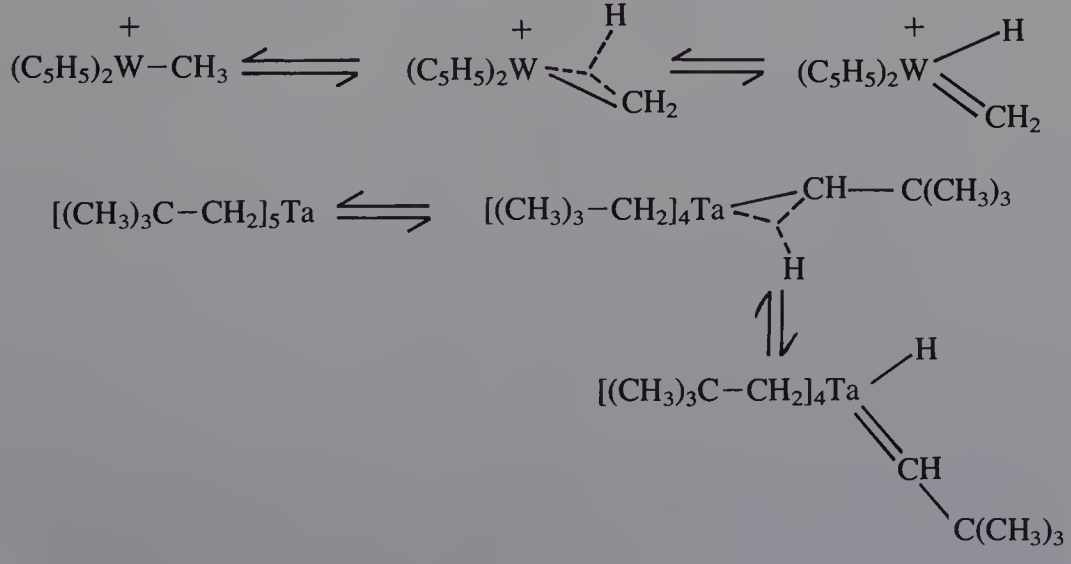
diphosphines.[86] Such a transformation occurs via an α-hydride elimination (Scheme 7.46).

Scheme 7.46



Similar α-elimination reactions resulting in metal carbenes have been studied extensively[87] in the case of tungsten and tantalum complexes (Scheme 7.47).

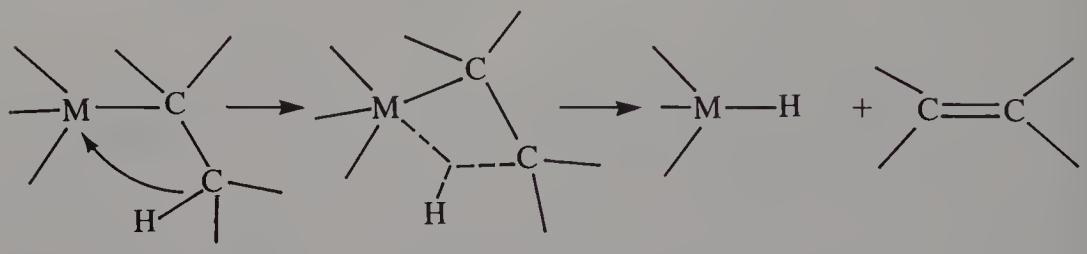
Scheme 7.47



An α-C−H bond interaction of this type has been proposed to rationalize the stereospecificity of reactions catalyzed by the cobalt containing coenzyme B-12.[88]

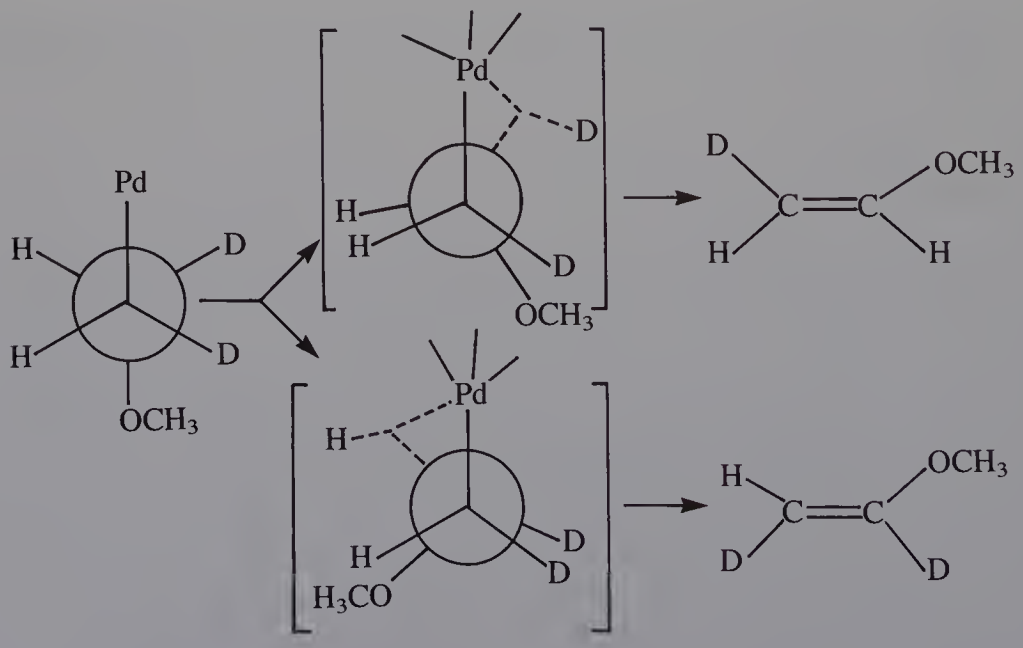
The reaction of a C−H bond at the carbon atom β to the metal in an alkyl metal complex leads to a facile elimination of an alkene (i.e., β-hydride elimination), Scheme 7.48.

Scheme 7.48



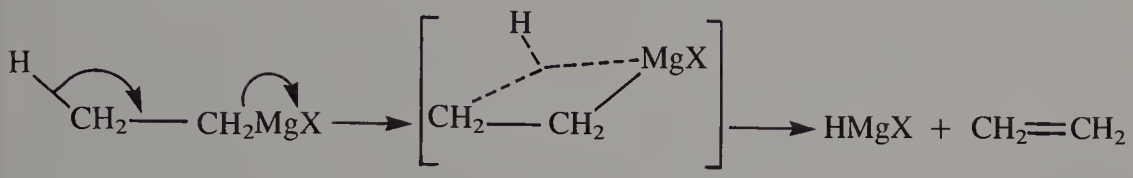
In cases where it has been possible to follow the stereochemical course of the β elimination,[89–91] it has been found to occur stereospecifically in a *syn* fashion. Consequently, the dideuterated organopalladium complex affords the two olefins via syn elimination (Scheme 7.49), consistent with the intermediacy of bridged intermediates containing higher coordinate carbon atoms.[92]

Scheme 7.49



β-Elimination is also common in many organoaluminum and organomagnesium compounds. The β-hydride eliminations of ethylmagnesium halides and diethylmagnesium are well recognized (Scheme 7.50).[93]

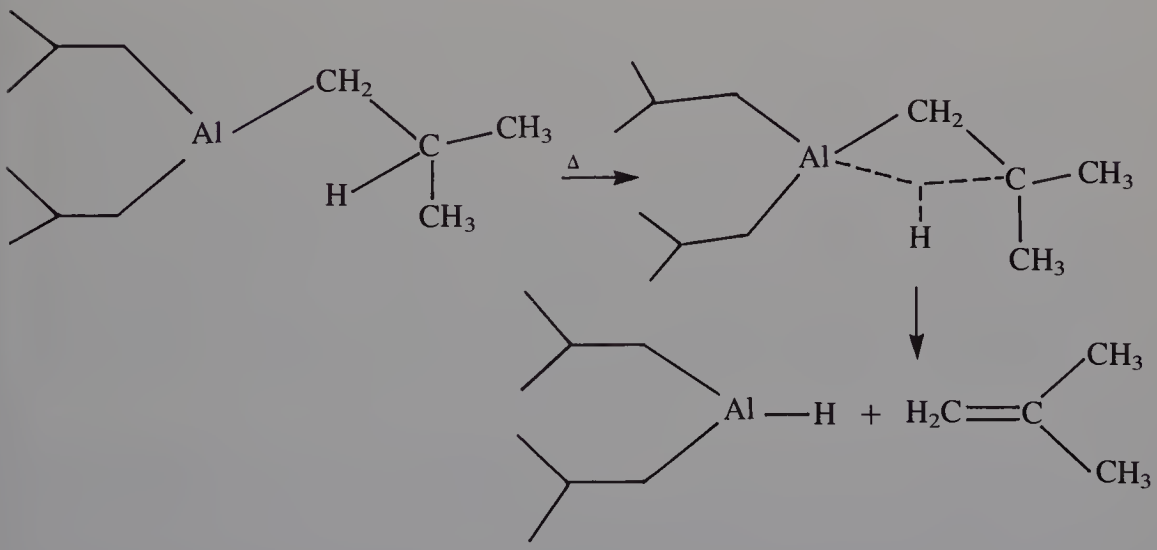
Scheme 7.50



$$Mg(CH_2{-}CH_3)_2 \xrightarrow{\Delta} MgH_2 + CH_2{=}CH_2$$

Thermal decomposition of isobutylaluminum produces diisobutylaluminum hydride and isobutylene (Scheme 7.51).[94]

Scheme 7.51



Even *n*-buLi in refluxing octane undergoes β-hydride elimination to give 1-butene (Scheme 7.52)[95]

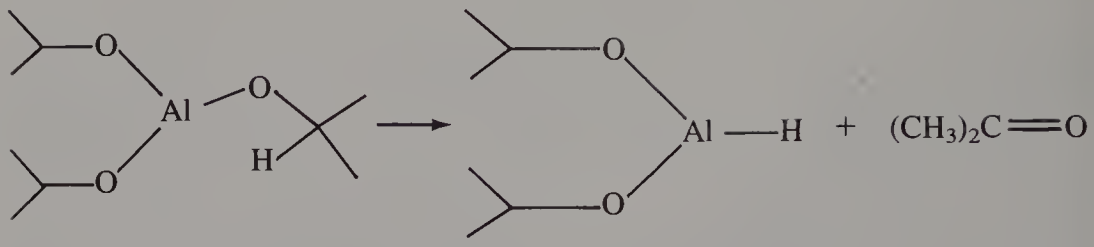
Scheme 7.52

$$CH_3CH_2CH_2CH_2Li \xrightarrow[\text{octane}]{\text{reflux}} CH_3CH_2CH{=}CH_2 + LiH$$

Similarly, tris-isopropylboron also undergoes β-hydride elimination. Decomposition of aluminum-isopropoxide thermally produces acetone by β-hydride elimination (Scheme 7.53).[96]

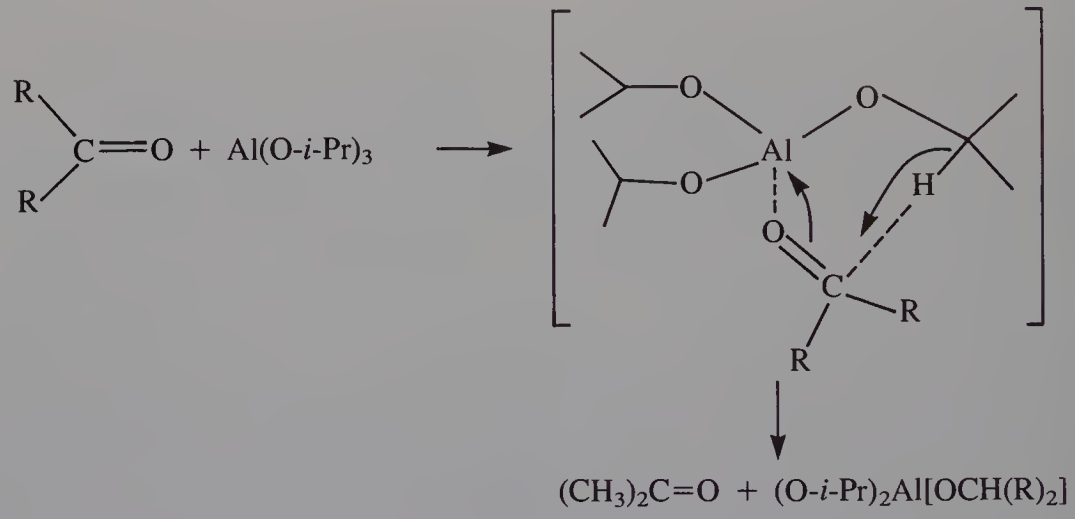
In fact, a variation of this reaction has been utilized in the well-known Meerwein–Ponndorf–Verley reduction (reverse of Oppenauer oxidation) of carbonyl compounds by aluminum–isopropoxide.[97] The reaction involves a six-centered

Scheme 7.53



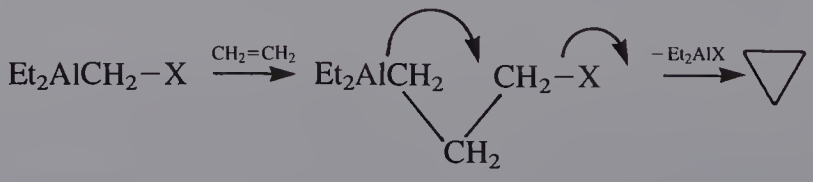
transition state, wherein the β hydride is delivered into an incoming carbonyl group (Scheme 7.54). The stereochemistry of this reaction has been studied in detail.[96]

Scheme 7.54



A number of heteroatom substituted dialkylaluminum compounds, R_2AlCH_2-X, can undergo apparent α, αβ, or αγ eliminations. The apparent α elimination when halomethylaluminum compounds cyclopropanate alkenes is actually a combination of carbalumination and αγ elimination (Scheme 7.55).[98] Such eliminations involve hypercarbon intermediates or transition states.

