THE ORGANOMETALLIC CHEMISTRY OF THE TRANSITION METALS

SECOND EDITION

ROBERT H. CRABTREE

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Second Edition

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PREFACE TO THE SECOND EDITION

In revising the book, I have taken the opportunity of correcting the errors kindly pointed out by readers. I would particularly like to thank Jack Faller and Mike Heinekey, as well as Ged Parkin (Columbia) and Dr. Takashi Ito (Yokohama) and the many students and teachers who wrote with suggestions.

It is surprising how far the field has come in a few years, but I have been particularly careful to make changes only when really needed and to avoid the temptation to add too many new sections. Even so, I think it is still possible to say that this is what you need to know to get started in the field.

ROBERT H. CRABTREE

Bethany, Connecticut
November 1993

PREFACE TO THE FIRST EDITION

This book is intended for senior undergraduate and graduate courses in organometallic chemistry. It is based on a course given at Yale University for a number of years by the author. It should also prove useful to research workers in allied fields who want to become better acquainted with the subject.

The chapters are relatively self-contained and some (e.g., Chapter 10 or 16) may be omitted if desired. There are frequent cross-references and references to the literature, which should prove useful to graduate students and organometallic chemists in general. Problems and solutions are included.

I thank Rich Uriarte (General Electric) for encouraging me to write this book, my former student Charles Parnell (du Pont) for technical help, and my colleague Jack Faller for helpful suggestions. I also thank my teachers Malcolm Green and Joseph Chatt, who helped me think more deeply about the subject, and Hugh Felkin, who sensitized me to the organic implications of organometallic chemistry. I thank Ms. Lisa Crocker for helpful suggestions. Yale University gave me a semester leave to write this book; part of it was also written during the tenure of an Albright and Wilson Visiting Professorship at Warwick University and an Esso Visiting Lectureship at the University of Toronto.

ROBERT H. CRABTREE

Bethany, Connecticut
September 1987

CONTENTS

LIST OF ABBREVIATIONS

[ ]	Encloses complex molecules or ions
□	Vacant site or labile ligand
1°, 2°, . . .	Primary, secondary, . . .
A	Associative substitution (Section 4.4)
acac	Acetylacetone
a.o.	Atomic orbital
at.	Pressure in atmospheres
bipy	2,2′-Bipyridyl
Bu	Butyl
cata	Catalyst
CIDNP	Chemically induced dynamic nuclear polarization (Section 6.3)
C.N.	Coordination number
cod	1,5-Cyclooctadiene
coe	Cyclooctene
cot	Cyclooctatetraene
Cp,Cp*	C_5H_5,C_5Me_5
Cy	Cyclohexyl
∂^+	Partial positive charge
δ	Chemical shift (NMR)
Δ	Crystal field splitting (Section 1.4)
D	Dissociative substitution mechanism (Section 4.3)
d_σ,d_π	σ-Acceptor and π-donor metal orbitals (see Section 1.4)
dpe	$Ph_2PCH_2CH_2PPh_2$

dmf	Dimethylformamide
dmg	Dimethyl glyoximate
dmpe	$Me_2PCH_2CH_2PMe_2$
dmso	Dimethyl sulfoxide
d^n	Electron configuration (Section 1.4)
η	Descriptor for hapticity (Section 2.1)
E,E^+	Generalized electrophile such as H^+
e	Electron, as in 18e rule
e.e.	Enantiomeric excess (Section 9.2)
en	$H_2NCH_2CH_2NH_2$
eq	Equivalent
Et	Ethyl
eu	Entropy units
Fp	$(C_5H_5)(CO)_2Fe$
fac	Facial (stereochemistry)
$HBpz_3$	Tris(pyrazolyl)borate
homo	Highest occupied molecular orbital
I	Nuclear spin
I	Intermediate substitution mechanism
IPR	Isotopic perturbation of resonance (Section 10.8)
IR	Infrared
L	Generalized ligand, in particular a 2e ligand (L model for ligand binding is discussed in Section 2.1)
L_nM	Generalized metal fragment with n ligands
lin	linear
lumo	Lowest unoccupied molecular orbital
μ	Descriptor for bridging (Section 1.1)
m-	Meta
Me	Methyl
mer	Meridional (stereochemistry)
m_r	Reduced mass
m.o.	Molecular orbital
ν	Frequency
nbd	Norbornadiene
NMR	Nuclear magnetic resonance (Sections 10.2–10.8)
NOE	Nuclear Overhauser effect (Section 10.7)
Np	Neopentyl
Nu,Nu^-	Generalized nucleophile, such as H^-
o-	Ortho
OAc	Acetate
oct	Octahedral (Table 2.5)
ofcot	Octafluorocyclooctadiene
O.S.	Oxidation state (Section 2.4)
p-	Para
Ph	Phenyl

py	Pyridine
r.f.	Radio frequency
SET	Single electron transfer (Section 8.6)
solv	Solvent
sq. py.	Square pyramidal (Table 2.5)
T_1	Spin-lattice relaxation time
tbe	t-BuCH=CH_2
thf	Tetrahydrofuran
triphos	$MeC(CH_2PPh_2)_3$
TBP or trig. bipy	Trigonal bipyramidal (Table 2.5)
TMEDA	$Me_2NCH_2CH_2NMe_2$
TMS	Trimethylsilyl
v.b.	Valence bond
X	Generalized 1e anionic ligand (Section 2.1) (X_2 model for ligand binding is discussed on pp. 106–107)

THE ORGANOMETALLIC CHEMISTRY OF THE TRANSITION METALS

CHAPTER 1

INTRODUCTION

Transition metal organometallic chemistry lies at the interface between classical organic and inorganic chemistry because it looks at the interaction between inorganic metal ions and organic molecules. A series of important industrial processes relies on organometallic chemistry, and new ones continue to be developed. In the last few years the field has provided some powerful new synthetic methods in organic chemistry. The area is beginning to make links with biochemistry with the discovery of several metalloenzymes that involve organometallic intermediates. The controlled pyrolysis of organometallic species has proved to be a useful way of preparing certain solid-state materials. It played an important part in the modern renaissance of inorganic chemistry that began in the 1950s and 1960s.

Transition metal ions can bind *ligands* (L) to give a coordination compound, or *complex* ML_n, as in the familiar aqua ions $[M(OH_2)_6]^{2+}$ (M = V, Cr, Mn, Fe, Co, or Ni). Organometallic chemistry is a subfield of coordination chemistry in which the complex contains an M—C or M—H bond [e.g., $Mo(CO)_6$]. Organometallic species tend to be more covalent, and the metal is often more reduced, than in other coordination compounds. Typical ligands that usually bind to metals in their lower oxidation states are CO, alkenes, and arenes, for example, $Mo(CO)_6$, $(C_6H_6)Cr(CO)_3$, or $Pt(C_2H_4)_3$.

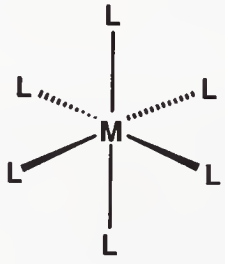
In the first few sections of this chapter we will review some fundamental ideas of coordination chemistry, which also apply to organometallic complexes.

1.1 WERNER COMPLEXES[1]

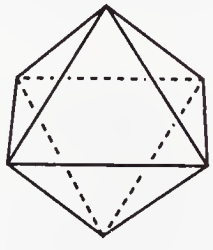
Complexes in which the metal binds to noncarbon ligands have been known longest and are often called *classical* or *Werner complexes*. The simplest

metal–ligand bond is perhaps $L_nM—NH_3$, where an ammonia binds to a metal fragment. This fragment will usually have other ligands, represented here by L_n. The bond consists of the lone pair of electrons present in free NH_3 that are donated to the metal to form the complex. The metal is a polyvalent Lewis acid capable of accepting the lone pairs of several ligands L, which act as Lewis bases.

The most common type of complex is ML_6, which adopts an octahedral coordination geometry[1] (**1.1**), based on one of the Pythagorean regular solids. The ligands occupy the six vertices of the octahedron, which allows them to minimize their M—L bonding distances, while maximizing their L···L nonbonding distances. From the point of view of the coordination chemist, it is perhaps unfortunate that Pythagoras decided to name his solids after the number of faces (octa = eight) rather than the number of vertices. After **1.1**, ML_4 and ML_5 are the next most common types.



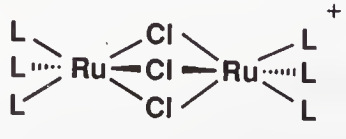
1.1



octahedron

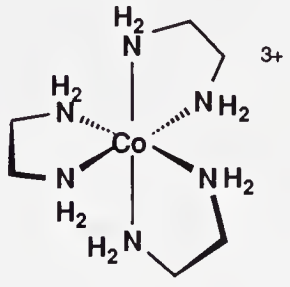
The assembly of metal and ligands that we call a *complex* may have a net charge, in which case it is a complex ion (e.g., $[PtCl_4]^{2-}$). Together with the counterions, we have a complex salt (e.g., $K_2[PtCl_4]$). In some cases both the cation and the anion may be complex, as in the picturesquely named *Magnus's green salt* $[Pt(NH_3)_4][PtCl_4]$. Square brackets are used to enclose the individual complex molecules or ions where necessary to avoid ambiguity.

Those ligands that have a donor atom with more than one lone pair can donate one to each of two or more metal ions. This gives rise to polynuclear complexes, such as the orange crystalline compound **1.2** (L = PR_3). The bridging group is represented in formulas by using the Greek letter μ (pronounced "mu") as in $[Ru_2(\mu\text{-}Cl)_3(PR_3)_6]^+$. Note how **1.2** can be considered as two octahedral fragments sharing the face that contains the three chloride bridges.



1.2

Other ligands can have more than one donor atom, each with its lone pair; an example is ethylenediamine ($NH_2CH_2CH_2NH_2$, often abbreviated "en"). Such ligands most commonly donate both lone pairs to the same metal to give a ring compound, known as a *chelate,* from the Greek word for "claw"; **1.3** is a typical example of such a complex



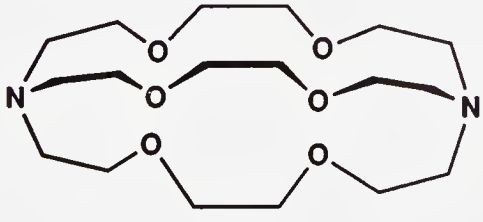
1.3

The early Russian investigator Chugaev first drew attention to the fact that chelating ligands are much less easily displaced from a complex than are monodentate ligands of the same type. The reason is illustrated in Eq. 1.1

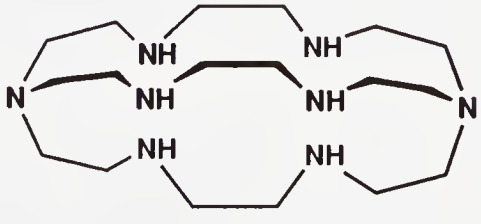
$$[M(NH_3)_6]^{n+} + 3\ \text{en} \longrightarrow [M(\text{en})_3]^{n+} + 6\ NH_3 \qquad (1.1)$$

Formation of the chelate releases six NH_3 molecules so that the total number of particles increases from 4 to 7. This creates entropy, and so favors the chelate form. Each chelate ring usually leads to an additional factor of about 10^5 in the equilibrium constant for reactions like Eq. 1.1. Equilibrium constants for complex formation are usually called *formation constants;* the higher the value, the more stable the complex.

Chelation not only makes the complex more stable but also forces the donor atoms to take up adjacent or cis sites in the resulting complex. Polydentate chelating ligands with three or more donor atoms also exist. Macrocyclic ligands, such as **1.4** and **1.5** confer an additional increment in the formation constant (the macrocyclic effect); they tend to be given rather lugubrious trivial names, such as *cryptates* (**1.4**) and *sepulchrates* (**1.5**).[1]



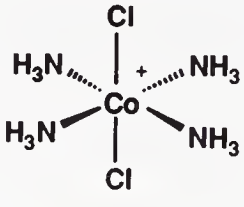
1.4



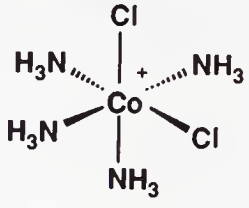
1.5

Alfred Werner developed the modern picture of coordination complexes in the 20 years that followed 1893, when, as a young scientist, he proposed

that in the well-known cobalt ammines (ammonia complexes) the metal ion is surrounded by six ligands in an octahedral array as in **1.6** and **1.7**. In doing so, he was opposing the views of all the major figures in the field, who held that the ligands were bound to one another in chains, and that only the ends of the chains were bound to the metal as in **1.8** and **1.9**. Jørgensen, who led the traditionalists against the Werner insurgency, was not willing to accept that a trivalent metal, Co^{3+}, could form bonds to six groups; in the chain theory, there were never more than three bonds to Co. Each time Werner came up with what he believed to be proof for his theory, Jørgensen would find a way of interpreting the chain theory to fit the new facts. For example, coordination theory predicts that there should be two isomers of $[Co(NH_3)_4Cl_2]^+$ (**1.6** and **1.7**). Up to that time, only a green one had ever been found. We now call this the *trans isomer* (**1.6**), because the two Cl ligands occupy opposite vertices of the octahedron. According to Werner's theory, there should also have been a second isomer, **1.7** (cis), in which the Cl ligands occupy adjacent vertices. On the other hand, Werner was able

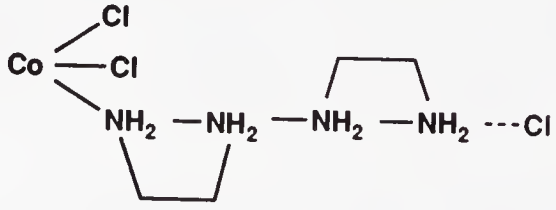


1.6



1.7

to obtain both green and purple isomers of the nitrite complex $[Co(NH_3)_4(NO_2)_2]^+$. Jørgensen quite reasonably (but wrongly) countered this finding by arguing that the nitrite ligands in the two isomers were simply bound in a different way *(linkage isomers)*, via N in one case (Co—NO_2) and O (Co—ONO) in the other. Werner then showed that there were two isomers of $[Co(en)_2Cl_2]^+$, one green and one purple, in a case where no



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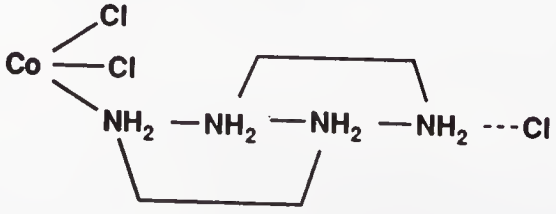
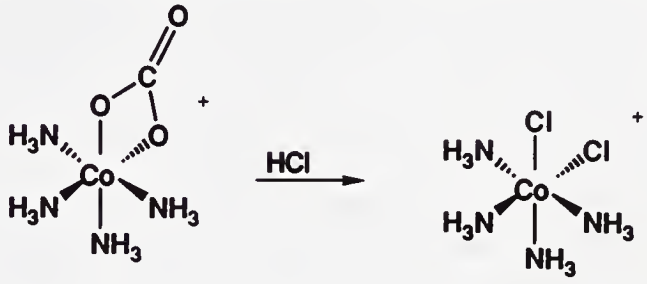


1.9

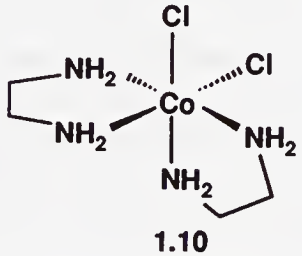
linkage isomerism was possible. Jørgensen brushed this observation aside by invoking the two chain isomers **1.8** and **1.9**, in which the topology of the chains differ.

In 1907, Werner finally succeeded in making the elusive purple isomer of $[Co(NH_3)_4Cl_2]^+$. This was done by an ingenious route (Eq. 1.2) via the carbonate $[Co(NH_3)_4(O_2CO)]$, in which two oxygens of the chelating dianion are necessarily cis. Treatment with HCl at 0°C liberates CO_2 and gives the cis dichloride. Jorgensen, receiving a sample of this purple cis complex by mail, conceded defeat. Finally, Werner resolved optical isomers of some of his compounds of the general type $[Co(en)_2X_2]^{n+}$ (**1.10** and **1.11**).

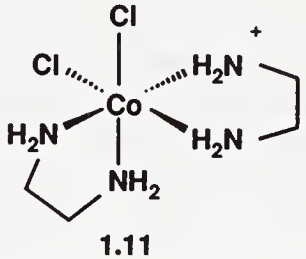


(1.2)

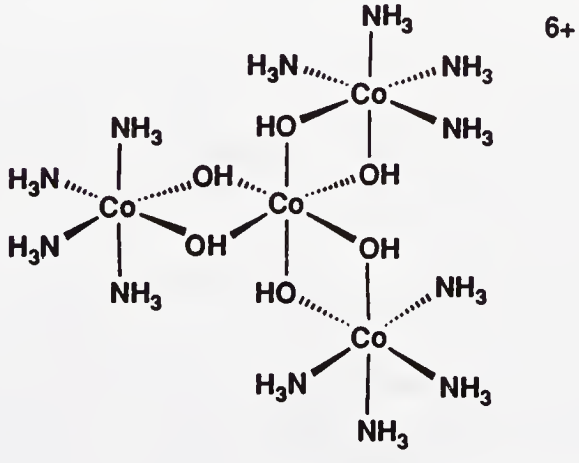
Only an octahedral array can account for the optical isomerism of these complexes. Even this point was challenged on the grounds that only organic compounds can be optically active, and so the optical activity must reside in the organic ligands. Werner responded by resolving a complex (**1.12**) containing only inorganic elements. This species has the extraordinarily high



1.10



1.11



1.12

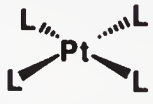
specific rotation of 36,000°, and required 1000 recrystallizations to resolve. Werner won the chemistry Nobel Prize for this work in 1913.

1.2 THE TRANS EFFECT

In the 1920s, Chernaev discovered that certain ligands facilitate the departure of a second ligand trans to the first, and their replacement or *substitution,* by an external ligand. Ligands that are more effective at this labilization are said to have a higher *trans effect.* We will consider in detail how this happens in Section 4.4, for the moment we need only note that the effect is most marked in substitution in Pt(II), and that the highest trans-effect ligands either form unusually strong σ bonds, such as H^-, Me^-, or $SnCl_3^-$, or unusually strong π bonds, such as CO, C_2H_4, and thiourea ($(NH_2)_2CS$, a ligand often represented as "tu").

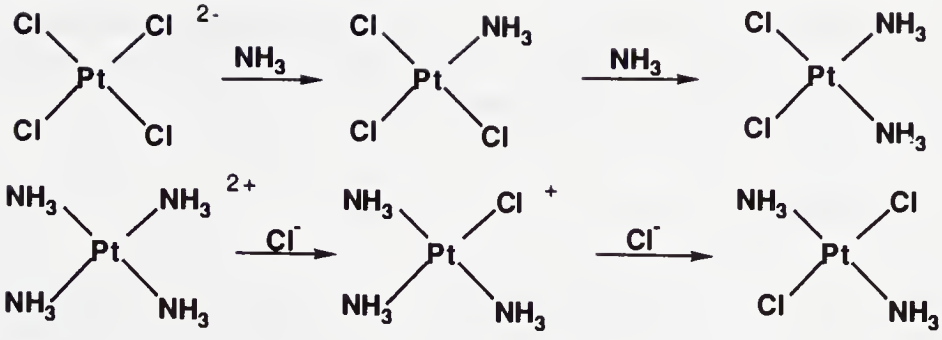
The same ligands also weaken the trans M—L bonds, as shown by a lengthening of the M—L distances found by X-ray crystallography or by some spectroscopic measure, such as M,L coupling constant in the NMR, or the ν(M—L) stretching frequency in the IR (infrared) spectrum. A change in the ground-state thermodynamic properties, such as these, is usually termed the *trans influence* to distinguish it from the parallel effect on the properties of the transition state for the substitution reaction, which is the trans effect proper, and refers to differences in *rates* of substitution and is therefore a result of a change in the energy difference between the ground state and transition state for the reaction.

Note that Pt(II) adopts a coordination geometry different from that of Co(III). The ligands in these Pt complexes lie at the corners of a square with the metal at the center. This is called the *square planar geometry* (**1.13**).



1.13

An important application of the trans effect is the synthesis of specific isomers of coordination compounds. Equations 1.3 and 1.4 show how the cis and trans isomers of $Pt(NH_3)_2Cl_2$ can be prepared selectively by taking advantage of the trans-effect order $Cl > NH_3$. This example is also of practical interest because the cis isomer is an important antitumor drug, but the trans isomer is ineffective. In each case the first step of the substitution can give only one isomer. In Eq. 1.3, the cis isomer is formed in the second step because the Cl trans to Cl is more labile than the Cl trans to the lower trans-effect ligand, ammonia. On the other hand, in Eq. 1.4, the first Cl to substitute labilizes the ammonia trans to itself to give the trans dichloride as final product.



(1.3)

(1.4)

1.3 SOFT VERSUS HARD LIGANDS

Chatt[2] pointed out in the 1950s that most metal ions in their usual oxidation states tend to bind saturated ligands such as NH_3, H_2O, or F^-. These are often called *hard* ligands in allusion to their low polarizability. On the other hand, a small group of ions, including the platinum metals, Ag^+, Hg^{2+}, and a few others, form stronger complexes with unsaturated or polarizable ligands, such as Br^-, I^-, PPh_3, or C_2H_4 (often called *soft*). Soft ligands either have donor atoms from the second or subsequent rows of the Periodic Table (e.g., Br^-, PPh_3, or Me_2S), or they have double or triple bonds (ethylene, acetylene, benzene). We now know that essentially all the transition metals can become soft if they are reduced to a sufficiently low valence state. The peculiarity of the small group of metals identified by Chatt is that they normally occur in low oxidation states, and so had long been known to form soft complexes. Table 1.1 shows some formation constants that illustrate the differences that are found. Low-oxidation-state metals tend to bind soft ligands because these metals have excess electron density by virtue of their reduced state. They therefore avoid strong donor ligands, but prefer ligands with which they can form covalencies, and that have available empty orbitals into which they can donate some of their excess electron density. (We will see how this happens in Section 1.6.) High-oxidation-state metals, on the other hand, are short of

TABLE 1.1 Hard and Soft Acids and Bases: Some Formation Constants[a]

	Ligand			
Metal Ion	F^-	Cl^-	Br^-	I^-
H^+	3	−7	−9	−9.5
Zn^{2+}	0.7	−0.2	−0.6	−1.3
Cu^{2+}	1.2	0.05	−0.03	–
Hg^{2+}	1.03	6.74	8.94	12.87

[a]The values are the negative logarithms of the equilibrium constant for $[M.aq]^{n+} + X^- \leftrightharpoons [MX.aq]^{(n-1)+}$, and show how H^+ and Zn^{2+} are hard acids, forming stronger complexes with F^- than with Cl^-, Br^-, or I^-. Cu^{2+} is a borderline case, and Hg^{2+} is a very soft acid, forming much stronger complexes with the more polarizable halide ions.

electron density and require good donor ligands. This idea is at the heart of that part of organometallic chemistry concerned with low-valent metals and soft ligands, such as metal carbonyl chemistry.

1.4 THE CRYSTAL FIELD

An important advance in understanding the spectra, structure, and magnetism of transition metal complexes is provided by the *crystal field* model. The idea is to try to find out how the *d* orbitals of the transition metal are affected by the presence of the ligands. To do this, we make the simplest possible assumption about the ligands—that they act as negative charges. For Cl^- as a ligand, we just think of the net negative charge on the ion; for NH_3, we think of the lone pair on nitrogen acting as a local concentration of negative charge. If we imagine the metal ion isolated in space, then the *d* orbitals are degenerate (have the same energy). As the ligands L approach the metal from the six octahedral directions $\pm x$, $\pm y$, and $\pm z$, the *d* orbitals take the form shown in Fig. 1.1. Those *d* orbitals that point toward the L groups ($d_{x^2-y^2}$ and d_{z^2}) are destabilized by the negative charge of the ligands and move to higher energy. Those that point away from L (d_{xy}, d_{yz}, and d_{xz}) are less destabilized.

The pair of orbitals that are most strongly destabilized are often identified by their symmetry label, e_g, or simply as d_σ, because they point along the M—L σ-bonding directions. The three more stable orbitals have the label t_{2g}, or simply d_π; these point away from the ligand directions but can form π bonds with the ligands. The magnitude of the energy difference between the d_σ and d_π set, usually called the *crystal field splitting,* and labeled Δ (or

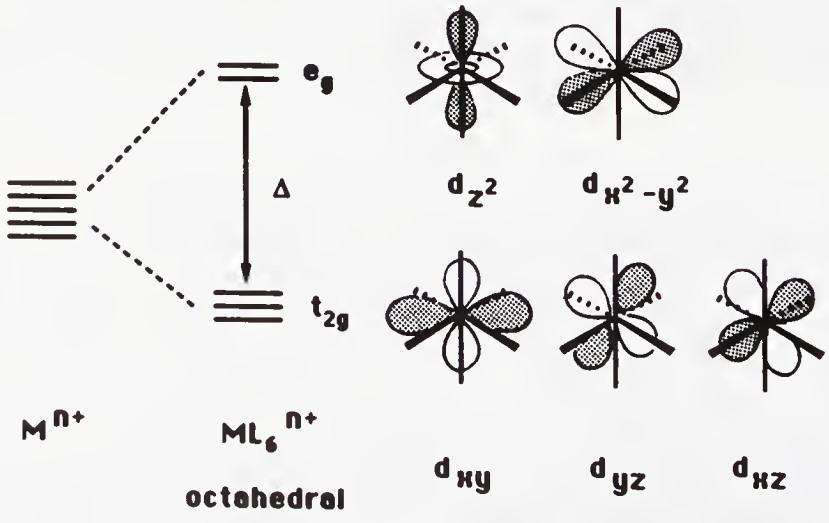


FIGURE 1.1 The effect on the *d* orbitals of bringing up six ligands along the $\pm x$, $\pm y$, and $\pm z$ directions. In this figure, shading represents the symmetry (not the occupation) of the *d* orbitals; shaded parts have the same sign of ψ.

sometimes $10Dq$) depends on the value of the effective negative charge and therefore on the nature of the ligands.

This picture explains why Co^{3+}, the metal ion Werner studied, has such a strong preference for the octahedral geometry. As a Group 9 element, Co has 9 electrons. The 3+ ion, of course, has (9 − 3) or 6 electrons, and is therefore said to have a d^6 configuration. Six electrons just fill the three low-lying d_π orbitals of the crystal field diagram, and leave the d_σ empty. This is a particularly stable arrangement, and other d^6 metals, Mo(0), Re(I), Fe(II), Ir(III), and Pt(IV) also show a very strong preference for the octahedral geometry. In spite of the high tendency to spin-pair the electrons in the d^6 configuration (to give the *low-spin* form $t_{2g}{}^6e_g{}^0$), if the ligand field splitting is small enough, then the electrons may rearrange to give the *high-spin* form $t_{2g}{}^4e_g{}^2$. In the high-spin form all the spins are aligned, as prescribed for the free ion by Hund's rule. This is shown in Fig. 1.2. The factor that favors the high-spin form is the fact that fewer electrons are paired up in the same orbitals and so the electron–electron repulsions are reduced. On the other hand, if Δ becomes large enough, then the energy gained by dropping from the e_g to the t_{2g} level will be sufficient to drive the electrons into pairing up. The spin state of the complex can usually be determined by measuring the magnetic moment of the complex. This is done by placing a sample of the complex in a magnetic field gradient. In the low-spin form of a d^6 ion, the molecule is *diamagnetic,* that is, it is very weakly repelled by the field. This behavior is exactly the same as that found for the vast majority of organic compounds, which are also spin-paired. On the other hand, the high-spin form is *paramagnetic,* in which case it is attracted into the field. The complex does not itself form a permanent magnet as will a piece of iron or nickel (this property is called *ferromagnetism*), because the spins are not aligned in the crystal in the absence of an external field, but they do respond to the external field by lining up together when we measure the magnetic moment.

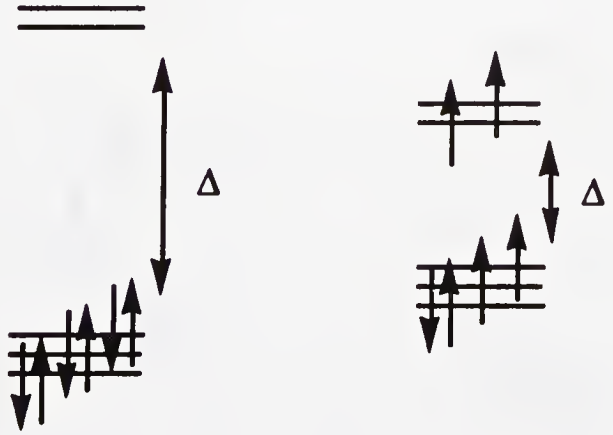


FIGURE 1.2 In a d^6 metal ion, both low- and high-spin complexes are possible depending on the value of Δ. A high Δ leads to the low-spin form.

Although the great majority of organometallic complexes are diamagnetic, because Δ is usually large in these complexes, we should not lose sight of the possibility that any given complex may be paramagnetic. This will always be the case for molecules like $V(CO)_6$, which have an uneven number of electrons. For molecules with an even number of electrons, a high-spin configuration is more likely for the first row metals, where Δ tends to be smaller than in the later rows. Sometimes the low- and high-spin forms have almost exactly the same energy. Each state can now be populated, and the relative populations of the two states vary with temperature; this happens for $Fe(S_2CNEt_2)_3$, for example.

In an octahedral d^7 ion we are obliged to place one electron in the higher-energy (less stable) d_σ level to give the configuration $t_{2g}^6 e_g^1$, and this will normally make the complex paramagnetic (Fig. 1.3). The net stabilization, often termed the *crystal field stabilization energy* (CFSE) of such a system will also be less than for d^6 (low spin), where we can put all the electrons into the more stable t_{2g} level. This is reflected in the chemistry of d^7 ions [e.g., Co(II)], which, as long as they remain octahedral, are more reactive than their d^6 analogs. For example, they undergo ligand dissociation much more readily. The reason is that the d_σ levels are really M—L σ-antibonding in character, as we see later. Werner was able to study his chemistry with Co(III) because the ligands tend to stay put. This is why Co(III) and other d^6 ions are often referred to as *coordinatively inert;* d^3 ions like Cr(III) are also coordination-inert because the t_{2g} level is now exactly half-filled, another favorable situation. On the other hand, Co(II) and other non-d^6 and -d^3 ions can be *coordinatively labile.*

The colors of transition metal ions often arise from the absorbtion of light that corresponds to the d_π–d_σ energy gap, Δ. The spectrum of the complex can then give a direct measure of this gap, and therefore of the crystal field strength of the ligands. So-called *high-field ligands* such as CO and C_2H_4 give rise to a large value of Δ. Low-field ligands, such as H_2O or NH_3, can give

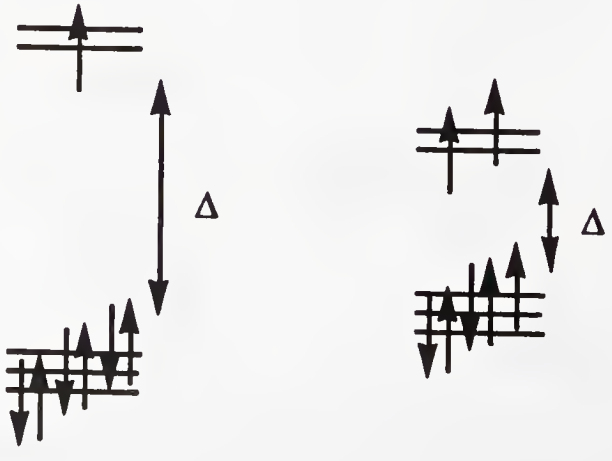


FIGURE 1.3 A d^7 ion is paramagnetic even in the low-spin form.

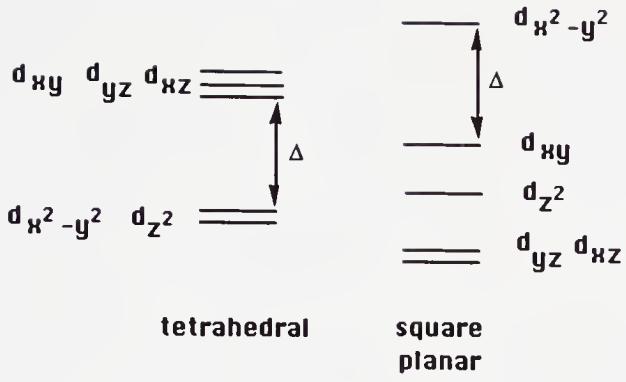


FIGURE 1.4 Crystal field splitting patterns for the common coordination geometries: tetrahedral and square planar. For the square planar arrangement, the z axis is conventionally taken to be perpendicular to the square plane.

such a low Δ, that the spin pairing is lost and even the d^6 configuration can become paramagnetic (Fig. 1.2, right hand side). This rarely occurs for organometallic ligands, since they tend to induce a large Δ splitting, and are therefore high-field ligands.

Other important crystal field splitting patterns are shown in Fig. 1.4. For the same ligand set, the tetrahedral splitting parameter is smaller than that for the octahedral geometry by a factor of $\frac{2}{3}$ because we now have only four ligands, not six, and so the chance of having a high-spin species is greater. The ordering of the levels is also reversed; three increase and only two decrease in energy. This is because the d_{xy}, d_{yz}, and d_{xz} orbitals now point toward, and the $d_{x^2-y^2}$, and d_{z^2} orbitals away from, the ligands. The d^{10} ions [e.g., Zn(II), Pt(0), Cu(I)] are often tetrahedral. The square planar splitting pattern is also shown. This geometry tends to be adopted by d^8 ions such as Au(III), Ni, Pd or Pt(II), and Rh or Ir(I), in which case the complex is diamagnetic; it is also common for paramagnetic d^9, such as Cu(II).

1.5 THE LIGAND FIELD

The crystal field picture gives a useful understanding, which is widely used for "*back of the envelope*" (qualitative) discussions. Once having established an idea of what to expect, we may need to turn to the more sophisticated *ligand field* model, which is really a conventional molecular orbital[3b] or m.o. picture for accurate electronic structure calculations. In this model (Fig. 1.5), we consider the s, the three p, and the five d, orbitals of the valence shell of the isolated ion as well as the six lone pair orbitals of a set of pure σ-donor ligands in an octahedron around the metal. Six of the metal orbitals, the s, the three p, and the two d_σ, which we will call the dsp_σ set, find symmetry matches in the six ligand lone pair orbitals. In combining the six metal orbitals with the six ligand orbitals, we make a bonding set of six (the M—L σ bonds)

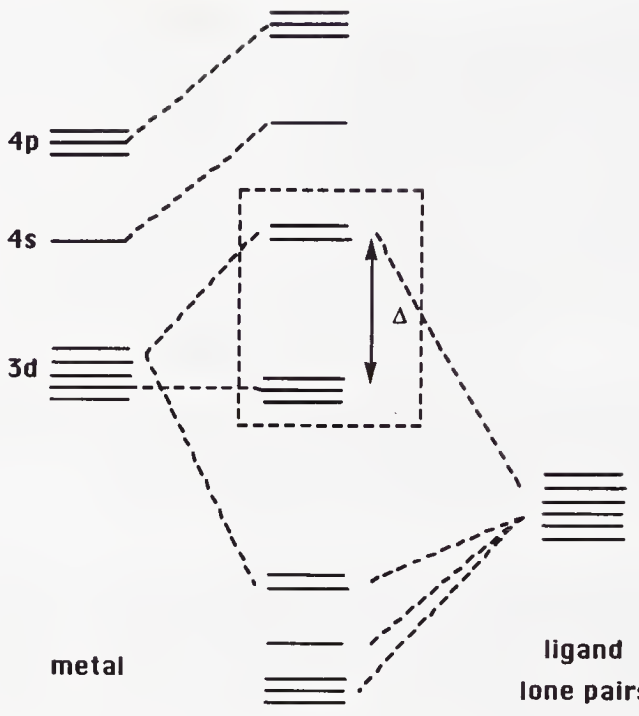


FIGURE 1.5 The molecular orbital, or ligand field picture of metal ligand bonding in an ML_6 complex.

that are stabilized, and an antibonding set of six (the M—L σ^* levels) that are destabilized when the six L groups approach bonding distance. The remaining three d orbitals, the d_π set, do not find a match among the ligand orbitals, and remain nonbonding. In a d^6 ion, we have 6e (six electrons) from Co^{3+} and 12e from the ligands, giving 18e in all. This means that all the levels up to and including the d_π set are filled, and the M—L σ^* levels remain unfilled. Note that we can identify the familiar crystal field splitting pattern in the d_π and two of the M—L σ^* levels. The Δ splitting will increase as the strength of the M—L σ bonds increase. The bond strength is the analog of the effective charge in the crystal field model. In the ligand field picture, high-field ligands are ones that form strong σ bonds. We can now see that a d_σ orbital is better described in the crystal field picture as an M—L σ antibonding orbital.

The L lone pairs start out in free L as pure ligand electrons but become bonding electron pairs shared between L and M when the M—L σ bonds are formed; these are the six lowest orbitals in Fig. 1.5 and are always completely filled (12 electrons). Each M—L σ-bonding m.o. is formed by the combination of the ligand lone pair, L(σ), with M(d_σ) and has both metal and ligand character, but L(σ) predominates. Any m.o. will more closely resemble the parent atomic orbital that lies closest in energy to it, and L(σ) almost always lies below M(d_σ) and therefore closer to the M—L σ-bonding orbitals. This means that electrons that were purely L lone pairs in the free ligand gain

some metal character in the complex; in other words, the L(σ) lone pairs are partially transferred to the metal. As L becomes more basic, the energy of the L(σ) orbital increases, and the extent of electron transfer will increase. An orbital that is higher in energy will appear higher in the m.o. diagram, and will tend to occupy a larger volume of space, and any electrons in it will tend to be less stable and more available for chemical interactions.

Using the language of organic chemistry, ligands are generally *nucleophilic* because they have available (high-lying) electron lone pairs. The metal ion is *electrophilic* because it has available (low-lying) empty *d* orbitals. The nucleophilic ligands, which are lone pair donors, tend to attack the electrophilic metal, which is an acceptor for lone pairs, to give the metal complex. One special feature of metal ions is their ability to accept multiple lone pairs so that the complex formed is not just ML but ML_n (n = 2–9).

1.6 BACK BONDING

Ligands like NH_3 are good σ donors but are not significant π acceptors. CO, in contrast, is an example of a good π acceptor, sometimes also called a π-*acid ligand*. Such ligands are of very great importance in organometallic chemistry. They tend to be very high-field ligands and form strong M—L bonds. All have empty orbitals of the right symmetry to overlap with a filled d_π orbital of the metal. In the case of CO, this orbital is the CO π*. Figure 1.6 shows how overlap takes place to form the M—C π bond. It may seem paradoxical that an antibonding orbital like the π*(CO) can form a bond, but this orbital is antibonding only with respect to C and O, and can still be bonding with respect to M and C.

We can make the ligand field diagram of Fig. 1.5 appropriate for the case of $W(CO)_6$ by including the π* levels of CO (Fig. 1.7). The d_π set of levels still find no match with the six CO(σ) orbitals, which are lone pairs on C.

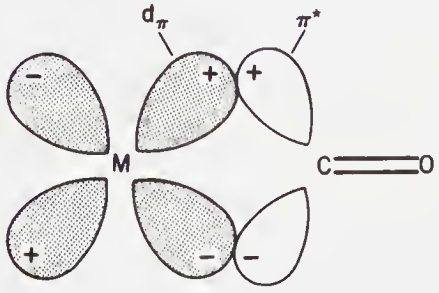


FIGURE 1.6 The overlap between a filled metal d_π orbital and an empty CO π* orbital to give the π component of the M—CO bond. The shading refers to occupancy of the orbitals and the + and − signs, to the symmetry. The M—CO sigma bond is formed by the donation of a lone pair on C into an empty d_σ orbital on the metal (not shown).

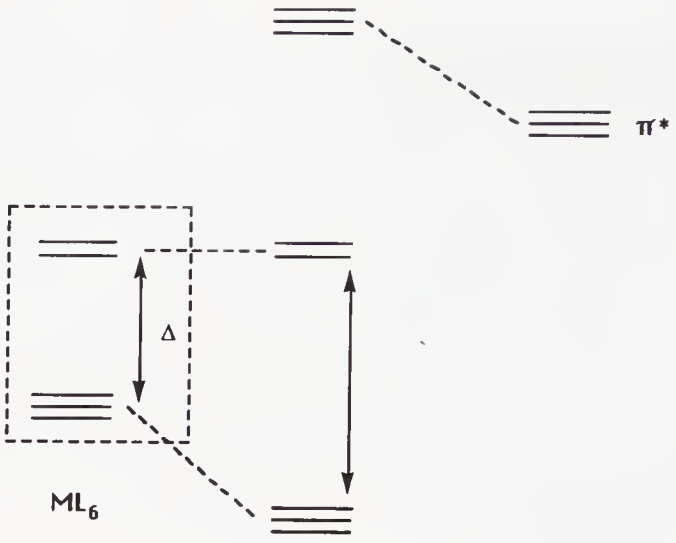


FIGURE 1.7 The effect of "turning on" the π interaction between a π-acceptor ligand and the metal. The unoccupied, and relatively unstable π^* orbitals of the ligand are shown on the right. Their effect is to stabilize the filled d_π orbitals of the complex and so increase Δ. In $W(CO)_6$, the lowest three orbitals are filled.

They do interact strongly with the empty CO π^* levels. Since the Md_π set are filled in this d^6 complex, the result is that d_π electrons that were metal-centered now spend some of their time on the ligands: this means that the metal has donated some electron density to the ligands. This is called *back bonding* and is a key feature of M—L bonds where L is an unsaturated molecule (i.e., has double bonds). Note that this can only happen in d^2 or higher configurations; a d^0 ion like Ti^{4+} cannot back bond and does not form stable carbonyl complexes.

As antibonding orbitals, the CO π^* levels are high in energy, but they are able to stabilize the d_π set as shown in Fig. 1.7. This has two important consequences: (1) the ligand field splitting parameter Δ rises, explaining why π-bonding ligands have such a strong ligand field; and (2) back bonding allows electron density on the metal makes its way back to the ligands. This, in turn, allows low-valent or zero-valent metals to form complexes. Such metals are in a reduced state, and already have a high electron density. (They are said to be very *electron-rich*.) They cannot accept further electrons from pure σ donors; this is why $W(NH_3)_6$ is not a stable compound. By back bonding, the metal can get rid of some of this excess electron density. In $W(CO)_6$ back bonding is so effective that the compound is air-stable and relatively unreactive; the CO groups have so stabilized the electrons that they have no tendency to be abstracted by an oxidizing agent. In $W(PMe_3)_6$, in contrast, back bonding is inefficient and the compound is very air-sensitive and reactive.

Spectroscopic and theoretical studies show that for CO this π back donation is usually comparable to or greater than the CO-to-metal electron donation

that constitutes the σ bond. One of the most direct arguments is structural. The M=C bond in metal carbonyls is usually substantially shorter than an M—C single bond. This is easiest to test when both types of bond are present in the same complex, such as $CpMo(CO)_3Me$, where M—C is 2.38 Å, and M=CO is 1.99 Å. We have to remember that a putative M—CO single bond would be shorter than 2.38 Å by about 0.07 Å, to allow for the higher *s* character (and therefore shorter bond length) of the *sp* hybrid on CO compared to the sp^3 hybrid of the methyl group. The remaining shortening of 0.32 Å is still substantial.

We now need to confirm that it really is the π* orbital of CO that is involved in the back bonding. To do this we turn to IR (infrared) spectroscopy. If CO were bound to the metal by its carbon lone pair, which is nonbonding with respect to CO, then the ν(CO) frequency in the complex would be very little different from that in free CO. The compound BH_3, which is as pure as a σ acceptor as will bind to CO, shows a slight shift of ν(CO) to higher energy: free CO, 2149 cm^{-1}; H_3B—CO, 2178 cm^{-1}. Metal complexes, in contrast, show ν(CO) coordination shifts of hundreds of wavenumbers to lower energy, consistent with the weakening of the C—O bond that would be expected if the π* orbital were being filled [e.g., $Cr(CO)_6$, ν(CO) = 2000 cm^{-1}]. Not only is there a coordination shift, but the shift is larger in cases where we would expect stronger back donation and vice versa. A net positive charge raises ν(CO), and a net negative charge lowers it (e.g., $V(CO)_6^-$, 1860 cm^{-1}; $Mn(CO)_6^+$, 2090 cm^{-1}). The effect of replacing three π-acceptor COs by the three pure σ-donor nitrogens of the tren ligand ($H_2NCH_2CH_2NHCH_2$-CH_2NH_2) is almost as great as changing the net ionic charge by one unit (e.g., $Cr(tren)(CO)_3$, 1880 cm^{-1}). This makes ν(CO) a good indicator of how electron-rich a metal is, and it often correlates well with other ways of estimating electron-rich character, such as the ease of removing an electron.[4]

Series of compounds such as $V(CO)_6^-$, $Cr(CO)_6$, and $Mn(CO)_6^+$ are said to be *isoelectronic complexes* because they have the same number of electrons distributed in very similar structures. Isoelectronic ligands are CO and NO^+ or CO and CN^-, for example. Strictly speaking, CO and CS are not isoelectronic, but as the difference between O and S lies in the number of core levels, the valence shell being the same, the term *isoelectronic* is often extended to cover such pairs. A comparison of isoelectronic complexes or ligands can be useful in making analogies and pointing out contrasts.[5]

The dipole moments of a variety of coordination compounds show that the bond moments of the M—L bonds of most σ-donor ligands are about 4 D, with the donor atom positive. In contrast, metal carbonyls show an M—C bond moment that is essentially zero because the M → L back donation and L → M direct donation cancel out. Formation of the M—CO bond weakens the C—O bond relative to free CO. This will still lead to a stable complex as long as the energy gained from the M—C bond exceeds the loss in C—O. Bond weakening in L on binding is a very common feature in many M—L systems.

Frontier Orbitals The picture we have sketched out for CO holds with slight modifications for a whole series of π acceptor (or soft) ligands, such as alkenes, alkynes, arenes, carbenes, carbynes, NO, N_2, and PF_3. Each of these ligands has a filled orbital that acts as a σ donor and an empty orbital that acts as a π acceptor. These orbitals are almost always the highest filled *(homo)* and lowest unoccupied molecular orbitals *(lumo)* of L, respectively. The homo of L is a donor to the lumo of the metal, which is normally d_σ. The lumo of the ligand accepts back donation from a filled d_π orbital of the metal. The homo and lumo of each fragment are the so-called *frontier orbitals,* and it is nearly always the case that these dominate the bonding. This is because strong interactions between orbitals require not only that the overlap between the orbitals be large but also that the energy separation be small. The homo of each fragment, M and L, is usually closest in energy to the lumo of the partner fragment than to any other vacant orbital of the partner. Strong bonding is expected if the homo–lumo gap of both partners is small. A small homo–lumo gap usually makes a ligand soft, because it is a good π acceptor.

π-Donor Ligands Ligands such as OR^-, F^-, and Cl^- are π donors as a result of the lone pairs that are left after one lone pair has formed the M—L σ bond. Instead of stabilizing the d_π electrons of a d^6 ion as does a π acceptor, these electrons are now destabilized by what is effectively a repulsion between two filled orbitals. This lowers Δ, as shown in Fig. 1.8 and leads to a weaker M—L bond than in the π-acceptor case. Lone pairs on electronegative atoms such as Cl and O are much more stable than the M(d_π) level, and this is why they are lower in Fig. 1.8 than are the π^* orbitals in Fig. 1.7. If the metal

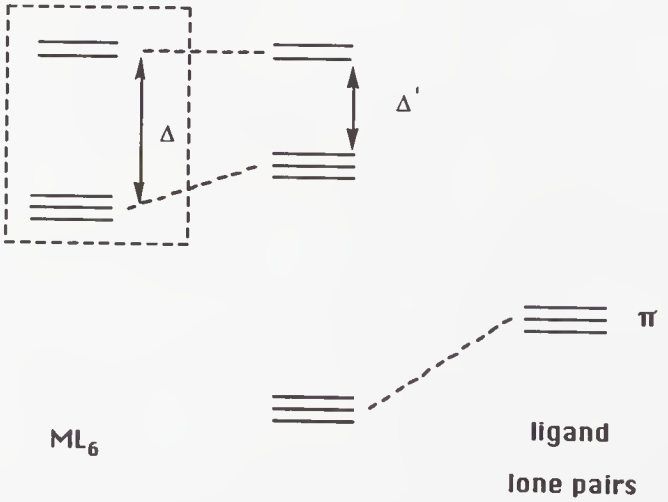


FIGURE 1.8 The effect of "turning on" the π interaction between a π-donor ligand and the metal. The occupied, and relatively stable, lone pair (π) orbitals of the ligand are shown on the right. Their effect is to destabilize the filled d_π orbitals of the complex and so decrease Δ. This is effectively a repulsion between two lone pairs, one on the metal and the other on the ligand.

has empty d_π orbitals, as in the d^0 ion Ti^{4+}, π donation from the ligand to the metal d_π orbitals now leads to stronger metal-ligand bonding; d^0 metals therefore form particularly strong bonds with π donor ligands.

1.7 ELECTRONEUTRALITY

In 1948 Pauling proposed the powerful *electroneutrality principle.* This says that the atoms in molecules arrange themselves so that their net charges fall within rather narrow limits, from about $+1$ to -1 overall. In fact, the range for any given element is likely to be narrower than this, and will tend toward a preferred charge, which will differ according to the electronegativity of the element concerned. The nonmetals, such as C, N, or O, will tend to be closer to -1, and the metals, such as Li, Mg, and Fe, will tend to be closer to $+1$. This implies that as far as electroneutrality arguments go, an element will bond best to other elements that have complementary preferred charges. In this way, each can satisfy the other. An electropositive element will prefer an electronegative one, as in the compounds NaCl and TiO_2, and elements with an intermediate electronegativity will tend to prefer each other, as in HgS and Au metal. An isolated Co^{3+} ion is not a electroneutral species, as it has an excessively high positive charge. In its compounds it will therefore seek good electron donors as ligands, such as O^{2-} in Co_2O_3, or NH_3, in the ammine complexes. On the other hand, an isolated W(0) atom is too electron-rich for its electronegativity, so it will prefer net electron-attracting ligands such as CO.

There is a deeper reason why the *d* orbitals of transition metals are available for back donation only in electron-rich complexes. Co(III), for example, has a filled d_π level, but it does not bind CO, because the d_π orbital is too low in energy and therefore not sufficiently basic. The reason is that the *s*, *p*, and *d* orbitals respond differently to a change in the charge on the metal. If the metal is in a high oxidation state, like Co(III), then there are electron "holes" in the valence shell compared with the neutral atom. This means that the valence shell of the ion is positive with respect to the situation in the atom. Since *d* orbitals tend to have their maximum electron density far away from the nucleus (because they have two planar nodes or planes of zero electron density that pass through the nucleus), *p* orbitals reach their maximum somewhat closer to the nucleus (one planar node), and *s* orbitals reach their maximum at the nucleus (no planar nodes), the orbitals will be less sensitive to the 3+ change in the net charge that took place on going from Co(0) to Co(III), in the order $d > p > s$. In other words, the *d* orbitals will be much more strongly stabilized than the others on going from the atom to the ion. This is why the atomic electron configuration for the transition metals involves *s*-orbital occupation (e.g., Co, d^7s^2), but the configuration of the ion is d^6, not d^4s^2. On the other hand, the more electron-rich (i.e., the more reduced, or low-oxidation-state) the metal complex, the less positive will be the charge

on the metal. This will destabilize the *d* orbitals and make them more available for back donation.

We also alter the orbital energies as we go from left to right in the transition series. For each step to the right, a proton is added to the nucleus. This extra positive charge stabilizes all the orbitals. The earlier metals are the more electropositive because it is easier to remove electrons from their less stable energy levels. The sensitivity of the orbitals to this change is different from what we saw above. This time the order is $d \sim s > p$, because the *s* orbital, having a maximum electron density at the nucleus, is more stabilized by the extra protons that we add for each step to the right in the Periodic Table, than are the *p* orbitals, which have a planar node at the nucleus. The *d* orbitals are stabilized because of their lower principal quantum number (e.g., 3*d* versus 4*s* and 4*p* for Fe). The special property of the transition metals is that all three types of orbital are in the valence shell and have similar energies so they are neither too stable nor too unstable to contribute significantly to the bonding. Metal carbonyls, for example, are most stable for Groups 4–10 because CO requires *d*-orbital participation to bind effectively.

Finally, as we go down a group from the first-row transition element to the second row, the outer valence electrons become more and more *shielded* from the nucleus by the extra shell of electrons that has been added. They are therefore more easily lost, and the heavier element will be the more basic and more electronegative, and high oxidation states will be more stable. This trend also extends to the third row, but as the *f* electrons that were added to build up the lanthanide elements are not as effective as *s*, *p*, or even *d* electrons in shielding the valence electrons from the nucleus, there is a smaller change on going from the second- to the third-row element than was the case for moving from the first row to the second. Compare, for example, Cr(VI) in Na_2CrO_4 and Mn(VII) in $KMnO_4$, which are unstable and are powerful oxidizing agents, with their stable analogs in the second and third rows, Na_2MoO_4, Na_2WO_4, and $KReO_4$, which are only very weakly oxidizing. Similarly, the increase in covalent radii is larger on going from the first to the second row than it is on going from the second to the third. This is termed the *lanthanide contraction*.

Another aspect of electroneutrality is that ionic compounds with excessively high positive or negative charges are not normally formed. The great majority of compounds are neutral, net charges of ± 1 are not uncommon, but net ionic charges of ± 2 or greater are increasingly rare unless there is some special reason to expect them, such as the presence of several metals to share the ionic charge.

1.8 TYPES OF LIGAND

Most ligands form the M—L σ bond by using a lone pair, that is, a pair of electrons that are nonbonding in the free ligand. For ligands that have them,

lone pairs are often the homo and the most basic electrons in the molecule. Classical Werner coordination complexes always involve lone pair donor ligands. There are two other types of ligand found in organometallic compounds of which C_2H_4 and H_2 are typical examples.

Ethylene is an example of a molecule that has no lone pairs, yet it binds strongly to low-valent metals. In this case the homo is the C=C π bond, and it is these electrons that form the M—L σ bond, as shown in Fig. 1.9*a*. The arrow marked "1" represents the π-bonding electron pair of ethylene being donated to the metal. There is also a back-bonding component (marked "2") where the π^* orbital of ethylene plays the role of acceptor. Since the C=C π bond lies both above and below the molecular plane, the metal has to bind out of the plane, where the electrons are. This type of binding is sometimes represented as (η^2-C_2H_4) (pronounced "eta–two ethylene") where η represents the *hapticity* of the ligand, defined as the number of atoms in the ligand bonded to the metal.

Molecular hydrogen has neither a lone pair nor a π bond, yet it also binds as an intact molecule to metals in such complexes as [W(η^2-H_2)$(CO)_3L_2$]. The only available electron pair is the H—H σ bond, and this becomes the donor ("3" in Fig. 1.9*b*). Back donation in this case ("4" in Fig. 1.9*b*) is accepted by the H_2 σ^* orbital. The metal binds side-on to H_2 to maximize σ–d_σ overlap. Related *σ-bond complexes*[6] are formed with C—H, Si—H, B—H, and M—H bonds. In general, the basicity of electron pairs decreases in the following order: lone pairs > π-bonding pairs > σ-bonding pairs, because being part of a bond stabilizes electrons. The usual order of binding ability is therefore as follows: lone pair donor > π-bond donor > σ-bond donor.

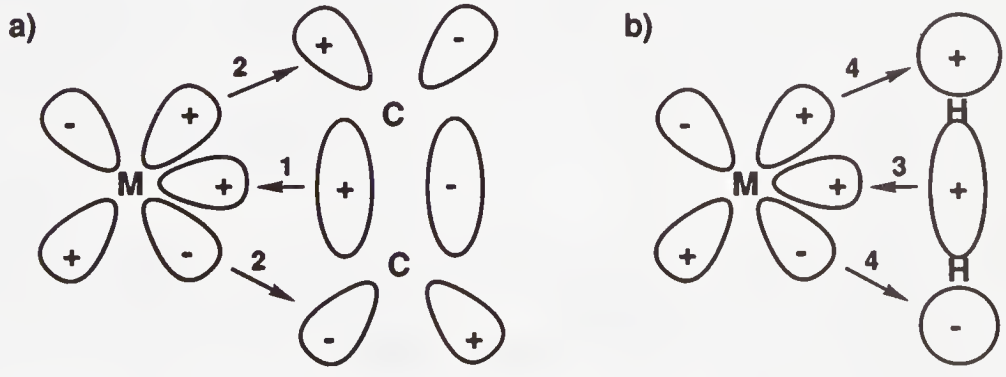


FIGURE 1.9 (*a*) The bonding of a π-bond donor, ethylene, to a metal. The arrow labeled "1" represents electron donation from the filled C=C π bond to the empty d_σ orbital on the metal; "2" represents the back donation from the filled M(d_p) orbital to the empty C=C π^*. (*b*) The bonding of a σ-bond donor, hydrogen, to a metal. The label "3" represents electron donation from the filled H—H σ bond to the empty d_σ orbital on the metal, and "4" represents the back donation from the filled M(d_p) orbital to the empty H—H σ^*. Only one of the four lobes of the d_σ orbital is shown.

For lone pair donors the M—L π bond can have 2e and be attractive, as we saw for M—CO (M = d^6 metal, Figs. 1.6 and 1.7) or 4e and be repulsive, as is the case for M—F^- (M = d^6 metal, Fig. 1.8). For the more weakly binding σ- and π-bond donors, the M—L π bond is nearly always attractive because if it were not, L would not bind strongly enough to form an isolable complex. In the π bond, a M(d_π) electron pair is donated to an empty antibonding orbital of the ligand, usually a π^* for π-bond donors and a σ^* for σ-bond donors (Fig. 1.9). In the case of a π-bond donor like ethylene, this back bonding weakens the C=C π bond but does not break it because C_2H_4 is still held together by strong C—C and C—H σ bonds that are not involved in M—L bond formation. The C=C distance of 1.32 Å in free ethylene is lengthened only to 1.35–1.5 Å in the complex.

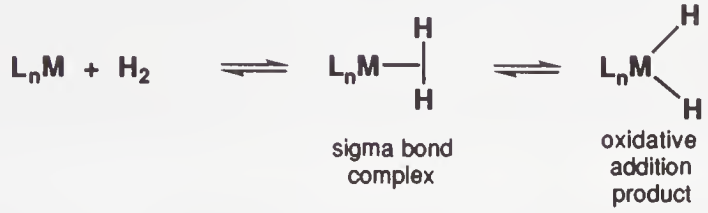
For σ-bond donors such as H_2, forming the M—L σ bond partially depletes the H—H σ bond because electrons that were fully engaged in keeping the two H atoms together in free H_2 are now also delocalized over the metal (hence the name *two-electron, three-center bond* for this type of interaction). Back bonding into the H—H σ^* causes additional weakening of the H—H σ bond because the σ^* is antibonding with respect to H—H. Free H_2 has an H—H distance of 0.74 Å, but the H—H distances in H_2 complexes go all the way from 0.82 to 1.5 Å. Eventually the H—H bond breaks and a dihydride is formed (Eq. 1.5). This is called the oxidative addition reaction (see Chapter 6). Formation of a σ-bond complex can be thought of as an incomplete oxidative addition. Table 1.2 classifies common ligands by the nature of the

TABLE 1.2 Types of Ligands[a]

σ \ π	Strong π Acceptor	Weak π-Bonding	Strong π Donor
Lone pair donor	CO PF_3 CR_2^+[b]	CH_3^- H^-[c] NH_3	CR_2^- OR^- F^-
π-Bonding electron pair donor	C_2F_4 O_2	C_2H_4 RCHO[d]	
σ-Bonding electron pair donor	Oxidative addition[e]	$R_3Si—H$, H_2 $R_3C—H$[f]	

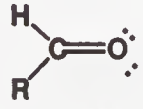
[a]Ligands are listed in approximate order of π-donor/acceptor power, with acceptors to the left.
[b]CH_2^- and CH_2 refer to Fischer and Schrock carbenes of Chapter 11.
[c]Ligands like this are considered here as anions rather than radicals.
[d]Can also bind as a lone pair donor (Eq. 1.5).
[e]Oxidative addition occurs when σ-bond donors bind very strongly (see text).
[f]A stable complex is formed only when the C—H bond is part of a ligand such as PPh_3 or C_2H_5.

M—L σ and π bonds. Both σ and π bonds bind side-on to metals when they act as ligands.

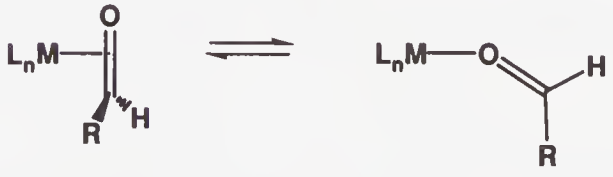


(1.5)

Some ligands have several types of electron pair available for bonding. For example, aldehydes (**1.14**) have the C=O π bond and lone pairs on the oxygen. When they act as π-bond donors, aldehydes bind side-on (**1.15**) like ethylene, when they act as lone pair donors, they bind end-on (**1.16**). Sometimes an equilibrium is found (Eq. 1.6) but strongly π-donor metals favor **1.15**, and strong σ acceptors favor **1.16**. Alkenes have both a C=C π bond and C—H σ bonds. Gladysz[7] has shown how metals can move from one face of a C=C bond to the other via intermediate binding to the C—H bond (Eq. 1.7).

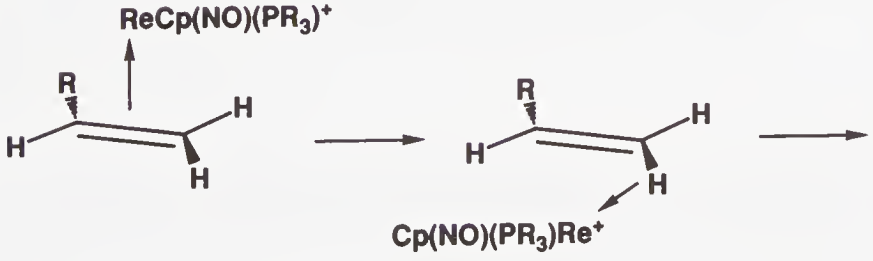


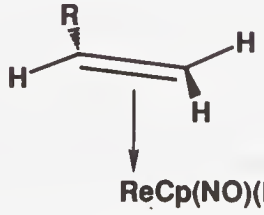
1.14



1.15 **1.16**

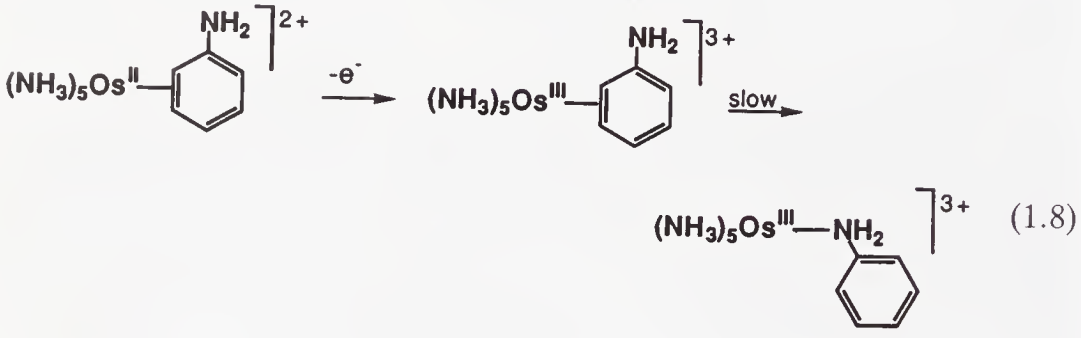
(1.6)





(1.7)

The $\{(NH_3)_5Os^{II}\}^{2+}$ fragment in Eq. 1.8 is a strong π donor because NH_3 is strongly σ donor but not a π-acceptor ligand, and it prefers to bind to one C=C bond of aniline. Oxidation to Os^{III} causes a sharp falloff in π-donor power because the extra positive charge stabilizes the *d* orbitals, and the complex rearranges to the *N*-bound aniline form.[8] This illustrates how the electronic character of a metal can be altered by changing the ligand set and oxidation state.



(1.8)

REFERENCES

1. A. M. Sargeson, *Pure Appl. Chem.*, **56,** 1603, 1984.
2. S. Ahrland, J. Chatt, and N. R. Davies, *Chem. Soc. Rev.*, **12,** 265, 1958.
3. K. W. Whitten, K. D. Gailey, and R. E. Davis, *General Chemistry*, 4th ed., Saunders, New York, 1992: (a) pp. 981–89; (b) pp. 304–351.
4. A. D. Hunter et al., *Organometallics,* **11,** 2251, 1992.
5. T. P. Fehlner et al., *Adv. Organometal. Chem.*, **30,** 189, 1990.
6. R. H. Crabtree, *Angew. Chem., Int. Ed.*, **32,** 789, 1993.
7. T. S. Peng and J. A. Gladysz, *J. Am. Chem. Soc.*, **114,** 4174, 1992.
8. H. Taube, *Pure Appl. Chem.*, **63,** 651, 1991.

PROBLEMS

1. How many isomers would you expect for a complex with the empirical formula $Pt(NH_3)_2Cl_2$?

2. Draw the structure of $[Me_3Pt(\mu_3\text{-}I)]_4$. The arrangement of the Pt and I atoms is often considered to be analogous to that of the vertices in one of the Pythagorean regular solids; which one do you think it is?

3. Why do you think that $H_2NCH_2CH_2NH_2$ is so much better as a chelating ligand than $H_2NCH_2NH_2$? Why do you think H_2O is a lower-field ligand than NH_3?

4. How would you design a synthesis of the complex *trans*-$[PtCl_2(en)(tu)]$, {the trans descriptor refers to the fact that a pair of identical ligands, Cl in this case, is mutually trans}, given that the trans effect order is tu > Cl > NH_3 [tu = $(H_2N)_2CS$)]?

5. Consider the two complexes $MeTiCl_3$, and $(CO)_5W(thf)$. Predict the order of reactivity in each case toward the following sets of ligands: NMe_3, PMe_3, CO.

6. How could you distinguish between a square planar and a tetrahedral structure in a nickel(II) complex of which you have a sample, without using crystallography?

7. You have a set of different ligands of the PR_3 type, and a large supply of $(CO)_5W(thf)$, with which to make a series of complexes $(CO)_5W(PR_3)$. How could you estimate the relative ordering of the electron-donor power of the different PR_3 ligands?

8. The stability of metal carbonyl complexes falls off markedly as we go to the right of Group 10 in the Periodic Table. For example, copper forms only a few weakly bound complexes with CO. Why is this? What oxidation state, of the ones commonly available to copper, would you think would form the strongest CO complexes?

9. Low-oxidation-state complexes are often air-sensitive (i.e., they react with the oxygen in the air), but are rarely water-sensitive. Why do you think this is so?

10. $MnCp_2$ is high-spin, while $MnCp_2^*$ ($Cp^* = \eta^5\text{-}C_5Me_5$) is low-spin. How many unpaired electrons does each metal have, and which ligand has the stronger ligand field?

11. Make up a problem on the subject matter of this chapter and provide an answer. This is a good thing for you to do for subsequent chapters as well. It gives you an idea of topics and issues on which to base questions and will therefore guide you in studying for tests.

CHAPTER 2

GENERAL PROPERTIES OF ORGANOMETALLIC COMPLEXES

Organometallic chemistry is concerned with the metal–carbon bond, of which the simplest is the M—C single bond of metal alkyls. As σ-bonding ligands, alkyls are closely related to the ligands found in coordination compounds, such as Cl, H_2O, and NH_3. A larger class of organometallic ligands are soft, and can π-bond. Of these, we have met CO already. If you examine the structures of some typical organometallic compounds, for example by leafing through the later chapters of this book, you will see many examples of such π-bonding ligands as butadiene, benzene, cyclopentadienyl (C_5H_5, often symbolised as Cp), and allyl. There are several differences between complexes of these ligands and coordination compounds containing Cl^-, H_2O, and NH_3. The metals are more electron-rich, in the sense that the metal bears a greater negative charge in the organometallic complex. The M—L bonds are much more covalent and often have a substantial π component. The metal *d* orbitals are higher in energy, and by back donation perturb the electronic structure of the ligands much more than is the case for coordination compounds. The organometallic ligands can be polarized and therefore activated toward chemical reactions, σ and π bonds in the ligands can be weakened or broken, and chemical bonds can be made or broken within and between different ligands. This rich pattern of reactions is one of the characteristic features of organometallic chemistry.

In this chapter, we look at the 18-electron rule and at the ionic and covalent models that are commonly used in connection with electron counting. We then examine the ways in which binding to the metal can perturb the chemical character of a ligand, an effect that lies at the heart of organometallic chemistry.

2.1 THE 18-ELECTRON RULE

The 18e rule[1] is a way to help us decide whether a given *d*-block transition metal organometallic complex is likely to be stable. Not all the organic formulas we can write down correspond to stable species. For example, CH_5 requires a 5-valent carbon, and is therefore not stable. Stable compounds, such as CH_4, have the noble gas octet, and so carbon can be thought of as following an 8e rule. This corresponds to carbon using its *s* and three *p* orbitals to form four filled bonding orbitals, and four unfilled antibonding orbitals. On the covalent model, we can consider that of the eight electrons required to fill the bonding orbitals, four come from carbon and one each comes from the four H substituents. We can therefore think of each H atom as being a 1e ligand to carbon.

We sometimes find it useful to assign a formal oxidation state to carbon in an organic molecule. For this we impose an ionic model on the compound by artificially dissecting it into ions. In doing this, each electron pair in any bond is assigned to the most electronegative of the two atoms or groups that constitute the bond. For methane, this dissection gives $C^{4-} + 4H^+$, with carbon as the more electronegative element. This makes methane an 8e compound with an oxidation state of -4, which is usually written C(-IV). Note that the net electron count remains the same, whether we adopt the covalent (4e {C atom} + 4 × 1e {4 H atoms} = 8e), or ionic models (8e {C^{4-} ion} + 4 × 0e {4 H^+ ions} = 8e).

The 18e rule, which applies to many low-valent transition metal complexes, follows a similar line of reasoning. The metal now has one *s*, and three *p* orbitals, as before, but now also five *d* orbitals. We will need 18e to fill all nine orbitals: some will come from the metal, the rest from the ligands. Only a limited number of combinations of metal and ligand will give an 18e count. Figure 1.5 shows that 18e will fill the m.o. diagram of the complex ML_6 up to the d_π level, and leave the d_σ orbitals empty. The resulting configuration is analogous to the closed shell present in the Group 18 elements and is therefore called the *noble gas configuration*. Each atomic orbital (a.o) on the metal that remains nonbonding will clearly give rise to one molecular orbital (m.o.) in the complex; each a.o. that interacts with a ligand orbital will give rise to one bonding m.o., which will be filled in the complex, and one antibonding m.o., which will normally be empty. Our nine metal orbitals will therefore give rise to nine low lying orbitals in the complex and to fill these we will need 18 electrons.

A glance at Table 2.1 will show how the first-row carbonyls mostly follow the 18e rule. Each metal contributes the same number of electrons as its group number, and each CO contributes 2e for its lone pair; π back bonding makes no difference to the electron count for the metal. In the free atom, it had one atomic orbital (a.o.) for each pair of d_π electrons it uses for back bonding; in the complex it still has one filled molecular orbital (m.o.), now delocalized over metal and ligands.

TABLE 2.1 The First-Row Carbonyls

$V(CO)_6$	17e; 18e $V(CO)_6^-$ also stable
$Cr(CO)_6$	Octahedral
$(CO)_5Mn—Mn(CO)_5$	The M—M bond contributes 1e to each metal; all the CO groups are terminal
$Fe(CO)_5$	Trigonal bipyramidal
$(CO)_3Co(\mu\text{-}CO)_2Co(CO)_3$	A μ-CO contributes 1e to each metal, and there is also an M—M bond
$Ni(CO)_4$	Tetrahedral

In cases where we start with an odd number of electrons on the metal, we can never reach an even number, 18, by adding 2e ligands like CO. In each case the system resolves this problem in a different way. In $V(CO)_6$, the complex is 17e, but is easily reduced to the 18e anion $V(CO)_6^-$. Unlike $V(CO)_6$, the $Mn(CO)_5$ fragment, also 17e, does dimerize, probably because, as a 5-coordinate species, there is more space available to make the M—M bond. This completes the noble gas configuration for each metal because the unpaired electron in each fragment is shared with the other in forming the bond, much as the 7e methyl radical dimerizes to give the 8e compound, ethane. In the 17e fragment $Co(CO)_4$, dimerization also takes place via a metal–metal bond, but a pair of COs also move into bridging positions. This makes no difference in the electron count, because the bridging CO is a 1e ligand to each metal, so an M—M bond is still required to attain 18e. The even-electron metals are able to achieve 18e without M—M bond formation, and in each case they do so by binding the appropriate number of COs, the odd electron metals need to form M—M bonds.

Unfortunately, there are two conventions for counting electrons: the ionic and covalent models, both of which have roughly equal numbers of supporters. Both methods lead to *exactly the same net result;* they differ only in the way that the electrons are considered as "coming from" the metal or from the ligands. Let us take $HMn(CO)_5$ as an example. We can adopt the covalent model and argue that the H atom, a 1e ligand, is coordinated to a 17e $Mn(CO)_5$ fragment. On the other hand, on the ionic model, one can consider the complex as being derived from an anionic 2e H^- ligand, coordinated to a cationic 16e $Mn(CO)_5^+$ fragment. The reason is that H is more electronegative than Mn and so is formally assigned the bonding electron pair when we dissect the complex. Fortunately, no one has yet suggested counting the molecule as arising from a 0e H^+ ligand and an 18e $Mn(CO)_5^-$ anion; ironically, protonation of the anion is the most common preparative method for this hydride.

These different ways of assigning electrons are simply models. Since all bonds between dissimilar elements have at least some ionic and some covalent character, each model reflects a facet of the truth. The covalent model is probably more appropriate for the majority of low-valent transition metal complexes, especially with the unsaturated ligands we will be studying. On

the other hand, the ionic model is more appropriate for high-valent complexes with N, O, or Cl ligands, such as are found in coordination chemistry or in the organometallic chemistry described in Chapter 15. Before the advent of organometallic chemistry, the oxidation state model played a dominant role in transition metal chemistry because the oxidation state of the types of compound studied could almost always be unambiguously defined. The rise of the covalent model has paralleled the growth in importance of organometallic compounds, which tend to involve more covalent M—L bonds and for which oxidation states cannot always be unambiguously defined (see Section 2.4). We have therefore preferred the covalent model as being most appropriate for the majority of the compounds with which we will be concerned. It is important to be conversant with both models, however, because each can be found in the literature without any indication as to which is being used, so you should practise counting under the other convention after you are happy with the first. We will also refer to any special implications of using one or other model as necessary.

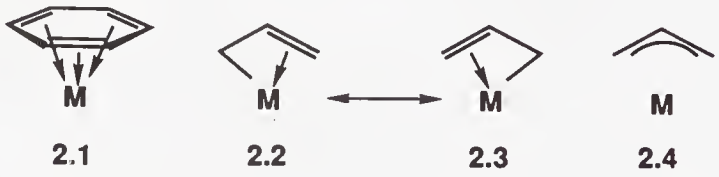
In Table 2.2 we see some of the common ligands and their electron counts on the two models. The symbol L is commonly used to signify a neutral ligand, which can be a lone pair donor, such as CO or NH_3, a π-bond donor, such as C_2H_4, or a σ-bond donor such as H_2, which are all 2e ligands on both models. The symbol X refers to ligands such as H, Cl, or Me, which are 1e X ligands on the covalent model and 2e X^- ligands on the ionic model. In the covalent model we regard them as 1e $X\cdot$ radicals bonding to the neutral metal atom; in the ionic model, we regard them as 2e X^- anions bonding to the M^+ cation. Green has developed a useful extension of this nomenclature by which more complicated ligands can be classified. For example, benzene (**2.1**) can be considered as a combination of three C=C ligands, and therefore

TABLE 2.2 Common Ligands and Their Electron Counts

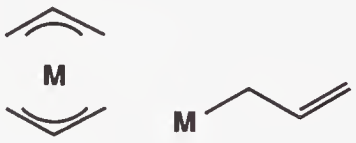
Ligand	Type	Covalent Model	Ionic Model
Me, Cl, Ph, Cl, η^1-allyl, NO (bent)[a]	X	1e	2e
Lone pair donors: CO, NH_3	L	2e	2e
π-Bond donors: C_2H_4	L	2e	2e
σ-Bond donors: (H_2)	L	2e	2e
η^3-Allyl, η^3-acetate	LX	3e	4e
NO (linear)[a]	LX	3e	2e
η^4-Butadiene	L_2[b]	4e	4e
η^5-Cp	L_2X	5e	6e
η^6-Benzene	L_3	6e	6e

[a]Linear NO is considered as NO^+ on the ionic model; see Section 4.1.
[b]The alternative LX_2 structure sometimes adopted gives the same electron count.

as L_3.* The allyl group can be considered as a combination of an alkyl and a C=C group. The two canonical forms **2.2** and **2.3** show how we can consider allyl groups in which all three carbons are bound to the metal as LX ligands. This can also be represented in the delocalized form as **2.4**. In such a case, the *hapticity* of the ligand, the number of ligand atoms bound to the metal, is 3 and so **2.5**, referred to as bis-π-allyl nickel in the older literature, is now known as bis-η^3-allyl nickel, or $[Ni(\eta^3\text{-}C_3H_5)_2]$. Occasionally the letter "h" is used instead of η, and sometimes η is used without a superscript as a synonym for the older form, π; such things tend to be frowned on. The electron count of the η^3 form of the allyl group is 3e on the covalent model and 4e on the ionic model, as suggested by the LX label. The advantage of the LX label is that those who follow the covalent model will translate LX as meaning a 3e ligand, and the devotees of the ionic model will translate LX as meaning a 4e ligand.



2.1 2.2 2.3 2.4

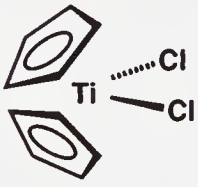


2.5 2.6

The allyl group can also bind in another way (**2.6**). Since only one carbon is now bound to the metal, this is the η^1-allyl, or σ-allyl form. In this bonding mode, the allyl behaves as an X-type ligand, like a methyl group, and is therefore a 1e ligand on the covalent model and a 2e ligand on the ionic model. Some examples of electron counting are shown in Fig. 2.1. Note the dissection into atoms and radicals in the covalent model and into ions in the ionic model.

Bridging ligands are very common in organometallic chemistry and are prefixed by the symbol μ. Bridging CO ligands are usually counted as shown in Table 2.1. Next we will look at bridging halide. This carries a lone pair, which is donated to the second metal in forming the bridge. An L_nMCl group is effectively acting as a ligand to the second metal. If $ML_n = M'L_n$, then

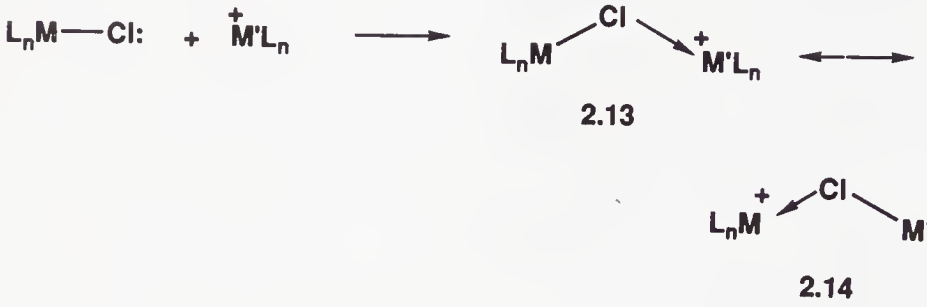
*Undergraduates will need to become familiar with organic "line notation," in which only C—C bonds are shown and enough H groups must be added to each C to make it 4-valent. For example, **2.6** represents $MCH_2CH{=}CH_2$.

Ionic Model			Covalent Model	
				
$C_5H_5^-$	6e		$C_5H_5\bullet$	5e
$C_5H_5^-$	6e	Fe	$C_5H_5\bullet$	5e
Fe^{2+}	6e		Fe	8e
	18e			18e
		2.7		
Mo^{4+}	2e	$MoH_4(PR_3)_4$	Mo	6e
$4 \times H^-$	8e	**2.8**	$4 \times H\bullet$	4e
$4 \times PR_3$	8e		$4 \times PR_3$	8e
	18e			18e
				
Ni^{2+}	8e	Ni	Ni	10e
$2 \times C_3H_5^-$	8e		$2 \times C_3H_5\bullet$	6e
	16e			16e
		2.9		
				
Mo	6e	Mo	Mo	6e
$2 \times C_6H_6$	12e		$2 \times C_6H_6$	12e
	18e			18e
		2.10		
$2 \times Cl^-$	4e		$2 \times Cl$	2e
Ti^{4+}	0e		Ti	4e
$2 \times C_5H_5^-$	12e		$2 \times C_5H_5\bullet$	10e
	16e			16e
		2.11		
				
Co^{3+}	6e	Co	Co	9e
$2 \times C_5H_5^-$	12e		$2 \times C_5H_5\bullet$	10e
	18e		Positive charge[a]	−1e
				18e
				
		2.12		

[a]To account for the positive ionic charge on the complex as a whole; for anions, the net charge is added to the total.

FIGURE 2.1 Electron counting on the covalent and ionic models.

the two bonds to Cl are indistinguishable by resonance between **2.13** and **2.14**:



(2.1)

For electron counting purposes, we can consider that the chlorine atom is a 1e donor to M and a 2e donor to M′ via its lone pair (or, on the ionic model, that Cl^- is a 2e donor to each metal via two lone pairs). The same usually holds true for other X-type ligands, such as halide, —SR, —OR, or $—PR_2$. A bridging carbonyl is like a ketone from the point of view of electron counting; it is a 1e donor to each metal. (This is true for both models, because users of the ionic model regard CO as a neutral ligand even when bridging.) Other ligands of the same type are bridging methylene, $M—CH_2—M$, and bridging oxo, M—O—M, which are 1e ligands to each metal on the covalent model and 2e ligands on the ionic model.

As shown in **2.13** and **2.14**, we often write M—X to signify the covalent bond, but L → M for the coordinate bond, as an indication that both electrons are regarded as "coming from" the ligand L.

For complex ions, we have to adjust for the net ionic charge in making the electron count. For example, $CoCp_2^+$ (**2.12** in Fig. 2.1) is counted on the covalent model as follows. The neutral Co atom has 9e because it is Group 9; from Table 2.2, the two neutral Cp groups add 10e; the net ionic charge is 1+, so one electron has been removed to make the cation. The electron (e) count is therefore 9 + 10 − 1 = 18e. Electron counting can be summarized by Eq. 2.2, which shows the electron count for a generalized complex $[MX_aL_b]^{c+}$, where N is the group number of the metal (and therefore the number of electrons in the neutral M atom).

$$\text{e count} = N + a + 2b - c \tag{2.2}$$

When we use the ionic model for electron counting, we first have to calculate the oxidation state of the metal. The oxidation state is the ionic charge left on the metal after removal of the ligands, taking care to assign the electron pairs in the M—L bonds to the more electronegative atom in each case. (If two atoms have the same electronegativity, one electron is assigned to each; see also Section 2.4.) For $CoCp_2^+$, we must remove two Cp's as Cp^- ions (as C is more electronegative than Co); this leaves Co^{3+}, which has a d^6 configuration. This means that $CoCp_2^+$ has 6 + (2 × 6) = 18 electrons. For the

general case of $[MX_aL_b]^{c+}$, this procedure leaves the metal as $M^{(c+a)+}$, and therefore the metal is in the oxidation state $(c + a)$, and has $N - c - a$ electrons. We now have to add 2e for each X^-, and 2e for each L in putting the complex back together:

$$\text{e count} = N - a - c + 2a + 2b = N + a + 2b - c \qquad (2.3)$$

You will see that this reduces to Eq. 2.2 and so the two methods of electron counting are equivalent.

2.2 LIMITATIONS OF THE 18-ELECTRON RULE

There are many cases in which the electron count for a stable complex is not 18; examples are $MeTiCl_3$, 8e; Me_2NbCl_3, 10e; WMe_6, 12e; $Pt(PCy_3)_2$, 14e; $[M(H_2O)_6]^{2+}$ (M = V, 15e; Cr, 16e; Mn, 17e; Fe, 18e), $CoCp_2$, 19e; and $NiCp_2$, 20e. For the 18e rule to be useful, we need to be able to predict when it will be obeyed and when it will not.

The rule works best for hydrides and carbonyls, because these are sterically small, high-field ligands. Because they are small, as many will generally bind as are required to achieve 18e. With high-field ligands, Δ for the complex will be large. This will mean that the d_σ^* orbitals that would be filled if the metal had more than 18e are high in energy and therefore poor acceptors. On the other hand, the d_π orbitals, which would have to give up electrons if the molecule had less than 18e are low in energy because of π bonding by CO (or, in the case of H, because of the very strong σ bond and the absence of repulsive π interactions with lone pairs). The d_π level is therefore a good acceptor, and to be stable, a complex must have this level filled (otherwise the electrophilic metal will gain electrons by binding more CO, or the solvent or some functional group in the ligands until the 18e configuration is attained).

Conversely, the rule works least well for high-valent metals with weak-field ligands. In the hexaaqua ions $[M(H_2O)_6]^{2+}$ (M = V, Cr, Mn, Fe, Co, Ni), the structure is the same whatever the electron count of the metal and so must be dictated by the fact that six H_2O's fit well around a metal ion. H_2O has two lone pairs, one of which it uses to form a σ bond. This leaves one remaining on the ligand, which acts as a π donor to the metal and so lowers Δ; H_2O is therefore a weak field ligand. If Δ is small, then the tendency to adopt the 18e configuration is also small because it is easy to add electrons to the low-lying d_σ^*, or to remove them from the high-lying d_π.

An important class of complexes follow a 16e, rather than an 18e, rule because one of the nine orbitals is very high-lying and is usually empty. This can happen for the d^8 metals of Groups 8–11 (Table 2.3). Group 8 shows the least, and Group 11 the highest tendency to become 16e. When these metals are 16e, they normally adopt the square planar geometry, which makes the $d_{x^2-y^2}$ orbital very high in energy because it experiences crystal field repulsion

TABLE 2.3 The d^8 Metals that Can Adopt a 16e Configuration

Group			
8	9	10	11
Fe(0)[a]	Co(I)[b]	Ni(II)	Cu(III)[c]
Ru(0)[a]	Rh(I)[b]	Pd(II)	—
Os(0)[a]	Ir(I)[b]	Pt(II)	Au(III)

[a]These metals prefer 18e to 16e.
[b]The 16e configuration is more often seen, but 18e complexes are common.
[c]A rare oxidation state.

from all four ligands. To go to an 18e species, the metal has to rehybridize to give a trigonal bipyramidal geometry, so as to direct the empty orbital toward the incoming fifth ligand and, by avoiding crystal field repulsions, lower its energy. Some examples of 16e complexes of this sort are $RhClL_3$, $IrCl(CO)L_2$, $PdCl_2L_2$, and $[PtCl_4]^{2-}$, $[AuMe_4]^-$ (L = 3° phosphine).