Scheme 7.55

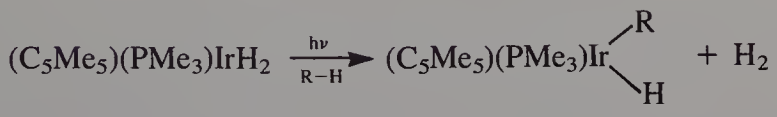


Although insertion of metals into C−H bonds of alkanes, alkenes, and aromatics has been known for a long time, the direct intermolecular insertion of a metal

fragment into a C–H bond of an alkane to provide a stable alkyl hydride adduct was achieved only in 1982.[99] The intermediate 16 electron, electron-deficient, transition metal fragment (of metals such as Ir, Rh, Ru, etc.) was generated photochemically by the decomposition of the appropriate metal dihydride or metal carbonyl.

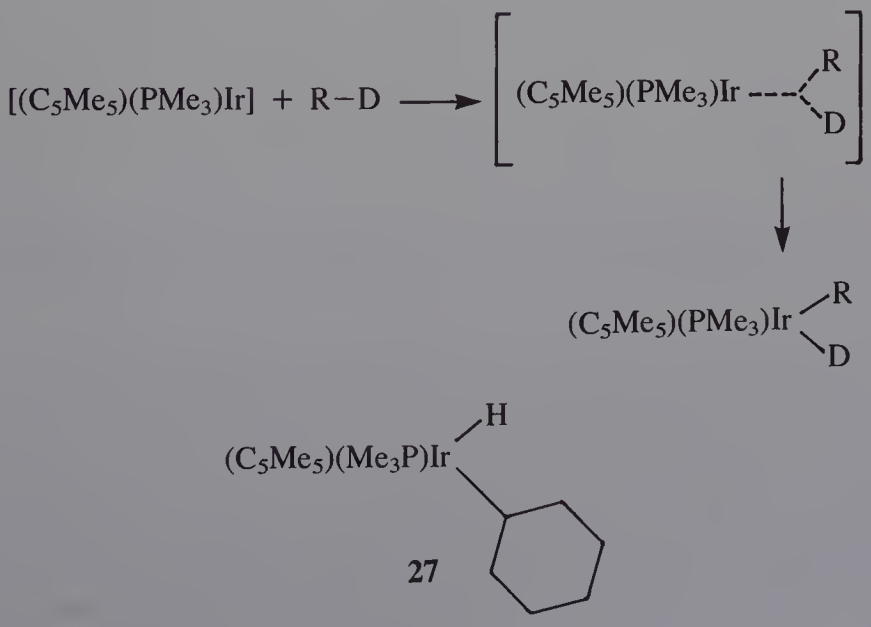
Bergman and Janowicz[100] showed that photolysis of $(C_5Me_5)(Me_3P)IrH_2$ in a variety of alkane solvents gave the corresponding alkyl hydride adducts with elimination of H_2 (Scheme 7.56). These adducts were also found to eliminate alkanes thermally at 110 °C and exchange with other alkanes.

Scheme 7.56



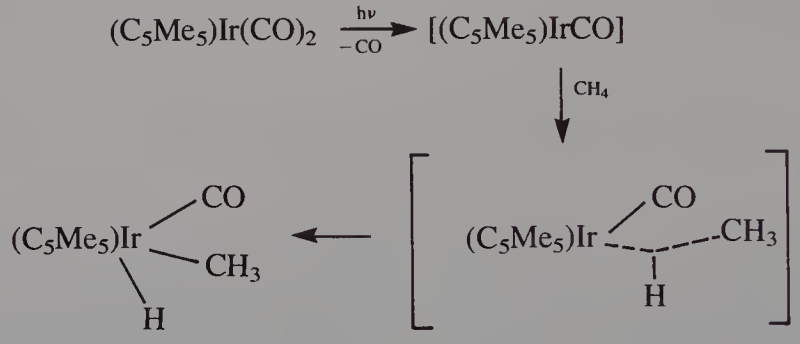
Photolysis of the iridium hydride in C_6D_6 gave the adduct $(C_5Me_5)(Me_3P)IrDC_6D_5$ and H_2 with no H/D exchange (Scheme 7.57), clearly ruling out photoextrusion of hydrogen atoms or any free radical mechanism. When the photolysis was carried out in the presence of a mixture of neopentane and cyclohexane-d_{12} less than 10% crossover occurred indicating the direct insertion of a photogenerated coordinatively unsaturated metal fragment $(C_5Me_5)(Me_3P)Ir$. The kinetic isotope effect of $kH/kD = 1.38$ is also consistent with a direct insertion mechanism involving a hypercoordinated carbon intermediate. The cyclohexyl hydride $(C_5Me_5)(Me_3P)IrH(C_6H_{11})$, **27**, has been structurally characterized.[101]

Scheme 7.57



It was also found that insertion into a primary C−H bond was more facile than into a secondary or tertiary C−H bond.[102] This indicated that insertion into a methane C−H bond would be more favorable. Graham and Hoyano[103] have independently photolyzed $C_5Me_5Ir(CO)_2$ in neopentane to obtain the neopentyl hydride with the loss of CO. Under these conditions, methane was also found[104] to react at 8-atm pressure in perfluorohexane solution (Scheme 7.58).

Scheme 7.58



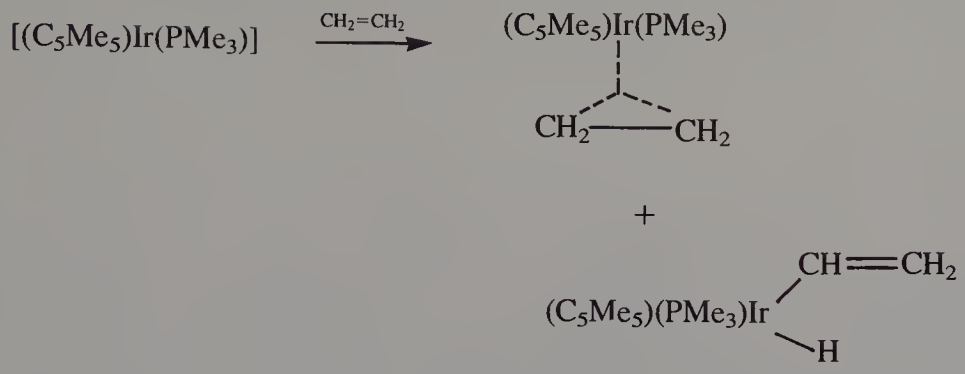
Graham and co-workers[105] have shown that insertion into the methane C−H bond occurs even at 12° K indicating a very low kinetic barrier for the process. Jones and Feher[106] studied a related rhodium complex, $(C_5Me_5)Rh(PMe_3)H_2$, which upon photolysis in alkanes and arenes gave similar C−H inserted complexes. Saillard and Hoffmann[107] suggested that general C−H addition to a square planar ML_4 is favored by folding back two trans L groups. This explains why the isolobal "CpML" fragments are so reactive towards C−H bonds.

Furthermore, Bergman et al.[101] succeeded in generating the transient "$CpRe(PMe_3)_2$" fragment by the irradiation of the $CpRe(PMe_3)_3$ complex. However, with this bulky rhenium species only methane, cyclopropane, and primary alkane C−H bonds were found reactive. Interestingly the transient iridium complex $(C_5Me_5)Ir(PMe_3)$ was also found to react with ethylene to give both the π complex and the σ-C−H inserted complex indicating the facile nature of the latter reaction (Scheme 7.59).

One other approach for the activation of alkane C−H bonds is to choose a metal that forms a strong metal to carbon bond. Main group and early *d*-block elements [e.g., $Al(R)_3$, $Ta(R)_5$, etc.] as well as lanthanides and actinide alkyls fall into this category.

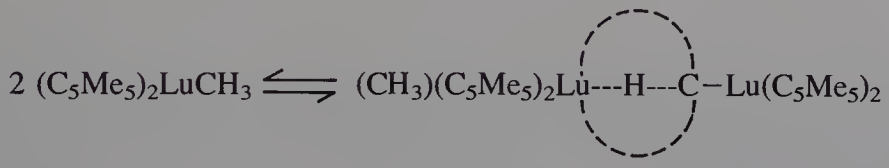
Watson[108] demonstrated alkane activation among *f*-block metals. Lutetium and ytterbium metals form complexes that are capable of inserting into C−H σ bonds. The coordinatively unsaturated complexes $(C_5Me_5)_2M-CH_3$(M = Yb, Lu) show a variety of interesting reactions (mainly of the Ziegler–Natta type). For example, the lutetium complex under solvent free conditions exists as a dimer (Scheme 7.60, confer Chapter 2). The crystal structure of the dimer indicates it to be unsymmetrical in which a methyl group from one coordinates to vacant metal orbitals of the second

Scheme 7.59



molecule.[109] In cyclohexane solution about 15% of this compound exists as a monomer and equilibration is rapid on the NMR time scale.

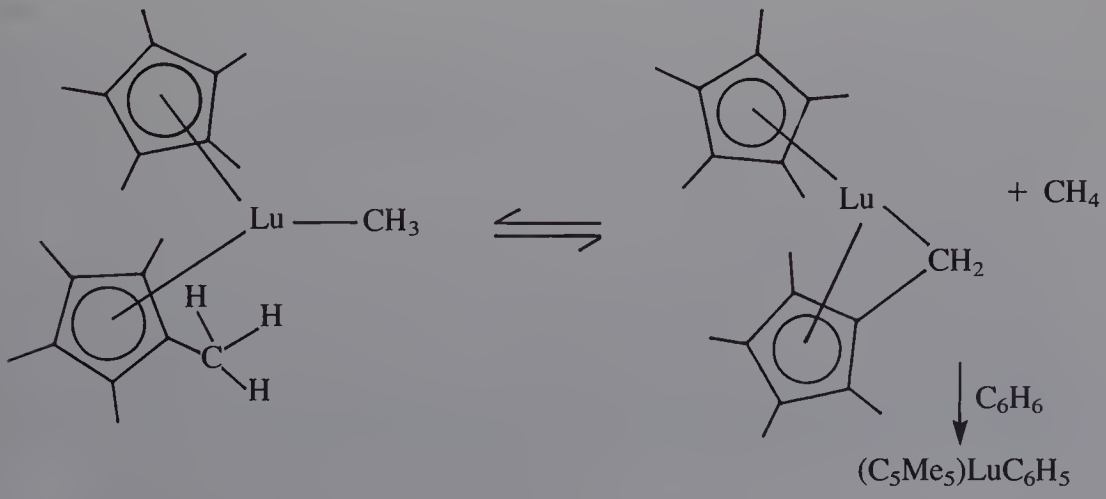
Scheme 7.60



For the dissociation of the dimer to monomers, $\Delta H^0 = 12.6$ kcal mol^{-1} and $\Delta S^0 = 32.8$ eu in cyclohexane was reported.[109]

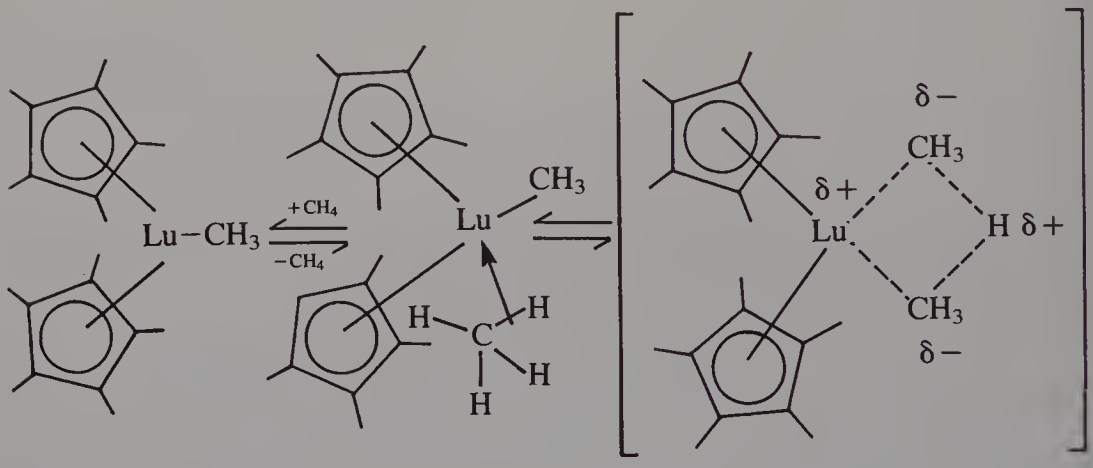
The monomer reacts with C_6H_6 at 70 °C via the following pathway through initial methane elimination followed by aromatic C–H insertion (unimolecular pathway),[109] Scheme 7.61.