The smaller metal clusters, such as $Os_3(CO)_{12}$, often obey the 18e rule for each metal, but for clusters of six metals or more, there are deviations, for which special cluster counting rules have been devised (Chapter 13). The rule is not useful for Main Group elements, such as $ZnMe_2$, 14e; $MeHg(bipy)^+$, 16e; $[I(py)_2]^+$, 20e; $[SbF_6]^-$, 22e; and IF_7, 24e, where no particular electron count is favored. The lanthanides and actinides have seven *f* orbitals to fill before they even start on the *d* orbitals, and so they are essentially never able to bind a sufficient number of ligands to raise the electron count to the $s^2p^6d^{10}f^{14}$, or 32e configuration of the appropriate noble gas; some examples are $U(cot)_2$, 22e, and Cp_2LuMe, 28e. This means that the stoichiometry of an *f* block complex tends to be decided by steric saturation of the space around the metal. Paramagnetic complexes (e.g., $V(CO)_6$, 17e; Cp_2Fe^+, 17e; Cp_2Ni, 20e) generally do not obey the 18e rule, but many of these have reactions in which they attain an 18e configuration, for example, the 19e $CpFe(\eta^6\text{-arene})$ is a powerful 1e donor.[2]

2.3 ELECTRON COUNTING IN REACTIONS

It is often useful to consider changes in the electron count of a metal during a reaction. For example, an 18e complex would not be expected to add a 2e ligand, such as PPh_3, without first losing a 2e ligand or rearranging in some way to generate a 2e vacancy at the metal. The 20e intermediate (or transition state) that would be involved if an extra ligand were to bind, is likely to be less stable than the 16e intermediate (or transition state) involved in the loss of a ligand. If all the ligands originally present are firmly bound, as in $FeCp_2$, then we do not expect a 2e reagent, such as a phosphine, to bind. On the other hand, H^+ is a zero-electron (0e) reagent, and can react with an 18e

species, such as ferrocene (Eq. 2.4). This protonation also illustrates the electron-rich (basic) character of the metal common for organometallic compounds, but not seen for aqua complexes and other coordination compounds.

$$Cp_2Fe + H^+ = [Cp_2FeH]^+ \quad (2.4)$$

Because H^- is a 2e reagent like PPh_3, we would not expect H^- to attack the metal in ferrocene. Note that this result is the same whether we use the ionic or covalent model. The reagents on the left-hand side of Eq. 2.4 are already separated for us, on any model, H^+ is 0e and Cp_2Fe is 18e. Ironically, neither model applied to $[Cp_2FeH]^+$ gives the dissection shown on the left-hand side of Eq. 2.4. We will therefore speak of H^+ and H^- as 0e and 2e *reagents,* respectively, even though H is a 1e ligand (ionic model: 2e) to make the distinction clear.

In terms of electron counting, any X ligand that bears a negative charge, as in Cl^-, is a 2e reagent, like PPh_3. Table 2.4 shows the effect of net charges on some other reagents. This table also tells us about possible isoelectronic replacements of one ligand by another. So, for example, an X^- group can replace an L ligand without a change in the electron count.

$$W(CO)_5(thf) + Cl^- = [W(CO)_5Cl]^- \quad (2.5)$$

The reaction of Eq. 2.6 turns a 1e alkyl group into a 2e alkene group. To retain the 18e configuration, the complex must become positively charged, which implies that the H must be lost as H^- and that an electrophilic reagent (like Ph_3C^+) must be used. In this way the 18e rule helps us pick the right reagent.

$$Cp(CO)_2Fe{-}CH(CH_3)_2 + Ph_3C^+ = [Cp(CO)_2Fe(\eta^2\text{-}CHMe{=}CH_2)]^+ + Ph_3CH \quad (2.6)$$

TABLE 2.4 Reagent Electron Counts

0e	1e	2e	3e	4e
H^+	$H^{\bullet}$[a]	$H^-(LiAlH_4)$[b]	NO	$C_3H_5^-(C_3H_5MgBr)$
$Me^+(MeI)$	$Me^{\bullet}$[a]	$Me^-(LiMe)$		Butadiene
$Br^+(Br_2)$[c]		PPh_3, NO^+		NO^-
		Cl^-, CO, H_2		

[a]These species are unstable and so they are invoked as reactive intermediates in mechanistic schemes, rather than used as reagents in the usual way.

[b]The reagents in parentheses are the ones most commonly used as a source of the species in question.

[c]Br_2 can also be a source of $Br^{\bullet}$, a 1e reagent, as well as of Br^+, depending on conditions.

As you look at the equations in the pages to come, it is worth trying to become familiar with electron counting of stable complexes, and with counting the ligands that are gained or lost in reactions.

2.4 OXIDATION STATE

The oxidation state of a metal in a complex is simply the charge that the metal would have on the ionic model. In practice, all we have to do for a neutral complex is to count the number of X ligands. For example, Cp_2Fe has two L_2X ligands and so can be represented as MX_2L_4; this means that the oxidation state (O.S.) is 2+, so Cp_2Fe is said to be Fe(II). For a complex ion, we need also to take account of the net charge as shown for $[MX_aL_b]^{c+}$ in Eq. 2.7. For example, Cp_2Fe^+ is Fe(III), and $[W(CO)_5]^{2-}$ is W(-II). Once we have the oxidation state, we can immediately obtain the corresponding d^n configuration. This is simply the number of d electrons that would be present in the free metal ion, which corresponds to the oxidation state we have assigned. For Cp_2Fe^+ the O.S. is Fe(III), which corresponds to the Fe^{3+} ion. The iron atom, which is in Group 8, has 8e, and so the ion has $8 - 3 = 5$e. Cp_2Fe^+ is therefore said to be a d^5 complex. Equation 2.8 gives the value of n in a general form. The significance of the d^n configuration is that it tells us how to fill up the crystal field diagrams we saw in Section 1.4. For example, the odd number for Cp_2Fe^+ implies paramagnetism because in a mononuclear complex we cannot pair 5 electrons whatever the d-orbital splitting.

$$\text{O.S.} = c + a \tag{2.7}$$

$$n = N - (c + a) = N - c - a \tag{2.8}$$

Many organometallic compounds have low or intermediate formal oxidation states. High oxidation states are still rather rare, although in Chapter 15, we look at these interesting species in detail. The reason is that back donation is severely reduced in higher oxidation states because (1) there are fewer (or no) nonbonding d electrons available and (2) the increased partial positive charge present on the metal in the high-oxidation-state complex strongly stabilizes the d levels so that any electrons they contain become less available. Those high-valent species that do exist, generally come from the third-row metals. The extra shielding provided by the f electrons added in building up the lanthanides makes the outer electrons of the third-row metals less tightly bound and therefore more available.

There are many situations in which it is useful to refer to the oxidation state and d^n configuration, but they are a useful classification only and do not allow us to deduce the real partial charge present on the metal. It is therefore important not to read too much into oxidation states and d^n configurations.

Organometallic complexes are not ionic, and so an Fe(II) complex, such as ferrocene, does not contain an Fe^{2+} ion. Similarly, WH_6L_3, in spite of being W(VI), is certainly closer to $W(CO)_6$ in terms of the real charge on the metal than to WO_3. In real terms, the hexahydride may even be more reduced and more electron-rich than the W(0) carbonyl. The reason is that CO groups are excellent π acceptors, so the metal in $W(CO)_6$ has a much lower electron density than a free W(0) atom; on the other hand, the W—H bond in WH_6L_3 is only weakly polar, and so the polyhydride has a much higher electron density than the W^{6+} suggested by its W(VI) oxidation state (which assumes a dissection: $W^+ H^-$). For this reason, the term *formal oxidation state* is often used for the value of O.S. as given by Eq. 2.7.

Ambiguous Oxidation States More serious are cases in which even the formal oxidation state is ambiguous and cannot be specified. Any organometallic fragment that has several resonance forms that contribute to a comparable extent to the real structure can be affected. For example, this is the case for the resonance forms **2.15** and **2.16** in butadiene complexes. One structure is L_2 (or π_2), the other LX_2 (or $\pi\sigma_2$).* The binding of butadiene as **2.15** leaves the oxidation state of the metal unchanged, but as **2.16** it becomes more positive by two units. On the covalent model, each gives exactly the same electron count: 4e. On the ionic model, the count changes by 2e (**2.15**, 4e; **2.16**, 6e) but this is compensated by a 2e "oxidation" of the metal. In the case of W(butadiene)$_3$, we can attribute any even oxidation between W(0) and W(VI) to the molecule by counting one or more of the ligands as LX_2, rather than L_2. To avoid misunderstandings it is therefore necessary to specify the resonance form to which the formal oxidation state applies. For neutral ligands like butadiene, the neutral L_2 form is generally used because this is the stable form of the ligand in the free state. Yet structural studies show that the ligand often more closely resembles **2.16** than **2.15**. Clearly, we can

2.15 **2.16**

place no reliance on the formal oxidation state to tell us about the real charge on the metal in W(butadiene)$_3$. We will see later (e.g., Section 4.2) several ways in which we can learn something about the real charge. In spite of its ambiguities, the oxidation state convention is almost universally used in classifying organometallic complexes.

One very useful generalization is that the oxidation state of a complex can never be higher than the group number of the transition metal involved.

*We use the LX notation because it holds for all types of ligands, including carbenes and nitrosyls where a $\pi\sigma$ notation does not apply.

Titanium can have no higher oxidation state than Ti(IV), for example. This is because Ti has only four valence electrons with which to form bonds and $TiMe_6$ therefore cannot exist.

2.5 COORDINATION NUMBER AND GEOMETRY

The coordination number (C.N.) of a complex is easily defined in cases in which the ligands are all monodentate; it is simply the number of ligands present [e.g., $[PtCl_4]^{2-}$, C.N. = 4, $W(CO)_6$, C.N. = 6]. A useful generalization is that the coordination number cannot exceed 9 for the transition metals. This is because the metal only has 9 valence orbitals, and each ligand will need its own orbital. In most cases the C.N. will be less than 9, and some of the 9 orbitals will either be lone pairs on the metal or engaged in back bonding.

Each coordination number has one or more coordination geometries associated with it. Table 2.5 lists some examples. In order to reach the maximum coordination number of 9, we need relatively small ligands (e.g., $[ReH_9]^{2-}$). Coordination numbers lower than 4 tend to be found with bulky ligands, which cannot bind in greater number without prohibitive steric interference between the ligands [e.g., $Pt(PCy_3)_2$]. Certain geometries are favored by particular d^n configurations, for example, d^6 strongly favors octahedral, d^8 prefers square planar, trigonal bipyramidal, or square pyramidal, and d^4 and d^{10} prefer tetrahedral. In each case, the preferred geometry leads to a favorable occupation pattern of the orbitals in the appropriate crystal field diagram. For example, eight electrons just fill the four most stable orbitals in the square planar splitting pattern and four electrons just fill the two most stable orbitals of the tetrahedral splitting pattern of Fig. 1.4.

Unfortunately, the definition of coordination number and geometry is less clear-cut for organometallic species, such as Cp_2Fe. Is this molecule 2-coordinate (there are two ligands), 6-coordinate (there are six electron pairs involved in metal–ligand bonding), or 10-coordinate (the 10 C atoms are all within bonding distance of the metal)? Most often, it is the second definition that is used, which is equivalent to adding up the number of L's and X's from all the ligands.

Equations 2.9–2.12 summarize the different counting rules as applied to our generalized transition metal complex $[MX_aL_b]^{c+}$, where N is the Group number, and n is the d^n configuration.

Coordination number: $$\text{C.N.} = a + b \leq 9 \tag{2.9}$$

Electron count: $$N + a + 2b - c = 18 \tag{2.10}$$

Oxidation state: $$\text{O.S.} = a + c \leq N \tag{2.11}$$

d^n configuration: $$n = N - \text{O.S.} = N - a - c \tag{2.12}$$

TABLE 2.5 Some Common Coordination Numbers and Geometries

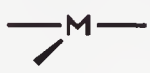
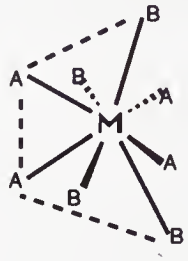
2 linear		$(Me_3SiCH_2)_2Mn$
3 trigonal		$Al(mesityl)_3$
T-shaped		$Rh(PPh_3)_3^+$
4 square planar		$RhCl(CO)(PPh_3)_2$
tetrahedral		$Ni(CO)_4$
5 trigonal bipyramidal		$Fe(CO)_5$
square pyramidal		$Co(CNPh)_5^{2+}$
6 octahedral		$Mo(CO)_6$
7 capped octahedron		$ReH(PR_3)_3(MeCN)_3^+$
pentagonal bipyramid		$IrH_5(PPh_3)_2$

TABLE 2.5 (*Continued*)

8 Dodecahedral [a]		$MoH_4(PR_3)_4$
square antiprism		TaF_8^{3-}
9 tricapped trigonal prism [b]		ReH_9^{2-}

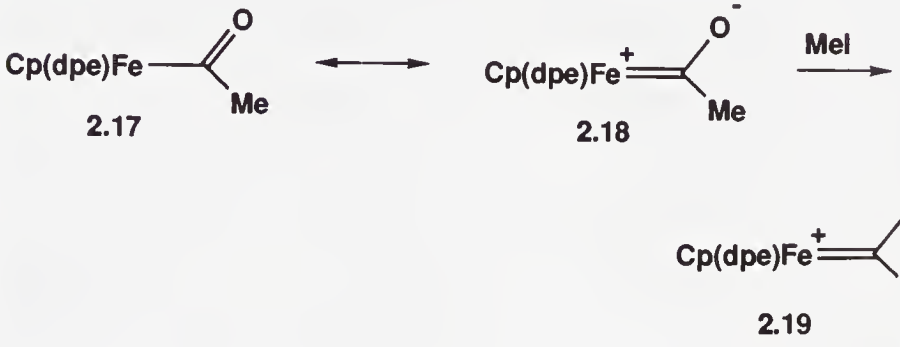
[a]The smaller ligands tend to go to the less hindered A sites. Two A and two B sites each lie on a plane containing the metal. One such plane is shown dotted, the other lies at right angles to the first.

[b]The tricapped trigonal prism is shown as viewed along its threefold axis. The vertices of the triangles are the axial ligand positions. The equatorial M—L bonds are shown explicitly.

2.6 EFFECTS OF COMPLEXATION

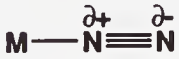
Much of the interest and importance of organometallic chemistry comes from the fact that the chemical character of many ligands is profoundly modified on binding to the metal. For the typical range of metal fragments L_nM, there is a smooth gradation of properties from strongly σ acceptor to strongly π-basic. A typical unsaturated ligand Q will be depleted of charge and made more electrophilic by a σ-acceptor L_nM fragment, and be made to accept electrons and therefore become more nucleophilic for a π-basic L_nM fragment. As an example, free benzene is very resistant to attack by nucleophiles, but reacts readily with electrophiles. In the complex $(C_6H_6)Cr(CO)_3$, in contrast, the $Cr(CO)_3$ fragment is a good acceptor, by virtue of its three CO ligands and so depletes the electron density on the aromatic ring. This makes it susceptible to nucleophilic attack, but resistant to electrophilic attack. A factor that increases the electrophilic character of the ligands is a net positive charge on the complex, such as $[Ru(\eta^6\text{-}C_6H_6)_2]^{2+}$. On the other hand, both

Cp groups and phosphines are strong donors, and so the acetyl **2.17** in Eq. 2.13 is very largely in the carbene (see Chapter 11) form **2.18**. It is subject to electrophilic attack to give **2.19**:



(2.13)

There is a third important situation that we need to consider. If the metal fragment is somewhere in the middle of the range of electronic properties mentioned above, and is both a σ acceptor and a π donor, then it might be thought that the unsaturated ligand would differ little in its chemical character from the situation in the free state. In fact, the ligand can still be strongly activated by polarization. This is because the σ donation from the ligand to the metal usually depletes the electron density of one atom or set of atoms in the ligand, but π back donation from the metal raises the electron density on a different set of atoms. For example in the case of molecular nitrogen, N_2, σ donation to the metal comes from a lone pair on the nitrogen directly bonded to the metal. The back bonding from the metal goes into a π^* orbital that is delocalized over both nitrogens. This means that the nitrogen directly bound to the metal tends to become positively charged, and the terminal nitrogen negatively charged on binding:



2.20

This polarization activates the coordinated N_2 toward chemical reactions, such as protonation at the terminal nitrogen and nucleophilic attack at the vicinal nitrogen; the free ligand is, of course, notably unreactive. The general situation is summarized in Table 2.6. If a ligand is normally reactive toward, say, nucleophiles, we can deactivate it by binding to a nucleophilic metal. The metal can then be thought of as acting as a protecting group. A ligand that is inert toward nucleophilic attack can be activated by binding to an electrophilic metal.

Free ≠ Bound The bound form of a given ligand is usually very different in properties compared to the same ligand in the free state. A knowledge of

TABLE 2.6 The Effect of the Electronic Character of a Metal Fragment on the Tendency for an Attached Ligand to Undergo Nucleophilic or Electrophilic Attack

Character of Free Ligand	Character of ML_n Fragment[a]		
	σ Acid	Polarizing	π Base
Susceptible to electrophilic attack	Suppresses susceptibility	May enhance susceptibility	Enhances
Susceptible to nucleophilic attack	Enhances susceptibility	May enhance susceptibility	Suppresses
Unreactive	May allow nu. attack	May allow both nu. and el. attack	May allow el. attack

[a]Abbreviations: nu. = nucleophilic; el. = electrophilic.

the behavior of carbenes, dienes, or other species can be misleading in trying to understand the chemistry of their complexes. For example, a notable feature of diene chemistry is their reaction with dienophiles in the Diels–Alder reaction. Dienes coordinated in the η^4 fashion do not give this reaction. In a sense, we might consider that the complex is already a Diels–Alder adduct, with the metal as the dienophile.

The properties of the metal ions as well as those of the ligands are both altered on complex formation. For example, Co(III) is very strongly oxidizing in a simple compound such as the acetate, which will even oxidize hydrocarbons. We know from Werner's work that almost all of this oxidizing power can be quenched by binding six ammonias to the Co(III) ion. The resulting $[Co(NH_3)_6]^{3+}$ ion lacks the severe electron deficiency of the acetate because of the presence of six strong σ-donor ligands. Conversely, molybdenum atoms are strongly reducing, yet $Mo(CO)_6$ is an air-stable compound with only modest reducing properties, because CO removes electron density from the metal by back donation.

Finally, it is important to remember that donor and acceptor are relative terms. If we take a complex L_nM—H, in which the hydride ligand bears no strong positive or negative charge, then we can consider the complex as arising from $L_nM^+ + H^-$, $L_nM\bullet + H\bullet$, or $L_nM^- + H^+$. We would have to regard H^- as a strong donor to L_nM^+, H^+ as a strong acceptor from L_nM^-, and H• as being neither with respect to $L_nM\bullet$. Normally the ionic model is assumed and the first type of dissection is implied.

2.7 DIFFERENT METALS

Changing the metal has an important effect on the properties of the resulting complexes. So great are the differences that it is not unusual for a single

research group to confine itself to one part of the Periodic Table. As we move from left to right, the electronegativity of the elements increases substantially. This means that the orbitals in which the electrons are located start out relatively high in energy and fall steadily as we go to the right. Table 2.7 shows the Pauling electronegativities of the transition elements. The early transition metals are electropositive and so readily lose all their valence electrons. These elements are therefore often found in the highest permissible oxidation state, such as d^0 Zr(IV) and Ta(V). Lower oxidation states, such as d^2 Zr(II) and Ta(III), are very easily oxidized, because the two d electrons are in an orbital of relatively high energy, and therefore are easily lost. These systems can be very air sensitive. Not only are they easily lost to an oxidizing agent but also have a strong tendency to be lost to the π^* orbitals of an unsaturated ligand in back donation. This makes d^2 early metal ions very π-basic and able to bind π ligands strongly with the effects we saw in Section 2.6. Ligands like CO, C_6H_6, and C_2H_4, which require back bonding for stability, will tend to bind only weakly, if at all, to d^0 metals.

Late metals, in contrast, are relatively electronegative, so they tend to retain their valence electrons. The low oxidation states, such as d^8 Pd(II), tend to be stable, and the higher ones, such as d^6 Pd(IV), often find ways to return to Pd(II); that is, they are oxidizing. Back donation is not so marked as with the early metals, and so any unsaturated ligand attached to the weak π-donor Pd(II) will accumulate a positive charge. As we see later (Eq. 5.10), this makes the ligand subject to attack by nucleophiles Nu^- and is the basis for important applications in organic synthesis.

A net anionic charge on a complex (e.g., $[MoCO)_5]^{2-}$) or the presence of donor ligands (e.g., PR_3 or Cp) tends to enhance the π basicity of the metal. Conversely, a net positive charge or the presence of π-acceptor ligands, such as NO or CO, will tend to diminish the π basicity of the metal. The extent of the effects produced can be estimated from the ν(CO) frequency changes in a series of CO complexes as shown in Table 2.8. As can be seen, the effect of net charge is surprisingly large.

First-row metals have lower M—L bond strengths and crystal field splittings compared with their second- and third-row analogs. They are more likely to

TABLE 2.7 Pauling Electronegativities of the Transition Elements[a]

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
1.3	1.5	1.6	1.6	1.6	1.8	1.9	1.9	1.9
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
1.2	1.3	1.6	2.1	1.9	2.2	2.3	2.2	1.9
La	Hf	Ta	W	Re	Os	Ir	Pt	Au
1.1	1.3	1.5	2.3	1.9	2.2	2.2	2.3	2.5

[a]Lanthanides and actinides: 1.1–1.3. The electronegativities of important ligand atoms are H, 2.2; C, 2.5; N, 3.0; O, 3.4; F, 4; Si, 1.9; P, 2.2; S, 2.6; Cl, 3.1; Br, 2.9; I, 2.6. Effective electronegativities of all elements are altered by their substituents, for example, the electronegativities estimated for an alkyl C, a vinyl C and a propynyl C are 2.5, 2.75, and 3.3 respectively.

TABLE 2.8 Effects of Changing Metal, Net Charge, and Ligands on π Basicity of a Metal, as measured by the ν(CO) values in the IR Spectrum

Changing Metal

$V(CO)_6$	$Cr(CO)_6$	$Mn_2(CO)_{10}$	$Fe(CO)_5$	$Co_2(CO)_8$	$Ni(CO)_4$
1976	2000	2013 (av)[a]	2023 (av)[a]	2044 (av)[b]	2057

Changing Net Ionic Charge in an Isoelectronic Series

$[Ti(CO)_6]^{2-}$	$[V(CO)_6]^-$	$Cr(CO)_6$	$[Mn(CO)_6]^+$
1747[c,d]	1860[d]	2000	2090

Replacing π-Acceptor CO Groups by Non-π-Acceptor Amines

$[Mn(CO)_6]^+$	$[(MeNH_2)Mn(CO)_5]^+$	$[(en)Mn(CO)_4]^+$	$[(tren)Mn(CO)_3]^+$
2090	2043(av)	2000(av)	1960

[a]Several bands are seen, average ν(CO) reported.
[b]Of isomer without bridging CO groups.
[c]This value is extremely low, well into the bridging CO region.
[d]The IR bands of this species may be lowered by coordination of the counter cation to the CO oxygen.
en = $H_2NCH_2CH_2NH_2$. tren = $H_2NCH_2CH_2NHCH_2CH_2NH_2$.

undergo 1e redox changes rather than the 2e changes often associated with the second and third rows. Finally, the first-row metals do not attain high oxidation states so easily as the second and especially the third row. Mn(V), (VII), and (VII) (e.g., MnO_4^-) are rare and usually highly oxidizing; Re(V) and (VII) are not unusual and the complexes are not strongly oxidizing.

REFERENCES

1. C. Tolman, *Chem. Soc. Rev.*, **1,** 337, 1972.
2. D. Astruc, *Acct. Chem. Res.*, **24,** 36, 1991.

PROBLEMS

Answering Problems

It is important that any intermediate you suggest in an organometallic reaction be reasonable. Does it have an appropriate electron count, coordination number, and oxidation state? If it is the only known Rh(V) carbonyl, it may be open to criticism. Check that the organic fragment is also reasonable. Sometimes students write diagrams without stopping to consider that their structure contains 5-valent carbon. Indicate the hapticity of each ligand.

1. Give the electron counts, formal oxidation states, and d^n configurations of the following: $[Pt(NH_3)_4]^{2+}$, $PtCl_2(NH_3)_2$, $PtCl_4^{2-}$, $(\eta^5\text{-}C_5H_5)_2Ni$,

$[(R_3P)_3Ru(\mu\text{-}Cl)_3Ru(PR_3)_3]^+$, ReH_9^{2-}, $CpIrMe_4$, $TaMe_5$, $(\eta^5\text{-}C_5H_5)_2TiCl_2$, and $MeReO_3$.

2. A complex is found to correspond to the empirical formula $(CO)_3ReCl$. How could it attain the 18e configuration without requiring any external ligands?

3. How could a complex of empirical formula $Cr(CO)_3(C_6H_5)_2$ attain the 18e configuration?

4. A complex $Ti(\eta^2\text{-}MeN{=}CH{-}CH{=}NMe)_2$ is found to be chelated via nitrogen. What oxidation state should we assign to Ti? Is any alternative assignment possible?

5. Count the valence electrons in the complexes shown in problem 1, but using a different model (ionic or covalent) from the one you used originally.

6. Given the existence of $(CO)_5Mn{-}Mn(CO)_5$, deduce the electron counting rule that applies to M—M bonds. Verify that the same holds for $Os_3(CO)_{12}$, which contains three Os—Os bonds and only terminal CO groups. What structure do you think is most likely for $Rh_4(CO)_{12}$?

7. Show how the valence electron count for the carbon atom $CH_3NH_3^+$ can be evaluated considering the molecule as an ammonia complex. Can the methylene carbon in $CH_2{=}C{=}O$ be treated in a similar way?

8. Water has two lone pairs. Decide whether both or only one of these should normally be counted, given that the following typical complexes exist: $IrH_2(H_2O)_2(PPh_3)_2^+$, $(\eta^6\text{-}C_6H_6)Os(H_2O)_3^{2+}$.

9. Acetone can bind in an η^2 (via C and O) and an η^1 fashion (via O). Would you expect the electron count to be the same or different in the two forms? What kind of metal fragments would you expect would be most likely to bind acetone as (a) an η^1 and (b) an η^2 ligand? Would either binding mode be expected to enhance the tendency of the carbonyl carbon to undergo nucleophilic attack?

10. Predict the hapticity of each Cp ring in $Cp_2W(CO)_2$, and of each "triphos" in $[Pd\{(PPh_2CH_2CH_2)_3CPh\}_2]^{2+}$.

11. Assign the oxidation states, d^n configurations, and electron counts for the two species shown below, which are in equilibrium in solution. Use both the covalent and ionic models.

$$W(\eta^2\text{-}H_2)(CO)_3(PR_3)_2 \rightleftharpoons W(H)_2(CO)_3(PR_3)_2$$

CHAPTER 3

METAL ALKYLS, ARYLS, AND HYDRIDES AND RELATED σ-BONDED LIGANDS

Metal alkyls and aryls are perhaps the simplest organometallic species. Yet transition metal examples remained very rare until the principles governing their stability were understood in the 1960s and 1970s. These principles make a useful starting point for our study of alkyls, because they introduce some of the most important organometallic reactions, which we will go on to study in more detail in later chapters.

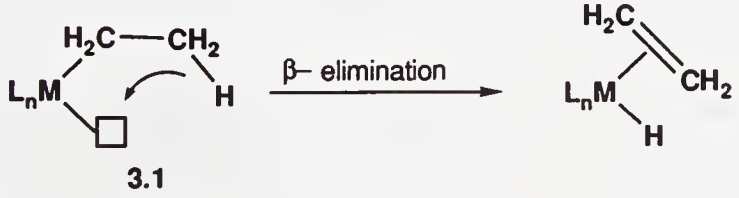
3.1 THE STABILITY OF TRANSITION METAL AKYLS AND ARYLS

In 1848, Edward Frankland attempted to prepare free ethyl radicals by the reaction of EtI with metallic zinc. Instead, he became the founder of organometallic chemistry by showing that the colorless liquid formed was diethylzinc, the first compound known to contain a metal–carbon bond. Victor Grignard's organomagnesium halides of 1900 made organometallic compounds indispensable in organic chemistry. Pope and Peachey's Me_3PtI (1909) was an early but isolated example of a *d*-block metal alkyl.

Attempts during the 1920s through 1940s to make further examples of *d*-block alkyls all failed. This was especially puzzling because by then almost every nontransition element had been shown to form stable alkyls. These failures led to the view that transition metal–carbon bonds were unusually weak; for a long time after that, few serious attempts were made to look for them. In fact, we now know that such M—C bonds are reasonably strong (30–65 kcal/mol is typical). It is the existence of several decomposition pathways that makes many metal alkyls unstable. Kinetics, not thermodynamics,

was to blame for the synthetic failures. This is fortunate because it is easier to manipulate the system to block decomposition pathways than it is to increase the bond strength. In order to be able to design stable alkyls, we must look at some of these pathways to see how they can be inhibited. This example of the historical evolution of our ideas implies that just as some of the early assumptions in this area proved to be wrong, several of our ideas today will probably turn out to be wrong, too—the problem is we do not know which ones!

β *Elimination* The major decomposition pathway for alkyls is β-*elimination*[1] (Eq. 3.1), which converts a metal alkyl into a hydridometal alkene complex. We study it in detail in Section 7.4. For the moment we need only note that the most common mechanistic type can occur whenever (1) the β carbon of the alkyl bears a hydrogen substituent; (2) the M—C—C—H unit can take up a roughly coplanar conformation,[1b] which brings the β hydrogen close to the metal; (3) there is a vacant site on the metal, symbolized here as □, cis to the alkyl; and (4) the reaction is very much more rapid for *d*-block than for Main Group alkyls. Requirements 1 and 3 arise because it is the β hydrogen of the alkyl that is transferred to the metal to give the product hydride. The geometry of the situation means that a cis site is required on the metal and a coplanar M—C—C—H arrangement in the ligand. The elimination is believed to be concerted; that is, C—H bond breaking and M—C and M—H bond making happen at the same time.



3.1

(3.1)

$$\longrightarrow \quad L_nM{-}H \quad + \quad H_2C{=}{=}CH_2$$

The term "vacant site" of requirement 3 needs some clarification. It does *not* simply mean that there be a gap in the coordination sphere large enough to accommodate the incoming ligand. There must also be an empty orbital ready to accept the β-H, or more exactly, the pair of electrons that constitutes the β-C—H bond. Another way of looking at this is to say that the electron count of the product alkene hydride is 2e more than that of the alkyl starting material. An 18e alkyl is much more reluctant to β-eliminate via a 20e intermediate than is a 16e alkyl, which can go via an 18e alkene hydride. Even if the alkene subsequently dissociates, which is often the case, we still have to stabilize the transition state leading to the alkene hydride intermediate if we want the reaction to be fast. An 18e alkyl, on the other hand, is said to be *coordinatively saturated.* By this we mean that an empty orbital is not

available. Some 18e alkyls do β-eliminate, but detailed mechanistic study often shows that the prior dissociation of some ligand is required in the rate determining step.

Main Group alkyls can also β-eliminate (e.g., Eq. 3.2), but this usually happens much more slowly. The reason for this difference is believed to be the greater ability of *d*-block metals to stabilize the transition states involved. We shall see shortly how in rare cases stable complexes exist in which transition metals stabilize what appear to be intermediate forms between simple alkyls and the hydride alkene product of β elimination.

$$[(EtMeCH)_3Al]_2 \xrightarrow{\text{reflux}} [(EtMeCH)_2Al(\mu\text{-}H)]_2 + \text{butene} \qquad (3.2)$$

To have a stable alkyl, we must block the β-elimination pathway for decomposition. This can happen for

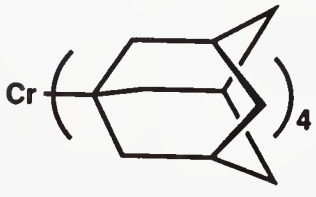
1. Alkyls that have no β hydrogen:

WMe_6, $Ti(CH_2Ph)_4$, $W(CH_2SiMe_3)_6$, $TaCl_2(CH_2CMe_3)_3$, $C_2F_5Mn(CO)_5$, $LAuCF_2CF_2Me$, $Pt(C{\equiv}CCF_3)_2L_2$, $Pt(CH_2COMe)Cl(NH_3)_2$

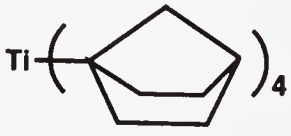
2. Alkyls for which the β hydrogen is unable to approach the metal as a result of the geometry of the ligand or because the system is very bulky:

$PtH(C{\equiv}CH)L_2$, $PdPh_2L_2$, $Cr(CMe_3)_4$, $Cr(CHMe_2)_4$, $CpL'_3MoCH{=}CHCMe_3$

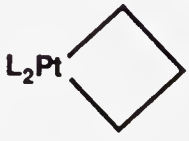
3. Alkyls in which the M—C—C—H unit cannot become *syn*-coplanar:



$[Cr(1\text{-adamantyl})_4]$



$Ti(6\text{-norbornyl})_4$

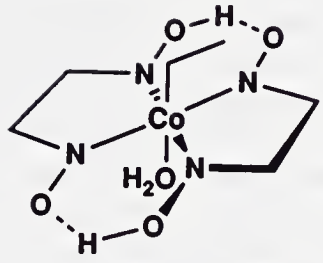


$L_2Pt(CH_2)_3$

4. A species with firmly bound ligands, which will not dissociate to generate a vacant site:

$Cp(CO)_2FeCH_2CH_3$, $Cp(CO)_3MoCH_2CH_3$,

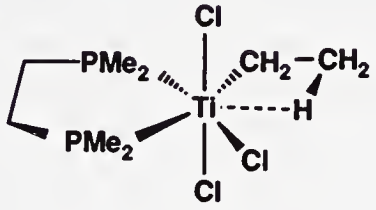
3.2 **3.3**



3.4

$Cp(CO)IrPrH$, **3.5** $[Cr(H_2O)_5Et]^{2+}$ **3.6**

5. Some d^0 alkyls:



3.7

Some of these cases call for special comment. WMe_6 has the trigonal prismatic structure **3.8**,[2a] not the octahedral structure usually found for ML_6 species. Albright and Eisenstein[2b] had previously predicted that d^0 MX_6 species would be trigonal prismatic where X is not a π donor. Methyl compounds are especially numerous, and the small size of this ligand allows the formation of polyalkyls. Often, substitution with electron-withdrawing or bulky groups (e.g., $—CH_2Ph$, $—CH_2SiMe_3$) also gives stable alkyls. The vinyl and phenyl groups both have β hydrogens, but they do not β-eliminate easily. One reason may be that the β hydrogen is further from the metal in these sp^2-hybridized systems with 120° angles at carbon, than in the sp^3 ethyl group (109°). In addition, as is the case for other electronegative alkyl groups, the phenyl and vinyl groups have stronger M—C bonds than does the ethyl group.

3.8

The *iso*-propyl and *tert*-butyl chromium complexes are unusual. Presumably, it is steric bulk that is preventing the β-C—H bond from reaching the metal. These structures seem to be sterically saturated. The examples containing noncoplanar M—C—C—H groups mainly involve cyclic alkyls, in which the rigidity of the ring system holds the M—C—C—H dihedral angle near 60°

and away from the value of 0° required for β-elimination. The fourth group includes those systems with no vacant site (**3.2**, **3.3**, and **3.5**), and others that have such a site, but not cis to the alkyl (**3.4**, assuming that the aqua ligand can dissociate). Compound **3.6** is not an 18e species, but as a d^3 Cr(III) complex it is coordination inert. Rarer are those species in which all criteria 1–3 appear to be favorable but in which β elimination still does not occur. In some of these (e.g., **3.7**) the β-C—H bond is bound to the metal in a way that suggests that the alkyl is beginning the approach to the transition state for β elimination, but the reaction has been arrested in some way. These are called *agostic* alkyls. They can be detected by X-ray or neutron crystal structural work and by the high-field shift of the agostic H in the proton NMR. The lowering of the J(C,H) and ν(CH) in the NMR and IR, respectively, on binding is symptomatic of the reduced C—H bond order in the agostic system.[3a] The most likely reason that β elimination does not occur in the case of **3.7** is that the d^0 Ti has no electron density to back-donate into the σ* orbital of the C—H bond. It is believed to be this back donation that breaks the C—H bond in the β-elimination reaction. Some d^0 alkyls are capable of β elimination, however (e.g., Eq. 3.2) but the reaction probably goes by a different mechanism, sigma bond metathesis (see Section 6.5). Agostic binding of C—H bonds also provides a way to stabilize coordinatively unsaturated species. They are also found in transition states for reactions such as alkene insertion/β-elimination either by experiment (see Fig. 11.4) or in theoretical work.[3b]

We saw earlier that we need a 2e vacant site (an empty *d* orbital) on the metal for β elimination. Now we see that we also need an available electron pair (a filled *d* orbital). There is a very close analogy between these requirements and those for binding a soft ligand such as CO. Both processes require a metal that is both σ-acidic and π-basic. In the case of CO, binding merely leads to a reduction in the CO bond order. In the case of the β-C—H bond of an alkyl group, this binding can reduce the C—H bond order to zero, by cleavage to give the alkene hydride complex. Alternatively, if the metal is a good σ acid but a poor π base, an agostic system may be the result, and the C—H bond is only weakened, not completely broken. Many of the characteristic reactions of organometallic chemistry require both σ-acid and π-base bifunctional character. This is why transition metals, with their *partly* filled *d* orbitals, give these reactions so readily.

β Elimination of halide can also occur. Early transition metals, such as Ti, the lanthanides and the actinides do not tend to form stable fluoroalkyls, because the very high M—F bond strengths of these elements encourages β elimination of the halide. The late transition metals have weak M—F bonds and do form stable fluoroalkyls. Not only do these ligands lack β-H's, but the M—C bond strengths are very high, as is also true for other alkyls MCH_2X, where X is an electronegative group. CF_3, like PF_3, can also act as a π acceptor via the σ* orbitals of the C—F bond (see Section 4.2), which also makes the M—C bond stronger for the π-basic late metals. The C_6F_5 group forms ex-

tremely stable aryls with the late transition metals in which an aryl π^* orbital acts as electron acceptor.[3c]

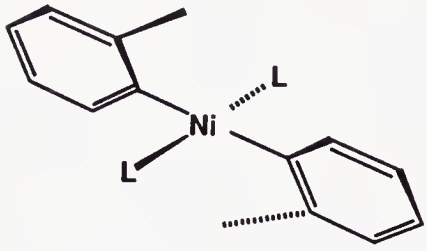
Reductive Elimination A second very common decomposition pathway for metal alkyls is *reductive elimination* (Eq. 3.3).[4] This leads to a decrease by two units in both the electron count and the formal oxidation state. (This is why the reaction is labeled "reductive.") We study it in detail in Chapter 6. In principle it is available to all complexes, even if they are d^0 or 18e, provided a stable oxidation state exists two units more reduced than the oxidation state in the starting alkyl. In fact, in many instances reductive elimination is not observed, for example, if X in **3.9** is a halogen. The reason is that for alkyl halides, the position of equilibrium for Eq. 3.3 usually lies well over to the side of **3.9**; in other words, **3.9** is usually more stable thermodynamically. Some examples of the loss of alkyl halide are known, however.

$$\underset{\textbf{3.9},\ 18e}{L_nM(Me)X} \xrightarrow{\text{red. elim.}} \underset{\textbf{3.10},\ 16e}{L_nM'} + MeX \qquad (3.3)$$

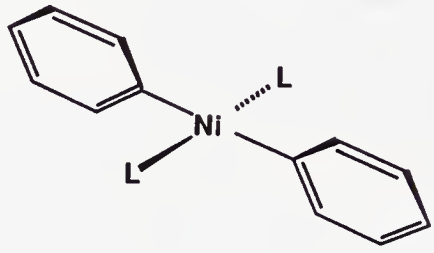
On the other hand, when X = H, the reaction is usually both kinetically facile and thermodynamically favorable, so isolable alkyl hydrides are rare. Where X = CH_3, the thermodynamics still favor elimination, but the reaction is generally much slower kinetically. It is often the case that reactions involving the movement of a hydrogen atom are much faster than those involving another element; this is because H carries no electrons other than bonding electrons, and these are in a 1*s* orbital, which is capable of making and breaking bonds in any direction in the transition state. The sp^3 orbital of the CH_3 fragment is directed in space, and so most reactions require extensive rehybridization at carbon in the transition state.

Stability from Bulky Substituents Associative decomposition pathways, such as by reaction with the solvent or with another molecule of the complex, can also be important, especially for 16e metals. These can often be supressed with bulky coligands. For example, square planar Ni(II) alkyls are vulnerable to attack along the *z* direction perpendicular to the plane. The *o*-tolyl complex **3.11**, in which this approach is blocked, is more stable than the analogous diphenyl, **3.12**, for example. This steric factor has made the use of bulky alkyl groups, such as neopentyl (CH_2CMe_3) or trimethylsilylmethyl (CH_2SiMe_3) common in organometallic chemistry.[5] It is true not only for alkyls but also for a great many other types of organometallic species that a judicious use of bulky ligands makes for a more stable complex. We see in Section 4.2 that phosphines (PR_3, R = alkyl or aryl) constitute one of the most extensive and useful series of ligands because by changing R we have good control of their steric size.

Where β elimination cannot occur for the reasons discussed above, α elimination sometimes takes over. This leads to the formation of species called



3.11



3.12

carbenes, which have M=C double bonds. The first step in the thermal decomposition of $Ti(CH_2t\text{-}Bu)_4$ is known to be α elimination to $Ti(=CHt\text{-}Bu)(CH_2t\text{-}Bu)_2$. Equations 3.4 and 3.5 show a typical decomposition pathway for a dimethyl complex. Similarly, attempts to prepare $Ta(CH_2t\text{-}Bu)_5$ led to t-BuCH=$Ta(CH_2t\text{-}Bu)_3$. Carbenes and α elimination are discussed in Sections 11.1 and 7.4.

$$L_nM(CH_3)_2 \longrightarrow L_nM{=}CH_2 + CH_4 \tag{3.4}$$

$$2\ L_nM{=}CH_2 \longrightarrow CH_2{=}CH_2 \tag{3.5}$$

3.2 THE PREPARATION OF METAL ALKYLS

The chief methods for the synthesis of alkyls involve (1) an R^- reagent, (2) an R^+ reagent, (3) oxidative addition, and (4) insertion. Typical examples of these are shown in Eqs. 3.6–3.15:

1. From an R^- reagent (nucleophilic attack on the metal):

$$WCl_6 \xrightarrow{LiMe} WMe_6 + LiCl \tag{3.6}$$

$$NbCl_5 \xrightarrow{ZnMe_2} NbMe_2Cl_3 + ZnCl_2 \tag{3.7}$$

2. From an R^+ reagent (electrophilic attack on the metal):

$$Mn(CO)_5^- \xrightarrow{MeI} MeMn(CO)_5 + I^- \tag{3.8}$$

$$CpFe(CO)_2^- \xrightarrow{Ph_2I^+} Cp_2Fe(CO)_2Ph + PhI \tag{3.9}$$

$$[Mn(CO)_5]^- \xrightarrow{CF_3COCl} CF_3COMn(CO)_5 \xrightarrow{-CO} CF_3Mn(CO)_5 \tag{3.10}$$

3. By oxidative addition:

$$IrCl(CO)L_2 \xrightarrow{MeI} MeIrICl(CO)L_2 \tag{3.11}$$

$$PtL_4 \xrightarrow{MeI} MePtIL_2 \tag{3.12}$$

$(L = PPh_3)$

$$Cr^{2+}(aq) \xrightarrow{MeI} CrMe(H_2O)_5^{2+} + CrI(H_2O)_5^{2+} \qquad (3.13)$$

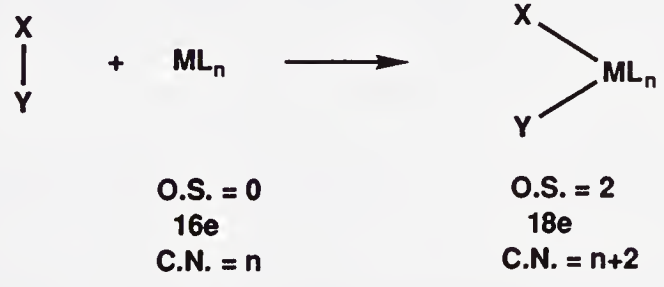
4. By insertion:

$$PtHCl(PEt_3)_2 + C_2H_4 \longrightarrow PtEtCl(PEt_3)_2 \qquad (3.14)$$

$$Cp(CO)_3MoH \xrightarrow{CH_2N_2} Cp(CO)_3MoCH_3 \qquad (3.15)$$

A Grignard or organolithium reagent usually reacts with a metal halide or a cationic metal complex to give an alkyl, often by nucleophilic attack on the metal, although other pathways can give the same products. Alternatively (case 2), a sufficiently nucleophilic metal can undergo electrophilic attack. Both these pathways have direct analogies in reactions that make bonds to carbon or nitrogen in organic chemistry (e.g., the reaction of MeLi with Me_2CO or of NMe_3 with MeI). Transfer of an alkyl group from one metal, such as Zn, Mg, or Li, to another, such as a transition metal, is called *transmetalation.* In Eq. 3.10, we use the fact that acyl complexes can often be persuaded to lose CO (Section 7.1). This is very convenient in this case because reagents that donate CF_3^+ are not available; CF_3I, for example, has a ∂^- CF_3 group and a ∂^+ I.

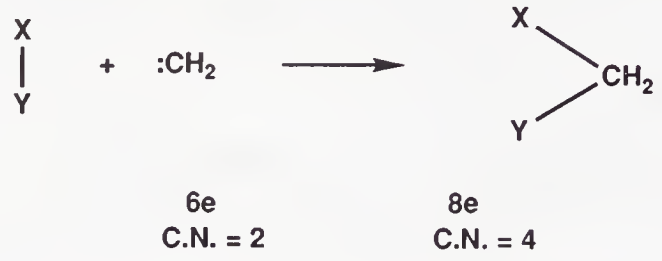
Oxidative Addition With the third general method of making alkyls, we encounter a new and very important reaction in organometallic chemistry, called *oxidative addition,* which we study in detail in Chapter 6.[6] This term is used any time we find that an X—Y bond has been broken by the insertion of a metal fragment L_nM into the X—Y bond. X and Y can be any one of a large number of groups, some of which are shown in Eq. 3.16.



(3.16)

($XY = H_2$, R_3C-H, Cl—H, RCO-Cl, Cl-Cl, Me—I, R_3Si-H)

Certain L_nM fragments are often considered carbene-like because there is an analogy between their insertion into X—Y bonds and the insertion of an organic carbene, such as CH_2, into a C—H, Si—H, or O—H bond (Eq. 3.17). In Section 13.2, we will see how the *isolobal principle* allows us to understand the orbital analogy between the two systems. There are several mechanisms



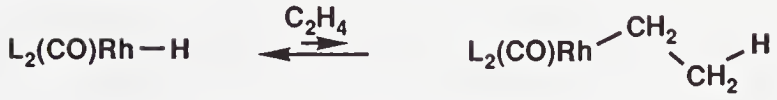
(3.17)

(XY = R_3C-H, R_3Si-H, RCO_2-H, $RO-H$)

for oxidative addition (Chapter 6). For the moment we need only note that the overall process fits a general pattern in which the oxidation state, the coordination number, and the electron count all rise by two units. This means that a metal fragment of oxidation state n can normally give an oxidative addition only if it also has a stable oxidation state of $(n + 2)$, can tolerate an increase in its coordination number by 2, and can accept two more electrons. This last condition requires that the metal fragment be 16e or less. An 18e complex can still undergo the reaction, provided at least one 2e ligand (e.g., PPh_3, or Cl^-) is lost first. Oxidative addition is simply the reverse of the reductive elimination reaction that we saw in Section 3.1.

The third example of oxidative addition (Eq. 3.13) calls for special comment. This is a binuclear variant of the reaction that is appropriate to those metals (usually from the first row) that prefer to change their oxidation state, coordination number, and electron count by one unit rather than two.

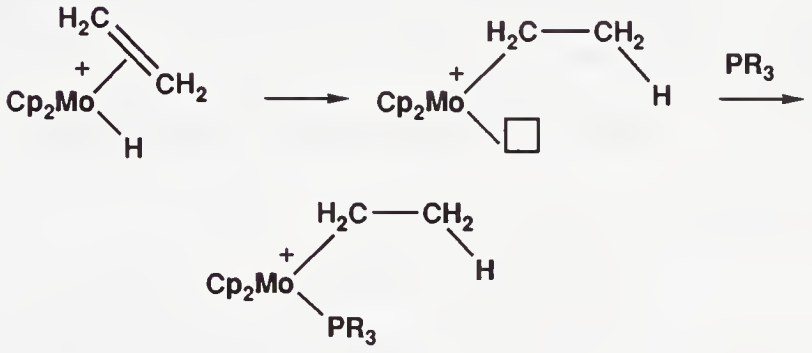
Insertion The fourth general route, *insertion* (studied in detail in Chapter 7), is particularly important because it allows us to make an alkyl from an alkene and a metal hydride. We shall see in Chapter 9 how this sequence can lead to a whole series of catalytic transformations of alkenes, such as hydrogenation with H_2 to give alkanes, hydroformylation with H_2 and CO to give aldehydes, and hydrocyanation with HCN to give nitriles. Such catalytic reactions are among the most important applications of organometallic chemistry. Olefin insertion is the reverse of the β-elimination reaction of Section 3.1. Since we insisted earlier on the kinetic instability of alkyls having β-H substituents, it might seem inconsistent that we can make alkyls of this type in this way. In practice, it is not unusual to find that only a small equilibrium concentration of the alkyl may be formed in such an insertion. This is enough to enable a catalytic reaction to proceed if the alkyl is rapidly trapped in some way. For example in catalytic hydrogenation, the alkyl is trapped by reductive elimination with a second hydride to give the product alkane. On the other hand, if the alkene is a fluorocarbon, then the product of insertion is a fluoroalkyl, and these are often very stable thermodynamically.[7] Compare the reversibility of Eq. 3.18 with the irreversible formation of the insertion product in Eq. 3.19. The reason is the high M—C bond strength in these cases, as discussed in Section 3.1.



(3.18)

(3.19)

Another way to trap the alkylmetal complex is to fill the vacant site that opens up on the metal in the insertion with another ligand:



(3.20)

Although oxidative addition can be seen as an insertion of L_nM into X—Y, the term "insertion" in organometallic chemistry is reserved for the insertion of a ligand into an M—X bond (Sections 7.1–7.3).

One final route to alkyls is the attack of a nucleophile on a metal alkene complex, but we will postpone a detailed discussion to Chapter 5. This route is more useful for the synthesis of metal vinyls from alkyne complexes; vinyls are also formed from alkyne insertion into M—H bonds:

$$[Cp(CO)(PPh_3)Fe(RC{\equiv}CR)]^+ + LiPh \xrightarrow{Cu(I)} [Cp(CO)(PPh_3)Fe{-}CR{=}CRPh] \quad (3.21)$$

3.3 CHARACTERIZATION AND PROPERTIES OF METAL ALKYLS

Metal alkyls[8] are generally characterized by ^1H and ^{13}C NMR. The strongest evidence for an M—C bond comes from the coupling of the ^{13}C and the ^1H nuclei of the alkyl to the metal, where this has a nuclear spin of $I = \frac{1}{2}$ (^{103}Rh, 100% abundance, ^{195}Pt, 34%; ^{183}W, 14%, ^{199}Hg, 17%; ^{187}Os, 1.6%, ^{199}Hg, 17%) or to phosphines, if present (^{31}P, 100%, $I = \frac{1}{2}$). The chemical shifts of the carbons and hydrogens alpha to the metal are often considerably to high field of those in the parent alkane. X-Ray crystallography is useful in characterizing alkyls, but IR spectroscopy is not, except if there is an agostic C—H, in which case it may show a C—H stretch at a frequency 100–200 cm^{-1} lower than normal. Sometimes the presence of an alkyl can be confirmed

chemically by removing it from the metal by using one of the reactions of type 3.24: the action of Br_2 to give R—Br or of $HgCl_2$ to give R—HgCl are typical examples.

Reactions of alkyls tend to fall into several general classes:

1. β Elimination (β elim.) and reductive elimination (red. elim.):

$$\mathrm{Cr}(t\text{-Bu})_3(\mathrm{thf})_3 \xrightarrow{\beta\text{-elim. } -\mathrm{CMe_2{=}CH_2}} \{\mathrm{Cr}(t\text{-Bu})_2\mathrm{H}(\mathrm{thf})_3\} \xrightarrow{\text{red. elim. } -\mathrm{CHMe_3}} \mathrm{Cr}(t\text{-Bu})(\mathrm{thf})_n \quad (3.22)$$

2. Migratory insertion:

$$\mathrm{MeMn(CO)_5} + \mathrm{CO} \longrightarrow \mathrm{(MeCO)Mn(CO)_5} \quad (3.23)$$

3. Electrophilic attack on an alkyl:

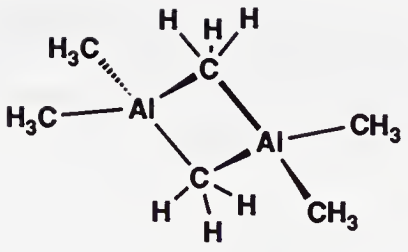
$$\mathrm{L}_n\mathrm{M{-}Me} + \mathrm{X}^+ \longrightarrow \mathrm{L}_n\mathrm{M}^+{-}\square + \mathrm{Me{-}X} \quad (3.24)$$

{X^+ = H^+ (from an acid), Br^+ (from Br_2), or $HgCl^+$ (from $HgCl_2$).
□ = empty site (2e vacancy)}

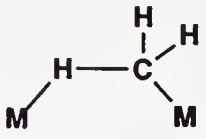
We have discussed β-elimination and reductive elimination, but the third reaction, *migratory insertion,* is new. Alkyls can migrate to a variety of unsaturated ligands of which CO is the most common. CO migration generates a metal acyl and a 2e vacant site that is filled by an incoming ligand, often CO itself. A typical example is shown in Eq. 3.23. The reaction is reversible, and so a 16e acyl can go to an 18e alkyl carbonyl complex. We study the details of migratory insertion in Section 7.1.

Electrophilic attack on an alkyl is often easy. By removing Me^-, the electrophile generates a vacant site on the metal, as well as functionalizing the R group. In these reactions the R group behaves as a weakly nucleophilic Grignard reagent, only weakly nucleophilic because a typical transition metal is much less electropositive than Mg (see Table 2.7). As expected from the electronegativity values, mercury–carbon bonds are among the most resistant to electrophilic attack, $[HgMe]^+$ being completely stable to water, and Ti alkyls are among the most nucleophilic among the transition metals.

Bridging Alkyls and Related Ligands Alkyls can also be bridging ligands. In the case of Main Group elements, such as Al, this seems to happen by a 2e, three-center bond involving only the metals and carbon [e.g., $Me_4Al_2(\mu\text{-}Me)_2$, **3.13**]. On the other hand, the transition metals tend to prefer to bridge by an agostic C—H bond (e.g., **3.14**). A number of remarkable bridges have also been found that involve an essentially planar methyl with the two metals coordinated each side of the plane (**3.15**).[2b]



3.13



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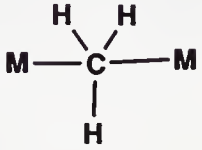
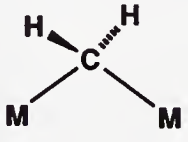


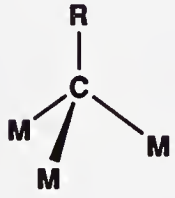
3.15

An important type of bridge related to the metal alkyl is the alkylidene, CR_2.[9] The carbon atom of this group is able to form two normal covalencies, one to each metal (e.g., **3.16**). The alkylidene can also act as a terminal ligand, in which case it forms a double bond to the metal (e.g., $Cp^*_2Ta(=CH_2)Me$), which gives it a distinctive chemistry, which we discuss



3.16

in Chapter 11. Alkylidynes, CR, can bridge to three, or to two metals or act as a terminal group with an M—C triple bond (e.g., **3.17**, **3.18**, and **3.19**). Finally, a carbon atom can bridge four metals as in $C(HgOAc)_4$ (**3.20**), but is more commonly found in *metal clusters* (Chapter 13), which are complexes that contain two or more metal–metal bonds. In the example shown (**3.21**), carbon is 6-coordinate!



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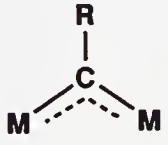
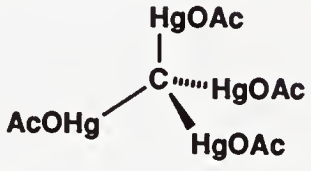


3.18

3.19



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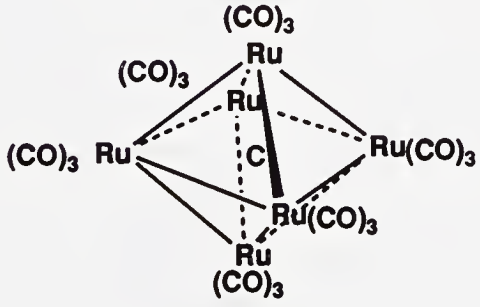


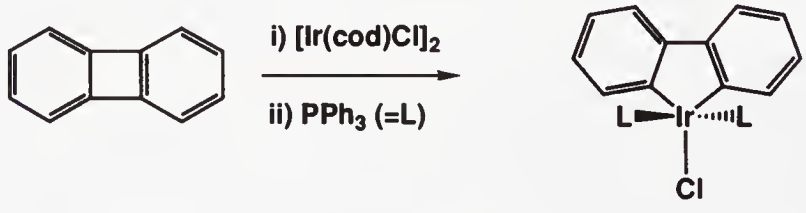
3.21

Metalacycles Cyclic dialkyls are examples of *metalacycles.*[10a] Metalacyclopropanes are more usefully thought of as metal–alkene complexes, but the higher homologs do indeed behave like dialkyls and have certain characteristic properties, such as the following interesting rearrangements:

(3.25)

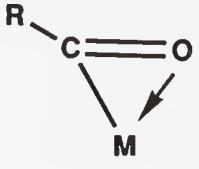
(3.26)

We look at these reactions in detail in Sections 11.3 and 6.6, respectively. For the moment we need only note that the β-C—H of these cyclic dialkyls is held away from the metal and so is not available for β elimination. The β-C—C bond *is* held close to the metal, however, and so these rearrangements are really β eliminations involving a C—C, rather than a C—H, bond. The reaction of Eq. 3.21 is of particular significance because it is the key step of an important catalytic reaction, alkene metathesis, which converts propene to butene and ethylene (Chapter 11). The anion of $[Li(tmeda)]_2[(CH_2)_4Pt(CH_2)_4]$ contains two tetramethylene rings bound to square planar Pt(II) and is thermally rather stable.[10b] Cyclic diaryls are rare; an interesting and very stable example is shown below:



(3.27)

Aryl, vinyl, and acyl ligands have empty π* orbitals that can accept electron density from the metal, and these also form strong M—C bonds. Pentahalophenyl ligands are exceptionally stable and strongly bound.[11a] Vinyls and acyls also have an alternative η^2-bonding mode[11b] shown as **3.22** and **3.23**, when the electron count goes from 1e to 3e. The η^2 forms are probable intermediates in the isomerization of metal vinyl complexes (Eq. 3.28).[11c]



3.22

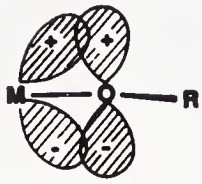
(3.28)

3.23

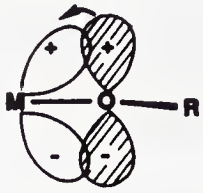
3.4 RELATED σ-BONDED LIGANDS

Group 14 Elements The closest noncarbon analog of the metal alkyl is the metal silyl M—SiR_3 (R = alkyl, aryl, or OH).[12] Trimethylsilyl transition metal complexes are much more numerous than are complexes of the *t*-butyl group, stable examples of which are rare. The most important reasons for this are probably that β elimination involving Me_3Si is inhibited by the instability of Si=C double bonds. The silyl complex is also less sterically congested than the CMe_3 group because the M—Si bond is much longer than M—C. Finally, M—SiR_3 bonds are strong because of the same π-interaction we discuss for M—PR_3 bonds in Section 4.2. Similar SnR_3 complexes are also known; an important class consists of $SnCl_3$ complexes. Polystannyl derivatives, such as $[Pt(SnCl_3)_3(cod)]^-$, are possible in this case. Many poly(trichlorostannyl) complexes are catalytically active, perhaps because the very high trans influence of this group helps labilize other ligands and so create sites for substrate binding.

Groups 15–17 On moving to the right of C in the Periodic Table, we encounter the dialkylamido, alkoxo,[13] and fluoro ligands. Examples are $[Mo(NMe_2)_4]$, $[W(NMe_2)_6]$, $[(PhO)_3Mo{\equiv}Mo(OPh)_3]$, $Zr(OtBu)_4$, and Cp_2TiF_2. Their most important feature is the presence on the heteroatom of one (—NR_2), two (—OR), or three (—F) lone pairs. In a late transition metal complex, which is 18e and so has filled *d* orbitals, these lone pairs only weaken the M—X bond by repulsion of the filled metal orbitals (**3.24**; shading denotes filled orbitals; see also Fig. 1.8). In the case of an early metal, in contrast, the complex is often d^0, and has less than 18e. There are therefore empty d_π orbitals available, which can accept electron density from the lone pairs of X and so strengthen the M—X bond (**3.25**). The early metals are therefore said to be *oxophilic* or *fluorophilic*. This effect is just one example of a general difference between the early and the late metals. As electropositive elements, the early metals are more often seen in high oxidation states. In these states they seek to attract electron density from the ligands, so hard, π-donor ligands such as NR_2, OR, or F are favored. The late metals, which are more electronegative and have more *d* electrons available, tend to prefer lower oxidation states and π-acceptor ligands such as CO (**3.26**); amide, alkoxo, and fluoro complexes of the late metals are known, however, especially in situations such as **3.27**, where the metal is 16e and so can accept some of the heteroatom lone pair electron density.[14]



3.24



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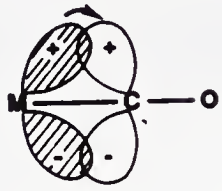

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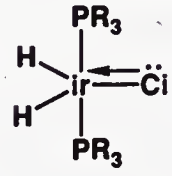
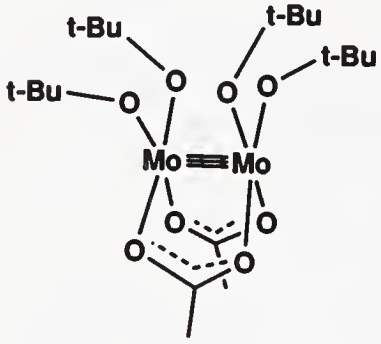
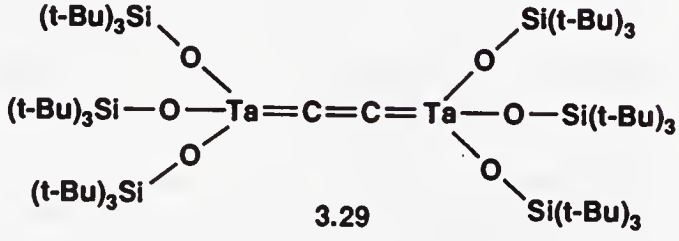


3.27

There are interesting structural consequences of this type of binding, especially in early metal complexes and with bulky alkoxides. The M—O—R angles tend to be larger than the usual tetrahedral angle. There are even cases where the angle is essentially 180°. What seems to be happening is that the oxygen rehybridizes so as to put one or both of the lone pairs in *p* orbitals, which makes them more available for overlap with empty metal *d* orbitals; this in turn makes the M—O—R angle open to 120° (**3.28**) or 180° (**3.29**).

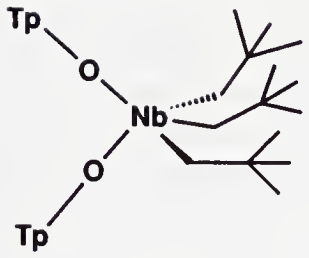


3.28



3.29

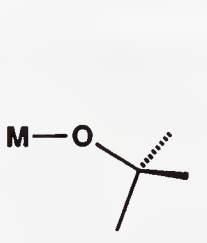
In many cases intermediate angles are also seen. The reason that the alkoxide needs to be bulky is that it can otherwise simply bridge to a second metal center, which achieves the same object of transferring electron density from the alkoxide to the metal without the necessity of rehybridizing; bulkiness strongly inhibits this bridging. A linear alkoxide can be considered as donating both of its lone pairs to the metal. As such it is now a 5e (ionic model: 6e) donor. A sufficiently bulky alkoxide of this type can give complexes reminiscent of the corresponding cyclopentadienyls (e.g., **3.30** resembles Cp_2NbX_3).[15]



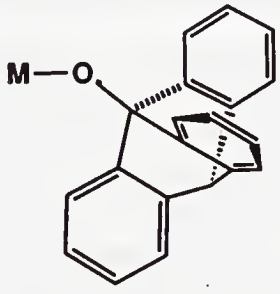
3.30
(Tp = trypticyl)

In dialkylamido ligands, NR_2, the lone pair is very basic and so the ligand often adopts a planar conformation, which puts the lone pair in a *p* orbital from which it can be donated to the metal. This resembles the situation in the planar NR_2 group found in organic amides, $RCONR_2$, where the π^* of the RCO group plays the role of acceptor.

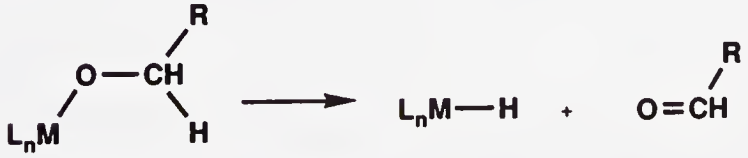
Metal alkoxides, although they lack M—C bonds, show certain similarities to alkyls; β Elimination can still occur as shown in Eq. 3.29, but instead of an alkene, a ketone or aldehyde is formed. This reaction has the important consequence that alcohols can act as reducing agents for metal complexes, especially in the presence of a base. The base converts the coordinated alcohol to the alkoxide, which can then β-eliminate. The alkoxides **3.31** and **3.32** are particularly useful ligands because they lack β hydrogens.



3.31



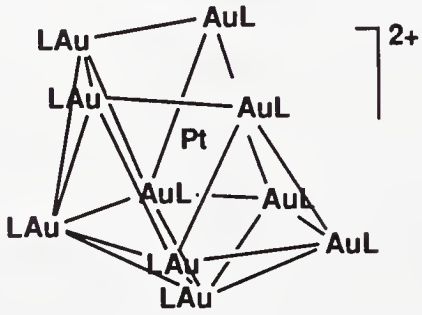
3.32



(3.29)

The heavier elements of Groups 15–17 also give σ-bonded complexes, but the ligands —PR_2, —SR, and —Cl have a much higher tendency to bridge than do their first-row analogs. This has been a serious problem in developing the chemistry of thiolate complexes, which is a particularly important area because cysteine thiolate is the soft ligand present in enzymes, the catalysts of biology.

Groups 12–13 Moving to the left of C, we come to $—BR_2$, which has an empty *p* orbital and so is in principle able to accept back-bonding electrons from a late transition metal; examples are still rare, however. M—X bonds where X is itself a metal have special properties and are considered in Chapter 13. In the case where X is $Au(PPh_3)$, the ligand is small enough to form polyaurated derivatives such as **3.33**, which show some resemblance to polyhydrides. As well as being bonded to the central metal, the gold atoms are also mutually bonded to give a *metal cluster* (Chapter 13.)



3.33

3.5 METAL HYDRIDE COMPLEXES

The M—H bond plays a very important role in organometallic chemistry because metal hydrides[16a] can undergo insertion with a wide variety of unsaturated compounds to give stable species or reaction intermediates containing M—C bonds. These are not only synthetically useful, but many of the catalytic reactions we study later involve hydride insertion as the key step.

Hieber was the first to report a metal hydride complex with the discovery of $H_2Fe(CO)_4$ in 1931. His claim that this compound contains an Fe—H bond remained controversial for many years, and the compound was generally regarded as having the structure $(CO)_2Fe(COH)_2$. Only with the discovery of Cp_2ReH, $PtHCl(PR_3)_2$, and the striking polyhydride $K_2[ReH_9]$ in the period 1955–1964, did the reality of the M—H bond as a normal covalency become widely accepted. The discovery of molecular hydrogen complexes in 1984 stimulated intense activity, which continues today. For such a simple ligand, H has a remarkably rich chemistry.

Characterization Hydrides are usually detected by ^1H NMR because they resonate to high field of TMS in a region (0–60δ) normally free of other ligand resonances. They couple with the metal, where this has ½ spin, and with cis (J = 15–30 Hz) and trans (J = 90–150 Hz) phosphines, which is often useful for determining the stereochemistry of the complex. Inequivalent

hydrogens also couple with each other (J = 1–10 Hz). IR studies show M—H stretching frequencies in the range 1500–2200 cm^{-1}, but the intensities are often weak, and so the method is not entirely reliable. Hydrides, especially paramagnetic hydrides can be very difficult to characterize.[16b]

Crystallographic studies are problematic because the hydride is such a poor scatterer of X rays. Hydrides may not be detected or may not be distinguishable with certainty from random electron density maxima in the neighborhood of the metal. Since X rays are scattered by electron density, not by the atomic nuclei, it is the M—H bonding electrons that are detected; these lie between the two nuclei, so that X-ray methods systematically underestimate the true M—H internuclear distance by approximately 0.1 Å. The best data for detecting hydrides are obtained at low temperatures (to reduce thermal motion) and at low angles (because hydride tends to give low angle scattering). Neutron diffraction detects the proton itself, which scatters neutrons relatively efficiently, so accurate distances can be obtained, but much larger crystals (1 mm^3 vs. 0.01 mm^3) are usually needed for neutron work.

Synthesis The main synthetic routes to hydrides are shown in Eqs. 3.30–3.36:

1. By protonation:

$$[Fe(CO)_4]^{2-} \xrightarrow{H^+} [HFe(CO)_4]^- \xrightarrow{H^+} H_2Fe(CO)_4 \qquad (3.30)$$

$$Cp_2WH_2 \xrightarrow{+H^+} [Cp_2WH_3]^+ \qquad (3.31)$$

2. From hydride donors:

$$WCl_6 + LiBEt_3H + PR_3 \longrightarrow WH_6(PR_3)_3 \qquad (3.32)$$

3. From H_2:

$$IrCl(CO)(PPh_3)_2 \xrightarrow{H_2} IrH_2Cl(CO)(PR_3)_2 \qquad (3.33)$$

$$WMe_6 + PMe_2Ph \xrightarrow{H_2} WH_6(PMe_2Ph)_3 \qquad (3.34)$$

4. From a ligand:

$$RuCl_2(PPh_3)_3 + KOCHMe_2 + PPh_3 \longrightarrow RuH_2(PPh_3)_4 + Me_2CO + KCl \qquad (3.35)$$

$$Cr(CO)_6 + OH^- \longrightarrow [Cr(CO)_5(COOH)]^- \xrightarrow{-CO_2} [CrH(CO)_5]^- \xrightarrow{Cr(CO)_6,\ -CO} [(CO)_5Cr—H—Cr(CO)_5]^- \qquad (3.36)$$

Protonation requires a basic metal complex, but the action of a Main Group hydride on a metal halide is very general. The third route, oxidative addition,

requires a metal that can undergo this reaction, but is of particular importance in catalysis. The reaction of hydrogen with the d^0 alkyl WMe_6 cannot go via oxidative addition because that would cause the W to exceed its maximum permitted oxidation state of six. This type of reaction is called *σ-bond metathesis*. Finally, hydrides are formed by the β elimination of a variety of groups.

Reactions Hydrides are kinetically very reactive species and undergo a wide variety of transformations; some of the more significant are shown in Eqs. 3.37–3.40. Hydride transfer and insertion are closely related; the former implies that a hydridic hydride is attacking an electrophilic substrate.

1. Deprotonation:

$$WH_6(PMe_3)_3 + NaH \longrightarrow Na[WH_5(PMe_3)_3] + H_2 \quad (3.37)$$

2. Hydride transfer and insertion:

$$Cp^*_2ZrH_2 + CH_2O \longrightarrow Cp^*_2Zr(OMe)_2 \quad (3.38)$$

$$Cp_2ZrHCl + RCH{=}CH_2 \longrightarrow Cp_2ZrCl(CH_2{-}CHR) \quad (3.39)$$

3. H atom transfer:

$$[Co(CN)_5H]^{3-} + PhCH{=}CHCOOH \longrightarrow [Co(CN)_5]^{3-} + PhC{\bullet}H{-}CH_2COOH \quad (3.40)$$

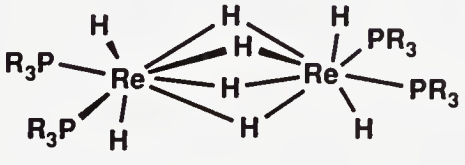
Several carbonyl hydrides are quite strong acids because the CO groups are able to delocalize the negative charge of the corresponding metal anion, such as $HCo(CO)_4$. When bound to the more electropositive early metals, the hydrogen tends to carry a significant negative charge, and these hydrides tend to be the most reactive toward transfer of H^- to an electrophilic substrate such as an aldehyde or ketone (Eq. 3.38). The later metals impart much less negative charge to the hydride (the hydride may even be positively charged in some cases), so that the word *hydride* should not be taken to imply the presence of H^-. Protonation of a hydride with loss of H_2 is a common method to open up a coordination site; for example, $IrH_5(PCy_3)_2$ reacts with HBF_4 in MeCN to give $[IrH_2(MeCN)_2(PCy_3)_2]^+$, the first step of which is shown in Eq. 3.45.

The reactivity of a hydride may depend strongly on the nature of the reaction partner. For example, $CpW(CO)_3H$ has been shown to be an H^+ donor toward simple bases, an $H\bullet$ donor toward styrene, and an H^- donor to a carbonium ion.[16c] Many hydrides react with excess CCl_4 to give $CHCl_3$ and the metal chloride, a reaction which has been used to detect metal hydride complexes.

Bridging Hydrides Hydrides have a high tendency to bridge two or more metals.[17] This bridge is bent and resembles a BHB bridge in boranes but is quite unlike the linear hydrogen bond, which results from an electrostatic attraction. It can be thought of as a σ-bond complex (Section 1.8) in which M—H as the donor binds to M′ as the acceptor. Note the difference between this situation, where the pair of electrons in the M—H bond is the donor, and that for other bridging ligands in which a lone pair on the bridging atom acts as the donor to the second metal (M—Cl: → M). One way of counting electrons in this system is to consider M—H as a 2e donor to M′. For example, in $[(CO)_5Cr—H—Cr(CO)_5]^-$, we can put the charge on one Cr and regard that Cr as the M—H donor to obtain $[(CO)_5Cr^-—H→Cr(CO)_5]$. Both Cr are now 18e species. The three-center bonding of a σ-bond complex implies the presence of M—M bonding. (In Section 13.1 we look at another convention for counting bridging hydrides.) The same idea can be applied synthetically;[18] for example, $L_nM—H$ often reacts with 16e $M'L'_n$ [or the equivalent system stabilized by a labile solvent $(solv)M'L'_n$] to give the bridged species $L_nM—H—M'L'_n$. Subsequent rearrangement to give multiply bridged systems, such as $[L_2HIr(\mu\text{-}H)_3IrHL_2]^+$ or $[H_2L_2Re(\mu\text{-}H)_4ReH_2L_2]$ (L = PPh_3), commonly occurs, however.

Typical preparative routes to complexes with bridging hydrides involve the generation of a vacant site in the presence of a hydride, but in the absence of any other species that would be a better ligand than M—H.[18] Some examples are shown in Eqs. 3.41–3.44:

$$ReH_7(PR_3)_2 \xrightarrow{-H_2}$$



(3.41)

3.34

$$(triphos)FeCl_2 + NaBH_4 \longrightarrow [\{(triphos)Fe\}_2(\mu\text{-}H)_3]^+ \quad (3.42)$$

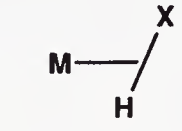
$$[(dpe)Rh(Me_2CO)_2]^+ + H_3IrL_3 \longrightarrow [(dpe)Rh(\mu\text{-}H)_3IrL_3]^+ \quad (3.43)$$

$$Cp_2NbH_3 + Fe(CO)_5 \longrightarrow Cp_2Nb—H—Fe(CO)_4 \quad (3.44)$$

(L = PEt_3)

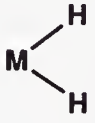
In Eq. 3.41 the 2e vacancy is probably created by loss of H_2 from the heptahydride. The product (**3.34**) is interesting in that it was the first and still is one of the very few $(\mu\text{-}H)_4$ species, and it is one of the rare cases in which the counting convention described above does not yield an 18e configuration (but 2 × 19e instead). We discuss these systems in more detail under metal clusters (Chapter 13).

H_2 Complexes and Nonclassical Hydrides As we saw in Section 1.8, H_2 and a number of X—H bonds such as C—H and Si—H can bind to 16e metal fragments as σ-bond complexes[19a] (e.g., **3.35**) or by oxidative addition (**3.36**). The stronger the back-donation component of the bonding (Fig. 1.9*b*), the more the bond is stretched relative to the free ligand until finally the X—H bond breaks completely in an oxidative addition. Hydrogen complexes (**3.37**) were discovered in 1984 by Kubas[19b], and many examples are now known

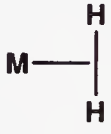


3.35

(X = R_3C or R_3Si)

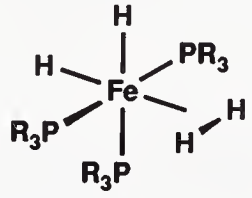


3.36

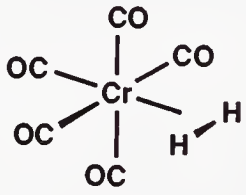


3.37

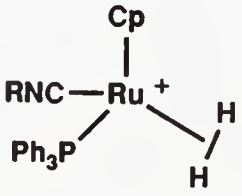
(**3.38–3.41**). Most have H—H distances of 0.82–1 Å, which are not very different from that in free H_2 (0.74 Å). These unstretched H_2 complexes are formed with the M→(H_2) π back-donation component of the bond is weak. The bound H_2 is very much more acidic than free H_2 [pK_a = 35 (free) or 0–15 (bound)], perhaps because the M—H_2 σ bond depletes the electron density on the H_2.



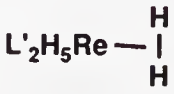
3.38



3.39



3.40



3.41

(L' = $P(o\text{-tol})_3$)

Complexes with H—H bonds are often called *nonclassical* hydrides.[20a] By the bonding model of Fig. 1.9*b*, we expect that more π-basic metals will tend to split the H_2 and form a classical dihydride **3.36**, while less π-basic metals will tend to form the dihydrogen complex, **3.37**. Morris[20b] has shown how increasing the electron density at the metal favors **3.37** by looking at the IR

stretching frequency of the corresponding N_2 complex: the lower $\nu(N_2)$ the more π-basic the site, and the more **3.37** is favored. Since π-basicity rises as we go down the Periodic Table, this accounts for the difference in structure between the nonclassical tetrahydride, $M(H_2)H_2(PR_3)_3$, where M is Fe or Ru, and the classical Os analog $OsH_4(PR_3)_3$. The role of a positive charge in reducing the basicity of a metal center is illustrated by Eq. 3.45, in which a classical pentahydride is protonated to give a bis(dihydrogen) dihydride cation.[20a]

$$Ir^{V}H_5(PCy_3)_2 + H^+ \longrightarrow [Ir^{III}(H_2)_2H_2(PCy_3)_2]^+ \qquad (3.45)$$

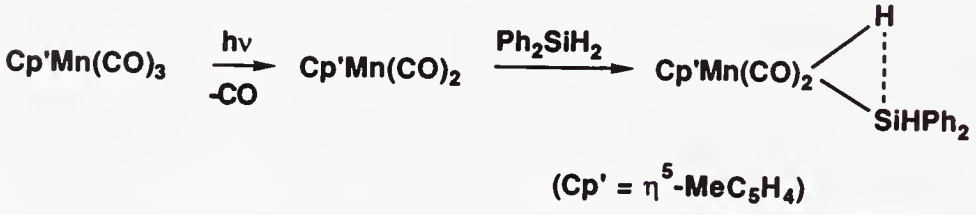
In some cases, including Kubas's complex itself, **3.36** and **3.37** are in tautomeric equilibrium in solution.

Coordinated dihydrogen can often be deprotonated with base;[20] for $[Ir(H_2)_2H_2(PCy_3)_2]^+$ this happens even with NEt_3. In $[CpRe(NO)(CO)(H_2)]^+$, the H_2 ligand has a pK_a of -2.5, making it a strong acid.[20c] Formation of an H_2 complex can be a good way to activate it heterolytically, in which case H^- is retained by the metal and H^+ is released. Several H_2 complexes can both exchange with free H_2 or D_2 and exchange with solvent protons and thus can catalyze isotope exchange between gas-phase D_2 and solvent protons.[20d]

The classical hexahydride $[WH_6(triphos)]$ (triphos = $PhP(CH_2CH_2PPh_2)_2$) protonates to give "$[WH_7(triphos)]^+$", which is stable below $-20°$. The product is particularly interesting because as written it would be d^{-2} W(VIII) and disobey the maximum oxidation state rule of Eq. 2.11, so the cation cannot be classical. It is probably $[WH_3(H_2)_2(triphos)]^+$, which would make it 8-coordinate d^2 W(IV).[20c] Cp*FeH(dppe) shows faster protonation at the Fe—H bond, so that $[Cp^*Fe^{II}(H_2)(dppe)]^+$ is obtained at $-80°C$; on warming above $-40°C$, the complex irreversibly converts to the classical form $[Cp^*Fe^{IV}(H)_2(dppe)]^+$. The Fe—H is the better kinetic base (faster protonation), but the Fe is the better thermodynamic base (more stable).[20g]

Characterization Dihydrogen complexes have been characterized by X-ray, or, much better, neutron diffraction. An IR absorbtion at 2300–2900 cm^{-1} is assigned to the H—H stretch, but it is not always seen. The H_2 resonance appears in the range 0 to -10δ in the ^1H NMR, and is often broad. The presence of an H—H(D) bond is shown by the H,D coupling constant of 20–34 Hz in the ^1H NMR spectrum of the H—D analog. This compares with a value of 43 Hz for free HD and ~1 Hz for classical H—M—D species. The H,D coupling is further reduced in *fluxional* polyhydrides, in which the protons rapidly exchange between classical and nonclassical sites. Relaxation time (T_1) and isotopic perturbation measurements in the ^1H NMR can still be used to give structural information. We will look at some of these NMR methods in detail in Chapter 10.

Stretched H_2 complexes with H—H distances above 1 Å are less common; for example, d(H—H) is 1.36 Å (n-diffraction) in **3.41**. They are difficult to distinguish from classical hydrides other than by neutron diffraction, because their J(H,D) and T_1 values resemble those of classical hydrides. Being on the classical/nonclassical borderline, their H—H distance is much more strongly affected by ligand electronic effects than for unstretched H_2 complexes. Just changing R in $[Re(H_2)H_5\{P(p\text{-}RC_6H_4)_3\}_2]$ from the donor —OMe to the acceptor —CF_3 is sufficient to change the H—H distance from 1.24 to 1.42 Å.[20f] Dihydrogen complexes are related to agostic alkyls in that both are σ-bond complexes where X—H (X = H or C) binds to a metal without breaking. σ-Bond complexes are now also known or suspected for X = Si, Sn, B, P, and S.[20a] While atoms in organic compounds are either bonded or nonbonded, inorganic compounds can have bond orders between 0 and 1. That is why many structures have dotted lines, indicating partial bonds, e.g., Eq. 3.46.



(3.46)

3.6 BOND STRENGTHS FOR CLASSICAL σ-BONDING LIGANDS

Classical σ-bonding ligands such as H, CH_3 and Cl form strong M—X bonds with metals. Bond strengths or bond dissociation energies (BDEs) are defined as the energy required to break the M—X bond homolytically, that is, by

$$L_nM—X \longrightarrow L_nM\bullet + X\bullet. \tag{3.47}$$

Bond strengths can be useful guides in predicting whether proposed steps in catalytic cycles are energetically reasonable. For example, oxidative addition of a C—F bond to a metal would require that the necessary loss of the large C—F bond energy of ~120 kcal/mol be compensated by the formation of sufficiently strong M—C and M—F bonds. It is much more difficult to determine BDEs in organometallic chemistry than it is for organic compounds because the latter usually burn cleanly to give defined products, and calorimetry is therefore possible. Instead, a number of other methods have been developed. For example, Fig. 3.1 illustrates a thermodynamic cycle that has proved useful for studies on metal hydrides. It relies on our ability to measure all the other steps in the cycle except the one involving the M—H BDE, and therefore to estimate the BDE by Hess's law. By measuring the acid dissociation constant of the hydride and the potential required for oxidizing the

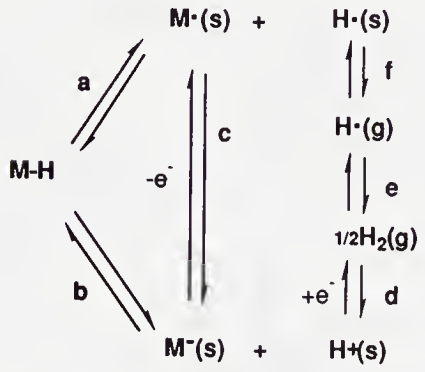


FIGURE 3.1 Thermodynamic cycle involved in one method of determining the M—H bond strength.

conjugate base, the metal anion, the ΔG values corresponding to steps *b* and *c* can be estimated from Eqs. 3.48–3.49.

$$\Delta G = -RT \ln K \tag{3.48}$$

$$\Delta G = \frac{RT}{F} \ln E_0 \tag{3.49}$$

The H^+/H_2 potential gives ΔG for step *d*, leaving the bond strength of H_2 and the solvation energy of H•, which are both known. The only unknown is now the M—H BDE. Methods useful for M—C BDEs are discussed in Section 16.2.[21]

Typical data[22] for M—X BDEs of various types are shown in Fig. 3.2, in which the M—X BDE is plotted against the H—X BDE. The good correlation between the two set of figures is rather surprising. The only significant deviation is the case of L_nM—H, which is normally stronger than L_nM—CH_3 by 15–25 kcal/mol. even though Me—H and H—H have almost the same BDEs. Labinger and Bercaw[23a] have discussed this problem in some detail.