Scheme 7.61



The monomer also exchanges a methyl group with the external ^{13}C enriched methane either by the unimolecular pathway or the bimolecular pathway as shown in Scheme 7.62 involving high coordinate carbon atoms.[109,110]

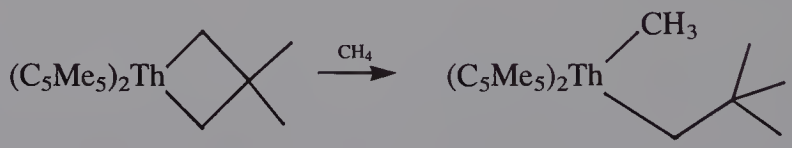
Scheme 7.62



However, such exchange does not occur very readily with higher alkanes such as cyclohexane and the reason may be steric. Linear alkanes such as ethane and propane react rather sluggishly.[109]

Marks and co-workers reported[110] that methane also reacts with a thorium metallacycle (Scheme 7.63).

Scheme 7.63

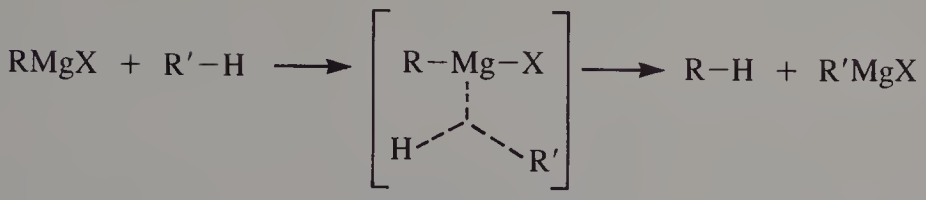


Many organomagnesium derivatives (e.g., RMgX) undergo alkyl group exchange when treated with reactive alkanes through C−H bond insertion. Cyclopentadiene, indene, fluorene, and their derivatives are readily metallated in the absence of a diethyl ether solvent (Scheme 7.64).[111]

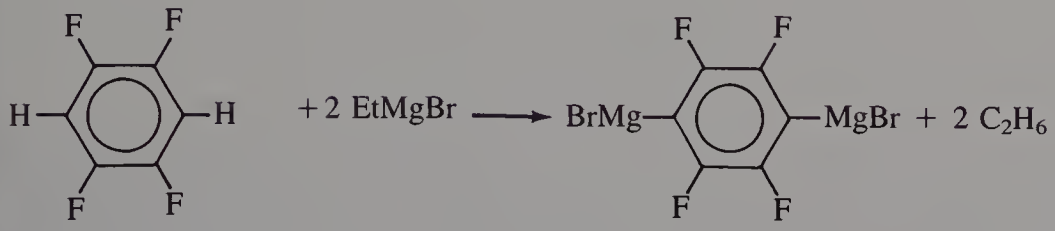
Tetrafluorobenzene is also easily metallated in the presence of ethylmagnesium bromide (Scheme 7.65).[112]

Apart from electron deficient metal fragments, free metal atoms as well as metal ions can insert into C−H and C−C bonds. In 1980, Billups et al.[113] demonstrated that photoexcited Fe atoms in a methane matrix reacted to provide $HFeCH_3$. Ozin and McCaffrey[114] subsequently studied this reaction in greater detail and found that the reaction is reversible at different wavelengths (Scheme 7.66).

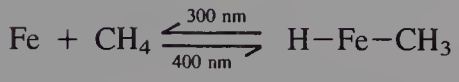
Scheme 7.64



Scheme 7.65



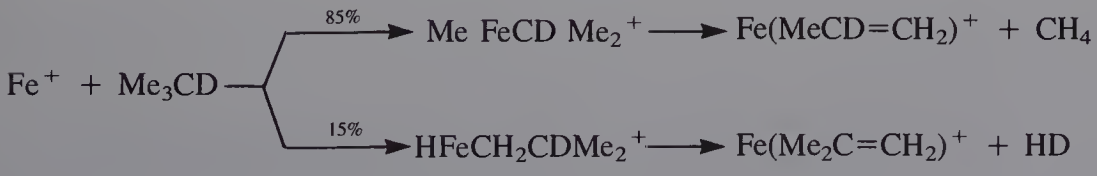
Scheme 7.66



Photoexcited Cu(^{2}P) was also found to react with methane in a matrix at 12° K. The photoadduct, conceived as $HCuCH_3$, decomposed photolytically to CuH and $CuCH_3$.[115]

The reaction of alkanes with simple or complex metal ions in the gas phase can be conveniently studied by ion beam mass spectrometry or by ion cyclotron resonance.[116] Ridge found[117] that "naked" Fe^+ ions could not only break C–H but also C–C bonds of *n*-butane and isobutane (Scheme 7.67).

Scheme 7.67

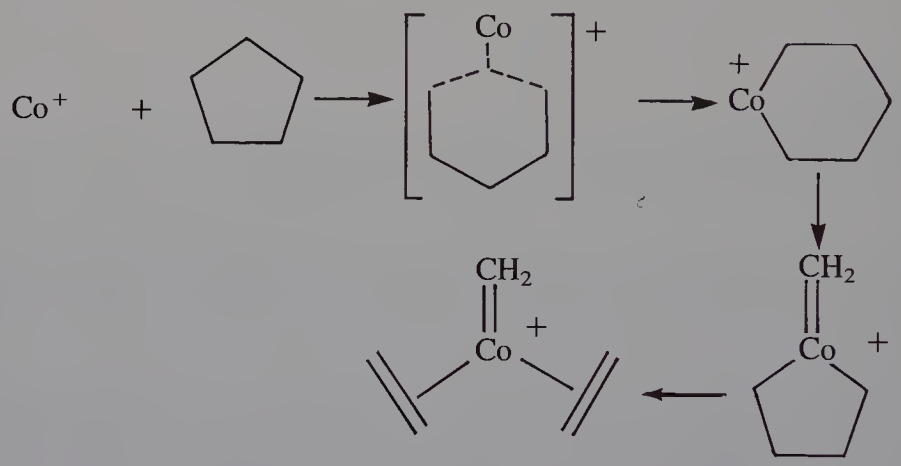


Beauchamp and Armentrout[118] studied the reaction of Co^+ with isobutane in an ion-beam apparatus connected to a mass spectrometer. They were able to see very similar chemistry to that observed by Ridge and co-workers.[117] Co^+ reacts with C–H and C–C bonds exothermically, the latter being preferred on thermodynamic grounds.

7.2.5.2. Carbon–Carbon Bond Insertions. Carbon–carbon bond breaking reactions in alkanes are of substantial importance, since they can lead to skeletal rearrangements and cracking. Some of these reactions were discussed in Section 7.2.1, where Brønsted and Lewis acids were used as catalysts. In a number of heterogeneous skeletal rearrangement reactions of alkanes involving C–C bond cleavages, transition metals have been implicated.

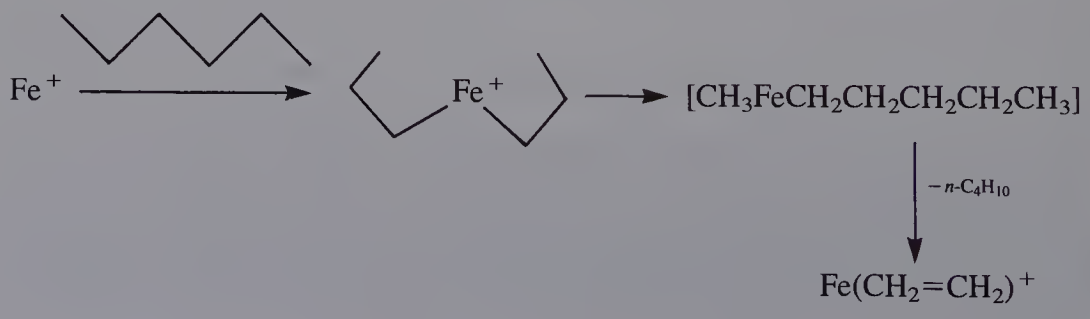
In the gas phase Fe^+, Co^+, and Ni^+ metal ions react with isobutane with facile C–C bond cleavage.[117] In fact, in the case of the Co^+ ion, the C–C bond cleavage appears to be preferred over C–H bond scission. The Co^+ ion reacts with C_3 to C_6 cycloalkanes exclusively by C–C bond insertion to provide metallacycles, which themselves decompose largely by C–C cleavage pathways.[118] All these reactions must proceed through the intermediacy of hypercarbon containing species. The reaction pathway for cyclopentane is shown in Scheme 7.68.[118,119]

Scheme 7.68



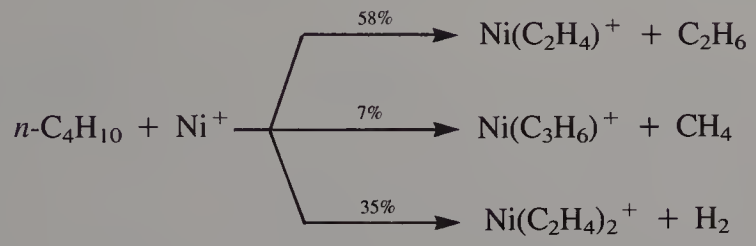
In the case of linear alkanes such as *n*-hexane, the Fe^+ ion inserts into the central C–C bond followed by β-methyl transfer (Scheme 7.69).[120] Again, these reactions presumably involve hypercarbon intermediates.

Scheme 7.69



The Ni^+ ion also reacts[121] with *n*-butane at the C–C bonds to provide a variety of products (Scheme 7.70).

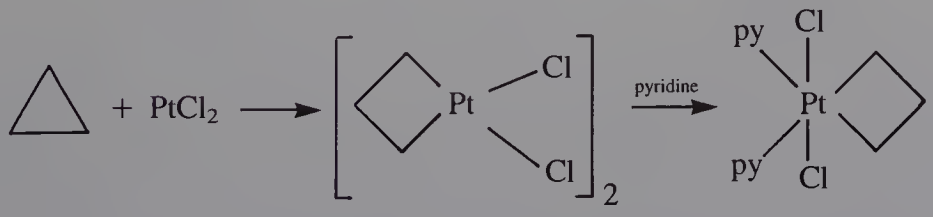
Scheme 7.70



The naked metal ion insertion reactions seem to indicate that high M–C bond strengths allow easy C–C bond cleavage for the bare ions. Apparently this is not the case for coordinated metals. Although C–C bond breaking appears to be kinetically facile as the initial step for the unhindered metal complexes, in the case of usual metal complexes, steric congestion at the metal center seems to retard such a process.[122]

The first example of a reaction with a strained C–C bond in a metal complex was studied in 1955 by Tipper.[123] $PtCl_2$ reacted with cyclopropane to give an adduct that was formulated as $[PtCl_2C_3H_6]_2$. The correct platinacyclobutane structure was later elucidated by Chatt and co-workers[124] by isolating it as a bis(pyridine) adduct (Scheme 7.71).

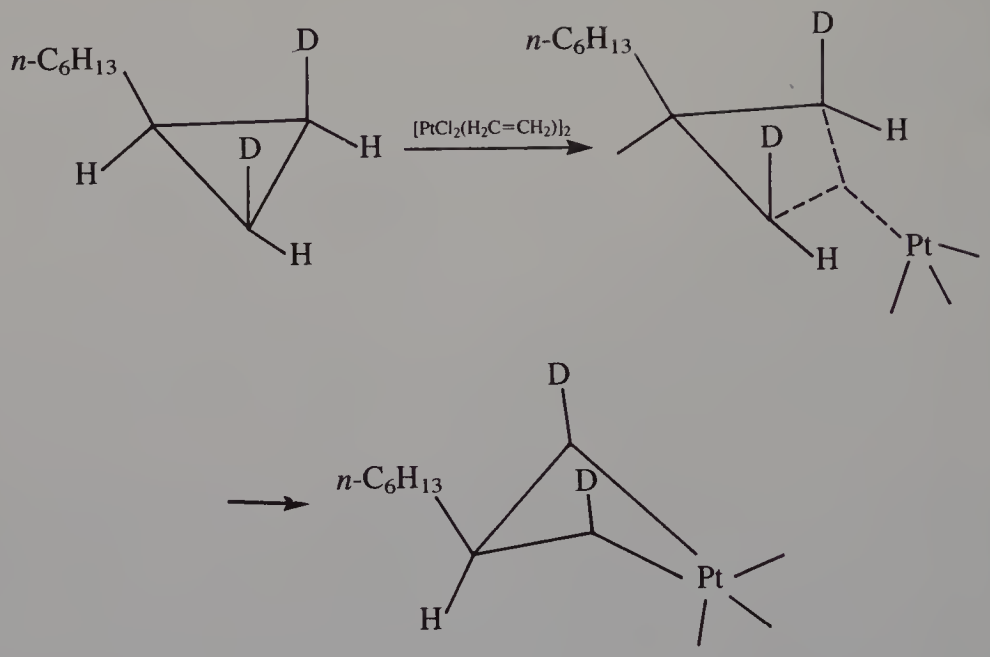
Scheme 7.71



The stereochemical course of such a reaction has been followed by[125] reacting $[PtCl_2(H_2C{=}CH_2)]_2$ with *n*-hexyl-*cis*-2,3-dideuterocyclopropane. A four membered metallacycle is produced where the configuration at C-2 and C-3 (of cyclopropane) is conserved indicating that the electron-deficient metal inserts into the (C-2)–(C-3) bond in a concerted fashion with retention of configuration through a three-center interaction in which neither carbon is free to lose its stereochemical integrity (Scheme 7.72).

The Walsh orbitals of cyclopropane adequately account for the high reactivity of the C–C bond.[126] The HOMO and LUMO interaction with metal $d\sigma$ and $d\pi$ orbitals, respectively, are each shown in Scheme 7.73.

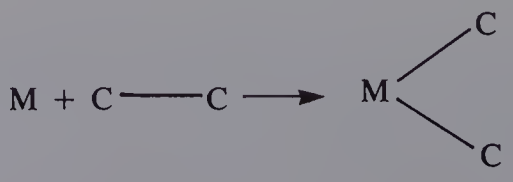
Scheme 7.72



Scheme 7.73

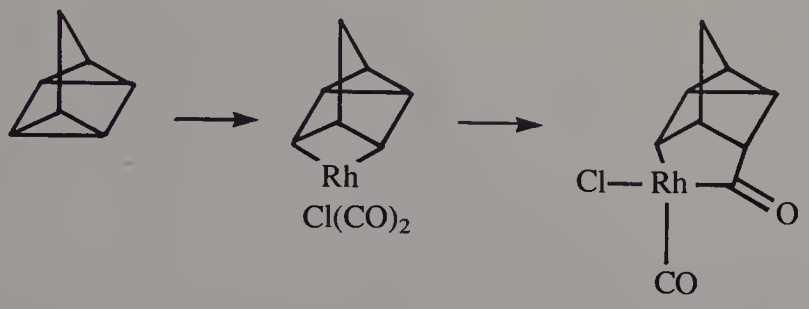
However, the lack of alkane C−C bond activation also arises from the fact that two relatively weak M−C bonds are formed in the process (Scheme 7.74). For a general unstrained alkane this can still be endothermic. However, in cyclopropanes and cyclobutanes, relief of steric strain is an additional favorable factor.

Scheme 7.74



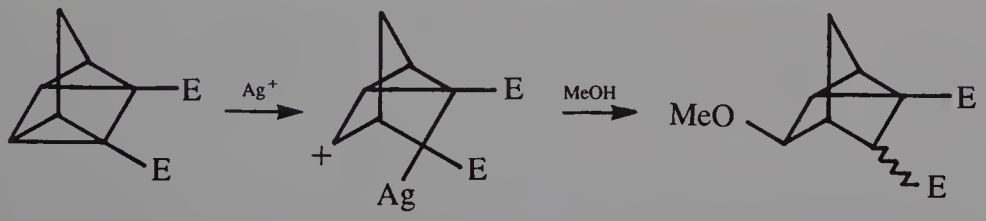
Halpern and Cassar[127] showed that $[Rh(CO)_2Cl]_2$ inserts into the strained σ bond of quadricyclane (Scheme 7.75).

Scheme 7.75



The Ag^+ ion catalyzed reaction of a quadricyclane derivative also appears to proceed through initial C–C bond insertion (Scheme 7.76).[128]

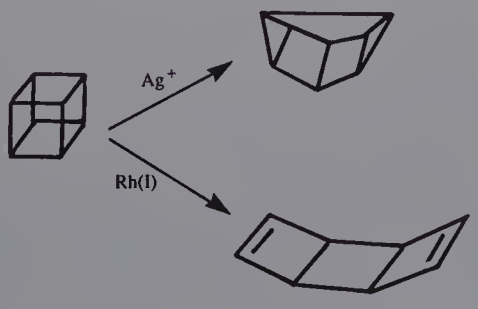
Scheme 7.76



E = CO_2R

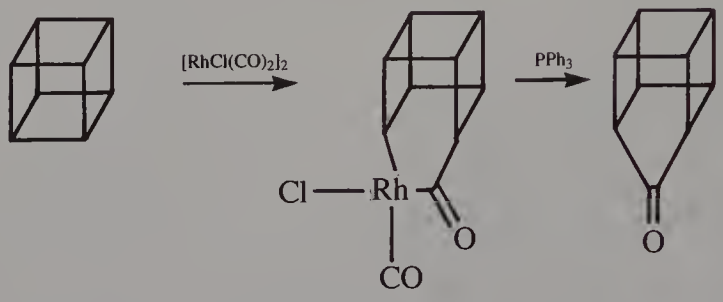
The rearrangement of cubane gives different types of products depending on the metal.[129] With Ag^+ ion catalysis cuneane is produced, whereas with Rh(I), tricyclooctadiene is obtained (Scheme 7.77). Again these reactions go through direct metal insertion.

Scheme 7.77



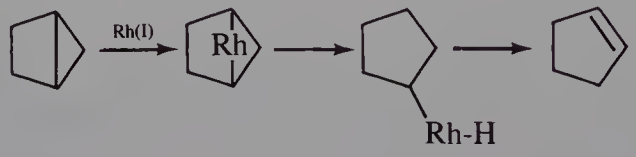
With the $[Rh(CO)_2Cl]_2$ complex the rhodium inserted cubane complex can be isolated (Scheme 7.78).[130]

Scheme 7.78



Rh(1) also inserts into the strained C−C bond of bicyclo[2.1.0]pentane (Scheme 7.79).[131]

Scheme 7.79



Formation and cleavage of C−C bonds can also occur in the case of main group elements. Trineopentylaluminum on thermolysis provides trimethylaluminum and isobutylene (Scheme 7.80).[132]

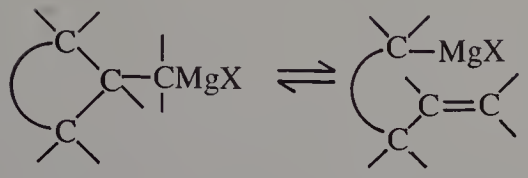
Scheme 7.80

$$(Me_3CCH_2)_3Al \overset{200\ ^\circ C}{\rightleftharpoons} Me_3Al + 3Me_2C{=}CH_2$$

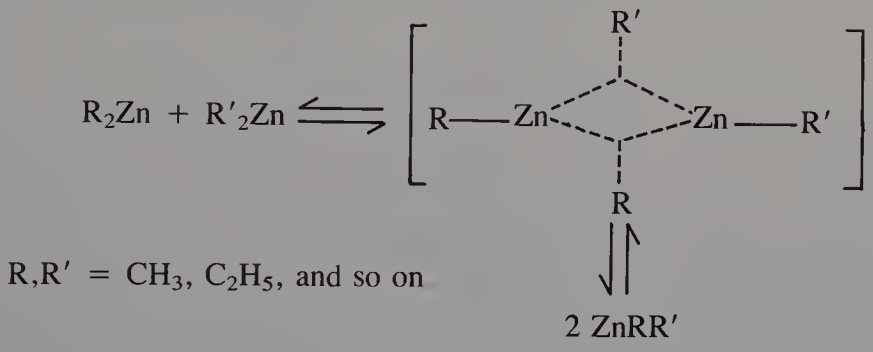
The bulky neopentyl groups prevent intermolecular bridging (trineopentyl aluminum is monomeric), but promote intramolecular C−C bond interaction with the electron-deficient aluminum center. Such intramolecular eliminations are also observed in some Grignard derivatives (Scheme 7.81).[133]

Gallium and zinc, the main group congeners of alkyl bridging metals such as aluminum and magnesium do not form stable dimeric alkyl bridged compounds. However, dialkyl zinc undergoes facile alkyl group exchange[134] through their dimeric forms involving hypercarbon intermediates or transition states (Scheme 7.82).

Scheme 7.81

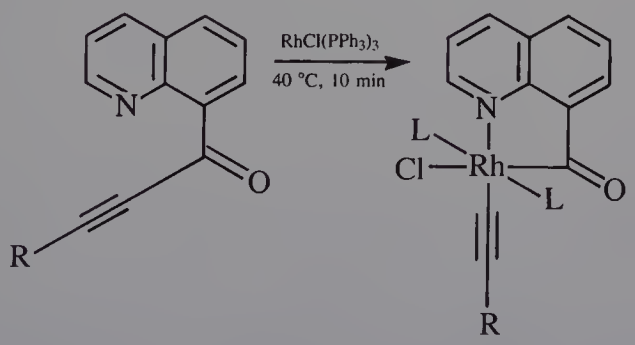


Scheme 7.82



A very interesting case of C–C cleavage in the late transition metals has been reported by Snuggs and Cox[135] involving the quinoline derivative (Scheme 7.83).

Scheme 7.83

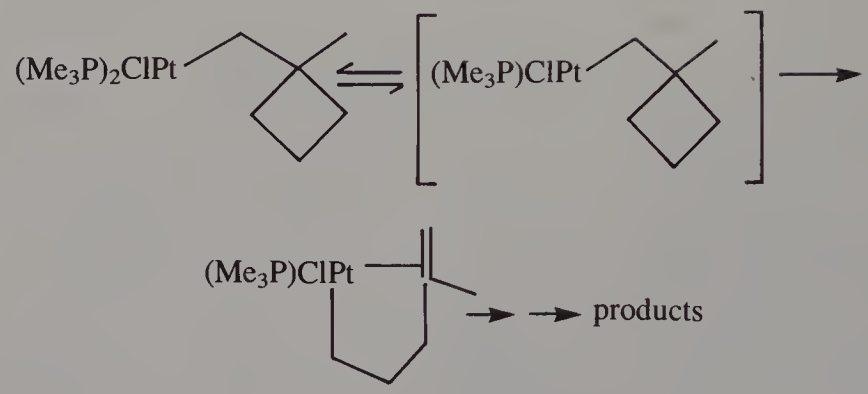


Flood and Statler[136] observed the cleavage of a cyclobutane ring C–C bond in (1-methylcyclobutyl)methyl-platinum(II) complexes (Scheme 7.84).

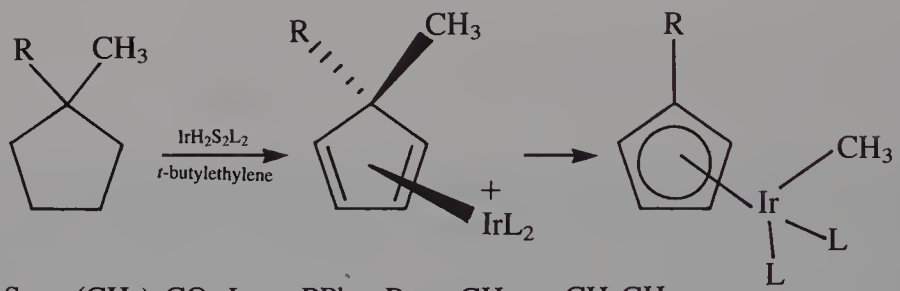
It appears that the activation of C–C bonds in unstrained alkanes by a *d*-block transition metal complex may require initial C–H bond activation to precede C–C bond breaking. However, in the case of early *d*-block and *f*-block metals, the M–C bond is much stronger and hence no such activation is required.[137]

Based on this premise, Crabtree and Dion[122] have successfully carried out indirect C–C bond cleavage of an unstrained alkane by an initial dehydrogenation reaction (Scheme 7.85).

Scheme 7.84



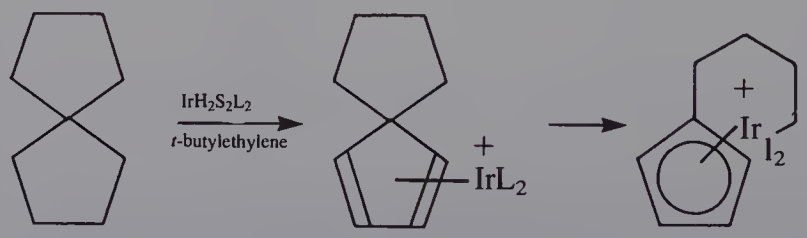
Scheme 7.85



S = $(CH_3)_2CO$; L = PPh_3; R = CH_3 or CH_3CH_2

Similar reactions have been observed[138] in the case of spiro[4.4]nonane (Scheme 7.86).

Scheme 7.86



S = $(CH_3)_2CO$; L = PPh_3

7.2.6. Reactions of Singlet Carbenes, Nitrenes, and Silylenes with C–H Bonds

Carbenes are highly reactive electron-deficient divalent carbon species generally having short lifetimes (under 1 s). They have been isolated only in matrices at very

low temperatures (77° K or less).[139,140] The two nonbonded electrons of a carbene may be either paired or unpaired. The species is termed a singlet if they are paired and a triplet if they are unpaired. The parent of carbenes is methylene ($:CH_2$).

Singlet methylene is much more reactive than triplet methylene. In fact, methylene is more stable in its triplet ground state by some 9 kcal mol^{-1} than its singlet state.[139,140] Apart from the well-known reaction with olefins,[139,140] methylene indiscriminately inserts into C–H bonds.[139–141] From the time of the original discovery of this latter reaction by Meerwein et al.[142] and Doering et al.,[143] there has existed the question of whether the mechanism of the reaction is a direct concerted reaction (Equation 7.1) or whether a two-step abstraction–recombination path takes place (Equation 7.2).