In organic chemistry it is a useful approximation to say that the same type of bond will have a very similar bond strength wherever it occurs. In organometallic compounds this seems to be true less often.[23b] The activation energy for phosphine loss from $Cp^*Ru(PMe_3)_2X$ (**3.42**) is a measure of the M—P bond strength, because the incoming ligand is believed not to bond significantly to the metal in the transition state and the PMe_3 is almost completely lost (D mechanism; see Section 4.3), so the barrier to the process is essentially equal to the M—P BDE. If the M—P BDE were constant, the activation energy would not change as X changes. Table 3.1 shows that for a series of σ-bonding ligands, the activation energy differences (and therefore M—P BDE differences) relative to the X = Me compound vary widely depending on the steric size of the ligand. Organic compounds, with 4-coordinate carbon, do not normally have strong intersubstituent repulsions. In contrast, metal ions in organometallic compounds often have much higher coordination num-

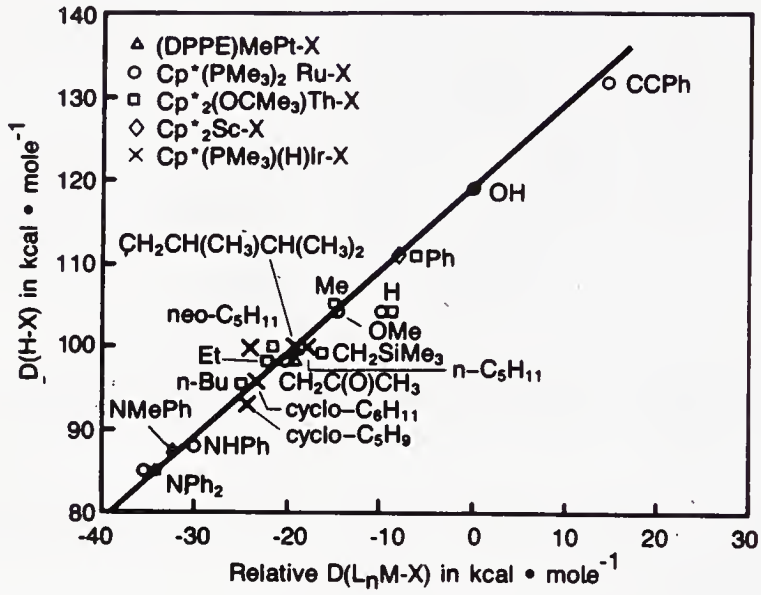
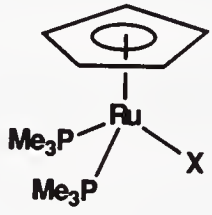


FIGURE 3.2 The relative bond energies $D(L_nM—X)$ versus the HX bond energy D(H—X) showing the good correlation obtained. Reproduced from ref. 22 with permission.

bers. For example, in **3.42**, 8 atoms are directly bonded to the metal. Intraligand repulsions are therefore common and relief of these repulsions on ligand dissociation favors ligand loss and makes the M—P bond weaker.



3.42

TABLE 3.1 M—P Bond Strength Differences in $Cp^*(Me_3P)XRu(—PMe_3)$ as a Function of the Nature of X

		σ-Donor Ligands			
H	>7	—C≡CPh	+2	CH_3	0[a]
CH_2Ph	−2	Ph	−3	CH_2SiMe_3	−6
		π-Donor Ligands			
CH_3	0[a]	−Cl	−7	OH	−11
NHPh	−12	Ph	−3		

[a]Zero by definition: this non-π-donor ligand is taken as a reference point for all the compounds studied.

3.43

The barrier for PMe_3 loss is also affected when X is a π-donor ligand, because X is then capable of stabilizing the 16e $Cp^*Ru(PMe_3)X$ fragment by π-electron donation from X to Ru (as illustrated in **3.43**). Relative to the non-π-bonding X = Me case, the barrier to PMe_3 loss is lowered by the presence of a π-donor X, to an extent that roughly corresponds with the π-donor power of X. This electronic effect is comparable in importance to the steric effect discussed above. All this may mean that no one set of BDE values is likely to be generally applicable in organometallic chemistry.

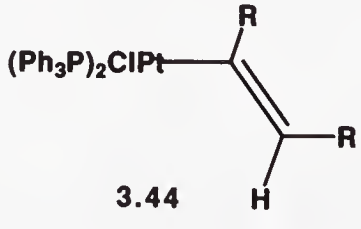
REFERENCES

1. G. M. Whitesides et al., *J. Am. Chem. Soc.*, **98,** 6521, 1976; (b) ibid., **94,** 5258, 1972.
2. (a) A. Haaland et al., *J. Am. Chem. Soc.*, **112,** 4547, 1990; (b) T. A. Albright, O. Eisenstein, et al., *Inorg. Chem.*, **28,** 1611, 1989.
3. (a) M. Brookhart and M. L. H. Green, *J. Organomet. Chem.*, **250,** 395, 1983; M. L. H. Green, *Prog. Inorg. Chem.*, **36,** 1, 1988; (b) N. Koga and K. Morokuma, Chap. 6 in *Transition Metal Hydrides,* A. Dedieu (ed.), VCH, Weinheim, 1992; (c) R. Usón et al., *J. Organometal. Chem.*, **447,** 137, 1993.
4. J. M. Brown and N. A. Cooley, *Chem. Rev.*, **88,** 1031, 1988; G. M. Whitesides et al., *Inorg. Chem.*, **21,** 2162, 1982.
5. R. R. Schrock, *Acct. Chem. Res.*, **23,** 158, 1990.
6. L. Vaska, *Acct. Chem. Res.*, **1,** 335, 1968.
7. T. J. Marks, *Bonding Energetics in Organometallic Compounds,* ACS (American Chemical Society) Symp. Ser., 1990.
8. R. R. Schrock and G. W. Parshall, *Chem. Rev.*, **76,** 243, 1976.
9. W. A. Herrman, *Angew. Chem., Int. Ed.*, **17,** 800, 1978.
10. (a) D. J. Cole-Hamilton et al., *Polyhedron,* **1,** 739, 1982; (b) H.-O. Fröhlich et al., *Angew. Chem. Int. Ed.*, **32,** 387, 1993.
11. (a) R. Usón et al., *Adv. Organometal. Chem.*, **28,** 219, 1988; (b) L. D. Durfee and I. P. Rothwell, *Chem Rev.*, **88,** 1059, 1988; (c) R. Tanke and R. H. Crabtree, *J. Am. Chem. Soc.*, **112,** 7984, 1990.
12. T. D. Tilley, in *The Chemistry of Organosilicon Compounds,* S. Patai (ed.), Wiley, Chichester, UK, 1989, Vol. 2, p. 1415; W. R. Roper, L. J. Wright, et al., *J. Am. Chem. Soc.*, **114,** 9682, 1992.
13. K. G. Caulton and L. G. Hubert-Pfalzgraf, *Chem. Rev.*, **90,** 969, 1990.
14. O. Eisenstein, K. G. Caulton, et al., *Organometallics,* 00,000 1992; in press; H. E. Bryndza and W. Tam., *Chem. Rev.*, **88,** 1163, 1988; M. D. Fryzuk et al., *Organometallics,* **5,** 2469, 1986.
15. P. T. Wolczanski et al., *Organometallics,* **4,** 1810, 1985.

16. (a) A. Dedieu, *Transition Metal Hydrides,* VCH, New York, 1992; (b) J. L. Kersten, A. L. Rheingold, K. H. Theopold, and C. P. Casey, *Angew. Chem.*, **31,** 1341, 1992; (c) R. M. Bullock et al., *Comments Inorg. Chem.*, **12,** 1, 1991; *J. Am. Chem. Soc.*, **112,** 6886, 1990; R. M. Bullock, J. R. Norton, et al., *Angew. Chem. Int. Ed.*, **31,** 1233, 1992.
17. R. Bau, R. G. Teller, S. W. Kirtley, and T. F. Koetzle, *Acct. Chem. Res.*, **12,** 176, 1979.
18. L. M. Venanzi, *Coord. Chem. Rev.*, **43,** 251, 1982.
19. (a) U. Schubert, *Adv. Organometal. Chem.*, **30,** 1, 1990; (b) G. J. Kubas et al., *J. Am. Chem. Soc.*, **106,** 451, 1984; *Acct. Chem. Res.*, **21,** 190, 1988.
20. (a) R. H. Crabtree, *Acct. Chem. Res.*, **23,** 95, 1990; *Ang. Chem., Int. Ed.*, **32,** 789, 1993; (b) R. H. Morris et al., *Coord. Chem. Rev.*, **121,** 155, 1992; (c) D. M. Heinekey et al., *J. Am. Chem. Soc.*, **112,** 5166, 1990, and references cited therein; (d) A. C. Albeniz, D. M. Heinekey, and R. H. Crabtree, *Inorg. Chem.*, **30,** 3632, 1991; A. C. Albeniz, R. H. Crabtree, et al., *Organometallics,* **11,** 242, 1992; (e) D. Michos, X.-L. Luo, J. W. Faller, and R. H. Crabtree, *Inorg. Chem.*, **32,** 1370, 1993; (f) D. Michos, X.-L. Luo, J. A. K. Howard, and R. H. Crabtree, *Inorg. Chem.*, **31,** 3914, 1992; (g) C. Lapinte et al., *J. Organometal. Chem.*, **428,** 49, 1992.
21. J. Halpern, *Inorg. Chim. Acta,* **100,** 41, 1985.
22. H. E. Bryndza, J. Bercaw, et al., *J. Am. Chem Soc.*, **109,** 1444, 1987.
23. (a) J. Labinger and J. E. Bercaw, *Organometallics,* **7,** 926, 1988; (b) H. E. Bryndza, J. E. Bercaw, et al., *Organometallics,* **8,** 379, 1989.

PROBLEMS

1. $[(Ph_3P)_2Pt(RC{\equiv}CR)]$ reacts with HCl to give **3.44**. Propose a mechanism for this process to account for the fact that the H in the product vinyl is endo with respect to the metal, as shown in **3.44**.



3.44

2. In which direction would you expect a late transition metal hydride to undergo insertion with $CH_2{=}CF_2$ to give the most stable alkyl product?

3. Suggest an efficient method for preparing $IrMe_3L_3$ from $IrClL_3$, LiMe, and MeCl.

4. Propose three alkoxides, which should be as different in structure as possible, that you would examine in trying to make a series of stable metal derivatives, say, of the type $Mo(OR)_6$. Would you expect $CpFe(CO)_2(OR)$ to be linear or bent at O? Explain.

4. What is the metal electron count for $H_2Fe(CO)_4$ and ReH_9^{2-}? Would the electron count be changed if any of these species had a nonclassical structure?

5. Ligands of type X—Y only give 2e three-center bonds to transition metals if either X or Y is a hydrogen. Why do you think this is so? (*Hint:* Consider possible alternative structures if X and Y are nonhydrogen groups.)

6. Reductive eliminations can sometimes be encouraged to take place by oxidizing the metal. Why do you think this is so?

7. Given that the homo of a d^8 square planar complex is the d_{z^2} orbital, predict which rotamer of the aryl groups in $NiPh_2L_2$ will be (a) electronically and (b) sterically favored.

8. Give the electron counts, oxidation states, and d^n configurations in the following: $L_3Ru(\mu\text{-}CH_2)_3RuL_3$, $[(CO)_5Cr(\mu\text{-}H)Cr(CO)_5]^-$, and WMe_6.

9. $Me_2CHMgBr$ reacts with $IrClL_3$ to give $IrHL_3$. How can this be explained, and what is the other product formed?

10. Certain 16e metal hydrides catalytically convert free 1-butene to free 2-butene. Propose a plausible mechanism, using the symbol [M]—H to represent the catalyst. Would an 18e metal hydride be able to carry out this reaction?

CHAPTER 4

CARBONYLS, PHOSPHINE COMPLEXES, AND LIGAND SUBSTITUTION REACTIONS

In this chapter, we first examine how CO, phosphines, and related species act as ligands, then look at ways in which one ligand can replace another by *substitution:*

$$L_nM—L + L' = L_nM—L' + L \tag{4.1}$$

This has been studied in most detail for the case of the substitution of CO groups in metal carbonyls by a variety of other ligands, such as tertiary phosphines, PR_3. The principles involved will be important later, for example, in catalysis.

4.1 METAL COMPLEXES OF CO, RNC, CS, AND NO

Unlike a simple alkyl, CO is an unsaturated ligand, by virtue of the C—O multiple bond. As we saw in Section 1.6, such ligands are soft because they are capable of accepting metal d_π electrons by back bonding; that is, these ligands are π acceptors. This contrasts to hard ligands, which are σ donors, and often π donors, too (e.g., H_2O, alkoxides).

As we saw in Section 1.6, we look first at the frontier orbitals of M and L because these usually dominate the bonding. The electronic structure of free CO is shown in Fig. 4.1*a* and 4.1*b*. We start with both the C and the O sp^2-hydridized. The singly occupied *sp* and p_z orbitals on each atom form a σ and a π bond, respectively. This leaves the carbon p_y orbital empty, and the oxygen p_y orbital doubly occupied, and so the second π bond is formed only

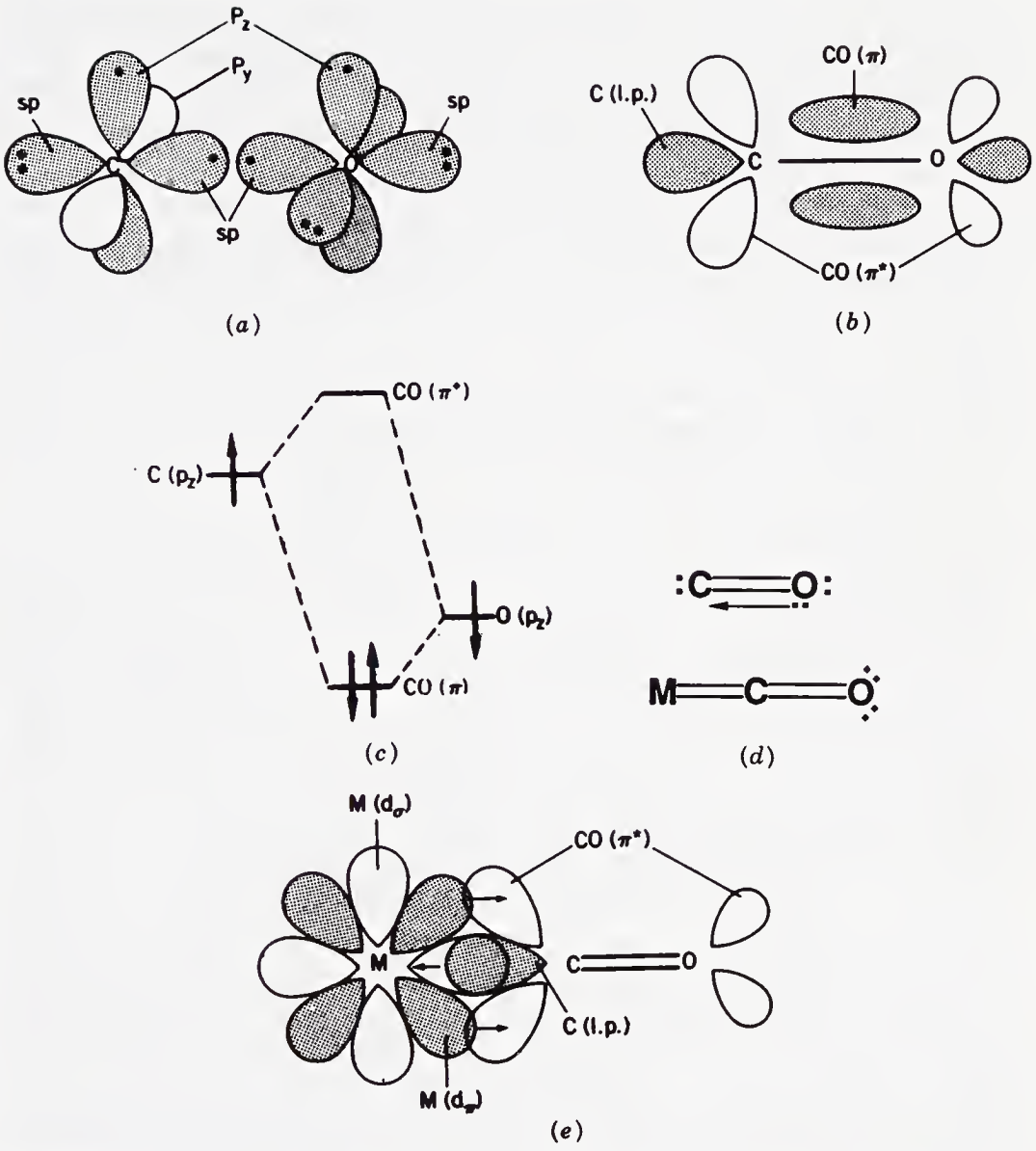


FIGURE 4.1 The electronic structure of CO and carbonyl complexes. Shading represents occupied orbitals (*a*) and (*b*) building up CO from C and O each atom having two *p* orbitals and two *sp* hybrids. In (*b*), only one of the two mutually perpendicular sets of π orbitals is shown. (*c*) An m.o. diagram showing a π bond of CO. (*d*) Valence bond representations of CO and the MCO fragment. (*e*) An m.o. picture of the MCO fragment. Again, only one of the two mutually perpendicular sets of π orbitals is shown.

after we have transferred one electron from the pair of O(p_y) electrons into the empty $C(p_y)$ orbital. This transfer leads to a C^-—O^+ polarization of the molecule, which is almost exactly canceled out by a partial C^+—O^- polarization of all three bonding orbitals because of the higher electronegativity of oxygen. The free CO molecule therefore has a net dipole moment very close

to zero. In Fig. 4.1*c* the reason for the polarization of the π_z orbital is shown in molecular orbital (m.o.) terms. An orbital is always polarized so as to favor the atomic orbital (a.o.) that is closest in energy and so the C—O π m.o. has more O than C character.[1a] The valence bond picture of CO and one form of the MCO system is shown in Fig. 4.1*d*.

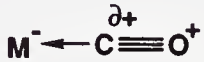
It is not surprising that the metal binds to C, not O, because the ligand homo is the C-, not the O-lone pair; this is because O is more electronegative and so its orbitals are deeper-lying. In addition, the CO(π^*) lumo is polarized toward C, and so M—CO π-overlap will also be optimal at C not O. Figure 4.1*e* shows how the CO homo donates electrons to the metal lumo, the empty M(d_σ) orbital, and metal homo, the filled M(d_π) orbital, back-donates to the CO lumo. While the former removes electron density from C, the latter increases electron density both at C and at O, because CO(π^*) has both C and O character. The result is that C becomes more positive on coordination, and O becomes more negative. This translates into a polarization of the CO on binding.

This polarization chemically activates the ligand. It makes the carbon more sensitive to nucleophilic, and the oxygen more sensitive to electrophilic attack. The polarization will be modulated by the effect of the other ligands on the metal and by the net charge on the complex. In $L_nM(CO)$, the CO carbon will be particularly ∂^+ in character if the L groups are good π acids or if the complex is cationic [e.g., $Mo(CO)_6$, or $[Mn(CO)_6]^+$], because the CO-to-metal σ-donor electron transfer will be enhanced at the expense of the metal to CO back donation. If the L groups are good donors or the complex is anionic [e.g., $Cp_2W(CO)$ or $[W(CO)_5]^{2-}$], back donation will be encouraged, the CO carbon will lose its pronounced ∂^+ charge, but the CO oxygen will become significantly ∂^-. The two extremes can be represented in valence bond terms as **4.1**, the extreme in which CO acts as a pure σ donor; and **4.2**, the extreme in which both the π_x^* and π_y^* are both fully engaged in back bonding. Neither extreme is reached in practice, but each can be considered to contribute differently to the real structure according to the circumstances. In general, polarization effects are of great importance in determining the reactivity of unsaturated ligands, and the same sort of effects we have seen for CO will be repeated for the others, with nuances in each case depending on the chemical character of the particular ligand. Note that, on the covalent model, the electron count of CO in both **4.1** and **2** is 2e. This seems always to be the case for true resonance forms.*

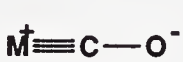
We can tell where any particular CO lies on the continuum between **4.1** and **4.2**, by looking at the IR spectrum. Because **4.2** has a lower C=O bond order than **4.1**, the greater the contribution of **4.2** to the real structure, the lower the observed CO stretching frequency will be; the normal range is 1820–2150 cm^{-1}. The m.o. picture leads to a similar conclusion. As the metal

*The + and − in **4.1–2** are *formal charges*[1b] and do not reflect the real charge, which is shown here by $\partial+$ or $\partial-$ signs.

to CO π^* back bonding becomes more important, we populate an orbital which is antibonding with respect to the C=O bond, and so we lengthen and weaken this bond. In a metal carbonyl, the M—C π bond is made at the expense of the C=O π bond. The high intensity of the CO stretching bands, also partly a result of polarization on binding, means that IR is extremely useful in a number of different ways. From the band position, we can tell how good is the metal as a π base. From the number and pattern of the bands, we can tell the number and stereochemistry of the COs present, as we shall see in detail in Chapter 10.



4.1



4.2

Preparations of CO Complexes Typical examples are shown in Eqs. 4.2–4.7.

1. From CO:

$$Fe \xrightarrow{CO,\ 200\ atm,\ 200^\circ} Fe(CO)_5 \qquad (4.2)^{2a}$$

$$IrCl(cod)L_2 + CO = IrCl(CO)L_2 \overset{CO}{\rightleftharpoons} IrCl(CO)_2L_2 \qquad (4.3)^{2b}$$

$(L = PMe_3)$

2. From CO and a reducing agent (reductive carbonylation):

$$NiSO_4 + CO + S_2O_4^{2-} = Ni(CO)_4 \qquad (4.4)^3$$

$$Re_2O_7 + 17CO \longrightarrow (CO)_5Re\text{–}Re(CO)_5 + 7CO_2 \qquad (4.5)$$

$$Cr(CO)_4(tmeda) \xrightarrow{Na} Na_4[Cr(CO)_4] \qquad (4.6)^4$$

4.3

$(tmeda = Me_2NCH_2CH_2NMe_2)$

3. From a reactive organic carbonyl compound:

$$RhClL_3 + RCXO \xrightarrow{\text{oxidative addition}} \{XRhCl(COR)L_3\} \xrightarrow{\text{retro migratory insertion}}$$

$$\{XRhCl(CO)RL_2\} \xrightarrow{\text{reductive elimination}} RX + RhCl(CO)L_2 \qquad (4.7)^5$$

$(L = PPh_3;\ X = H \text{ or } Cl)$

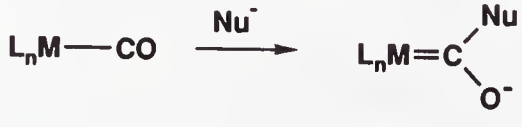
The first method requires that the metal already be in a reduced state, because only π-basic metals can bind CO. If a high-oxidation-state complex is the starting material, then we need to reduce it first as shown in the second method. Equation 4.5 illustrates the high tendency of CO groups to stabilize M—M bonds; not only are they small ligands but they also leave the metal atom with a net charge similar to that in the bulk metal. In this case the product has no bridging carbonyls, and the dimer is held together by the M—M bond only. Equation 4.6 shows the ability of CO to stabilize polyanionic species by acting as a strong π acceptor and delocalizing the negative charge over the CO oxygens. Compound **4.3** has the extraordinarily low ν(CO) of 1462 cm^{-1}, the extremely high anionic charge on the complex and binding of Na^+ to the carbonyl oxygen contribute to the lowering by favoring the M≡C—ONa resonance form, which is related to **4.2**.

The third route involves abstraction of CO from an organic compound. This can happen for aldehydes, alcohols, and even CO_2. In the example shown in Eq. 4.7, the reaction requires three steps; the second step is the reverse of migratory insertion. The success of the reaction in any given instance relies on the thermodynamic stability of the final metal carbonyl product, which is greater for a low-valent metal. Note that the first step in the case of an aldehyde is oxidative addition of the aldehyde C—H bond. It is much more difficult for the metal to break into a C—C bond. This means that ketones, R_2CO, are usually resistant to this reaction.

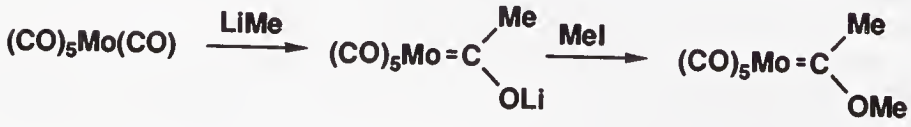
Since COs are small and strongly held ligands, as many will usually bind as are required to achieve coordinative saturation. This means that metal carbonyls, in common with metal hydrides, show a strong preference for the 18e configuration.

Reactions of Metal Carbonyls Typical reactions are shown in Eqs. 4.8–4.13. All of these depend on the polarization of the CO on binding, and so change in importance as the coligands and net charge change. For example, types 1 and 3 are promoted by the electrophilicity of the CO carbon and type 2, by nucleophilicity at CO oxygen.

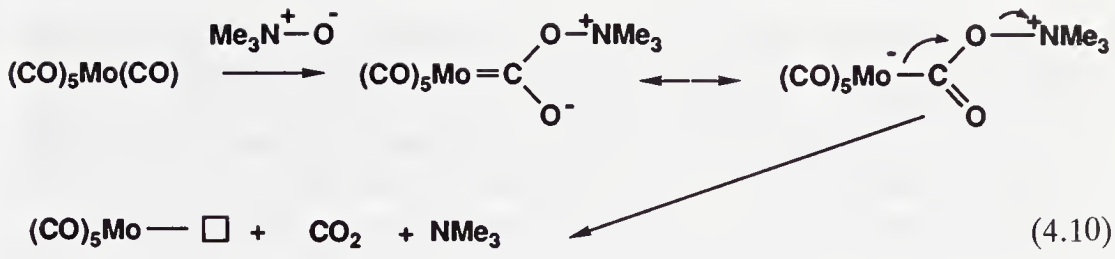
1. Nucleophilic attack at carbon:



(4.8)



(4.9)



(4.10)

These reactions give carbenes (Chapter 11) or carbene-like intermediates. The reaction of Eq. 4.10 is particularly important because it is one of the rare ways in which the tightly bound CO can be removed to generate an open site at the metal. In this way a ligand L′, which would normally not be sufficiently strongly binding to replace the CO, can now do so.

$$[Cp(NO)(PPh_3)ReCO]^+ \xrightarrow{LiBHEt_3} Cp(NO)(PPh_3)Re(CHO) \qquad (4.11)$$

This reaction (Eq. 4.11) produces the unusual formyl ligand, which is important in CO reduction to MeOH (Section 12.1). It is stable in this case because the 18e complex provides no empty site for rearrangement to a hydrido-carbonyl complex.

2. Electrophilic attack at oxygen:

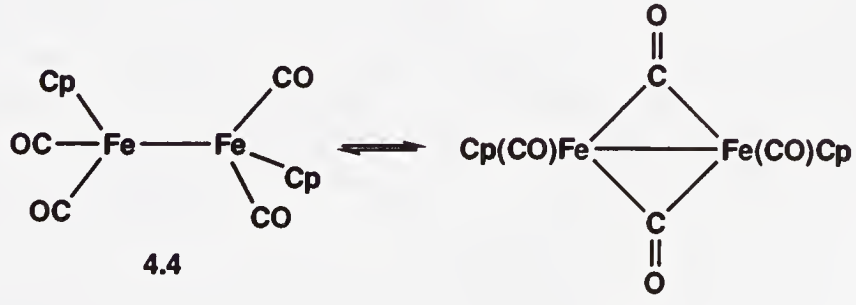
$$Cl(PR_3)_4Re{-}CO \xrightarrow{AlMe_3} [Cl(PR_3)_4Re{-}CO{\longrightarrow}AlMe_3] \qquad (4.12)$$

Protonation of this Re carbonyl occurs at the metal, as is most often the case, but the bulkier acid, $AlMe_3$, prefers to bind at the CO oxygen.

3. Finally, there is the migratory insertion reaction that we looked at in Section 3.3.

$$MeMn(CO)_5 \xrightarrow{PMe_3} (MeCO)Mn(CO)_4(PMe_3) \qquad (4.13)$$

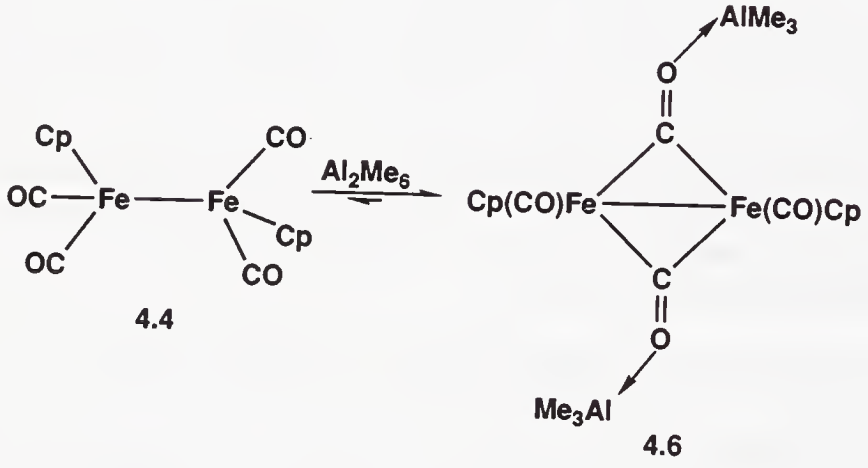
Bridging CO Groups CO has a high tendency to bridge two metals (e.g., **4.4** ⇌ **4.5**):



4.4 **4.5**

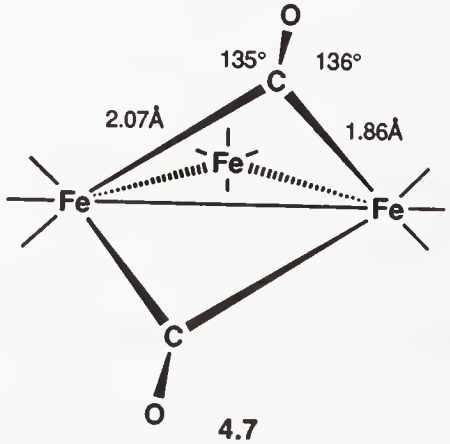
(4.14)

The electron count remains unchanged on going from **4.4** to **4.5**. The 15e CpFe(CO) fragment is completed in **4.4** by a M—M bond (1e) and a terminal CO (2e). In **4.5**, on the other hand, we count 1e from each of the two bridging CO (μ^2-CO) groups and 1e from the M—M bond. The bridging CO is not entirely ketone-like because an M—M bond seems almost always to accompany a CO bridge. The CO stretching frequency in the IR spectrum falls to 1720–1850 cm^{-1} on bridging. Consistent with the idea of a nucleophilic attack by a second metal, a bridging CO is more basic at O than the terminal ligand. A good illustration of this is the fact that a Lewis acid can bind more strongly to the oxygen of a bridging CO and so displace the equilibrium of Eq. 4.15 toward **4.6**. Similar $[CpM(CO)_x]_2$ species are known for many different metals.[6a]



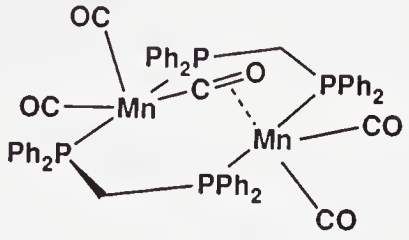
4.4 4.6 (4.15)

Cotton[6b] has studied the *semibridging carbonyl,* in which the CO is neither fully terminal nor fully bridging, but intermediate between the two. This is one of the many cases in organometallic chemistry where a stable species is intermediate in character between two bonding types and shows us a "stopped action" view of the conversion of one to the other. An example is **4.7**, in which you can see that the each semibridging CO is bending in response to the second metal atom being close by.



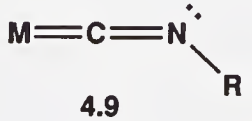
4.7

More recently, a second and rarer type of semibridging carbonyl has been recognized,[6c] one in which the semibridging CO remains linear as the second metal approaches (**4.8**). Triply bridging CO groups are also known in metal cluster compounds, for example, $(Cp^*Co)_3(\mu^3\text{-}CO)_2$. These have CO stretching frequencies in the range of 1600–1730 cm^{-1}. PdSiO, a very unstable molecule seen only at low temperatures, is the only SiO complex known.[7]



4.8

Isonitriles Many 2e ligands closely resemble CO. Replacement of the CO oxygen with the related, but less electronegative, fragment RN gives isonitrile, RNC, a ligand that is a significantly better electron donor than CO. It stabilizes more cationic and higher-oxidation-state complexes than does CO [e.g., $[Pt(CNPh)_4]^{2+}$], for which no CO analog is known, but tends to bridge less readily than does CO. It is also more sensitive to nucleophilic attack at carbon to give aminocarbenes (Eq. 11.3) and has a higher tendency for migratory insertion. Unlike the situation for CO, the CN stretching vibration in isonitrile complexes is often lower than in the free ligand. The reason is that the C lone pair is nearly nonbonding with respect to CO (i.e., does not contribute to the CO bond) for carbonyls but is much more antibonding with respect to CN in isonitriles. Depletion of electron density in this lone pair by donation to the metal therefore has little effect on ν(CO) but raises ν(CN). Back bonding lowers both ν(CO) and ν(CN). Depending on the balance of σ versus π bonding, ν(CN) is raised for weak π-donor metals, such as Pt(II), and lowered for strong π-donor metals, such as Ni(O). Recently, cases such as $NbCl(CO)(CNR)(dmpe)_2$ have been found in which back bonding to an isonitrile is so strong that the ligand becomes bent at N (129°–144°), indicating that the resonance form **4.9** has become dominant. The M—C bond is also unusually short (2.05 Å compared to 2.32 Å for a Nb—C single bond) in the bent isonitrile case, and the ν(CN) is unusually low (1750 cm^{-1} compared to ~2100 cm^{-1} for the linear type), again consistent with the structure **4.9**.[8] RNC usually fails to replace more than one or two carbonyls in a mononuclear or cluster carbonyl, unless a catalyst, such as Pt/Al_2O_3, is used.[9] The appalling stench of volatile isonitriles may be a result of their binding to a metal ion acting as a receptor in the human nose.



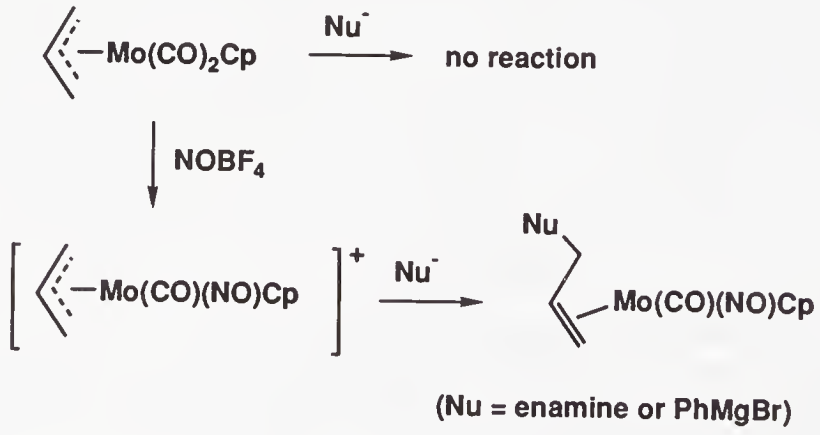
4.9

Thiocarbonyls CS is not stable above −160°C in the free state, but a number of complexes are known, such as $RhCl(CS)(PPh_3)$ (Eq. 4.16) and $Cp(CO)Ru(\mu^2\text{-}CS)_2RuCp(CO)$, but so far no "pure" or *homoleptic* examples $M(CS)_n$. They are usually made from CS_2 or by conversion of a CO to a CS group. Perhaps because of the lower tendency of the second row elements such as S to form double bonds, the $M^+{\equiv}C{-}S^-$ form analogous to **4.2** is more important for MCS than MCO: the MC bond therefore tends to be short and CS is a better π acceptor than CO. Perhaps for this reason, CO and not CS tends to be substituted in a mixed carbonyl–thiocarbonyl complex.

$$RhCl(PPh_3)_3 \xrightarrow{CS_2} \textit{trans}\text{-}RhCl(CS)(PPh_3)_2 + SPPh_3 \qquad (4.16)^{10}$$

Typical ν(CS) ranges for CS complexes are 1273 cm^{-1}, free CS; 1040–1080 cm^{-1}, $M_3(\mu_3\text{-}CS)$; 1100–1160 cm^{-1}, $M_2(\mu_2\text{-}CS)$; 1160–1410 cm^{-1}, M—CS.[11] CSe and CTe complexes are also known.[12]

Nitrosyls Free NO is a stable free radical, because the weak ON—NO bond inhibits dimerization. It forms an extensive series of diamagnetic nitrosyl complexes[13] by binding to odd-electron metal fragments. NO^+, available as the salt $NOBF_4$, is isoelectronic with CO and can often replace CO in a substitution reaction. In the majority of nitrosyl complexes, the MNO unit is linear, and in such cases, the NO is usually considered as behaving as the 2e donor NO^+ on the ionic model and as a 3e LX ligand on the covalent model. Replacing a CO by an NO^+ means that the complex will bear an extra positive (or one less negative) charge. This increases the reactivity of the system toward nucleophiles and is a standard strategy for activating an otherwise unreactive complex (e.g., Eq. 4.17).[14]



(4.17)

We can mentally construct NO from CO by adding an extra proton (and a neutron) to the carbon nucleus to give us NO^+, and a single electron to the π^* orbital to account for the extra valence electron of N versus C. We look first at the ionic model (Fig. 4.2). In bringing $CpMo(CO)_2$ and NO together to form $CpMo(CO)_2(\textit{lin}\text{-}NO)$, we first remove the unpaired electron

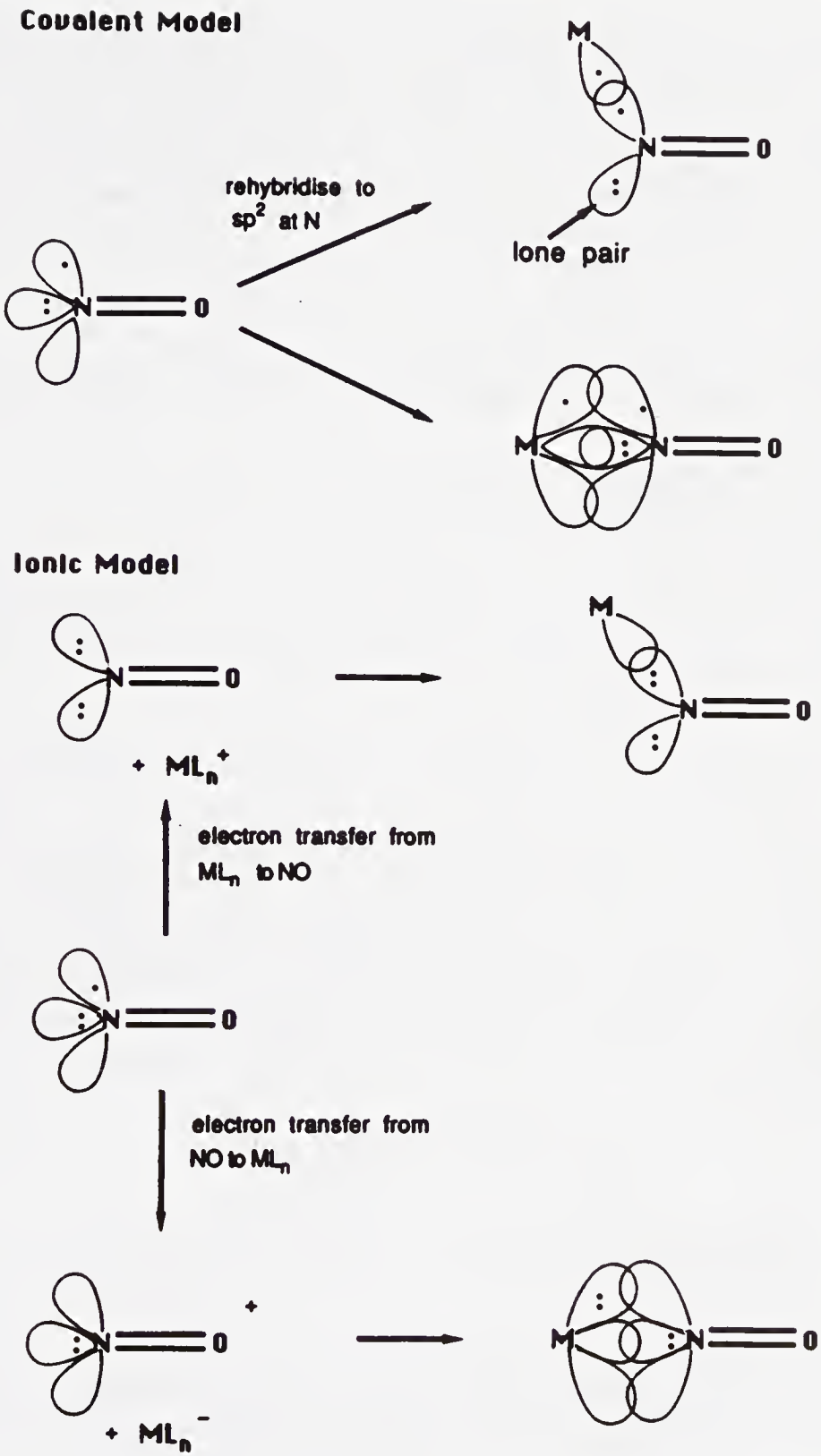


FIGURE 4.2 The electronic structure of NO and its binding to a metal fragment on the covalent and ionic models.

from NO to give NO^+ and place this electron on Mo, which gives it a zero oxidation state in this case. Binding of NO^+ as a 2e donor to $CpMo(CO)_2^-$, a 16e fragment, gives an 18e configuration. On the other hand, the 17e fragment, $[Co(diars)_2X]^+$, binds NO to give a complex with a bent nitrosyl structure. In this case, we first carry out an electron transfer from the metal to NO to get the 16e fragment $[Co(diars)_2X]^{2+}$ and NO^-; the NO^- is then a 2e ligand to bring the total electron count to 18. The conversion of a linear to a bent NO is considered to lead to an increase in the formal oxidation state by two units (e.g., Eq. 4.18). Raising the electron density on a metal will encourage the linear-to-bent conversion, because in the bent NO, a pair of electrons originally assigned to the complex becomes a lone pair on nitrogen; in the language of the ionic model, the electron-rich metal reduces the NO^+ to NO^-.

On the covalent model, a linear NO is a 3e LX ligand. In this case there is no need to rehybridize. The metal has a singly occupied d_π orbital, which binds with the singly occupied NO(π^*) to give a M—N π bond, and the N(l.p.) (lone pair) donates to the empty M(d_σ) in the normal way to give the σ bond. A bent NO is a 1e X ligand like a chlorine atom, but as the electron is in a π^* orbital in free NO, the N has to rehybridize to put this electron in an sp^2 orbital pointing toward the metal in order to bind.

A 17e L_nM fragment can bond to NO to give only a bent 18e nitrosyl complex, while a 15e L_nM fragment can give either an 18e linear or a 16e bent complex. 16e bent NO complexes are not uncommon. Some complexes have both bent and linear NO: e.g., $ClL_2Ir(lin\text{-}NO)(bent\text{-}NO)$.[15] Equations 4.18–4.20 show examples where the linear and bent nitrosyl complexes are in equilibrium.[16,17] For the Co case, the linear complex has ν(NO) at 1750 cm^{-1} and the bent NO has ν(NO) at 1650 cm^{-1}; unfortunately, the typical ν(NO) ranges for the two structural types overlap. These equilibria also show that it is not always possible to decide whether an NO is linear or bent by finding out which structure leads to an 18e configuration. Only if a linear structure would give a 20e configuration, as in **4.10** in Eq. 4.20, can we assign a bent structure.

$$\underset{\text{18e, Co(I)}}{CoCl_2L_2(lin\text{-}NO)} = \underset{\text{16e, Co(III)}}{CoCl_2L_2(bent\text{-}NO)} \qquad (4.18)^{16a}$$

$$\underset{\text{18e, Ir(I)}}{(o\text{-}C_6H_4O_2)_2L_2Ir(lin\text{-}NO)} \longrightarrow \underset{\text{16e, Ir(III)}}{(o\text{-}C_6H_4O_2)_2L_2Ir(bent\text{-}NO)} \qquad (4.19)^{16b}$$

$$(L = PPh_3)$$

$$\underset{\text{18e, Co(I)}}{[Co(lin\text{-}NO)(diars)_2]^{2+}} + X^- \longrightarrow \underset{\textbf{4.10}\text{, 18e, Co(III)}}{[CoX(bent\text{-}NO)(diars)_2]^{2+}} \qquad (4.20)$$

The recent discovery that NO and CO are important messenger molecules in the mammalian brain will certainly provoke increased interest in the area.[17]

Typical nitrosyls, together with some preparative routes, are shown in Eqs. 4.21–4.26. The first two cases show linear–bent equilibria. Equation 4.21 shows that NO, unlike most ligands can replace all the COs in a metal carbonyl to give a homoleptic nitrosyl. The last two cases show the use of the stable cation NO^+ (isoelectronic with CO) in synthesis. NO^+ is a powerful 1e oxidizing agent and it is even capable of oxidizing many bulk metals. The resulting higher-oxidation-state ions cannot bind NO, however.

$$Cr(CO)_6 + NO + h\nu = Cr(\textit{lin}\text{-}NO)_4 \qquad (4.21)^{18}$$

$$Mn(CO)_5I + NO = Mn(\textit{lin}\text{-}NO)_3(CO) \qquad (4.22)^{19}$$

$$IrH_5(PR_3)_2 + NO = (R_3P)(\textit{lin}\text{-}NO)_2Ir\text{—}Ir(\textit{lin}\text{-}NO)_2(PR_3)_2 \qquad (4.23)^{20}$$

$$(\text{toluene})Cr(CO)_3 + NO^+ + MeCN = \textit{trans}\text{-}[Cr(\textit{lin}\text{-}NO)_2(MeCN)_4]^{2+} \qquad (4.24)^{21}$$

$$Pd + NO^+ + MeCN = [Pd(MeCN)_4]^{2+} \qquad (4.25)^{22}$$

Like CO, coordinated NO can give the migratory insertion reaction:

$$[CpCo(NO)]^- \xrightarrow{RI} [CpCoR(NO)] \xrightarrow{PPh_3} [CpCo(NOR)PPh_3] \qquad (4.26)^{23}$$

4.2 PHOSPHINES AS LIGANDS

Tertiary phosphines, PR_3, are important because they constitute one of the few series of ligands in which electronic and steric properties can be altered in a systematic and predictable way over a very wide range by varying R. They also stabilize an exceptionally wide variety of ligands of interest to the organometallic chemist as their phosphine complexes $(R_3P)_nM\text{—}L$.