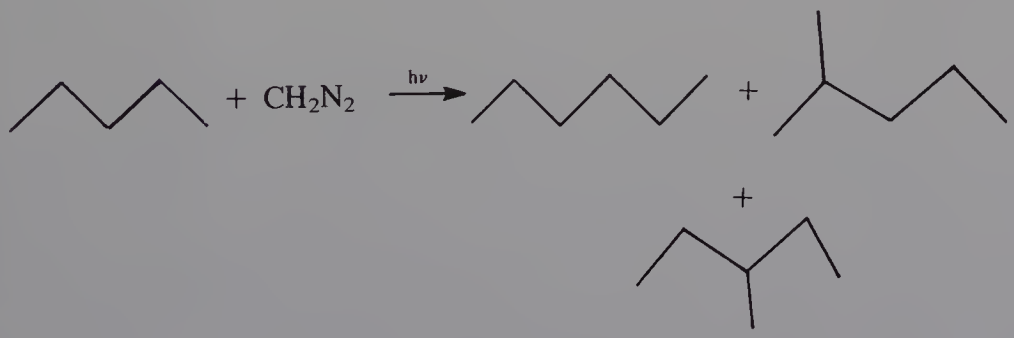
$$:CH_2 + R{-}H \longrightarrow R{-}CH_2{-}H \tag{7.1}$$

$$:CH_2 + R{-}H \longrightarrow CH_3^{\cdot} + R^{\cdot} \tag{7.2}$$

$$CH_3^{\cdot} + R^{\cdot} \longrightarrow R\text{-}CH_3$$

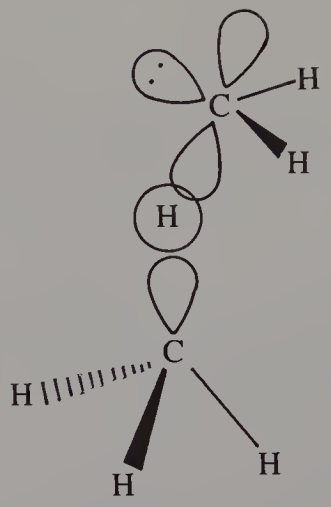
Although there is some evidence for the latter reaction, direct C–H insertion seems to predominate. Singlet methylene inserts into C–H bonds of hydrocarbons in a statistical fashion (Scheme 7.87).[144]

Scheme 7.87



Similar carbene insertion reactions with ethers are also very well known. Apart from direct C–H insertion, attack on oxygen can occur to form a very reactive dialkyloxonium methylide.[142,145]

The direct insertion of singlet methylene into methane has been theoretically probed by Hoffmann and co-workers.[146] The reaction on the C–H bond begins, in theory, by an attack of the methylene with its empty *p* orbital impinging in a slightly nonlinear geometry on the H atom. In the intermediate stage of the reaction the H atom is transferred to methylene with very little change in the C–C bond distance (Structure **28**). Clearly in such an insertion one must invoke the involvement of an incipient hypercoordinate carbon atom,

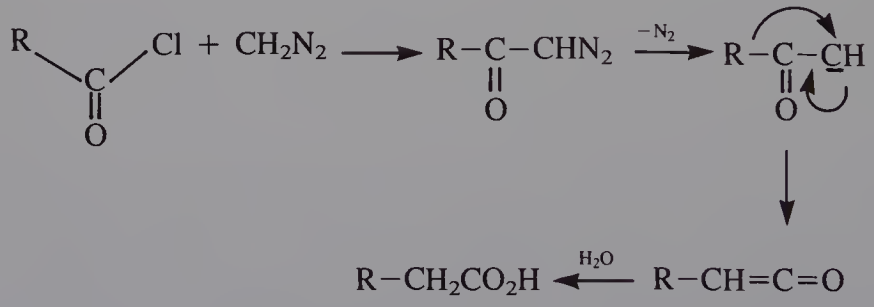


28

although the reaction qualitatively can also be considered similar to a linear hydrogen abstraction.[147]

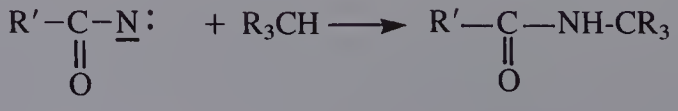
The well-known Arndt–Eistert homologation[148] of an acyl halide to a carboxylic acid also involves the migration of an R group (with its electron pair) to an electron-deficient acyl carbene (presumably through a hypercarbon species), Scheme 7.88. This rearrangement is also known as the Wolff rearrangement.

Scheme 7.88



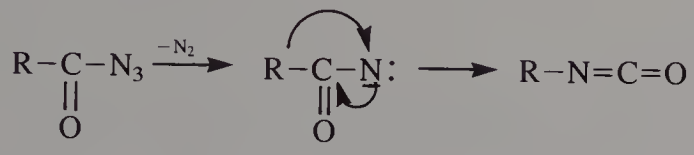
Similar to singlet carbenes, singlet nitrenes, R–N: (the nitrogen analog of carbenes) are also known to insert into C–H bonds. Acyl nitrenes and sulfonyl nitrenes insert rather readily into C–H bonds (Scheme 7.89).[22]

Scheme 7.89

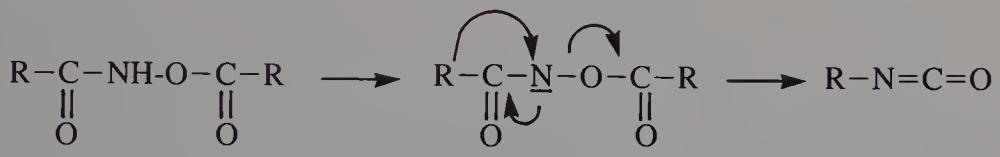


The Curtius[149] and Lossen[150] rearrangements (Schemes 7.90 and 7.91) also involve a migration of an R group to an acyl nitrene-type intermediate to form an isocyanate.

Scheme 7.90

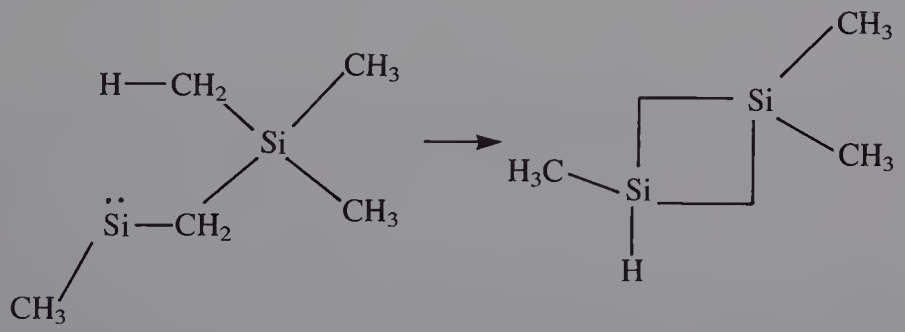


Scheme 7.91



The electron-deficient divalent silylenes, $R_2Si:$, are known to insert into C–H σ bonds. The silylene generated *in situ* undergoes facile C–H insertion to provide 1,3-disilacyclobutane (Scheme 7.92).[151]

Scheme 7.92

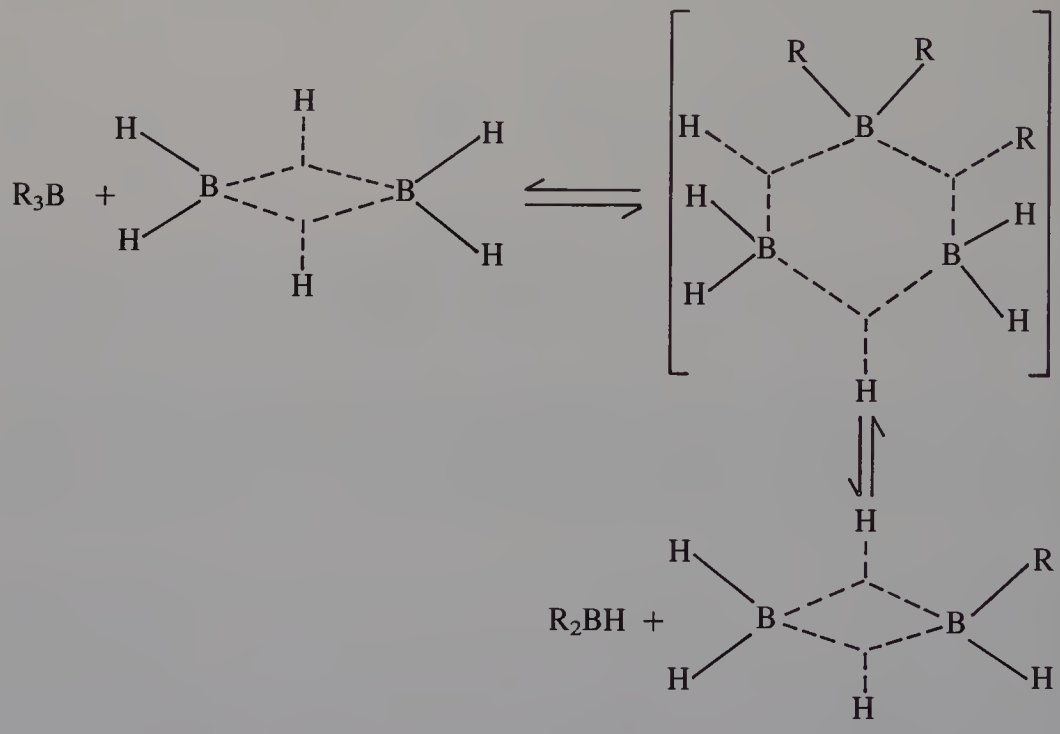


7.2.7. Rearrangements to Electron-Deficient Boron, Aluminum, Nitrogen, and Oxygen Centers

7.2.7.1. Isomerization, Rearrangement, and Redistribution of Alkyl-Boranes and AlkylAlanes. When heated with a catalytic amount of diborane (or alkylboron hydrides) alkylboranes equilibrate to a thermodynamic mixture of the possible alkyldiboranes and alkylboranes.[152–154] It has been proposed[155a] that the equilibration proceeds via the intermolecular attack of diborane (or an alkylboron

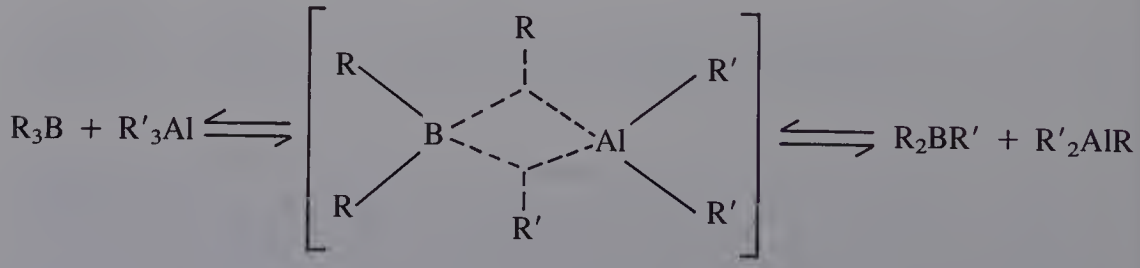
hydride) on an alkylborane to give a bridged species that can cleave to yield new boranes and diboranes. At low temperatures the redistribution of alkyl groups proceeds with retention of configuration in the migrating alkyl group.[156] This is consistent with the intermediacy of a bridged species incorporating a higher coordinate carbon atom (Scheme 7.93).

Scheme 7.93



In a similar fashion, the redistribution of alkyl groups between organoalanes and organoboranes proceeds via alkyl-bridged boron–aluminum species (Scheme 7.94).[157]

Scheme 7.94

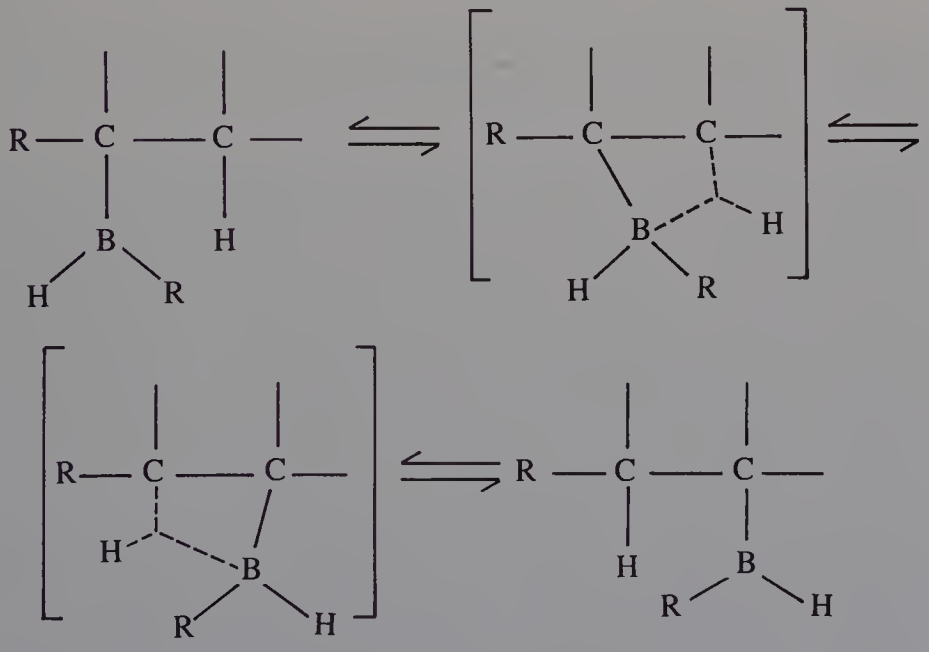


Hydroboration, the addition of borane (or diborane) to π-donor substrates such as olefins, actylenes, carbonyl compounds, and so on, is a most useful synthetic reaction

and was developed by the extensive work of Brown.[158,159] In the absence of more nucleophilic *n*- and π-donor sites, borane will also attack σ bonds in alkanes,[160] silanes,[161] and aromatic compounds[162] to yield addition, cleavage, and rearrangement products. The interaction of borane with hydrocarbons involves two-electron, three-center bonded five-coordinate carbons.

Alkylboranes rearrange intramolecularly (on heating) to thermodynamically more stable alkylboranes, typically with the boron atom attached to the sterically least hindered position on the alkyl chain (the hydroboration rearrangement[155,159]). Williams[155b] proposed that this equilibration occurs by a stepwise intramolecular attack of the electron-deficient center on the neighboring C–H σ bonds. The transition state of the intramolecular migration incorporates a five-coordinate carbon atom (Scheme 7.95).

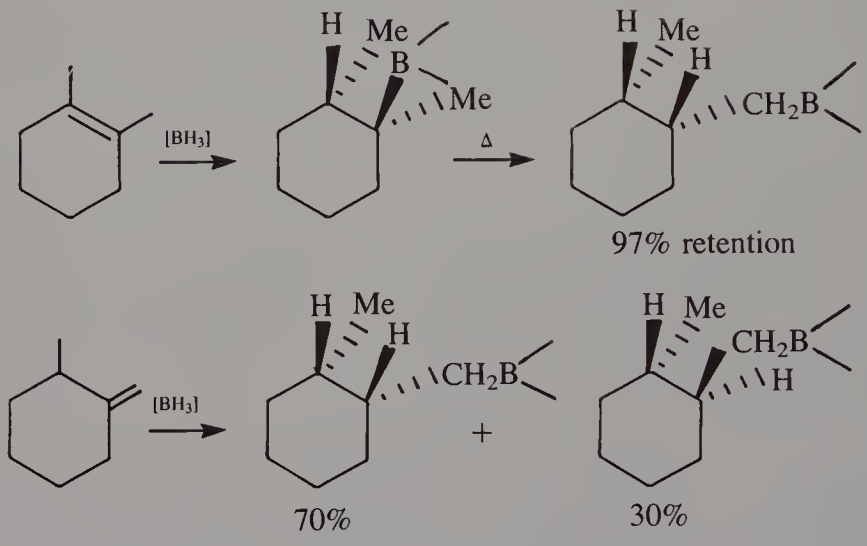
Scheme 7.95



An alternative mechanism for the hydroboration rearrangement has been advanced by Brown[159,163] who considers the rearrangement to be a sequence of reversible dehydroboration–hydroboration steps with stepwise migration of the double bond so formed. However, in cyclic systems where the stereochemistry of rearrangement can be readily followed,[164] the process occurs with retention of configuration and this would not be expected if a free olefin were a reaction intermediate (Scheme 7.96).

The intramolecular reaction of an electron-deficient boron atom with σ bonds is also well-established in other types of alkylborane rearrangements. The hydroboration of dienes, trienes, and polyenes invariably leads to a complex mixture of the possible organoboranes and polymeric organoboranes. On heating, the products rearrange to the thermodynamically most favorable organoboranes,[163,165] typically incorporating five- and six-membered boracycles. These rearrangements are

Scheme 7.96



extensions of the hydroboration rearrangement where the interaction of the boron atom with nearby σ bonds can provide a mechanism for equilibration of the carbon framework.

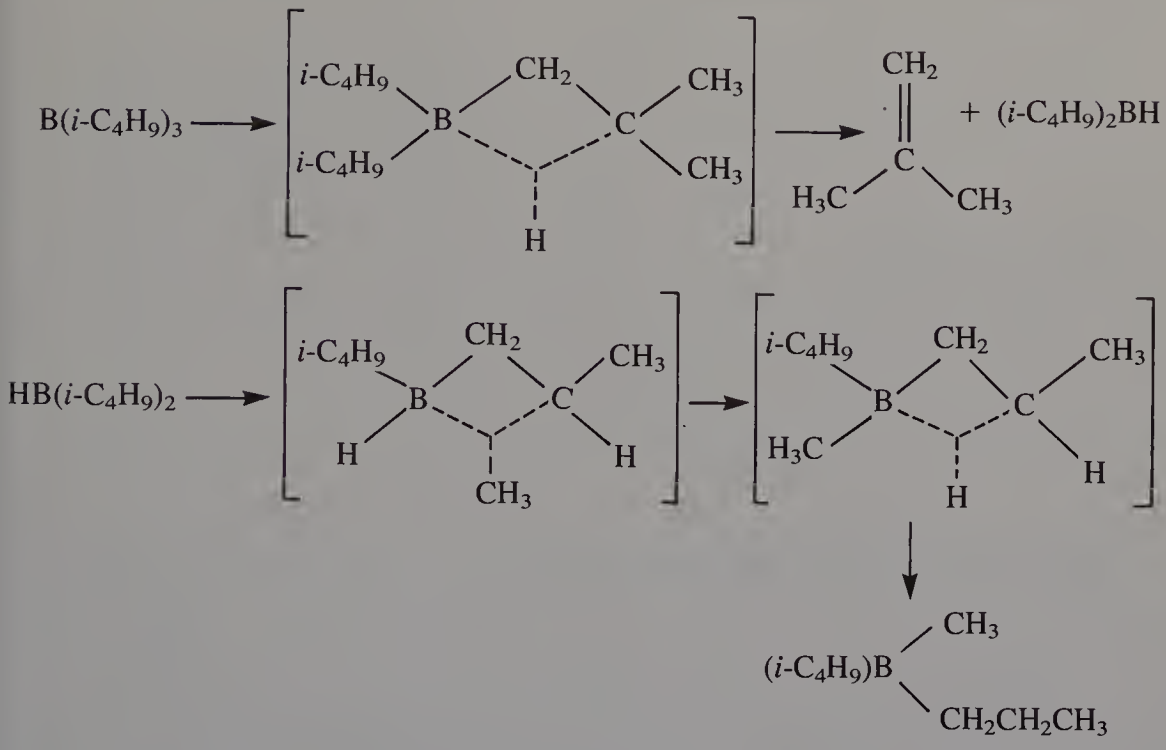
Alkylboranes also undergo a number of irreversible thermal transformations.[166] Pyrolysis of trialkylboranes containing more than one but fewer than four alkyl groups in the main alkyl chain affords methylated boranes and alkylboranes by cleavage of C−C and C−H bonds.[166–167] The reaction proceeds intramolecularly with the elimination of olefinic by-products and although the borane products generally do not contain any B−H bonds, compounds with C−H bonds are thought to be intermediates (Scheme 7.97). The mechanism of this type of transformation has not been fully investigated, but by analogy with the hydroboration rearrangement, intermediates containing five-coordinate carbon are indicated.

When heated vigorously, trialkylboranes with longer alkyl substituents form borocyclic compounds with the elimination of hydrogen gas and olefins (Scheme 7.98).[168] Dialkylboranes are considered to be reaction intermediates.

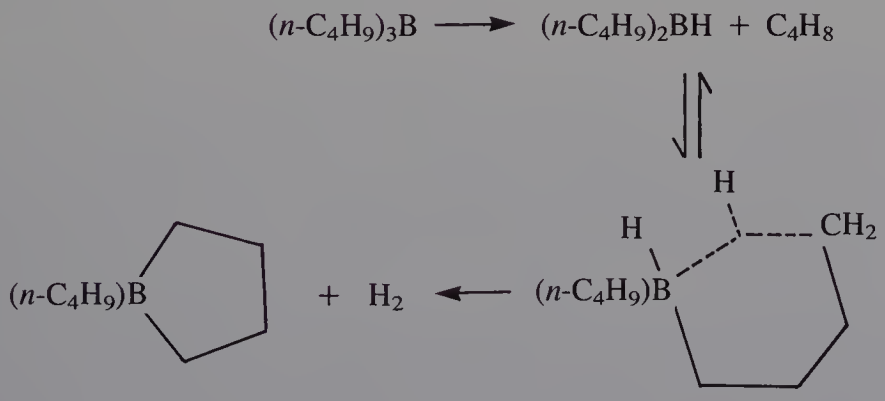
Although less thoroughly studied, alkylalanes undergo rearrangements and isomerizations[133] analogous to those known for alkylboranes. The greater tendency for aluminum to form stable alkyl bridged species is reflected in the milder conditions generally required to bring about rearrangements in organoaluminum species compared to their organoboron analogs.

7.2.7.2. Rearrangements to Electron-Deficient Nitrogen and Oxygen Centers. Migration of an alkyl group to a neighboring electron-deficient carbon center was discussed in Section 7.2.1.2. The well-known acid catalyzed Beckman[169] and nitrenium ion[170] rearrangements involve alkyl or hydrogen migration to an electron-deficient nitrogen centers. Similarly, the Baeyer–Villiger rearrangement[171] takes place on an electron-deficient oxygen center.

Scheme 7.97



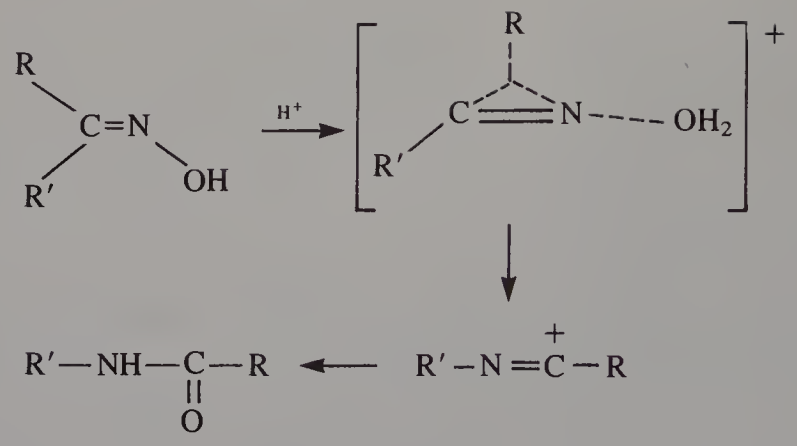
Scheme 7.98



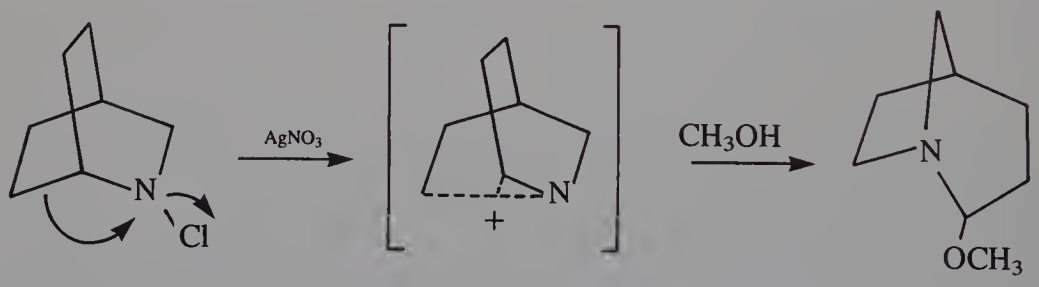
Beckman and nitrenium ion rearrangements are depicted in Schemes 7.99 and 7.100. Again in the migrating group the carbon atom becomes pentacoordinate during the migration.

In the Baeyer–Villiger rearrangement[171] involving oxidation of ketones to esters with peracids or hydrogen peroxide, the mechanism involving migration of an alkyl or aryl group to an electron-deficient oxygen center occurs (Scheme 7.101). During the migration, the migrating group carbon atom becomes hypercoordinate (for similar migrations, see Section 7.2.4).