Like NH_3, phosphines have a lone pair on the central atom that can be donated to a metal. Unlike NH_3, they are also π acids, to an extent that depends on the nature of the R groups present on the PR_3 ligand. For alkyl phosphines, the π acidity is weak; aryl, dialkylamino, and alkoxy groups are successively more effective in promoting π acidity. In the extreme case of PF_3, the π acidity becomes as great as that found for CO.

In the case of CO it has long been recognized that it is the π^* orbital that accepts electrons from the metal. It is only recently that the σ^* orbitals of the P—R bonds have been recognized as playing a role as an acceptor in PR_3.[24] Figure 4.3 shows the m.o. picture. You will see that as the R group becomes more electronegative, the orbital that the R fragment will use to bond to phosphorus becomes more stable. This implies that the σ^* orbital of the P—R bond also becomes more stable. At the same time, the phosphorus contribution to σ^* increases, and so the size of the σ^* lobe that points toward the metal increases (the larger the energy gap between two atomic orbitals, the more the more stable atomic orbital contributes to σ, and the least stable

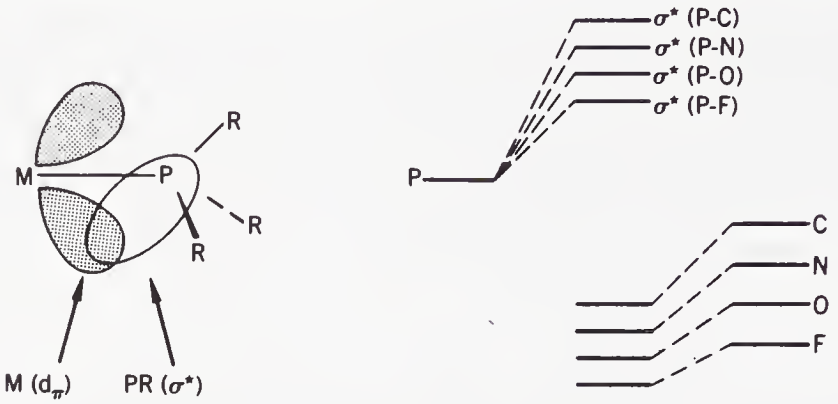


FIGURE 4.3 The σ* orbitals of the P—R bond play the role of acceptor in metal complexes of phosphorus ligands. As the atom attached to phosphorus becomes more electronegative, the empty σ* orbital of the P—X bond moves to lower energy and becomes a better acceptor from the metal.

to σ*). Both of these factors make the σ* more accessible for back donation. The final order of increasing π-acid character is

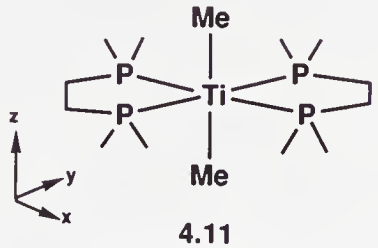
$$PMe_3 \approx P(NR_2)_3 < PAr_3 < P(OMe)_3 < P(OAr)_3 < PCl_3 < CO \approx PF_3$$

$P(NR_2)_3$ is a better donor than it should be based on the argument of Fig. 4.3. This is probably because the basic N lone pairs make the phosphorus a better donor.

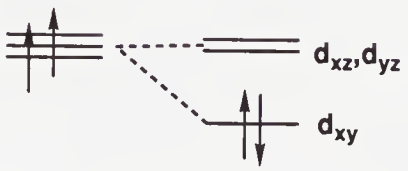
Occupation of the σ* by back bonding from the metal also implies that the P—R bonds should lengthen slightly on binding. In practice, this is masked by a simultaneous shortening of the P—R bond due to donation of the P lone pair to the metal, and the consequent decrease in P(lone pair)—R(bonding pair) repulsions. To eliminate this complication, Orpen[24a] has compared the crystal structures of pairs of complexes, such as $[(\eta^3\text{-}C_8H_{13})Fe\{P(OMe)_3\}_3]^{n+}$, where $n = 0$ or 1. The M—P σ bonds are similar in both cases, but the cationic iron in the oxidized complex is less π-basic and so back-donates less to the phosphite; this leads to a longer Fe—P distance (difference: +0.015 ± 0.003 Å), and a shorter P—O distance (−0.021 ± 0.003 Å). Once again, as in the case of CO, the M—L π bond is made at the expense of a bond in the ligand, but this time it is a σ, not a π bond.

Further evidence for the π-acceptor character of phosphines comes from the diamagnetism of the octahedral d^2 species, *trans*-$TiMe_2(dmpe)_2$ (**4.11**). In order to be diamagnetic, the three d_π orbitals have to split as shown in **4.12**. For this to happen, either the axial ligands have to be π donors or the equatorial ligands have to be π acceptors. Since —CH_3 was shown not to be a significant π donor, the dmpe must be an acceptor. In Fig. 1.7, six π-acceptor ligands caused all three d_π orbitals to drop in energy; here four π acceptors in the *xy* plane (2 × dmpe) cause the d_{xy} orbital to be lowered below d_{xz} and d_{yz} to give **4.12**.[25] Note that Ti(II) is a very strong π donor, as

we saw in Section 2.7, and so the situation is very favorable for detecting M—(PR_3) π bonding.



4.11



4.12

Tolman Electronic Parameter and Cone Angle The dependence of the electronic effect of various PR_3 ligands on the nature of the R group has been quantified by Tolman,[26] who compared the ν(CO) frequencies of a series of complexes of the type $LNi(CO)_3$, containing different PR_3 ligands. The stronger donor phosphines increase the electron density on Ni, which passes some of this increase along to the COs by back donation. This, in turn, lowers ν(CO) as shown in Fig. 4.4.

The second important feature of PR_3 as a ligand is the variable steric size, which can be adjusted by changing R. COs are so small that as many can

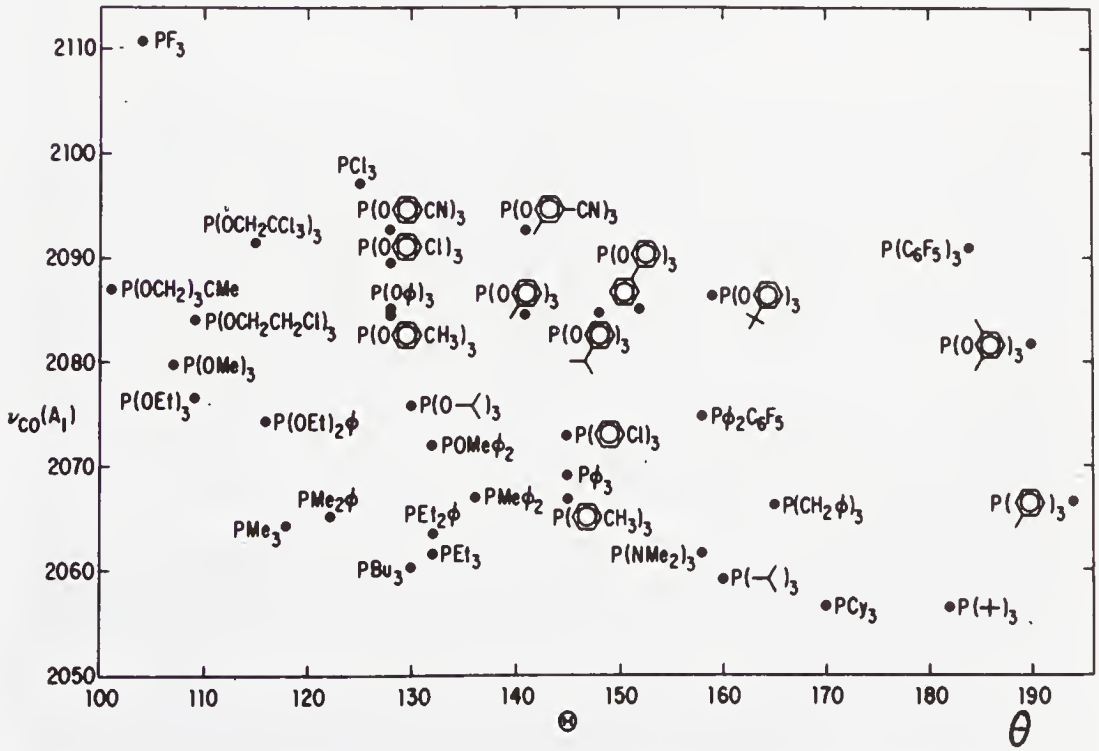
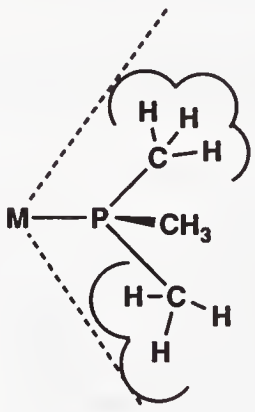


FIGURE 4.4 The electronic and steric effects of common P-donor ligands plotted on a map according to Tolman. (Reproduced from ref. 26 with permission of the American Chemical Society.)

bind as are needed to achieve 18e. In contrast, the same is rarely true for phosphines, where only a certain number of phosphines can fit around the metal. This can be a great advantage in that we leave room for small but weakly binding ligands, which would be excluded by a direct competition with a smaller ligand such as PMe_3 or CO. The usual maximum number of phosphines that can bind is two for PCy_3 or $P(i\text{-}Pr)_3$, three or four for PPh_3, four for PMe_2Ph, and five or six for PMe_3. Examples of stable complexes showing these principles at work are $Pt(PCy_3)_2$, and $[Rh(PPh_3)_3]^+$, both coordinatively unsaturated species that are stabilized by bulky phosphines, and $W(PMe_3)_6$.

Tolman has also quantified the steric effects of phosphines with his *cone angle*. This is obtained by taking a space-filling model of the $M(PR_3)$ group, folding back the R substituents as far as they will go, and measuring the angle of the cone that will just contain all of the ligand, when the apex of the cone is at the metal (**4.13**). Although the procedure may look rather approximate, the angles obtained have been very successful in rationalizing the behavior of a wide variety of complexes. The results of these studies also appear on Fig. 4.4 with the electronic parameters. The resulting "map" of phosphine properties is very useful in choosing the right ligand in any given case.



4.13

4.3 DISSOCIATIVE SUBSTITUTION

The reactions of phosphines with metal carbonyls, investigated by Basolo,[27] form the basis for our understanding of organometallic substitution reactions in general. The phosphine is usually refluxed with the carbonyl in an organic solvent, such as ethanol or toluene. One can distinguish two extreme mechanisms for substitution, one dissociative,[27,28] labeled D, and the other associative, labeled A. Intermediate cases are often labeled I: I_a if closer to A and I_d if closer to D.[28]

The dissociative extreme involves a slow initial loss of a CO to generate a vacant site at the metal, which is trapped by the incoming ligand L. Because

the rate determining step is dissociation of CO, the reaction is usually independent of the concentration of L and the rate is the same for any of a series of different L ligands. This leads to a simple rate equation:

$$\text{Rate} = k_1[\text{complex}] \tag{4.27}$$

$$L_nM{-}CO \underset{+CO,\ k_{-1}}{\overset{-CO,\ k_1}{\rightleftharpoons}} L_nM{-}\square \xrightarrow{+L',\ k_2} L_nM{-}L' \tag{4.28}$$

In some cases, the back reaction, k_{-1}, becomes important, in which case the intermediate, $L_nM{-}\square$, partitions between the forward and back reactions.[28] Increasing the concentration of L does now have an effect on the rate because it encourages the forward process. The rate equation derived for Eq. 4.28 is shown in Eq. 4.29. It reduces to Eq. 4.27, if the concentration of CO, and therefore the rate of the back reaction, is negligible.

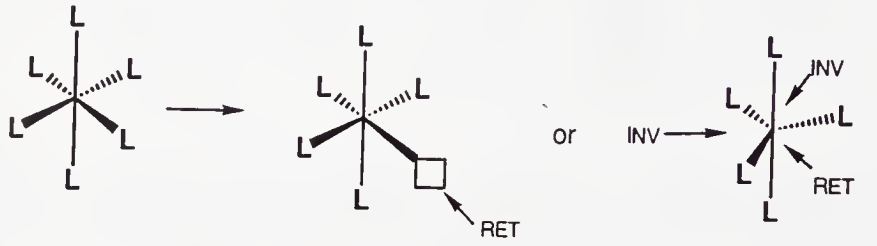
The overall rate is usually controlled by the rate at which the leaving ligand dissociates. Ligands which bind less well to the metal, dissociate faster than does CO. For example, $Cr(CO)_5L$ shows faster rates of substitution of L in the order L = CO < Ph_3As < py. For similar ligands, say, phosphines, the larger the cone angle, the faster the dissociation:[28a]

$$\text{Rate} = \frac{k_1k_2[\text{L}][\text{complex}]}{k_{-1}[\text{CO}] + k_2[\text{L}]} \tag{4.29}$$

This mechanism tends to be observed for 18e carbonyls. The alternative, initial attack of a phosphine, would generate a 20e species. While it is not forbidden to have a 20e transition state (after all, $NiCp_2$ is a stable 20e species), the 16e intermediate of Eq. 4.28 provides a lower-energy path in many cases. This is reminiscent of the S_N1 mechanism of substitution in alkyl halides. The activation enthalpy required for the reaction is normally close to the M—CO bond strength, because this bond is largely broken in going to the transition state. $\Delta S^{\ddagger}$ is usually positive and in the range 10–15 eu (entropy units), as expected for a dissociative process in which the transition state is less ordered.

The stereochemistry at a d^6 octahedral metal may be retained in the substitution if the 16e intermediate has the square pyramidal or T-shaped geometry (**4.14**). On the other hand, if the metal becomes distorted trigonal bipyramidal (TBP) or Y-shaped (**4.15**), the stereochemistry may be lost because the incoming ligand can attack at several different places in the equatorial plane (Eq. 4.30). Both Y and T structures[28e] have been found in the few known examples of stable 16e d^6 species; these are model compounds for the intermediates in D substitution. The Y-geometry is favored when one of the equatorial ligands, the one at the foot of the Y, is a good π donor (e.g., Cl, OR, or NR_2). In this case, the π-donor lone pair also donates to the metal and makes up the 2e deficit in what would otherwise be a 16e

species. The T-geometry is favored by having a high trans-effect ligand (e.g., H, Me, or CO) at the foot of the T, trans to the empty site. The stability of this T-shaped intermediate explains how a high trans-effect ligand can promote fast exchange trans to itself in a d^6 octahedral complex without rearrangement of the other ligands.



(4.30)

square pyramid

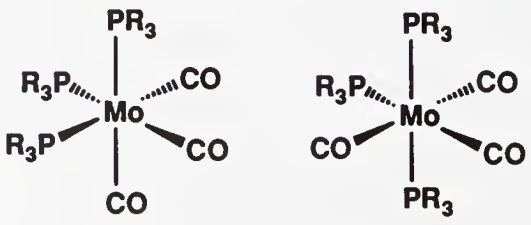
4.14

trigonal pyramid

4.15

The dissociative mechanism tends to be most favored in TBP d^8, followed by d^{10} tetrahedral and then d^6 octahedral. For example, d^8 $Co_2(CO)_8$ has a half-life for CO dissociation of a few tens of minutes at 0°, but for d^6 $Mn_2(CO)_{10}$ at room temperature the half-life is about 10 years! This order is consistent with the relative stabilities of the stereochemistries of the starting material and of the intermediates in each case, as predicted by crystal field arguments (Section 1.4). Substitution rates tend to follow the order 3rd row < 2nd row > 1st row.[18] For example, at 50°, the rate constants for CO dissociation in $M(CO)_5$ are Fe, 6×10^{-11}; Ru, 3×10^{-3}; Os, 5×10^{-8}. The rate for Fe is exceptionally slow, perhaps because $Fe(CO)_4$, but not the Ru or Os analog, is high-spin and less stable, leading to a higher activation energy.

Phosphines do not replace all the carbonyls in a complex, even in a case where the particular phosphine is sterically small enough to do so. The reaction of $Mo(CO)_6$ with a monodentate alkylphosphine never proceeds further than the *fac*-$Mo(CO)_3L_3$ stage. This is in part because the phosphines are much more electron-donating than the carbonyls they replace. The remaining COs therefore benefit from increased back donation and are more tightly held in consequence. The fac stereochemistry (**4.16**), in which the PR_3 ligands occupy a face of the octahedron, is preferred electronically to the mer arrangement (**4.17**), in which the ligands occupy a meridian. This is because



fac

4.16

mer

4.17

the COs have a higher trans effect than the phosphines, and so substitution continues until there are no COs trans to a CO. The mer arrangement is less sterically encumbered, however, and is seen for bulky L groups.

Dissociation of a ligand is accelerated for bulky ligands. We shall see in Section 9.4 how this affects the dissociation of a phosphite from NiL_4 in a key step in olefin hydrocyanation, an important catalytic reaction. The degree of dissociation can be predicted from the appropriate cone angles, and the bulky phosphite P(O-*o*-tolyl)$_3$ makes one of the very best catalysts. Triphenylphosphine is very useful in a wide variety of catalysts for the same reason.

Dissociation can sometimes be encouraged in various ways. For example, a chloride ligand can often be substituted in the presence of Ag^+, because AgCl is precipitated. Tl^+ is used in cases where Ag^+ oxidizes the complex and is therefore unsatisfactory. Protonation can also be used to remove ligands such as alkyl or hydride groups. Weakly bound solvents are often useful ligands synthetically, because they can be readily displaced. As a π donor, thf is a poor ligand for W(0):

$$W(CO)_5(thf) + PPh_3 = W(CO)_5(PPh_3) \qquad (4.31)$$

Substitution of halide for alkyl or hydride is often carried out with RMgX or $LiAlH_4$. Cyclopentadienyls may be prepared from CpNa or CpTl, in which case the insoluble TlCl precipitates and helps drive the reaction.

Certain types of ligands are more likely to dissociate than others. The chelate effect means that polydentate ligands will dissociate less easily, for example. Carbon-donor ligands of the L_n type, like η^6-C_6H_6 (L_3), or CO (L), will tend to dissociate more easily than L_nX ligands such as η^5-Cp (L_2X) or Me (X). This is because L_n ligands tend to be stable in the free state, but L_nX ligands would have to dissociate as radicals or ions, which is usually less favorable. Among non-carbon-donor ligands, the anions or cations can be very stable in solution (e.g., H^+ or Cl^-) and may well dissociate in a polar solvent. The electronic configuration of the metal is also important: substitution-inert d^6 octahedral complexes are much less likely to dissociate a ligand than are substitution-labile d^8 TBP metals, as we saw in Section 1.4.

Redox catalysis of substitution[28] is covered in Section 4.5.

4.4 THE ASSOCIATIVE MECHANISM

The slow step in associative substitution[29] is the attack of the incoming ligand L′ on the complex to form an intermediate that rapidly expels one of the original ligands L.

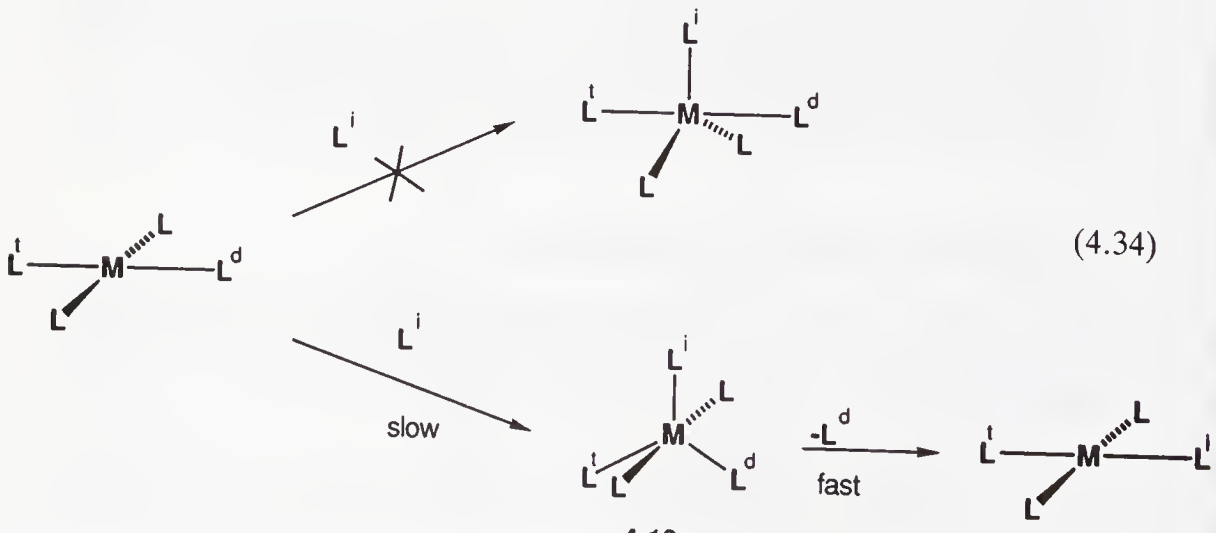
$$L_nM \xrightarrow{+L',\ k_1} L_nM{-}L' \xrightarrow{-L,\ \text{fast}} L_{n-1}M{-}L' \qquad (4.32)$$

The rate of the overall process is now controlled by the rate at which the incoming ligand can attack the metal in the slow step, and so L′ appears in the rate equation:

$$\text{Rate} = k_1[\text{L}'][\text{complex}] \tag{4.33}$$

This mechanism is often adopted by 16e complexes because the intermediate is 18e, and so can usually provide a lower energy route than the 14e intermediate that would be formed in dissociative substitution. The reaction is analogous to the nucleophilic attack of OH^- on a C=O in ester hydrolysis, for example. The entropy of activation is negative ($\Delta S^{\ddagger} = -10$ to -15 eu), as you might expect for the more ordered transition state required.[30]

The classic examples of the associative mechanism are shown by 16e, square planar species, such as complexes of Pt(II), Pd(II), and Rh(I). The 18e intermediate is a trigonal bipyramid with the incoming ligand in the equatorial plane (**4.18**). By microscopic reversibility, if the entering ligand occupies an equatorial site, the departing ligand must leave from an equatorial site. This has important consequences for the stereochemistry of the product and provides a simple rationale for the trans effect (Section 1.2). In Eq. 4.34, the incoming ligand is labeled L^i, the departing ligand L^d. We need only postulate that L^t, the ligand of highest trans effect, has the highest tendency to occupy the equatorial sites in the intermediate. This will ensure that the ligand L^d, trans to L^t, will also be in an equatorial site. Now, either L^t or L^d will be lost to give the final product; since L^t, as a good π-bonding ligand, is likely to be firmly bound, L^d, as the most labile ligand in the equatorial plane, is forced to leave. This is equivalent to saying that L^d is labilized by the trans effect of L^t. Good π-acid ligands are high in the trans effect series because they find the more π-basic equatorial sites in the TBP intermediate more congenial. Hydrogen also has a high trans effect, in part because of the lack of lone pairs, such as would be found for Cl^-, for example, minimize the ligand–metal (d_π) repulsions.



(4.34)

4.18

It is not uncommon for the solvent, present as it is in such high molarity, to act as L^i, and expel L^d to give a solvated 4-coordinate intermediate. This intermediate can then undergo a second associative substitution with the ultimate ligand to give the product. Substitutions of one halide for another on Pd and Pt(II) can follow this route:[31]

$$L_2MCl_2 \xrightarrow{+\text{solv, slow}} [L_2M(\text{solv})Cl]^+ \xrightarrow{+Br^-,\ \text{fast}} L_2MBrCl \qquad (4.35)$$

It is easy to imagine that, because it is cationic, the solvated intermediate would be much more susceptible to Br^- attack than the starting complex. Because the solvent concentration cannot normally be varied without introducing rate changes due to solvent effects, the [solv] term does not usually appear in the experimental rate equation, which therefore has the form

$$\text{Rate} = k_s[\text{complex}] + k_a[\text{complex}][L'] \qquad (4.36)$$

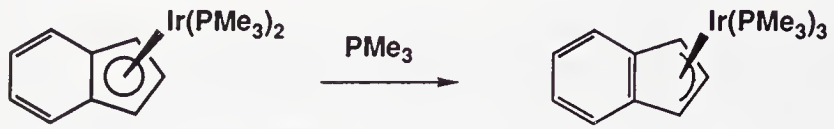
where the first term refers to the solvent assisted associative route, and the second to the direct associative reaction, which will become relatively more important as less strongly ligating solvents are used.

Eighteen-electron complexes can also undergo associative substitution. Such complexes usually contain a ligand capable of rearranging and so accepting the extra pair of electrons, so that the metal can avoid a 20e configuration. Nitrosyls, with their bent to linear rearrangements, are believed to do this. For example, $Mn(CO)_4(NO)$ shows a second-order rate law and a negative $\Delta S^{\ddagger}$, consistent with this mechanism:

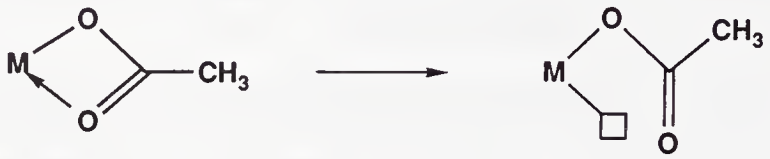
$$(CO)_4Mn(\textit{lin}\text{-NO}) \xrightarrow{L,\ \text{slow}} (CO)_4LMn(\textit{bent}\text{-NO}) \xrightarrow{-CO,\ \text{fast}} (CO)_3LCo(\textit{lin}\text{-NO}) \qquad (4.37)^{32a}$$

Indenyl complexes undergo associative substitution much faster than their Cp analogs. This is believed to be a result of the indenyl slipping from an η^5 to an η^3 structure. This is favorable for the indenyl group because the fused benzo ring regains its full aromatic stabilization energy as the 8- and 9-carbons dissociate from the metal and participate fully in the aromaticity of the benzo ring. These arguments have been strengthened recently by the isolation of several stable complexes with an η^3, or even an η^1 indenyl group, formed by the attack of a ligand on an η^5 indenyl complex. Having an indenyl is not required, $CpRh(CO)_2$ undergoes associative substitution, and the unsubstituted Cp is assumed to slip.[32b] Several other ligands are capable of rearranging in a similar way; some examples are shown in Eqs. 4.38–4.42:

(4.38)



(4.39)



(4.40)

(4.41)

(4.42)

Not all these cases give second-order kinetics; if the ligand rearrangement is rate determining and L^i rapidly traps the open site, then we will see first order kinetics and the substitution will be effectively a dissociative one, because L^i is not involved in the slow step.

4.5 REDOX EFFECTS, THE I MECHANISM, AND REARRANGEMENTS IN SUBSTITUTION

Because odd-electron species are more difficult to study and are often transients rather than stable compounds, their importance is only beginning to to be recognized.[33a]

17e and 19e Species As one might expect for a complex with an electron in an M—L σ^* orbital, 19e species[33b] tend to be more dissociatively labile than their 18e counterparts. This means that substitution of 18e species may be catalyzed by reduction. For example $Fe(CO)_5$ can be substituted with electrochemical catalysis as shown in Eq. 4.43, where $[Fe(CO)_5]^{\bullet -}$ is the chain carrier in the catalytic cycle:

$$Fe(CO)_5 \xrightarrow{+e^-} [Fe(CO)_5]^{\bullet -} \xrightarrow{-CO} [Fe(CO)_4]^{\bullet -} \xrightarrow{+L}$$
$$[Fe(CO)_4L]^{\bullet -} \xrightarrow{Fe(CO)_5} [Fe(CO)_5]^{\bullet -} + Fe(CO)_4L \quad (4.43)^{34a}$$

The substitution of $[(ArH)Mn(CO)_3]^+$ by PPh_3 to give $[(ArH)Mn(CO)_2L]^+$ is catalyzed in the same way.[34b]

Although the green-black 17e complex $V(CO)_6$ is stable, many 17e species,[35] such as $Mn(CO)_5\bullet$[36] and $Co(CO)_4\bullet$,[37] are isolable[38] only in matrices at low temperature or are transient intermediates at room temperature. These and other 17e species also undergo very rapid substitution, but usually by an associative pathway.[17] $V(CO)_6$, for example,[39] undergoes second-order (associative) ligand exchange at room temperature, while the 18e $[V(CO)_6]^-$ does not substitute or lose CO even in molten PPh_3. This means that substitution in an 18e species can be catalyzed by oxidation. The presence of air is sometimes enough to cause substitution to occur, which can lead to irreproducibility or to problems in interpreting the rate. It has been shown[40] that electrochemically oxidizing $CpMn(CO)_2(MeCN)$ in the presence of PPh_3 leads to the substitution of the acetonitrile not in just one but in as many as 250 molecules of the complex. The chain reaction of Eqs. 4.44 and 4.45 accounts for this result because the product radical reoxidizes the starting material, and the cycle can be repeated.

$$CpMn(CO)_2(MeCN) \xrightarrow{-e} [CpMn(CO)_2(MeCN)]\bullet^+ \xrightarrow{+L} [CpMn(CO)_2L]\bullet^+ \tag{4.44}$$

$$CpMn(CO)_2(MeCN) + [CpMn(CO)_2L]\bullet^+ \longrightarrow [CpMn(CO)_2(MeCN)]\bullet^+ + CpMn(CO)_2L \tag{4.45}$$

Alternatively, a trace of a free radical can abstract a le ligand from the metal, and the substitution be catalyzed by a chain reaction such as is shown in Eq. 4.46. The last step regenerates the chain carrier $(CO)_nM\bullet$:

$$(CO)_nMX \xrightarrow{O\cdot} (CO)_nM\bullet \xrightarrow{L} (CO)_{(n-1)}LM\bullet \xrightarrow{(CO)_nMX} (CO)_{(n-1)}LMX + (CO)_nM\bullet \tag{4.46}$$

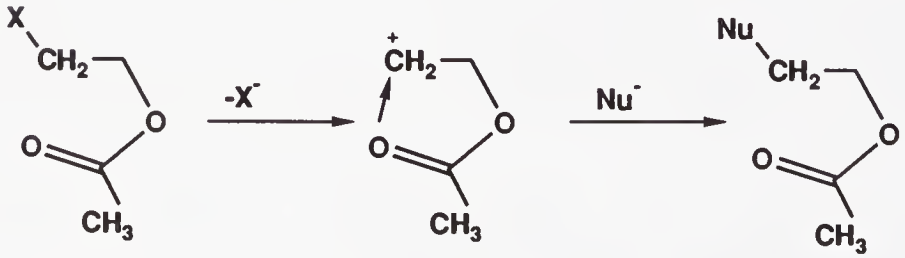
Note that Eqs. 4.43–4.46 all involve 17e/19e interconversions, while the previous examples of A and D mechanisms in diamagnetic molecules (e.g., Eqs. 4.28 and 4.32) involved 16e/18e interconversions.

While most 19e species are reactive transients, some are stable enough to isolate. Tyler[41a] has isolated $(\eta^5\text{-}Ph_4C_5H)Mo(CO)_2L_2$ (L_2 = 2,3-bis(diphenylphosphino)maleic anhydride) and Astruc[41b] $CpFe(\eta^6\text{-arene})$ as stable 19e species. Mössbauer and epr (electron paramagnetic resonance) data for the Fe(I) species suggested the 19th electron is largely located on the metal; the X-ray crystal structure shows that all 11 carbons of both rings are coordinated but the Fe—C(Cp) distances are 0.1 Å longer than in analogous 18e species. Sometimes the 19th electron is largely ligand-based, as in $CoCp_2$.[41b] The addition of a salt such as $NaPF_6$ can completely change the outcome of a substitution reaction to give ionic products instead of the neutral ones formed in the absence of a salt. This effect has so far been studied for 19e species,[41c] but it could be useful in other types of substitution.

The Interchange Mechanism There is evidence that certain soft nucleophiles show a second-order, associative component for their substitution even in cases such as $Mo(CO)_6$, where it is not obvious how the molecule can rearrange to avoid being 20e when the L^i binds. We have seen that 20e intermediates are unlikely, but a 20e transition state seems to be possible. An intermediate is a species that has to survive as an independent entity, if only briefly. The lifetime of a transition state, on the other hand, is comparable with a molecular vibration, or about 10^{-13} sec. It is necessarily an unstable entity, and 20e transition states are not uncommon. It is believed that in such cases that although both L^i and L^d bind simultaneously to the metal, they do so more weakly than they would in a more stable 18e intermediate. This is called the *interchange mechanism of substitution* and is designated I. The I mechanisms are further divided into I_a, in which L^i and L^d bind more strongly to the metal in the transition state, and I_d, in which they bind more weakly.[42] Experimentally, it is not easy to distinguish an I_a from an A mechanism, because the evidence for I_a is essentially negative: the absence of a detectable intermediate. In spite of the great sophistication of modern methods of detection of transient intermediates,[43] it may be that we do not see one and will therefore take an A mechanism to be I_a. This problem is fully discussed in a review by Darensbourg.[28]

Rearrangements of Coordinatively Unsaturated Species When an 18e complex loses a ligand, it is common for one of the remaining ligands to rearrange so as to fill the vacant site created. This is simply the reverse of the processes we saw in Eqs. 4.38–4.42. For example, an acetate might chelate as shown in Eq. 4.47. The rearrangement product may be stable, in which case it may be observed directly, or it may be unstable, and an incoming ligand L^i may displace it. The closest analogy in organic chemistry is neighboring group participation (Eq. 4.48):

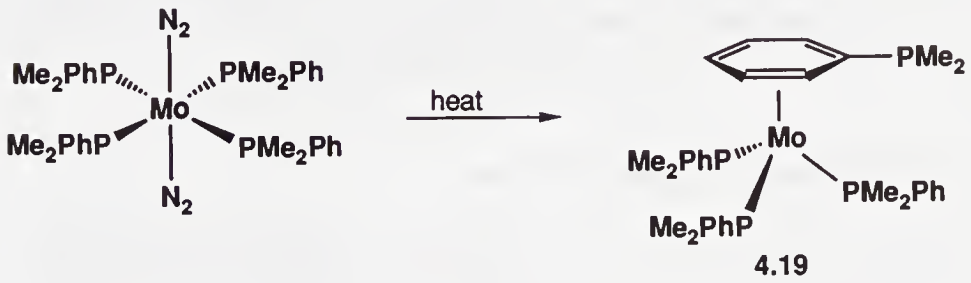
(4.47)



(4.48)

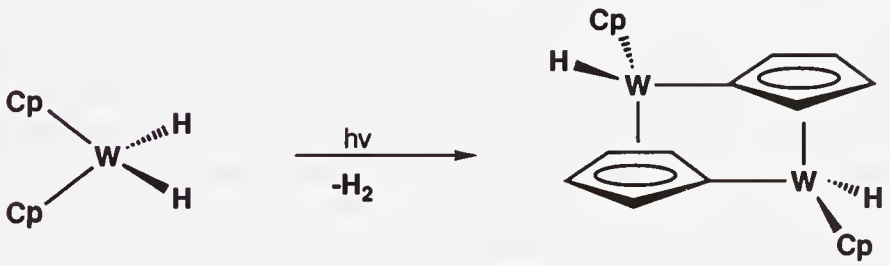
This stabilization of what would otherwise be coordinatively unsaturated intermediates can accelerate substitution reactions. In addition, species that appear from their stoichiometry to be coordinatively unsaturated interme-

diates may not in fact be what they seem. For example, on heating $Mo(N_2)_2(PMe_2Ph)_4$, N_2 is lost and $Mo(PMe_2Ph)_4$ (**4.19**) is formed:



(4.49)

Complex **4.19** might seem to have an electron count of 14e, but in fact it has rearranged to an 18e complex in which one of the phosphines binds via an η^6 arene ring, not via phosphorus at all. Other common ways that apparently 18e species can rearrange is by dimerization via a potentially bridging ligand (Eq. 4.51), via an agostic ligand (Eq. 4.53), or by the process known as *cyclometallation*[44] (e.g., Eqs. 4.50 and 4.52); this is simply the oxidative addition of a C—H bond in a ligand to the metal:



(4.50)

(4.51)

(4.52)

yellow purple

(4.53)

There are also cases in which there are reasons to believe that apparently highly coordinatively unsaturated species are authentic, for example, Cp_2^*ScMe, $Cr(CH_2Ph)_4$, $Pt(PCy_3)_2$, or $[Rh(PPh_3)_3]^+$, but it is always hard to rule out weak interactions with the ligands and solvent in solution. In such cases steric bulk may play a role in stabilizing the product.

4.6 PHOTOCHEMICAL SUBSTITUTION

Photochemical reactions can occur when light is absorbed by a compound. In this process, an electron is promoted and the ground-state electronic configuration is changed to that of one of the excited states. Even the longer-lived of these states only survive 10^{-6} to 10^{-9} sec, and so if any photochemistry is to occur, the excited state must react very quickly. If a molecule of product is formed for every photon absorbed, the quantum yield, Φ, is said to be unity. Otherwise the electron falls back to the ground state and the compound either emits light (luminescence) or is heated up thermally; in this case, chemistry does not occur and Φ for product formation will normally be less than unity.

Carbonyls Substitution reactions of carbonyls, such as $W(CO)_6$, are accelerated by UV or, for colored carbonyls, by visible light. For example, on irradiation in thf as solvent the pentacarbonyl $W(CO)_5$(thf) is obtained. As we saw in Eq. 4.23, this is a useful synthetic intermediate because it reacts with a variety of ligands L to give $W(CO)_5L$ cleanly by rapid thermal substitution, rather than more highly substituted species, such as *fac*-$W(CO)_3L_3$, which are obtained from $W(CO)_6$ and L on heating. The most reasonable mechanism for such reactions is the photon-induced promotion of a d_π electron into a d_σ level, which is M—L σ-antibonding in character, and so dissociative substitution is more rapid in the excited state. Knowing the UV–visible spectrum of the starting material is useful in designing the experiment. The complex must absorb at the wavelength to be used, but if the product also absorbs, then subsequent photochemistry may lower the yield. The buildup of highly absorbing decomposition products can stop the photochemistry by absorbing all the light.

The photolysis of $W(CO)_5L$ can lead either to loss of L or of a CO group cis to L, according to the wavelength used. This result can be understood[45] in terms of the crystal field diagram for the complex, shown in Fig. 4.5. Since the symmetry is lower than octahedral because of the presence of L, both the d_σ and the d_π levels split up in a characteristic pattern. The L ligand, conventionally placed on the z axis, is usually a lower-field ligand than CO and so the d_{z^2} orbital is stabilized with respect to the $d_{x^2-y^2}$. As we saw in Section 1.5, these are really M—L σ^* orbitals, $d_{x^2-y^2}$ (σ_{xy}^*) playing this role for ligands in the xy plane, and d_{z^2} (σ_z^*) for the ligands along the z axis. This means that irradiation at ν_1 tends to populate the σ_z^*, which will labilize the

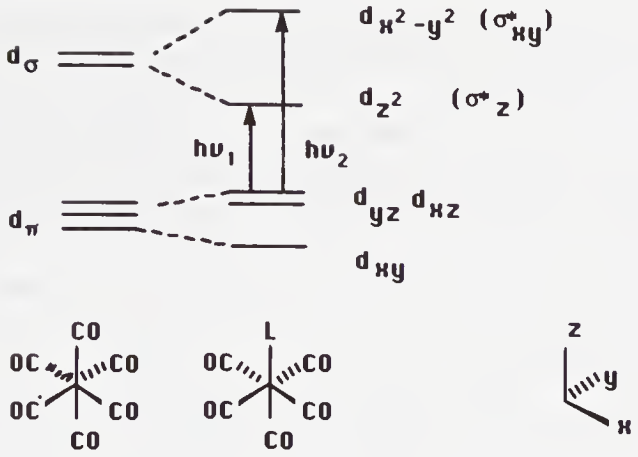


FIGURE 4.5 The crystal field basis for the selectivity observed in the photolysis of $M(CO)_5L$ complexes. Irradiation at a frequency ν_1 raises an electron from the filled d_p level to the empty $\sigma^*(z)$, where it helps to labilize ligands along the z axis of the molecule. Irradiation at ν_1 labilizes ligands in the xy plane.

L ligand because it lies on the z axis. Irradiation at ν_2 will tend to populate σ^*_{xy}, and so one of the cis COs will be labilized, because they lie in the xy plane, cis to L. Where L is pyridine, the appropriate wavelengths are ~400 nm (ν_1) and <250 nm (ν_2), respectively. The method has often been used to synthesize *cis*-$Mo(CO)_4L_2$ complexes.

$W(CO)_4$(phen) has near UV and visible absorbtions at 366 and 546 nm. The first corresponds to promotion of a d_π electron to the d_σ level, and is referred to as a ligand field (LF) band. The 546 nm band is a *metal-to-ligand charge transfer* (or MLCT) band and corresponds to promoting a metal d_π electron to a π^* level of the dipy ligand; the excited state therefore contains a 17e metal and a reduced ligand $W^{\bullet+}(CO)_4(phen^{\cdot-})$. Irradiation in either band leads to substitution by PPh_3, for example, to give $W(CO)_3(PPh_3)$(phen).

Increased pressure accelerates an associative process because the volume of the transition state $L_nM\cdots L'$ is smaller than that of the separated L_nM and L′ molecules; the reverse is true for a dissociative process because $L_{n-1}M\cdots L$ is larger than L_nM. Several hundred atmospheres are required to see substantial effects, however. Van Eldik[46a] has shown that pressure accelerates the MLCT photosubstitution of $W(CO)_4$(phen), but decelerates the LF photosubstitution. As the MLCT excited state is effectively a 17e W species, an A mechanism is reasonable for this process; the LF process is evidently dissociative, probably as a result of populating the M—L σ^* levels.