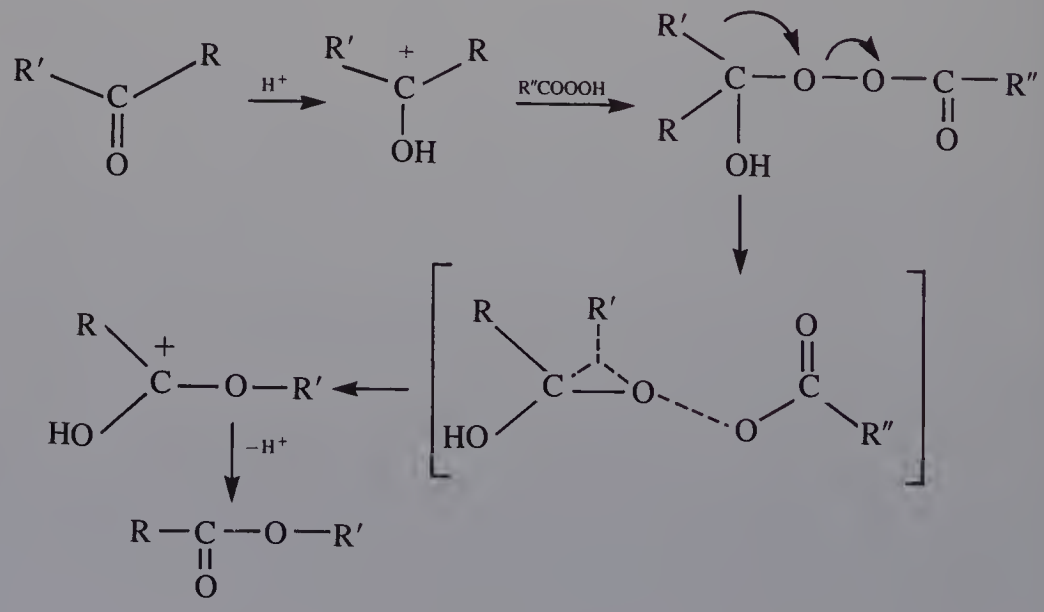
Scheme 7.99 Beckman Rearrangement



Scheme 7.100 Nitrenium Ion Rearrangement



Scheme 7.101

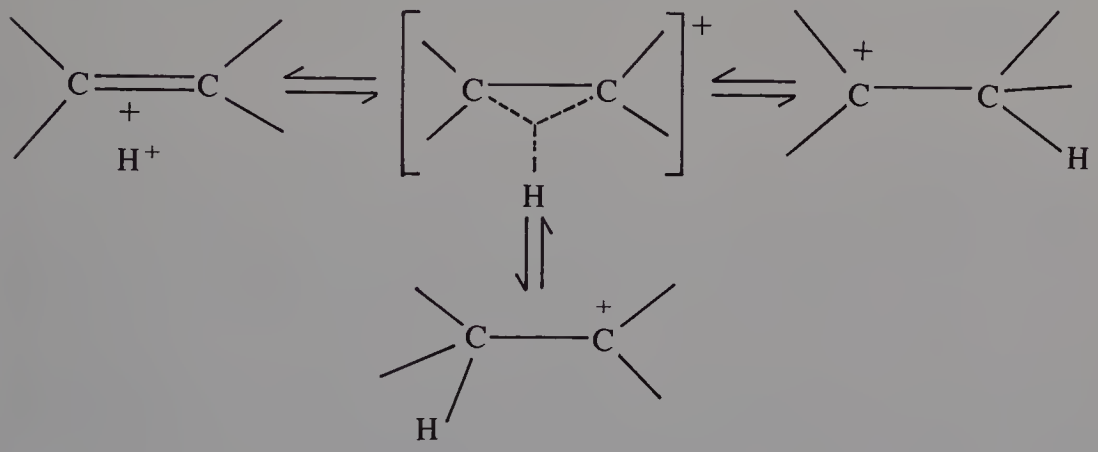


7.3. ELECTROPHILIC REACTIONS OF π-DONOR SYSTEMS

The reactivity of olefins, acteylenes, and aromatic hydrocarbons toward electrophiles in addition and substitution reactions is based on their π-donor ability. In any reaction involving the attack of an electrophile on a multiple bond, the initial interaction is between the electrophile and the electrons of the π bond.

The protonation of olefins (the essential first step in acid catalyzed olefin isomerization, alkylation, hydration, etc.) is considered to involve the initial overlap of the carbon *p* orbitals (forming the π bond) with the vacant *s* orbital of the proton, forming a three-center bonded interaction (or π-complex) (Scheme 7.102).[172]

Scheme 7.102



Opening of the three-center bond affords the carbenium ion of greatest stability (the well-known Markovnikov's rule[25]). It should be pointed out that except in extremely crowded cases (such as adamantylideneadamantane),[172e] there is no direct evidence that the three-center bonded π complex is an intermediate and thus it is only a depiction of the transition state (or a high-lying metastable intermediate) of the addition reaction.

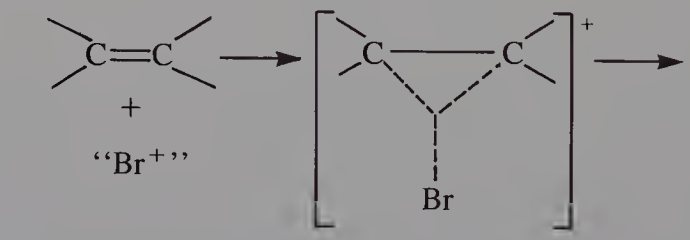
Olefin alkylation (also the initial step in cationic olefin polymerization) and nitration can likewise be considered to involve the initial formation of bridged transition states (or high-lying intermediates) containing three-center bonds (Scheme 7.103).

In the electrophilic halogenation of olefins, the initial interaction of the electrophilic halogenating agent (incipient halonium ion) with the double bond (considered of hypercoordinate π-complex nature) results via participation of the halogen nonbonded pairs in a three-membered alkelene halonium ion. Stable ions of this type have been observed spectroscopically and isolated in some cases.[173–174] Observation of a reversible π-complex stage was claimed[173] for the very crowded adamantylideneadamantane system based on NMR studies. Subsequent, x-ray

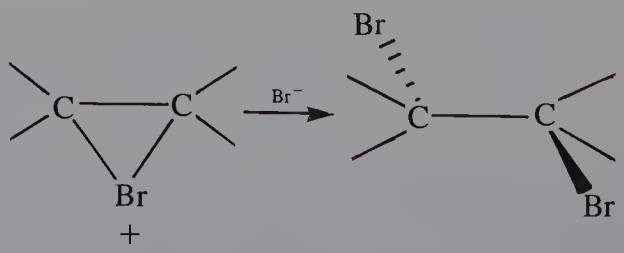
Scheme 7.103

crystal structure study[174b] indicated a three membered ring bromonium ion. However, no clear differentiation between a π-complex or a σ-bonded bromonium ion is possible since a bulky bromine atom sits over the crowded π-bond. Back-side S_N2 attack by a halide ion gives rise to the observed trans stereochemistry of halogenation (Scheme 7.104). A similar mechanism has been proposed for electrophilic mercuration.[175]

Scheme 7.104



π-Complex

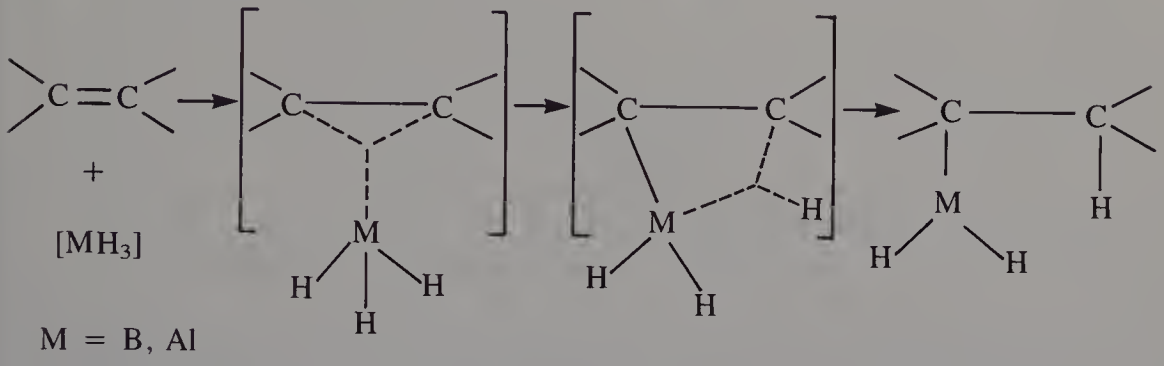


Bromonium ion
or σ-Complex
intermediate

The reaction of Lewis acids including borane or alane with olefins (hydroboration or hydroalanation,[176] respectively) is considered to involve an initial three-center interaction between the electrophile and the carbons of the double bond. The B−H or Al−H bonds can act as internal nucleophiles during opening of the three-center bond and it is for this reason that hydroboration and hydroalanation (and other

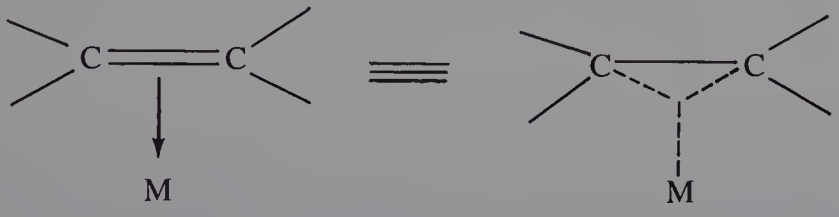
hydrometallation reactions) always yield *cis* addition products (Scheme 7.105) (for simplicity monomeric alane (borane) is shown to depict the reaction. However, the dimeric (or oligomeric) hydrogen bridged forms may also be involved).

Scheme 7.105



The interaction between metal atoms and ions with olefins (as well as other π-bonded systems) is the basis for the chemistry of metal π complexes. Such complexes can be formulated as "metal-bridged" species incorporating three-center bonds (Scheme 7.106).

Scheme 7.106

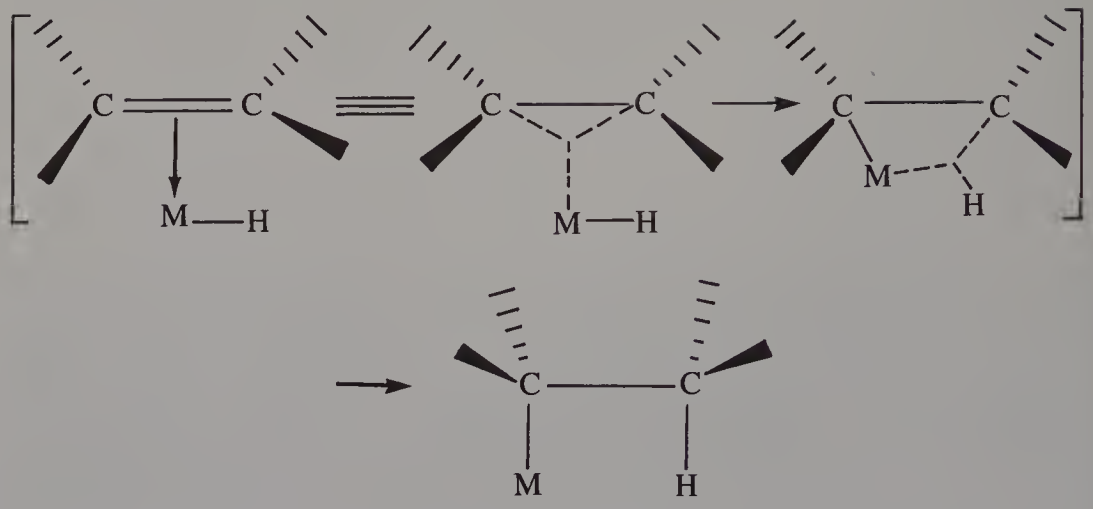


Coordination of an olefin to a coordinatively unsaturated transition metal hydride is an essential step in homogeneous hydrogenation.[177,178] In those cases where it has been possible to follow the reaction stereochemistry,[89,179] the transfer of hydride from the metal to the coordinated olefin has been observed to proceed in a stereospecifically *syn* fashion (Scheme 7.107).

An analogous scheme can be advanced to rationalize the stereospecificity with which alkyl migration proceeds in metal alkyl–transition metal catalyzed olefin oligimerization and polymerization reactions such as Ziegler–Natta polymerization[178,180] and olefin metathesis.[181]

Ziegler–Natta polymerization of olefins is an important industrial process for the manufacture of polyolefins. Although the original procedure involved use of the triethylaluminum–$TiCl_4$ complex as the catalyst, many other transition metal

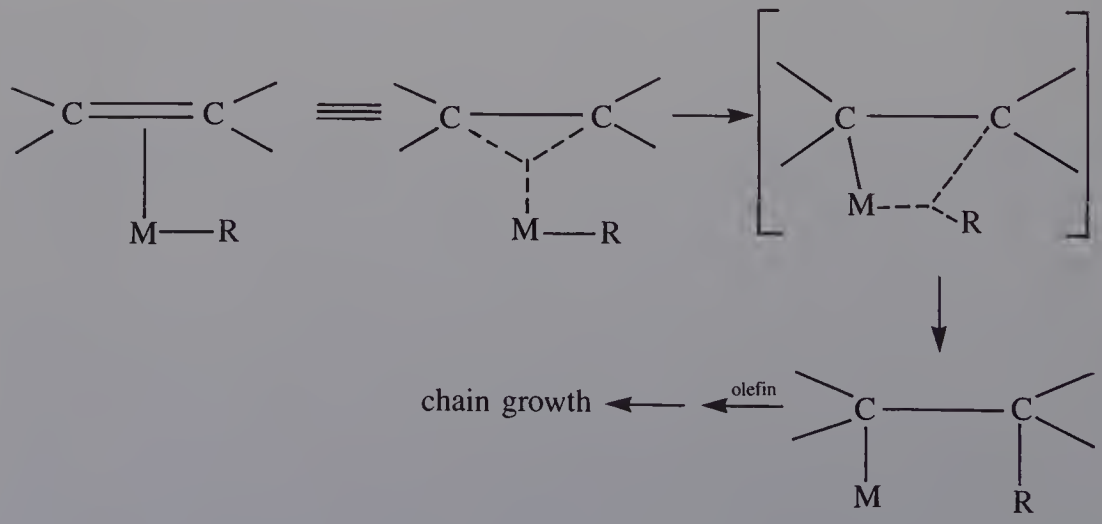
Scheme 7.107



complexes and *f*-block compounds (lanthanides) also catalyze the polymerization of olefins.