A complex such as $(\eta^6\text{-}C_7H_8)Cr(CO)_3$ undergoes thermal substitution by loss of cycloheptatriene. Although the triene is a polydentate ligand, this does not make up for the intrinsically much stronger binding of CO. In contrast, photochemical substitution (366 nm) gives $(\eta^6\text{-}C_7H_8)Cr(CO)_2L$. This is probably because monodentate ligands are more affected by occupation of "their" σ^* orbital than a polydentate ligand that binds simultaneously along two or

all three axes of the molecule. The arene is lost in photosubstitution of $[CpFe(\eta^6\text{-}PhCH_3)]PF_6$, however, because the Cp is also polydentate.[46b]

Hydrides The second most common photosubstitution is the extrusion of H_2 from a di- or polyhydride. This reaction was discovered[47] in the case of the yellow crystalline complex, Cp_2WH_2 (Eq. 4.54). This is most probably the result of the promotion of an electron into the M—L σ^* orbital corresponding to the MH_2 system. Sometimes the reductive elimination product is stable, or as in Eq. 4.54, it can also be very unstable and can oxidatively add to C—H or other bonds in the solvent or ligands.

$$Cp_2WH_2 \xrightarrow{h\nu,\ \text{benzene}} Cp_2WPhH + H_2 \qquad (4.54)$$

In some cases it has been shown that loss of phosphine can occur in preference to reductive elimination of H_2, presumably depending on which σ^* orbital is populated with the wavelength of light used.

$$ReH_5(PR_3)_3 \xrightarrow{h\nu} \{ReH_5(PR_3)_2\} + PR_3 \qquad (4.55)$$

M—M Bonds Another important photochemical process is the homolysis of M—M bonds. The fragments produced are likely to be odd-electron and therefore substitutionally labile. For example, the photosubstitution of CO in Mn_2CO_{10} by PPh_3 proceeds via the 17e intermediates $\bullet Mn(CO)_5$. Equation 4.57 is an interesting example,[48] because the replacement of three COs by the non-π-acceptor NH_3 leads to a buildup of electron density on the metal. This is relieved by an electron transfer from a 19e $Mn(CO)_3(NH_3)_3$ intermediate to a 17e $Mn(CO)_5$ fragment to give the *disproportionation* product **4.20** in a chain mechanism.[49]

$$Mn_2(CO)_{10} + PPh_3 \longrightarrow Mn_2(CO)_9(PPh_3) + CO \qquad (4.56)$$

$$Mn_2^0(CO)_{10} + NH_3 \longrightarrow [Mn^I(CO)_3(NH_3)_3]^+[Mn^{-I}(CO)_5]^- \qquad (4.57)$$

4.20

Ultrasound High-frequency sound waves can promote ligand dissociation and other reactions of organometallic species as a result of the high local temperatures that can be achieved by cavitation (the opening and closing of small bubbles of vapor in the solvent).[50]

4.7 STERIC AND SOLVENT EFFECTS IN SUBSTITUTION

As we saw in Section 4.4, the substitution rate for an associative reaction changes as we change the incoming ligand L, but what properties of L are important in deciding the rate? At first sight this looks complicated because

σ effects, π effects, and steric hindrance might all play a role. A promising approach[51] has been to assume that σ effects are dominant and compare observed rates with the pK_a of L. Since the pK_a measures the tendency for L to bind a proton, it correlates with the σ-donor power of L. For small ligands L, the rates are successfully predicted by Eq. 4.58. Both α and β need to be determined by experiment but are constant for any particular complex.

$$\log k_\sigma = \alpha + \beta(pK_a) \tag{4.58}$$

The α value measures the intrinsic reactivity of the complex, and β measures how much the rate is affected by the σ-donor strength of the ligand. The result is a Hammett-type linear free energy (LFE) relationship.

For more hindered ligands L, the predicted rate k_σ is larger than the observed rate k_{obs}, so hindered ligands react more slowly. Figure 4.6 shows a plot of ($\log k_{obs} - \log k_\sigma$) versus the cone angle θ for the substitution of (Ind)$Mn(CO)_3$(a) and $V(CO)_6$(b). With ($\log k_{obs} - \log k_\sigma$) as the ordinate, the points should lie on a horizontal line if Eq. 4.58 holds. This is indeed true for the smaller ligands, and so the rates depend only on σ effects. As we move to larger θ, there comes a threshold value θ_{st} at which steric effects become important; θ_{st} differs depending on the particular reaction studied. The rate falls off either sharply or slowly depending on how much the reaction is affected by steric effects. The resulting plot of Fig. 4.6 is the *steric profile* of the reaction. A more sophisticated version of this analysis is sometimes called *QALE* (quantitative analysis of ligand effects).

Solvents and Other Weakly Coordinating Ligands As we have seen in the last few sections, solvents can act as ligands. Of the common solvents, the ones most likely to bind, and therefore perhaps to divert the reaction from its intended goal are MeCN, pyridine, Me_2SO (dimethylsulfoxide, DMSO), and Me_2NCHO (dimethylformamide, DMF). Several species dissolve only in such solvents, which bind to the metal. DMF binds via the carbonyl because the nitrogen lone pair is tied up by resonance with the CO to give $Me_2N^+{=}CH{-}O^-$ (**4.21**). DMSO is a particularly interesting ligand because it can bind either via the S or the O. Both steric and hard and soft considerations seem to play a role in the choice. CS_2 is another solvent that finds restricted use in organometallic chemistry because it reacts with most complexes; SO_2 has been used successfully, especially as a low-temperature NMR solvent.

Tetrahydrofuran (THF), acetone, water, and ethanol are much less strongly ligating and are widely used. Early transition metal complexes can be very sensitive to solvents containing labile protons, but this depends on the case. All of these solvents can act as weak ligands, and their complexes can be synthetically useful. Ketones usually bind in the η^1 mode via O, as in **4.22**, but can also bind in the η^2 mode via both C and O, as in **4.23** (Eq. 4.59). The latter is favored by low steric hindrance and by a strongly back-donating

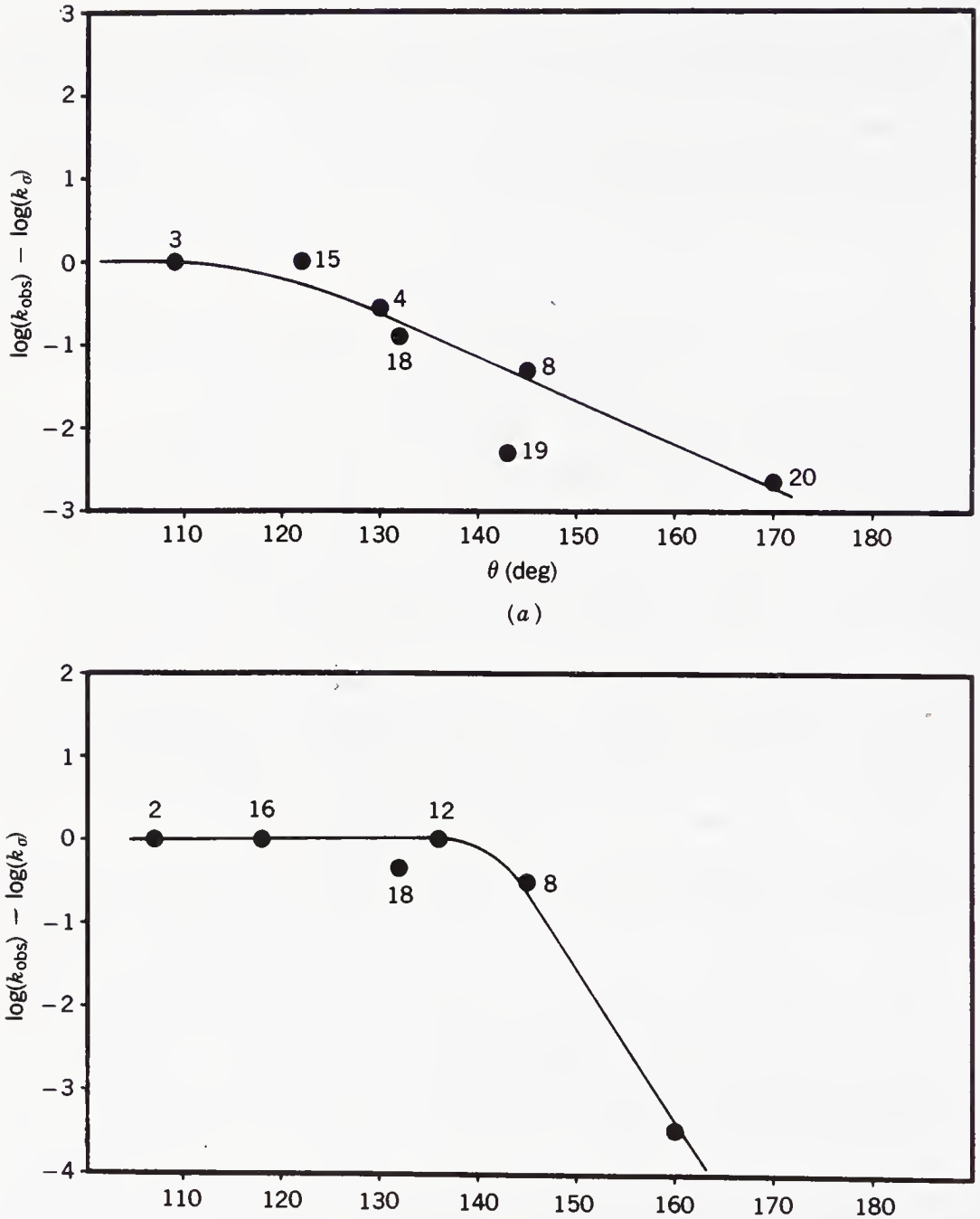
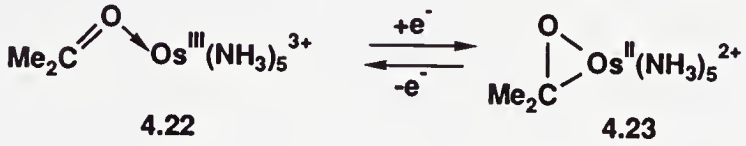


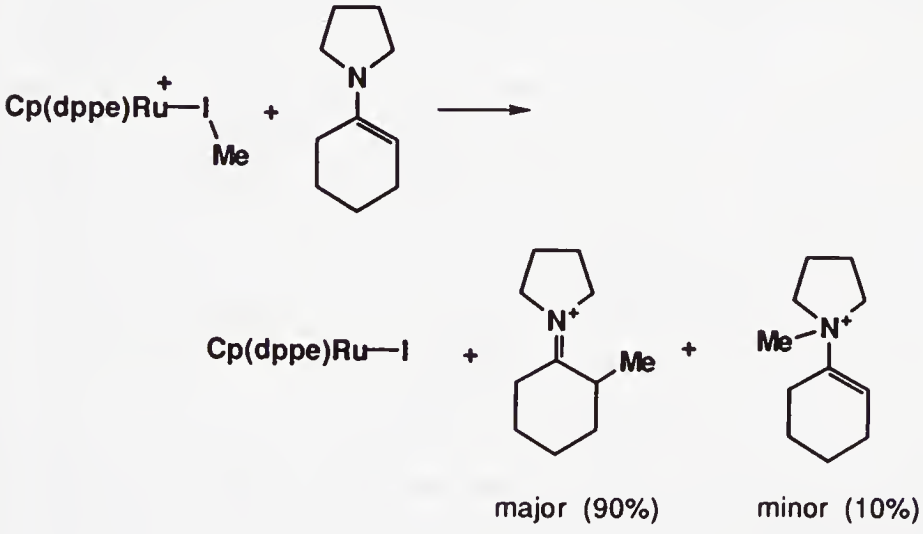
FIGURE 4.6 Steric profiles for the associative substitution reactions of (*a*), (η^5-indenyl)$Mn(CO)_3$ and (*b*) $V(CO)_6$. The labels refer to the following ligands: 2, $(MeO)_3P$; 3, $(EtO)_3P$; 4, $(i\text{-}PrO)_3P$; 8, Ph_3P; 12, $MePh_2P$; 15, Me_2PhP; 18, $(n\text{-}Bu)_3P$; 19, $(i\text{-}Bu)_3P$; 20, $(Cy)_3P$. (Reproduced from ref. 51 with permission of the American Chemical Society.)

metal fragment. Equation 4.59 shows how the η^1-to-η^2 rearrangement of acetone can occur on changing the oxidation state of the metal. The strong π-donor Os(II) favors the η^2 form.[52]



4.22 4.23 (4.59)

Halocarbon solvents tend to be oxidizing and can destroy sensitive compounds. Dichloromethane is probably the least reactive and most useful of them all. It has recently been shown that halocarbons can form stable complexes, some of which have been crystallographically characterized, such as $[IrH_2(IMe)_2(PPh_3)_2]^+$.[53] Although the binding is relatively weak, the presence of the metal greatly increases the rate of attack of nucleophiles at the halocarbon and, by manipulating the steric bulk, can strongly affect the selectivity of the reaction. For example, halocarbon binding favors the useful C alkylation rather than the usual N alkylation of enamines:[54]



major (90%) minor (10%) (4.60)

Arenes can in principle bind to metals, but the reaction is usually either sufficiently slow or thermodynamically unfavorable to permit the satisfactory use of arenes as solvents without significant interference. Alkanes are normally reliably noncoordinating (but see Section 12.3). Many complexes do not have sufficient solubility in the usual alkanes, but solvents such as ethylcyclohexane—the molecules of which pack poorly, leaving gaps in the liquid structure—are significantly better. IR spectra are best recorded in alkanes because they interact least with the solute and give the sharpest absorbtion peaks.

In the case of ionic complexes, the choice of counterion may be important, because they may bind to the metal.[55] Several anions in common use are

optimistically termed "noncoordinating." BF_4^- is useful, but F^- abstraction is a recognized problem, especially for the early metals, and many complexes are now known in which BF_4^- acts as a ligand via a B—F—M bridge; SbF_6^- appears to be less strongly coordinating. BPh_4^- can form η^6 arene complexes including $Ph_2B(\eta^6\text{-}Ph)_2Nb(MeC{\equiv}CMe)$ in which two rings bind to the same metal.[56] The $[B(3,5\text{-}\{CF_3\}_2C_6H_3)_4]^-$ is an excellent non-coordinating anion, and the corresponding acid is also available.[57] Among cations, $Ph_3P{=}N{=}PPh_3^+$ is one of the most widely used. In each case the counterions of choice are large, so as to stabilize the ionic lattice of the large organometallic ion.

REFERENCES

1. K. W. Whitten, K. D. Gailey, and R. E. Davis, *General Chemistry,* 4th ed., Saunders, New York, 1992; (a) pp. 337–351; (b) pp. 275–278.
2. (a) W. Hieber, *Z. Anorg. allgem. Chem.*, **245,** 295, 1940; (b) M. W. Burk and R. H. Crabtree, *Inorg. Chem.*, **25,** 931, 1986.
3. W. Hieber, E. O. Fischer, et al., *Z. Anorg. allgem. Chem.*, **269,** 308, 1952.
4. J. E. Ellis, *Adv. Organometal. Chem.*, **31,** 1, 1990.
5. M. C. Baird, J. A. Osborn, and G. Wilkinson, *Chem. Commun.*, 129, 1966.
6. (a) M. J. Winter, *Adv. Organometal. Chem.*, **29,** 101, 1989; (b) F. A. Cotton, *Prog. Inorg. Chem.*, **21,** 1, 1976; (c) M. D. Curtis, *J. Am. Chem. Soc.*, **100,** 5034, 1975; R. H. Crabtree and M. Lavin, *Inorg. Chem.*, **24,** 1949, 1985.
7. H. Schnöckel, *Angew. Chem., Int. Ed.*, **31,** 638, 1992.
8. L. G. Hubert-Pfalzgraf et al., *Inorg. Chem.*, **30,** 3105, 1991; S. J. Lippard et al., *J. Am. Chem. Soc.*, **112,** 3230, 1990.
9. N. J. Coville, E. Singleton, et al., *J. Organometal. Chem.*, **326,** 229, 1987.
10. G. Wilkinson et al., *J. Chem. Soc.* (*A*), 2037, 1967.
11. I. S. Butler, *Pure Appl. Chem.*, **60,** 1241, 1988.
12. H. Werner, *Angew. Chem., Int. Ed.*, **29,** 1077, 1990.
13. G. B. Richter-Addo and P. Legzdins, *Chem. Rev.*, **88,** 991, 1988; W. L. Gladfelter, *Adv. Organometal. Chem.*, **24,** 41, 1985.
14. J. W. Faller et al., *J. Organometal. Chem.*, **383,** 161, 1990.
15. D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **7,** 2345, 1968.
16. J. P. Collman, P. Farnham, and G. Dolcetti, *J. Am. Chem. Soc.*, **93,** 1788, 1971; (b) G. Dolcetti et al., *Inorg. Chem.*, **17,** 257, 1978.
17. D. E. Koshland et al., *Science,* **258,** 186, 1992; S. Snyder et al., *ibid.*, **259,** 381, 1993.
18. B. I. Swanson and S. K. Satija, *Chem. Commun.*, 40, 1973.
19. J. Lewis et al., *J. Chem. Soc.*, 4842, 1960.
20. M. Manassero et al., *Chem. Commun.*, 789, 1973.
21. L. F. Dahl et al., *Chem. Commun.*, 880, 1970.
22. B. B. Wayland and R. F. Schramm, *Inorg. Chem.*, 971, 1969.

23. R. G. Bergman et al., *J. Am. Chem. Soc.*, **105,** 3922, 1983.
24. (a) A. G. Orpen, *Chem. Commun.*, 1310, 1985; (b) G. Pacchioni and P. S. Bagus, *Inorg. Chem.*, **31,** 4391, 1992.
25. R. J. Morris and G. S. Girolami, *Inorg. Chem.*, **29,** 4167, 1990; H. Taube et al., *Inorg. Chem.*, **28,** 1310, 1989.
26. C. A. Tolman, *Chem. Rev.*, **77,** 313, 1977.
27. F. Basolo, *Polyhedron,* **9,** 1503, 1990; J. A. S. Howell and P. M. Burkinshaw, *Chem. Rev.*, **83,** 557, 1983.
28. (a) D. J. Darensbourg, *Adv. Organomet. Chem.*, **21,** 113, 1982; (b) P. H. Rieger et al., *Chem. Commun.*, 265 1981; (c) T. L. Brown et al., *J. Am. Chem. Soc.*, **100,** 4095, 1978; (d) T. L. Brown et al., *J. Am. Chem. Soc.*, **99,** 2982, 1977; (e) O. Eisenstein et al., *New J. Chem.*, **14,** 671, 1990; *Organometallics,* **11,** 729, 1992.
29. R. J. Cross, *Chem. Soc. Rev.*, **14,** 197, 1985.
30. F. Basolo et al., *J. Am. Chem. Soc.*, **85,** 3929, 1966; **89,** 4626, 1967.
31. R. G. Pearson, H. B. Gray, and F. Basolo, *J. Am. Chem. Soc.*, **82,** 787, 1960.
32. (a) H. Wawersik and F. Basolo, *J. Am. Chem. Soc.*, **89,** 4626, 1969; (b) R. van Eldik, *Organometallics,* **10,** 818, 1991.
33. (a) J. K. Kochi, *J. Organometal. Chem.*, **300,** 139, 1986; (b) W. C. Trogler (ed.), *Organometallic Radical Processes,* Elsevier, Amsterdam, 1991; D. R. Tyler et al., *Organometallics,* **11,** 3856, 1992; D. Astruc, *Chem. Rev.*, **88,** 1189, 1988; *Acct. Chem. Res.*, **24,** 36, 1991.
34. (a) P. H. Rieger et al., *Chem. Commun.*, 265, 1981; (b) D. A. Sweigert et al., *Chem. Commun.* 1993, 916.
35. M. C. Baird, *Chem. Rev.*, **88,** 1217, 1988.
36. D. R. Kidd and T. L. Brown, *J. Am. Chem. Soc.*, **100,** 4095, 1978.
37. M. Absi-Halabi and T. L. Brown, *J. Am. Chem. Soc.*, **99,** 2982, 1977.
38. G. A. Ozin et al., *J. Am. Chem. Soc.*, **97,** 7054, 1975.
39. T. L. Brown et al., *J. Am. Chem. Soc.*, **104,** 4007, 1982; W. C. Trogler, F. Basolo, et al., ibid, 4032.
40. J. K. Kochi et al. *Chem. Commun.*, 212, 1982.
41. (a) D. R. Tyler, *Coord. Chem. Res.*, **97,** 119, 1990; (b) D. Astruc, *New J. Chem.*, **16,** 305, 1992; (c) *J. Am. Chem. Soc.*, **114,** 8310, 1992.
42. H. Taube, *Comments Inorg. Chem.* **1,** 17, 1981; A. Poe and M. V. Twigg., *J. Chem. Soc.* Dalton, 1860, 1974; M. L. Tobe, *Inorg. Chem.*, **7,** 1260, 1968.
43. M. Poliakoff and E. Weitz, *Adv. Organometal. Chem.*, **25,** 277, 1986.
44. M. I. Bruce, *Angew. Chem., Int. Ed.*, **16,** 73, 1977.
45. M. Wrighton, *Chem. Rev.*, 401, 1974.
46. (a) R. van Eldik (ed.), *Inorganic High Pressure Chemistry: Kinetics and Mechanism,* Elsevier, Amsterdam, 1986; (b) D. Astruc et al., *J. Organometal. Chem.*, **377,** 309, 1989.
47. M. L. H. Green, *Pure Appl. Chem.*, **50,** 27, 1978.
48. M. Herberhold et al., *J. Organometal. Chem.*, **152,** 329, 1978.
49. D. R. Tyler et al., *Coord. Chem. Rev.*, **63,** 217, 1985.
50. K. S. Suslick, *Adv. Organomet. Chem.*, **25,** 73, 1986.

51. W. P. Giering et al., *Organometallics,* **4,** 1981, 1985; A. J. Poe, *Pure Appl. Chem.,* **60,** 1209, 1988; J. K. Kochi et al., *J. Am. Chem. Soc.,* **106,** 3771, 1984.
52. W. D. Harman, H. Taube, et al., *J. Am. Chem. Soc.,* **110,** 2439, 1988.
53. R. H. Crabtree, J. W. Faller, et al., *J. Am. Chem. Soc.,* **1,** 1361, 1982.
54. R. J. Kulawiec and R. H. Crabtree, *Coord. Chem. Rev.,* **99,** 89, 1990.
55. S. H. Strauss, *Chem. Rev.,* **93,** 927, 1993.
56. F. Calderazzo, U. Englbert, G. Pampaloni, and L. Rocchi, *Ang. Chem., Int. Ed.,* **31,** 1235, 1992.
57. M. Brookhart et al., *Organometallics,* **11,** 3920, 1992.

PROBLEMS

1. (a) Would you expect metal carbonyl halides $M(CO)_nX$, X = halide, to dissociate into halide anions and the metal carbonyl cation as easily as the hydrides, X = H, dissociate into H^+ and the metal carbonyl anion? (b) Given that we have a case where both of the above processes occur, contrast the role of the solvent in the two cases.

2. $Ni(CO)_4$ and $CO(lin\text{-}NO)(CO)_3$ are both tetrahedral. Why does the Ni compound undergo dissociative substitution and the Co compound undergo associative substitution?[55]

3. List the following in the order of decreasing reactivity you would predict for the attack of trimethylamine oxide on their CO groups: $Mo(CO)_6$, $Mn(CO)_6^+$, $Mo(CO)_2(dpe)_2$, $Mo(CO)_5^{2-}$, $Mo(CO)_4(dpe)$, $Mo(CO)_3(NO)_2$.

4. What single piece of physical data would you choose to measure as an aid to establishing the reactivity order of the carbonyl complexes above?

5. What are the electron counts, oxidation states, and coordination numbers of the metals in Eqs. 4.50–4.53.

6. Amines, NR_3, are usually only weakly coordinating toward low-valent metals. Why is this? Do you think that NF_3 would be a better ligand for these metals? Discuss the factors involved.

7. Phosphite dissociation from NiL_4 is only very slight for L = $P(OMe_3)$, yet for L = PMe_3 it is almost complete. Given that the two ligands have essentially the same cone angle, discuss the factors that might be responsible.

8. Determine whether associative or dissociative substitution is more likely for the following species (not all of which are stable): $CpFe(CO)_2L^+$, $Mn(CO)_5$, $Pt(PPh_3)_4$, $ReH_7(PPh_3)_2$, $PtCl_2(PPh_3)_2$, $IrCl(CO)(PPh_3)_2$.

9. Propose plausible structures for complexes with the following empirical formulas: $Rh(cod)(BPh_4)$, $(indenyl)_2W(CO)_2$, $PtMe_3I$, $(cot)(PtCl_2)_2$, $(CO)_2RhCl$.

10. Given a complex $M(CO)_6$ undergoing substitution with an entering ligand L′, what isomer(s) of the product would you expect to find in the products if L′ were (a) monodentate and a higher-trans-effect ligand than CO, or (b) L′ were bidentate and had a lower trans effect than CO.

11. NO^+ is isoelectronic with CO and often replaces CO in a substitution reaction, so it might seem that Eq. 4.61 should be a favorable reaction. Comment on whether the process shown is likely.

$$Mo(CO)_6 + NOBF_4 \longrightarrow Mo(NO)_6(BF_4)_6 + 6CO \qquad (4.61)$$

12. $Fe(CO)_5$ loses CO very slowly, but in the presence of an acid, substitution is greatly accelerated. Suggest possible explanations. For dissociative CO substitutions, the rate tends to be higher as the ν(CO) stretching frequency of the carbonyl increases. Suggest a reason.

CHAPTER 5

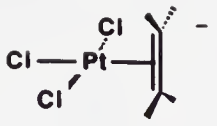
COMPLEXES OF π-BOUND LIGANDS

In this chapter we continue our survey of the different types of ligands by looking at cases in which the π electrons of an unsaturated organic fragment, rather than a lone pair, are donated to the metal to help form the M—L bond.

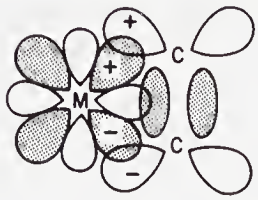
5.1 ALKENE AND ALKYNE COMPLEXES

In 1827, the Danish chemist Zeise obtained a new compound he took to be $KCl.PtCl_2.EtOH$ from the reaction of platinum chloride with EtOH. Only in the 1950s was it established that Zeise's salt, **5.1**, is really $K[PtCl_3(C_2H_4)].H_2O$, containing a coordinated ethylene, formed by dehydration of the ethanol, and a water of crystallization. The metal is bonded to both carbons of the ethylene, but the four C—H bonds bend slightly away from the metal, as shown in **5.1**; this allows the metal to bind efficiently to the π electrons of the alkene. For Zeise's salt, the best bonding picture is given by what is generally called the *Dewar–Chatt* model. This involves donation of the C=C π electrons to an empty d_σ orbital on the metal, so this electron pair is now delocalized over three centers: M, C, and C′. This is accompanied by back donation from a metal d_π orbital into the ligand lumo, the C=C π* level, as shown in **5.2**. By analogy with the bonding in CO, we will refer to the former as the "σ bond" and the latter as the "π bond." As is the case for CO, a σ bond is insufficient on its own to stabilize the complex, and so only metals capable of back donation, and not d^0 metals such as Ti(IV), bind alkenes.

The C=C bond of the alkene lengthens on binding. The M—alkene σ bond depletes the C=C π bond by partial transfer of these electrons to the

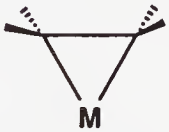


5.1

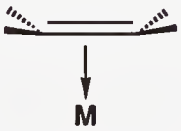


5.2

metal and so slightly weakens and, therefore, lengthens it. The major factor in lengthening the C=C bond, however, is the strength of back donation from the metal. By filling the π^* orbital of the C=C group, this back donation can sharply lower the C—C bond order of the coordinated alkene. For a weakly π-basic metal this reduction is slight, but for a good π base it can reduce it almost to a single bond. For Zeise's salt itself M—L σ bonding predominates because the Pt(II) is weakly π-basic, and the ligand (C—C: 1.375 Å) more nearly resembles the free alkene (1.337 Å). The substituents are only slightly bent back away from the metal, and the C—C distance is not greatly lengthened compared to free ethylene.[1] Pt(0), in contrast, is much more strongly π-basic, and in $Pt(PPh_3)_2(C_2H_4)$, the C—C distance becomes much longer (1.43 Å).[2] In such a case the metal alkene system is usually considered as approaching the *metalacyclopropane* extreme, **5.3**, as contrasted with the Dewar–Chatt model, **5.4**, involving minimal π back donation.



5.3
X_2



5.4
L

In the metalacyclopropane extreme, the substituents on carbon are strongly folded back away from the metal as the carbons rehybridize from sp^2 to something more closely approaching sp^3. The presence of electron-withdrawing groups on the alkene also encourages back donation and makes the alkene bind more strongly to the metal; for example, $Pt(PPh_3)_2(C_2CN_4)$ has an even longer C—C distance (1.49 Å) than the C_2H_4 complex.[3] In the Dewar–Chatt extreme, we can think of the ligand acting largely as a simple L ligand like PPh_3, but in the metalacyclopropane extreme, we have what is effectively a cyclic dialkyl, and so we can think of it as an X_2 (or σ_2) ligand. In both cases we have a 2e ligand on the covalent model, but while the L (or π) formulation, **5.4**, leaves the oxidation state unchanged, the X_2 picture, **5.3**, makes the oxidation state more positive by two units. By convention, the L model is usually adopted for the assignment of the oxidation state.

Structural studies are best for determining where any given alkene complex lies on the structural continuum between **5.3** and **5.4**. The position of any

vinyl protons, or of the vinyl carbons in the ^{1}H and ^{13}C NMR also shows a correlation with the structure. For example, at the metalacyclopropane X_2 extreme, the vinyl protons can resonate 5 ppm, and the vinyl carbons 100 ppm to high field of their position in the free ligand, as is appropriate for a change of hybridization from sp^2 to about sp^3 at carbon. Coordination shifts are usually much lower in the case of the L extreme.

The same factors that lead to lowering of ν(CO) in metal carbonyls also lead to greater metalacyclopropane character in alkene complexes: strong donor coligands, a net negative charge on the complex ion, and a particularly low oxidation state for the metal. This means that Pd(II), Hg(II), Ag(I), and Cu(I) alkene complexes tend to be L-type, or Dewar–Chatt, in character, while those of Ni(0), Pd(0), and Pt(0), tend to be X_2, or metalacyclopropane-like.

One chemically significant difference between the two extremes is that **5.4** tends to have a ∂^+ charge on carbon and therefore some of the character of a masked carbonium ion. This is because the ligand to metal σ donation depletes the charge on the ligand, and in the L-type extreme this is not recouped by back donation. These alkene complexes are therefore subject to nucleophilic attack, and resistant to electrophilic attack at the vinyl carbons. Since simple alkenes in the free state are subject to electrophilic but not nucleophilic attack, the effect of binding is very significant. It means that the appropriate metal fragment inverts the chemical character of the alkene, a phenomenon known as *umpolung*. The metal can act both to promote nucleophilic attack or to inhibit electrophilic attack at the ethylene carbons—that is to say, it can act either as an activating group or as a protecting group, depending on the reagents involved.

Strained alkenes, such as cyclopropene or norbornene (**5.5**), bind unusually strongly to metals because the rehybridization on binding leads to relief of strain. Much of the strain in a small ring compound arises because the real C—C—C angles are constrained to be smaller than the ideal ones. Such an alkene is therefore less strained when complexed because the ideal angles at the vinylic carbons drop from the value of 120°, appropriate for sp^2 hybridization close to 109°, appropriate for sp^3 hybridization. In some cases very strained alkenes are only stable in the complexed form. Nonconjugated dienes such as 1,5-cyclooctadiene (cod), and norbornadiene (nbd), can chelate to the metal and so bind more strongly than the corresponding monoenes, but conjugated dienes behave somewhat differently (Section 5.3). Ketenes (RCH=C=O) can bind in several ways, including η^2 via the C=C bond.[4]

5.5

Synthesis Alkene complexes are usually synthesized by one of the methods shown in Eqs. 5.1–5.7:

1. Substitution in a low-valent metal:

$$AgOSO_2CF_3 + C_2H_4 \longrightarrow (C_2H_4)AgOSO_2CF_3 \quad (5.1)^{5a}$$

$$PtCl_4^{2-} + C_2H_4 \longrightarrow [PtCl_3(C_2H_4)]^- + Cl^- \quad (5.2)^{5b}$$

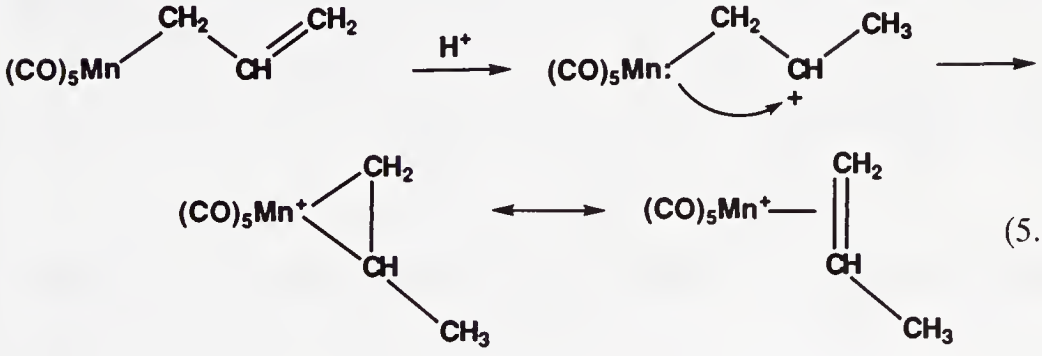
$$Cp(CO)_2Fe(Me_2C{=}CH_2) \xrightarrow{\text{1-hexene}} Cp(CO)_2Fe(\text{1-hexene}) \quad (5.3)^{6}$$

2. Reduction of a higher valent metal in the presence of an alkene:

$$(cod)PtCl_2 + C_8H_8^{2-} + cod \longrightarrow Pt(cod)_2 \quad (5.4)^{7}$$

$$RhCl_3 + nbd + CH_3CH_2OH \longrightarrow [(nbd)Rh(\mu\text{-}Cl)]_2 + CH_3CHO + HCl \quad (5.5)^{8}$$

3. From alkyls and related species:



(5.6)[9]

$$CpTaCl_3 \xrightarrow{n\text{-BuMgX}} \{Cp_2TaBu_3\} \xrightarrow{\beta \text{ elim., red. elim.}} Cp_2TaH(\text{1-butene}) + \text{butene} + \text{butane} \quad (5.7)^{10}$$

(where red. elim. = reductive elimination).

Reversible binding of alkenes to Ag^+ (Eq. 5.1) is used to separate different alkenes chromatographically on silver-doped gas chromatography columns. Less hindered alkenes usually bind more strongly (Eq. 5.3). The reducing agent in Eq. 5.4 is the dianion of cyclooctatetraene, which the authors may have intended to act as a ligand. If so, this is an example of a common event—a reaction with an unintended outcome. The alcohol solvent is the reductant in Eq. 5.5; this happens by the mechanism of Eq. 3.29. Protonation at the terminal methylene in the η^1-allyl manganese complex of Eq. 5.6 creates what may be regarded as a carbonium ion having a metal at the β position. Since the carbonium ion is a zero-electron ligand like a proton, it can coordinate

to the 18e metal to give the alkene complex. Equation 5.7 shows a common result of trying to make a metal alkyl in which the alkyl contains a β hydrogen.

Reactions Perhaps the most important reaction of alkene ligands is their insertion into M—X bonds to give alkyls as we saw in Chapter 3 (Eqs. 3.18–3.20). This goes very readily for X = H, often at room temperature. On the other hand, insertion into other M—X bonds is rarer. Strained alkenes and alkynes insert most readily; the first case is promoted by relief of strain in the alkyl product and the second, because the product M-vinyl bond strength is unusually high. Fluoroalkenes (e.g., Eq. 5.9) also insert readily because the resulting fluoroalkyl has a very high M—C bond strength (Section 3.6).

$$PtHCl(PEt_3)_2 + C_2H_4 \rightleftharpoons PtEtCl(PEt_3)_2 \qquad (5.8)^{11}$$

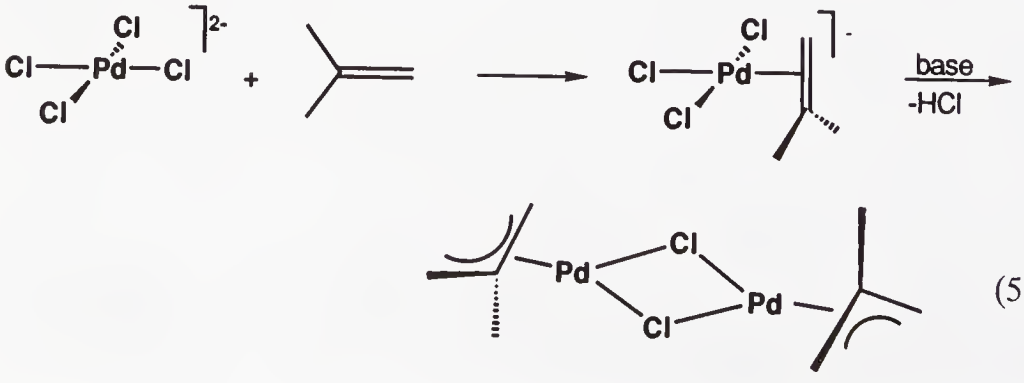
$$AuMe(PPh_3) + CF_2{=}CF_2 \longrightarrow \{(CF_2{=}CF_2)AuMe(PPh_3)\} \longrightarrow$$

$$Au(CF_2{-}CF_2Me)(PPh_3) \qquad (5.9)^{12}$$

When the metal fragment is a poor π base, the L model (**5.4**) applies and the vinylic carbons bound to the metal behave as masked, metal-stabilized carbonium ions. In such a case we often see nucleophilic attack (e.g., Eq. 5.10).[13] This is an example of a more general reaction type—nucleophilic attack on polyenes or polyenyls, and will be discussed in more detail in Section 8.3.

(5.10)

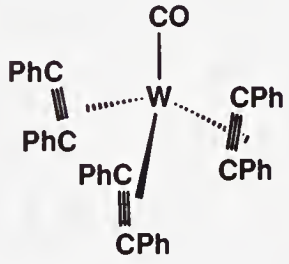
Finally, alkenes containing allylic hydrogens can undergo oxidative addition of the C—H bond in what is effectively a cyclometallation to give an allyl hydride complex. In the example shown, a base is also present so as to remove HCl from the metal and trap the allyl product.[14]



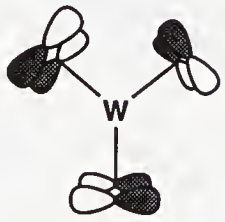
(5.11)

Alkyne Complexes Alkynes behave in ways broadly similar to alkenes, but being more electronegative, they tend to encourage back donation and bind more strongly. The substituents tend to fold back away from the metal by 30–40° in the complex, and the M—C distances are slightly shorter than in the corresponding alkene complexes. The metalacyclopropene model (**5.6**) seems often to be the most appropriate description when alkynes act as 2e donors. More interestingly, alkynes can form complexes that appear to be coordinatively unsaturated. For example, **5.7**[15a] appears to be 14e, and **5.8**,[15b] a 16e species if we count the alkyne as a conventional 2e donor. In such cases it is now clear that the alkyne is using its second C=C π-bonding orbital, which lies at right angles to the first. When this also interacts with the metal, the alkyne is a 4e donor[15c] and **5.8** can be formulated as an 18e complex. Compound **5.7** might seem to be a 20e complex on this model, but in fact one combination of ligand π orbitals, **5.7a**, finds no match among the *d* orbitals of the metal, and so the true electron count is 18e. An extreme valence bond formulation of the 4e donor form is to regard it as a bis-carbene (**5.9**), the bonding of which we look at in Chapter 11. 2e alkyne complexes are rare for d^6 metals because of a 4e repulsion between the filled metal d_π and the second alkyne C=C π bonding pair.

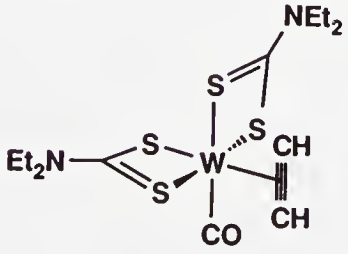
5.6



5.7



5.7a



5.8

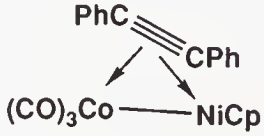
5.9

When the free alkyne has a structure which leads to bending of the C≡C triple bond, this induces strain, which is partially relieved on binding. Cyclohexyne and benzyne are both highly unstable species that bind very strongly to metals, as in $[(Ph_3P)_2Pt(\eta^2\text{-cyclohexyne})]$ or the product shown in Eq.

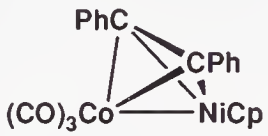
5.12.[16a] Cyclobutyne, normally inaccessible, has been trapped as its triosmium cluster complex.[16b]

$$Cp^*TaMe_4Ph \xrightarrow{heat} Cp^*TaMe_3(\eta^2\text{-benzyne}) + MeH \qquad (5.12)$$

Alkynes readily bridge an M—M bond, in which case they can act as conventional 2e donors to each metal (**5.10**). The alternative tetrahedrane form (**5.11**) is the equivalent of the metalacyclopropane picture for such a system.



5.10



5.11

5.2 ALLYL COMPLEXES

The allyl group[17] binds in one of two ways. In the monohapto form, **5.12**, it is a simple le X-type ligand like Me, and in the trihapto form, **5.13**, it acts as a 3e LX ligand. It is often useful to think of **5.13** in terms of the resonance forms **5.14a** and **5.14b**.