There were numerous mechanisms proposed for the Ziegler–Natta polymerization. Various valencies have been suggested for the involved titanium (the original catalyst system) ranging from four to two. Nevertheless, the most comprehensive and generally accepted mechanism is that of Cossee and Arlman.[182] The mechanism suggests that polymerization occurs at surface titanium atoms that possess vacant coordination sites. The general mechanism of coordination followed by insertion is shown in Scheme 7.108. The addition is highly stereoregular (*cis* addition). These addition migrations involve hypercoordinate carbon atoms.

Scheme 7.108

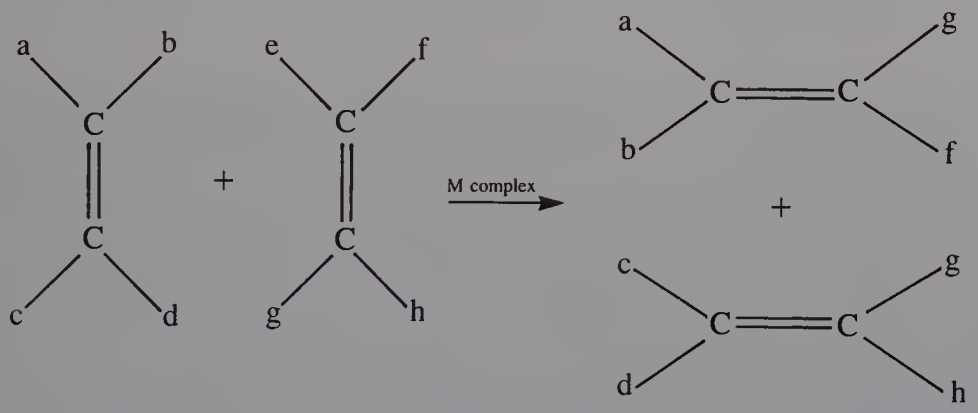


The intermediacy of an alkyl-bridged species containing a higher coordinate carbon atom dictates the stereoregularity of the polymer as each successive residue is added to the growing chain. Other mechanisms involving metallacyclobutanes (metatheses reaction)[183] and metallacyclopentane have been proposed. All the available evidence[184,185] on titanium systems now favors the Cossee–Arlman mechanism.

In a great variety of other organometallic reactions where alkyl groups migrate from a metal to a coordinated ligand, for example, carbonylation, acylation, reductive alkyl elimination, and so on, the migration generally occurs with retention of configuration at the migrating carbon.[89] In such cases a bridged species, where the migrating carbon adopts a higher coordination number, is a probable reaction intermediate.

Another important reaction of olefins with coordinatively unsaturated transition metal complexes is the olefin-metathesis reaction (depicted in Scheme 7.109).

Scheme 7.109



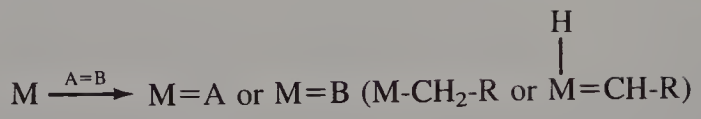
The currently accepted mechanism[186] involves the initial formation of a metal–carbene (alkylidene) complex that reacts with an olefin to form a three-center bound π complex. The three-center bound π complex subsequently rearranges to a metallacyclobutane intermediate. The sequence is depicted in Scheme 7.110.

Electrophilic additions to olefins can be considered, in accordance with the Hammond postulate,[187] to involve transition states resembling either the intermediate trivalent carbocations (or, in the case of halogenation, three-membered ring halonium ions) or the starting olefins. In the first case, a new covalent bond is more fully developed in the transition state than in the latter case. The position of the transition state can vary from reaction to reaction and resemble either the starting olefin or the carbenium ion intermediate.

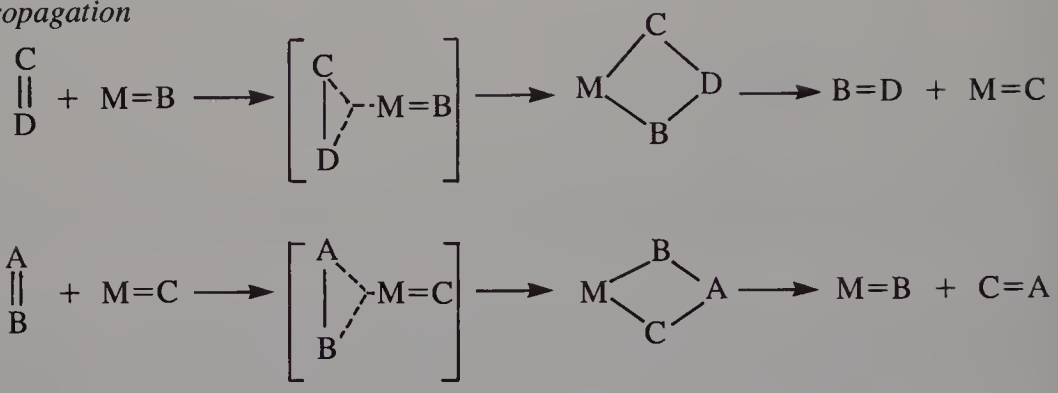
In aromatic electrophilic substitution[188a] the initial interaction between an electrophile and the aromatic π system is a multicenter interaction (of π-complex

Scheme 7.110

Initiation



Propagation



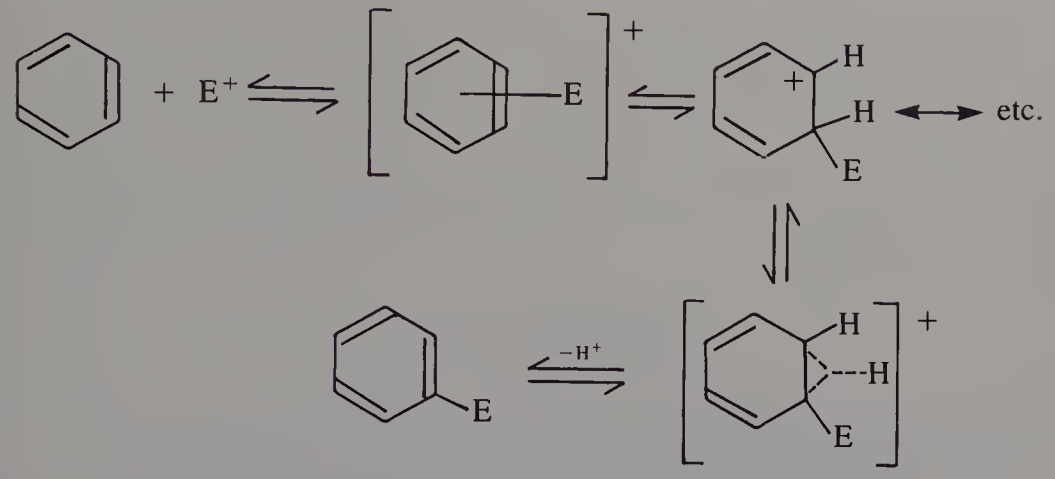
etc.

nature). The lack of substrate selectivity observed in some reactions of aromatic compounds with strong electrophiles (e.g., NO_2^+) indicates that the initial multicenter complex is a separate well-defined intermediate, although its nature is not yet fully clarified. Schofield et al. suggested[188b] it to be only an encounter complex with no specific structural nature, held together by a solvent cage. Perrin[188c] prefers a radical ion pair. Regardless, there is general agreement of an initial intermediate involving the aromatic as an entity. The subsequent step affords a trivalent benzenium ion intermediate (σ complex, Scheme 7.111). The transition state of highest energy thus can either resemble the starting compound (i.e., lie early on the reaction coordinate) or be of arenium ion nature (i.e., lie late on the reaction coordinate).

π-Electron pairs are better electron donors than σ bonds. In systems that contain both σ and π bonds, the π system is generally the reactive site (reflected by the first ionization potentials of the systems). In toluene, for example, electrophilic reactions lead to substitutions in the ring rather than in the methyl side chain. However, if the aromatic π system is less available (by steric crowding or by the presence of deactivating substituents) then the σ bonds become more reactive. For example, nitration of pentafluorotoluene with $NO_2^+BF_4$ gives pentafluorophenyl nitromethane.

Dewar[172b,189] should be credited with having suggested the concept of "π-complex" interactions of electrophiles with π-donor systems in the late 1940s. π Complexes till then were regarded only as weak donor–acceptor intereactions between the π-donor system and the electron-deficient reactant. Dewar was the first to consider much stronger "molecular bonds" formed by the overlap of a π-electron pair with the vacant orbital of an electron-deficient species. In a discussion of

Scheme 7.111

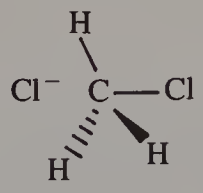


"nonclassical ions," Dewar and Marchand[189a] subsequently stated "in a true π complex, the π donor and acceptor are linked by a covalent bond, not by weak forces of the van der Waal's type." Dewar's complexes are indeed higher coordinate carbocations incorporating high coordinate carbon atoms in multicenter bonding.

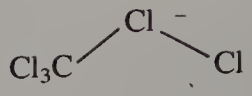
7.4. FIVE-COORDINATE S_N2 REACTION TRANSITION STATES AND CLAIMED INTERMEDIATES

The bimolecular nucleophilic substitution reactions (S_N2 reactions) involve pentacoordinate carbon in the transition state.[25,190] Whereas five-coordinate CH_5^+ like intermediates of S_E2 reactions represent only an 8 electron system around the carbocationic center involving (3*c*–2*e*) bonding (octet rule is obeyed) an S_N2 intermediate would represent a 10 electron system involving (3*c*–4*e*) bonding resulting in an unstable situation since carbon cannot accommodate 10 electrons in its valence shell. It is well known that S_N2 reactions occur with inversion of configuration.[25] Several attempts have been made to isolate and observe true S_N2 like intermediates. Ions like $CH_3Cl_2^-$ and related anion adducts[191] are known in the gas phase. However, $CH_3Cl_2^-$ is better regarded as the CH_3Cl solvated chloride ion, **29**. Compounds such as CCl_5^- are also known as stable species in the condensed state. However, it was shown that CCl_5^- is an analog Cl_3^-, with the CCl_3 pseudohalide group replacing a chlorine atom (structure **30**). All attempts to obtain five-coordinate S_N2 like intermediates failed until the work of Martin and co-workers who succeeded[192] in observing the stable system, **31**, which undergoes "bell-clapper" rearrangement. The system is uniquely designed to delocalize the additional two electrons in completing the aromatic sextet (the term bisipsoaromaticity is used to describe such a phenomenon, structure **32**).

It is thus indicated that whereas 10 electrons around a carbon atom cannot be a stable ground state, when the additional two electrons can be delocalized away onto the ligands (involving carbon nonbonding orbitals) then a stable intermediate can be

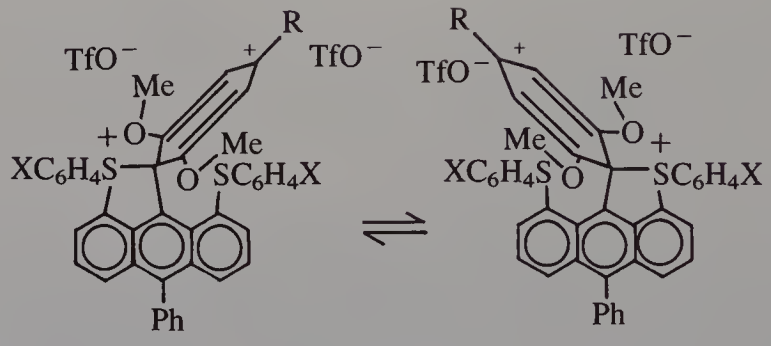


29

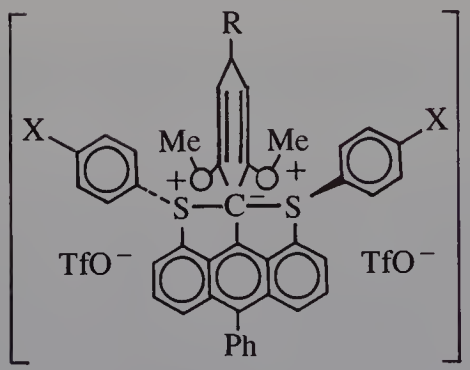


30

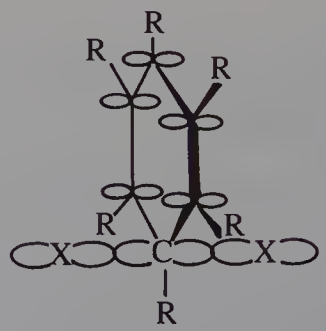
"Bell-clapper" rearrangement



31

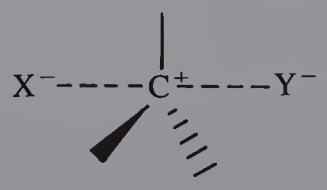


32



bis-ipsoaromatic

obtained. This has, however, no direct relevance to S_N2 reaction intermediates. The carbocationic center in an S_N2 transition state is solvated from both sides by the negatively charged nucleophile and the leaving group, that is, structure **33**.



33

7.5. CONCLUSIONS

We have attempted in this final chapter to give representative examples of the involvement of hypercarbon containing intermediates or transition states in a wide variety of organic and organometallic reactions. Our aim was not to give comprehensive coverage of such extensive and diverse fields. It is impressive to note the wide involvement of hypercarbon species in many diverse chemical reactions of substantial importance.

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