5.12

5.13

5.14a **5.14b**

Figure 5.1*a* shows that of the three m.o.'s of the allyl fragment, ψ_1 can interact with a suitable metal d_σ orbital, and ψ_2, with a M(d_π) orbital on the metal; ψ_3 is not a frontier orbital and so probably of lesser importance.[19] Note that as the number of nodes increases, the m.o.'s of the free ligand become less stable (Fig. 5.1*b*). Two peculiarities of the structures of η^3 allyl complexes can be understood on this picture. Firstly, the plane of the allyl is canted at an angle θ with respect to the coordination polyhedron around the metal, as shown in Fig. 5.1*c*; θ is usually 5–10°. The reason seems to be that the interaction between ψ_2 and the d_{xy} orbital on the metal is improved if the allyl group moves in this way, as can be seen in Fig. 5.1*c*. The structures also show that the terminal CH_2 groups of the allyl are twisted about the C—C vector in such a way as to rotate the anti hydrogens, H_a away from the metal, and the syn hydrogens, H_s, toward the metal as shown by the arrows in Fig. 5.1*d*. This seems to happen so that the *p* orbital on these carbons points more directly toward the metal, thus further improving the overlap.[20] Note the

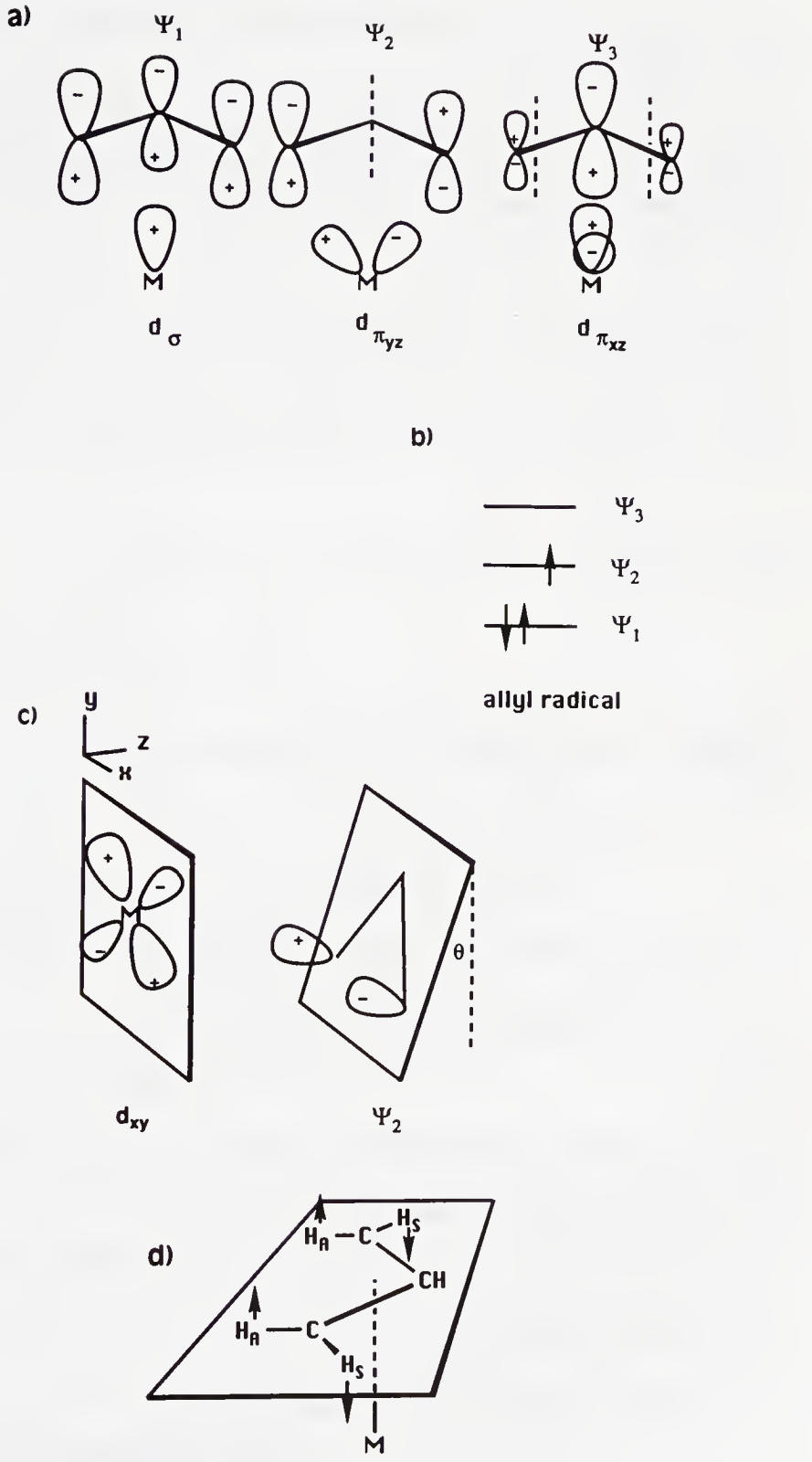
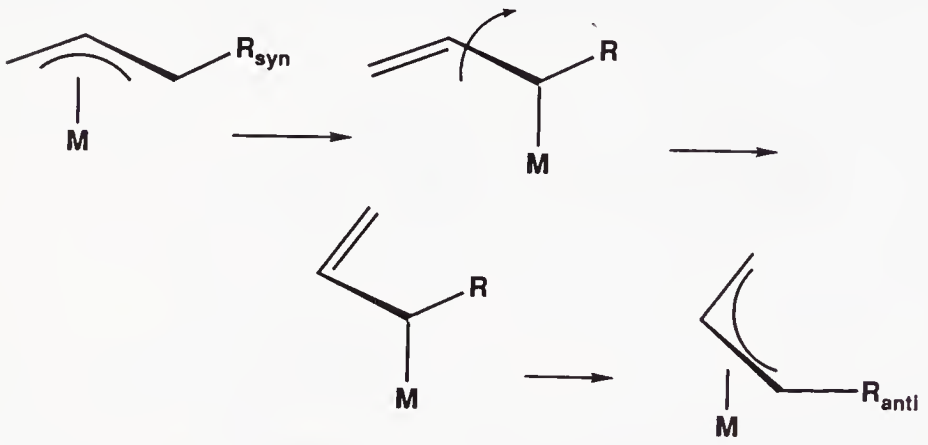


FIGURE 5.1 The electronic structure of the allyl ligand and some features of metal–allyl bonding. Nodes are shown as dotted lines in (a).

nomenclature of the allyl substituents, which are exo or endo with respect to the central CH.

The η^3-allyl group often shows exchange of the syn and anti substituents. One mechanism that accomplishes this goes through an η^1-allyl intermediate, as shown in Eq. 5.13. This kind of exchange can affect the appearance of the ^{1}H NMR spectrum (Section 10.2), and also means that an allyl complex of a given stereochemistry may rearrange with time.



(5.13)

Synthesis Typical routes to allyl complexes are shown below.

1. From an alkene (see also Eq. 5.11):

$$\text{Mo(dpe)}_2(\eta^2\text{-propene}) \rightleftharpoons \text{Mo(dpe)}_2(\eta^3\text{-allyl})\text{H} \quad (5.14)^{21}$$

2. From an allyl compound by nucleophilic attack on the metal:

$$\text{CH}_2{=}\text{CHCH}_2\text{SnMe}_3 + \text{Mn(CO)}_5\text{Br} \xrightarrow{\text{reflux}} (\eta^3\text{-CH}_2\text{CHCH}_2)\text{Mn(CO)}_4 \quad (5.15)^{22}$$

3. From an allyl compound by electrophilic attack on the metal:[23]

$$\text{CH}_2{=}\text{CHCH}_2\text{Cl} + \text{Mn(CO)}_5^- \longrightarrow (\eta^1\text{-CH}_2{=}\text{CHCH}_2)\text{Mn(CO)}_5 \xrightarrow{\text{heat}} (\eta^3\text{-CH}_2\text{CHCH}_2)\text{Mn(CO)}_4 \quad (5.16)$$

4. From diene complexes:[24,25]

$$(\eta^2\text{-CH}_2{=}\text{CH}{-}\text{CH}{=}\text{CH}_2)\text{Fe(CO)}_3 \xrightarrow{\text{HCl}} (\eta^3\text{-CH}_2\text{CHCHMe})\text{Fe(CO)}_3\text{Cl} \quad (5.17)$$

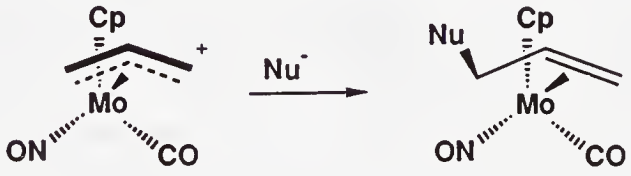
$$\text{Cp}_2\text{TiCl} \xrightarrow{i\text{-PrMgBr–propene}} \{\text{Cp}_2\text{TiH}\} \xrightarrow{\text{butadiene}} \text{Cp}_2\text{Ti}(\eta^3\text{-MeCHCHCHMe}) \quad (5.18)$$

$$[PtH(acetone)(PR_3)_2]^+ + CH_2{=}C{=}CH_2 \longrightarrow [(\eta^3\text{-allyl})Pt(PR_3)_2]^+ \quad (5.19)$$

The first route we saw in Section 5.1; the second and third resemble the synthetic reactions most commonly used for alkyl complexes. In Eqs. 5.15 and 5.16, the metal often attacks at the least hindered terminal CH_2 group. Equation 5.17 demonstrates an electrophilic attack on a diene complex; we shall see in the next section why attack takes place at the terminal carbon. Equation 5.18 shows that when one C=C group of a diene undergoes insertion into a M—H bond, the hydrogen tends to attach itself to the terminal carbon of the conjugated chain. This leaves a methylallyl group, which can become η^3 if a vacant site is available. Finally, Eq. 5.19 shows that allenes insert into an M—H bond to put the hydride on the central carbon and generate an allyl group.

Reactions The most important reactions of allyls are illustrated in Eqs. 5.20–5.23:

1. With nucleophiles (Eq. 5.20):



(5.20)[26]

2. With electrophiles:[27]

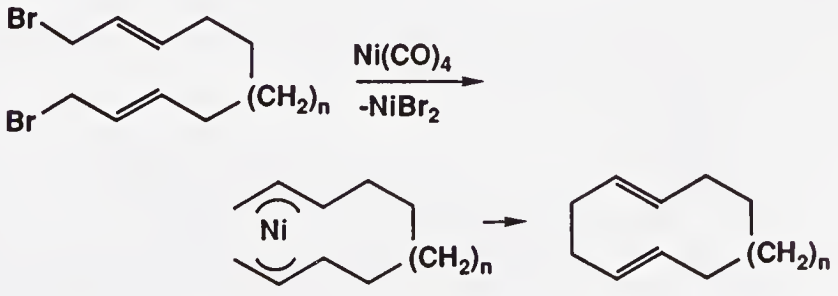
$$Cp(CO)_2FeCH_2CH{=}CH_2 + E^+ \longrightarrow [Cp(CO)_2Fe(CH_2{=}CHCH_2E)]^+$$

$$(E^+ = HgCl^+, Me^+, RCO^+, H^+, Br^+) \quad (5.21)$$

3. By insertion:[28]

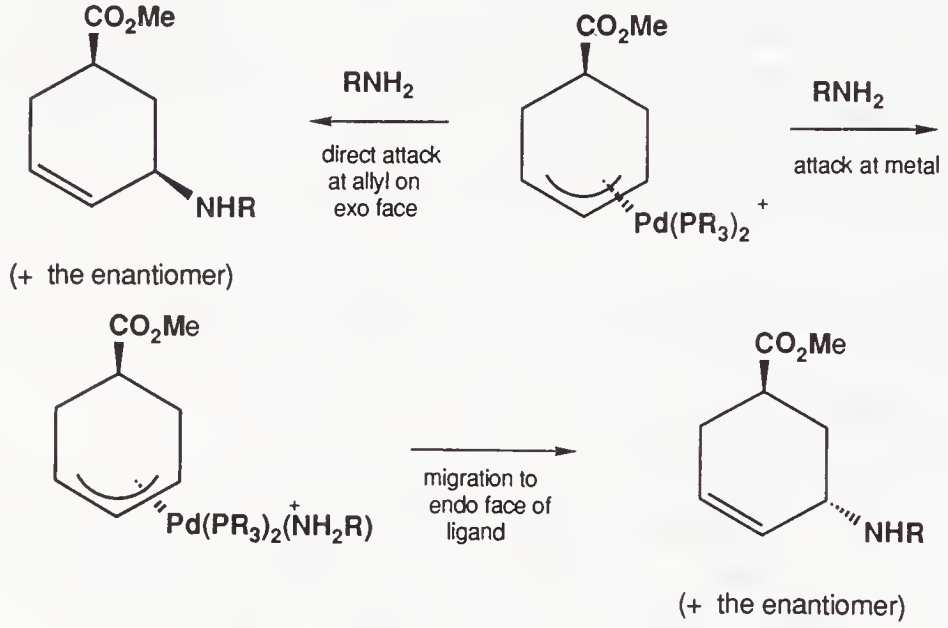
$$(\eta^3\text{-allyl})_2Ni \xrightarrow{CO_2} (\eta^3\text{-allyl})NiOCOCH_2CH{=}CH_2 \quad (5.22)$$

4. With reductive elimination (Eq. 5.23):[29]



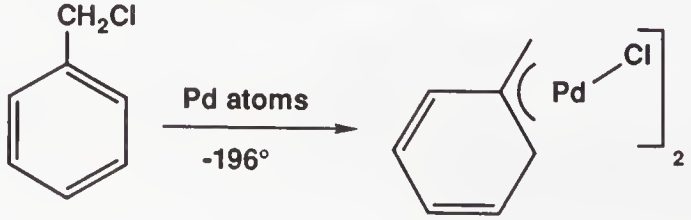
(5.23)

Nucleophilic attack at one of the terminal carbons of the allyl group most often takes place from the face of the allyl away from the metal. This happens when the nucleophile attacks directly. On the other hand, cases are known in which the nucleophile first attacks the metal and only then is transferred to the allyl group. The latter route can only take place when a vacant site is made available at the metal. An example of a system that gives products of both stereochemistries is shown in Eq. 5.24.[30]

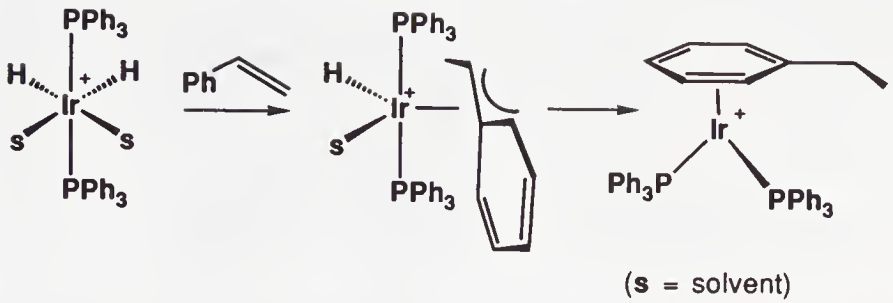


(5.24)

Other Ligands Cyclopropenyl complexes, such as $(\eta^3\text{-}Ph_3C_3)Co(CO)_3$,[31] are also known, but are less well studied than allyls. Benzyl groups can be persuaded to give η^3-benzyl species, but the aromatic C=C double bond is less available than that of the simple allyl group, so the complexes have a high tendency to go to the η^1 form. One example of such a complex is formed by cocondensing Pd atoms and benzyl chloride in a *metal vapor synthesis* experiment (Eq. 5.25). This technique requires special equipment, but allows preparatively useful quantities of metal atoms to be used as reagents. They are formed by firing an electron gun at the metal surface in a vacuum and condensing the atoms with ligand vapor at liquid N_2 temperature. The η^3-benzyl intermediate, shown in Eq. 5.25, has also been invoked in the unusual rearrangement of Eq. 5.26.[32a] The η^3-propargyl ligand ($^-CH_2—C{\equiv}CH$), which sometimes behaves as an η^3-allenyl group ($CH_2{=}C{=}CH^-$), is also known.[32b] The bis-triphenylphosphine Pt(II) complex readily undergoes nucleophilic attack at the central carbon.[32c]



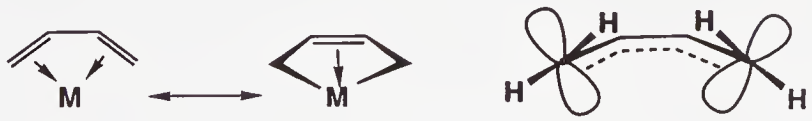
(5.25)



(5.26)

5.3 DIENE COMPLEXES

This ligand usually acts as a 4e donor in its cisoid conformation, as shown in **5.15**. This L_2 (or π_2) form is analogous to the Chatt–Dewar extreme for alkenes, while the LX_2 (or $\sigma_2\pi$) form **5.16** is related to the metalacyclopropane extreme. The first is rarely seen in pure form but (butadiene)$Fe(CO)_3$ has an intermediate character, with the C_1C_2, C_2C_3 and C_3C_4 distances about equal (1.46 Å) and C_1 and C_4 further from the metal than C_2 and C_3. Form **5.16** becomes more important as the back donation increases. Bound to the strongly back-donating $Hf(PMe_3)_2Cl_2$ d^2 system, 1,2-dimethylbutadiene shows an extreme LX_2 bonding pattern.[33] The substituents at C_1 and C_4 twist approximately 20–30° out of the plane of the ligand and bend back strongly so that the corresponding *p* orbitals can overlap better with the metal (**5.17**). The C_1C_2, and C_3C_4 distances [1.46 Å (average)] are much longer than C_2C_3 (1.40 Å), and C_1 and C_4 are closer to the metal than C_2 and C_3 by 0.18Å.



L_2 LX_2

5.15 **5.16** **5.17**

We expect the frontier orbitals of the butadiene, ψ_2 (homo) and ψ_3 (lumo), to be the most important in bonding to the metal. The m.o. diagram (Fig. 5.2) shows that both the depletion of electron density in ψ_2 by σ donation to the metal, and population of ψ_3 by back donation from the metal will have the effect of lengthening C_1C_2 and shortening C_2C_3, because ψ_2 is C_1C_2 antibonding and ψ_3 is C_2C_3 bonding in character. Protonation occurs at C_1 (Eq. 5.17) because the homo, ψ_2, has its highest coefficient there.

This is quite general—binding to a metal usually depletes the ligand homo and fills the ligand lumo. This is the main reason why binding has such a profound effect on the chemical character of a ligand (see Section 2.6). The structure of the bound form of a ligand is often similar to that of the first excited state of the free ligand, because to reach this state we promote an electron from the homo to the lumo, thus partially depleting the former and filling the latter.

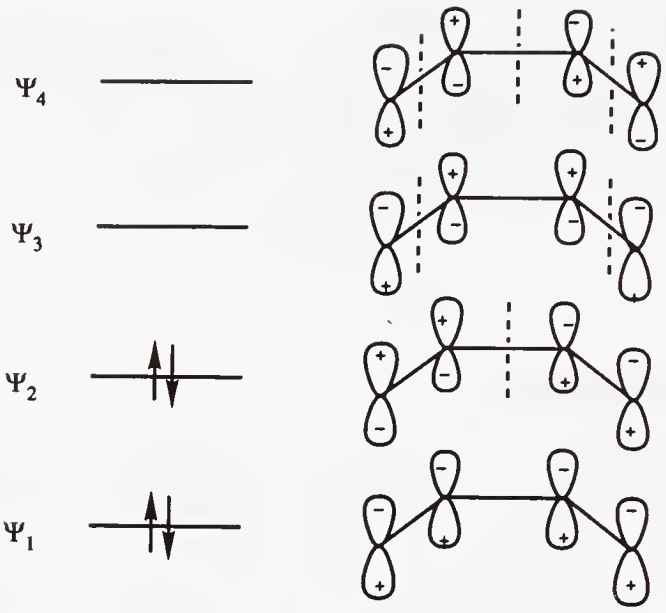
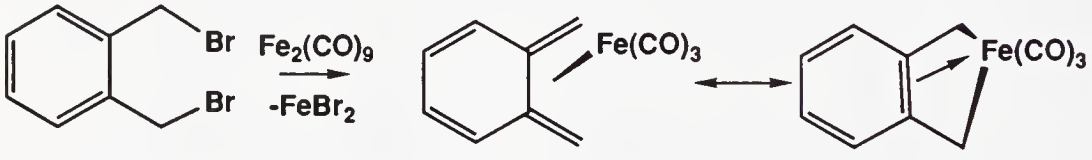
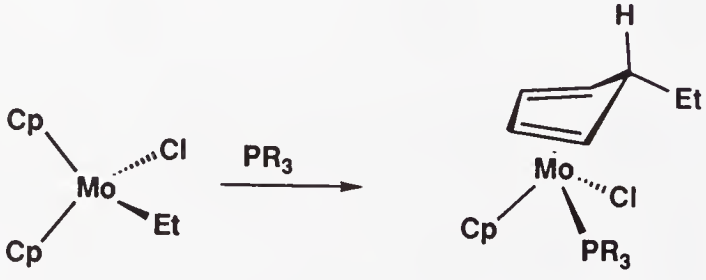


FIGURE 5.2 The electronic structure of butadiene. An electron-rich metal will tend to populate Ψ_3; an electron-poor metal will tend to depopulate Ψ_2.

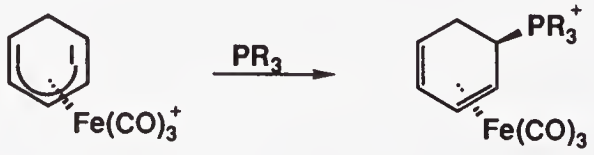
Butadiene complexes are usually prepared in ways very similar to those used for alkenes, but some interesting examples of methods specific to diene complexes are shown below (Eqs. 5.27–5.29):[34,35]



(5.27)



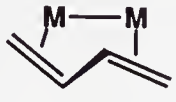
(5.28)



(5.29)

The binding of butadiene in the transoid form is much rarer. It is found in $Os_3(CO)_{10}(C_4H_6)$, **5.18**, in which the diene is η^2-bound to two different Os centers[36] and in $Cp_2Zr(C_4H_6)$, **5.19**, in which the diene is bound to a single

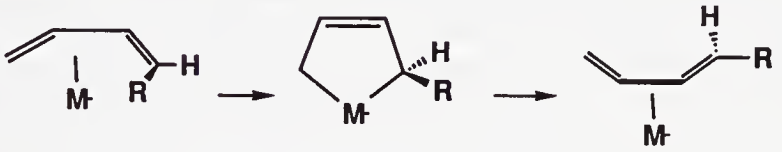
Zr.[37] In the zirconium case, the cisoid isomer also exists but it rearranges to give a 1:1 thermodynamic mixture of the two forms on standing; photolysis leads to conversion to give the trans form.



5.18

5.19

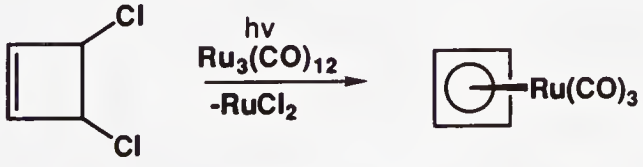
The interesting rearrangement called the "envelope shift" (shown in Eq. 5.30), is sometimes seen.[38] It has the effect of exchanging the anti and syn substituents on the diene via an X_2-type dialkyl intermediate, in which the central C=C group must be uncomplexed (i.e., unlike the case of **5.16**) because the metal lies in the plane of this C=C group and orthogonal to the C=C π electrons:



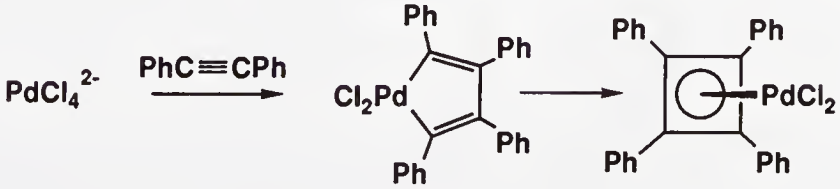
(5.30)

Cyclobutadiene Complexes Up to now, most the neutral ligands we have studied have been stable in the free state. With cyclobutadiene, we have a situation where the complexes are very stable and have been known for many years, but the free dienes are so highly reactive that stable examples have only been reported very recently. The free molecule, with four π electrons, is antiaromatic and rectangular, but the ligand is square and seems to be aromatic. The metal must stabilize the diene by populating the lumo of the free diene by back donation; by gaining partial control of two more π electrons, this gives the diene an electronic structure resembling that of the aromatic six π-electron dianion $R_4C_4^{2-}$; ligand-to-metal σ donation prevents the ligand from accumulating excessive negative charge. This is a good example of the free and bound forms of the ligand being substantially different from one another (Section 2.6).

Some synthetic routes are [39,40]



(5.31)

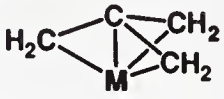


(5.32)

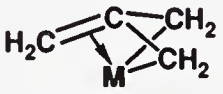
5.20

The ruthenium example probably involves oxidative addition of the dihalide to two $Ru(CO)_3$ fragments derived from the photolysis of the cluster; then the metals probably disproportionate, so that one becomes the observed product and the other carries away the halides in the form of undefined Ru(II) halo complexes. The reaction of Eq. 5.32 probably goes by an oxidative coupling to give **5.20**, which is very favorable for alkynes, followed by a reductive elimination of the cyclobutadiene ligand.

Other Ligands Another significant tetrahapto ligand that is very unstable in the free state is trimethylenemethane (**5.21**). It can be considered as an LX_2 ligand; one of the resonance forms is shown as **5.22**. The ligand shows an umbrella distortion from the ideal planar conformation, which means that the central carbon lies out of the plane away from the metal. Maintaining good delocalization within the ligand favors the planar form, but distorting allows the *p* orbitals on the terminal carbons to point more directly toward the metal and improve M—L overlap. In spite of the distortion, the central carbon is still closest to the metal.[41] Two synthetic routes[42] are illustrated in Eq. 5.33.

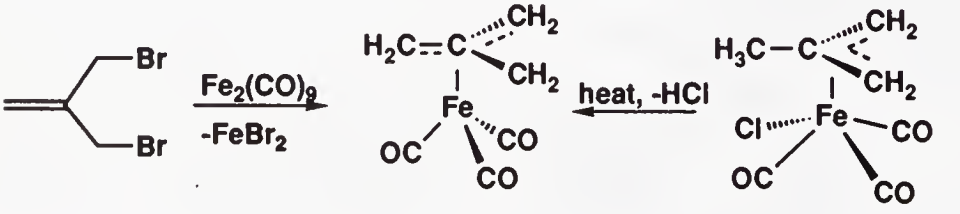


5.21

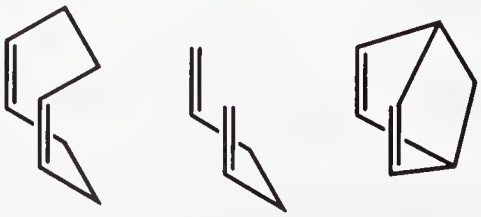


5.22

Nonconjugated diolefins behave much as simple olefin complexes, except that the chelation introduces rigidity and increases the binding constant to the metal. 1,5-cyclooctadiene (**5.23**), 1,5-heptadiene (**5.24**), and norbornadiene (**5.25**) are typical examples.



(5.33)



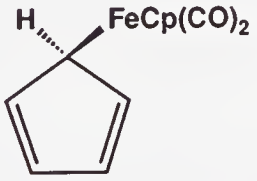
5.23 **5.24** **5.25**

5.4 CYCLOPENTADIENYL COMPLEXES

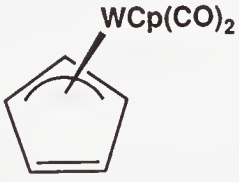
The cyclopentadienyl group is perhaps the most important of the polyenyls because it is the most firmly bound and the most inert to nucleophilic or electrophilic reagents. This makes it a reliable stabilizing ligand for a whole series of complexes $CpML_n$ (n = 2, 3, or 4) where we want chemistry to occur at the ML_n group. $CpML_n$ are often referred to as "two-, three-, or four-legged piano stools," with the Cp being regarded as the "seat" and the ligands as the "legs." The *metallocenes,* Cp_2M (see Fig. 5.5) are also important in the historical development of organometallic chemistry, but their chemistry is somewhat less rich than that of the piano stools, because fewer ligands can bind to the metallocenes without overstepping the 18e rule. Their most important application is alkene polymerization (Chapter 11).

The sandwich structure of the orange crystalline Cp_2Fe was deduced by Wilkinson and Woodward and by Fischer and their respective coworkers in 1954.[43] This is usually counted as one of the most significant discoveries during the early development of organotransition metal chemistry, and helped to launch it as an independent field in its own right.

The η^2 structure is also found where the coligands are sufficiently firmly bound so that the Cp cannot rearrange to η^5 (e.g., **5.26**). Trihapto-Cp groups are rather rare (e.g., **5.27**); the Cp folds so the uncomplexed C=C group can bend away from the metal. The tendency of an η^5 Cp group to "slip" to an η^3 or η^1 structure is small. Nevertheless, there are cases in which 18e piano stool complexes have been found to undergo substitution by an associative mechanism, and it is therefore assumed that the Cp can slip in the transition state.



5.26



5.27

$$CpRh(CO)_2 \xrightarrow{L} \{\eta^3\text{-}CpRh(CO)_2L\} \xrightarrow{-CO} CpRhL(CO) \quad (5.34)^{44}$$

A rare rearrangement of an η^5 Cp to a stable η^1 structure on the addition of a ligand has recently been observed:

$$CpReMe(NO)(CO) \xrightarrow{PMe_3} \eta^1\text{-}CpReMe(NO)(CO)(PMe_3)_2 \quad (5.35)^{45}$$

In this case the slip takes place in preference to two other possible rearrangements that might have relieved the electron count on the metal: bending of the NO, or methyl migration to CO. It is likely that one of these two processes

may be important in the initial attack of the phosphine, but that slip of the Cp gives the stable product shown. η^1-Cp groups tend to show both long and short C—C distances, as appropriate for an uncomplexed diene. The η^5 form has essentially equal C=C distances, and the substituents point very slightly toward the metal.

η^5-Cp groups usually show a resonance in the ^{1}H NMR at 4–6δ, as appropriate for an aromatic group. This aromaticity was one of the first properties of the Cp group to attract the attention of the early workers, who showed that ferrocene, like benzene, undergoes electrophilic acylation. η^1-Cp groups can show a more complex ^{1}H NMR pattern: the α hydrogen appears at about 3.5δ, and the β and γ hydrogens, at 5–7δ. As we shall see in Chapter 10, the η^1-Cp group can be fluxional, in which case the metal rapidly moves around the ring so as to make all the protons equivalent. Such complexes are picturesquely termed "ring whizzers."

The m.o. scheme for the C_5H_5 group is shown in Fig. 5.3. The five *p* orbitals on carbon give rise to five m.o.'s for the C_5H_5 group. In Fig. 5.3*a*, only the nodes are shown for simplicity, but Fig. 5.3*b* shows the orbitals in full in one case. The most important overlaps are ψ_1 with the metal *s*, and ψ_2 and ψ_3 with the d_{xz} and d_{yz} orbitals (an example is shown explicitly in Fig. 5.3*b*); ψ_4 and ψ_5 do not interact very strongly with metal orbitals, and the Cp group is therefore not a particularly good π acceptor. This means that Cp complexes are generally electron-rich, and that the presence of the Cp encourages back donation from the metal to the other ligands present.

If we put two Cp groups and one metal together, we obtain the m.o. diagram for a metallocene (Fig. 5.4). We now have to look at the symmetry of *pairs* of Cp orbitals and ask how they will interact with the metal orbitals. As an example, if we take the combination of the ψ_1's of both rings shown in Fig. 5.4*b*, which has the symmetry label a_{1g}, we find it can interact with the d_{z^2} orbital on the metal, also a_{1g}. Taking the opposite combination of ψ_1's (shown in Fig. 5.4*c*, and labeled a_{2u}) we find that the interaction now takes place with p_z. Similarly, ψ_2 and ψ_3 combinations are strongly stabilized by interactions with the d_{xz}, d_{yz}, p_x, and p_y orbitals. Although the details of the interaction are more complex in this case, the picture retains L → M direct-donation and M → L back-donation components as we saw for CO or C_2H_4.

As might be expected for what is essentially an octahedral complex, the *d*-orbital splitting pattern for an octahedral crystal field, highlighted in a box in Fig. 5.4*a*, appears in the final pattern. Because of the different choice of axes in this case (Fig. 5.3*c*) than previously, it turns out that the labels of the orbitals (d_{xy}, d_{yz}, etc.) are different in this diagram from what they were for the crystal field diagrams we saw before. This does not matter; labels are our convention, not Nature's.

In the case of ferrocene itself, all the bonding and nonbonding orbitals are exactly filled, so it is not surprising that the Group 8 metallocenes are the stablest members of the series. Metallocenes from Groups 9 and 10 have one or two electrons in antibonding orbitals; this is why $CoCp_2$ and $NiCp_2$ are

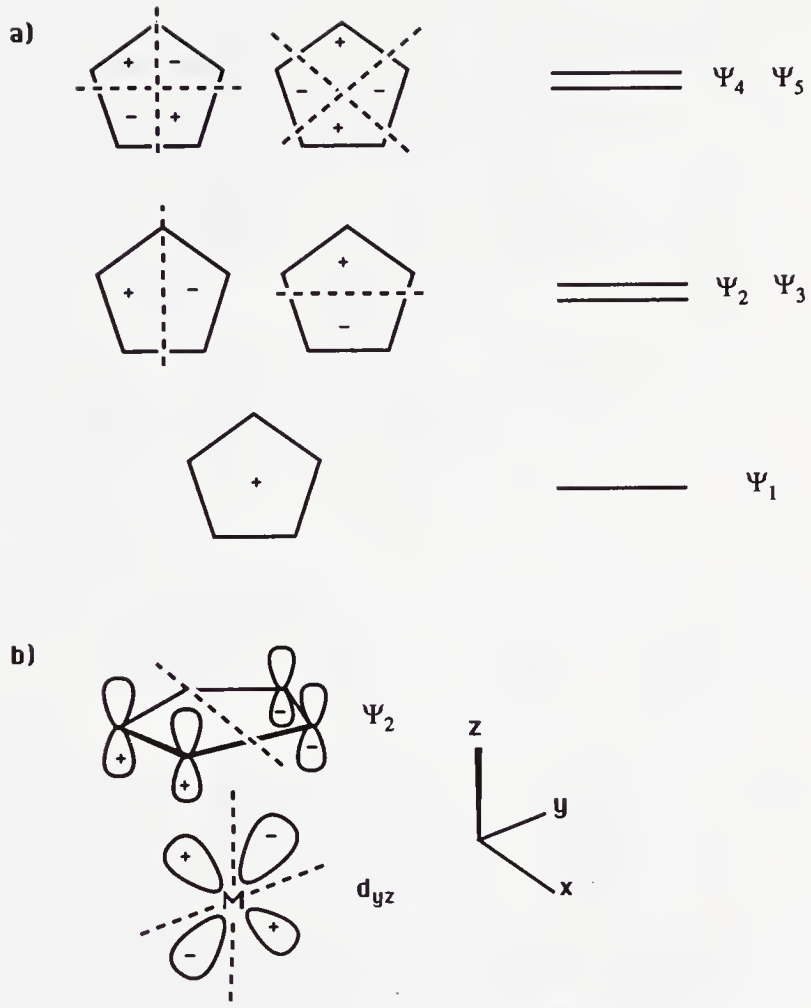


FIGURE 5.3 The electronic structure of the cyclopentadienyl ligand and one of the possible metal–Cp bonding combinations.

paramagnetic and much more reactive than ferrocene. Cobalticene also has an 18e cationic form, Cp_2Co^+. Chromocene and vanadocene have fewer than 18e and are also paramagnetic, as the electron occupation diagram (Fig. 5.5) predicts. Because d^5 ions have no crystal field stabilization in their high-spin form, high-spin $MnCp_2$ is very reactive and strongly ionic in character. The higher-field ligand C_5Me_5, on the other hand, gives a low-spin manganocene.

Another important series of metallocenes are those of Group 4, and of the heavier elements of Groups 5–7. These are capable of binding up to three ligands in addition to the two Cp groups. In doing so, the Cp's bend back away from the ligands as shown in Fig. 5.6. This bending rehybridizes the metal *d* orbitals labeled d_{z^2}, $d_{x^2-y^2}$, and d_{xy} in Fig. 5.6, so that they point out of the open side of the metallocene away from the rings and toward the additional ligands (**5.28**). In ferrocene itself, these are all filled, but one may still be protonated to give Cp_2FeH^+. "Cp_2Re" has one fewer electron and so

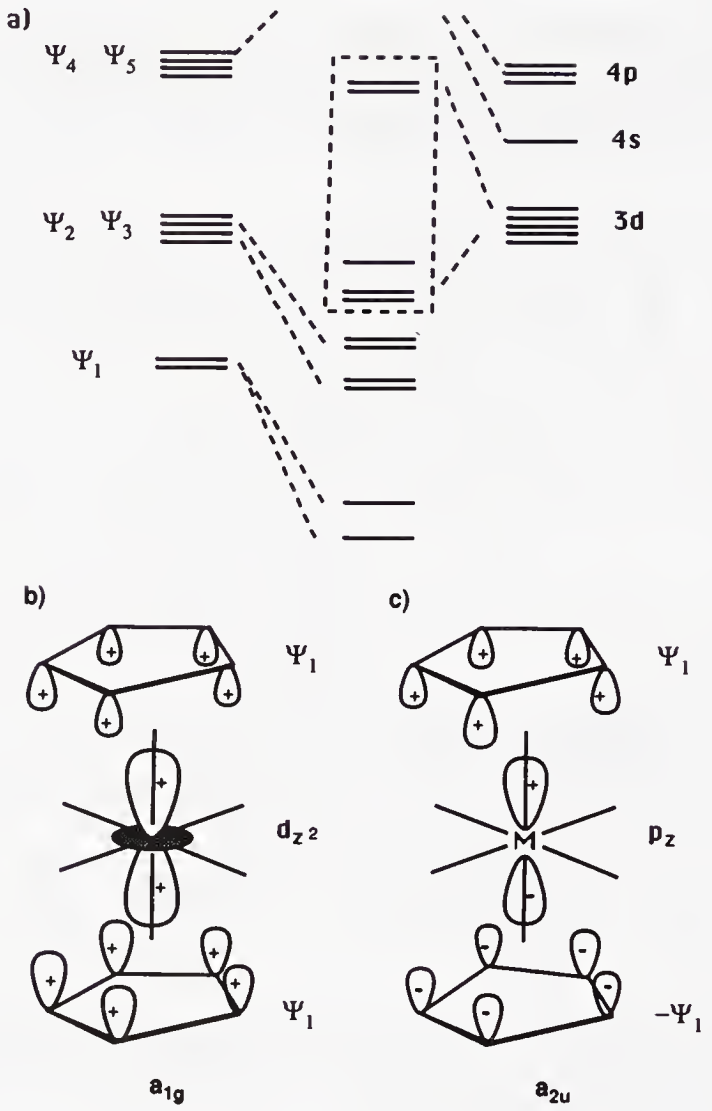


FIGURE 5.4 A qualitative m.o. diagram for a first-row metallocene. (*a*) The box shows the crystal field splitting pattern, only slightly distorted from its arrangement in an octahedral field. Because we now have two Cp groups, the sum and difference of each m.o. has to be considered. For example, Ψ_1 gives $\Psi_1 + \Psi_1'$, of symmetry a_{1g}, which interacts with d_{z^2}, as shown in (*b*), and $\Psi_1 - \Psi_1'$, of symmetry a_{2u}, which interacts with pz, as shown in (*c*). For clarity, only one lobe of the Cp p orbital is shown.

requires one 1e ligand to give a stable complex (e.g., Cp_2ReCl). "Cp_2Mo" and "Cp_2W" have two fewer electrons than ferrocene and so can bind two 1e ligands or one 2e ligand to reach 18e [e.g., Cp_2MH_2 or $Cp_2M(CO)$]. Only two of the three available orbitals are used in the metallocene dihydrides. One is a lone pair that points between the two substituents, and it can be protonated to give the water-soluble trihydride cations $Cp_2MH_3^+$. This lone

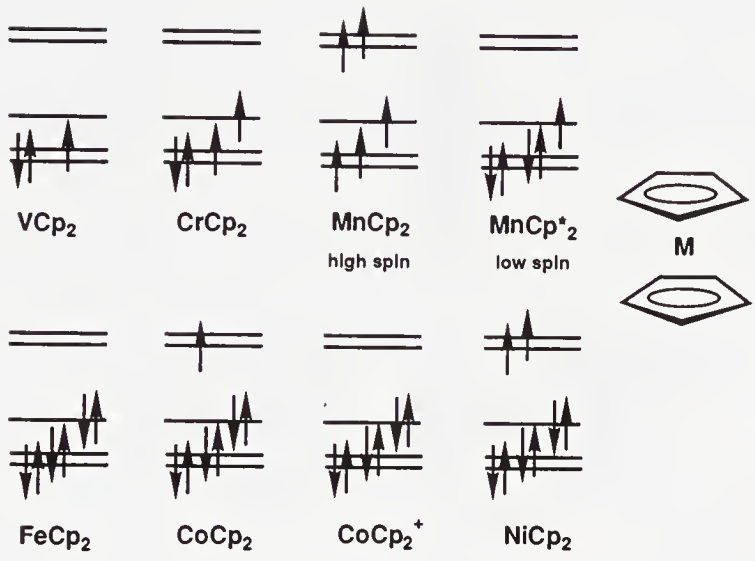


FIGURE 5.5 The orbital occupation patterns for some first-row metallocenes.

pair can also take part in back donation to stabilize any unsaturated ligands that may be present: e.g., $[Cp_2M(C_2H_4)Me]^+$. The Group 5 metals can bind three X ligands: e.g., Cp_2NbCl_3. The Group 4 metals bind only two X ligands, e.g., Cp_2TiCl_2; having only 4 valence electrons, their maximum oxidation state is M(IV). This leaves the 16e titanocene dihalide with an empty orbital (**5.29**), rather than a filled one as in the molybdocene dihalides (**5.30**). This accounts for many of the striking differences in the chemistry of the Group 4 and Group 6 metallocene complexes. The former act as Lewis acids and tend to bind π-basic ligands such as —OR, but the latter act as Lewis bases and tend to bind π-acceptor ligands such as ethylene.

The η^5-C_5Me_5 ligand, often designated Cp*, is a popular and important variant of Cp itself. It is not only higher field, but also more electron-releasing, and more bulky. It stabilizes a wider range of organometallic complexes than Cp itself. This is an example of a general strategy for producing more stable versions of interesting compounds—introducing steric hindrance. The Cp* derivatives are often also more soluble than the Cp compounds. Examples of Cp* compounds showing properties not shared by their Cp analogs are discussed in Sections 7.1, 11.1, and 15.3.

Synthesis The synthesis of cyclopentadienyls follows the general pattern shown in Eqs. 5.36–5.41. TlCp is an air-stable reagent that is often useful for making Cp complexes from halides; the product in Eq. 5.37 has the trivial name *cymantrene*. Some of the syntheses go in rather low yield (e.g., Eq. 5.38 typically gives 30%), and it is often the case that only one of the usual

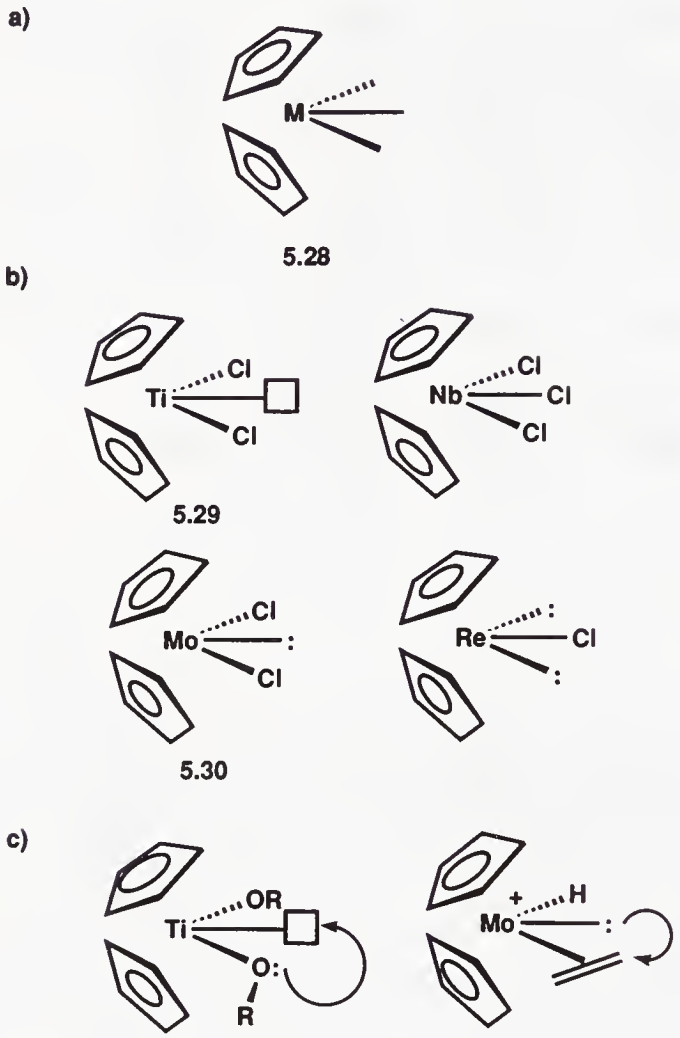


FIGURE 5.6 The bent metallocenes. (*a*) Note how all these metallocenes have three orbitals directed as shown for **5.28**. (*b*) The occupancy of these orbitals depends on how many electrons the metal provides. For Ti, the center orbital is left empty. This can act as a Lewis acid as shown in (*c*), where the Ti is interacting with a lone pair of a π-*basic* ligand. For Mo, this orbital is filled, and so can act as a Lewis base; in (*c*) it is shown in back donation to a π-*acid* ligand, ethylene.

reagents, NaCp, CpMgBr, TlCp, or $CpSnMe_3$, will work, but the others will not; the reasons are often unclear.

1. From a source of Cp^-:

$$NaCp + FeCl_2 = Cp_2Fe \qquad (5.36)^{46}$$

$$TlCp + Mn(CO)_2Cl \longrightarrow CpMn(CO)_3 \qquad (5.37)^{47}$$

$$MoCl_5 \xrightarrow{NaCp,\ NaBH_4,\ -100°C} Cp_2MoH_2 \qquad (5.38)^{48}$$

2. From a source of Cp^+:

$$CpFe(CO)_2^- + C_5H_5Br \longrightarrow CpFe(CO)_2(\eta^1\text{-}Cp) \xrightarrow{\text{heat, } -CO} FeCp_2 \qquad (5.39)$$

3. From the diene or a related hydrocarbon:

$$C_5Me_5H + MeRe(CO)_5 \longrightarrow Cp^*Re(CO)_3 \qquad (5.40)^{49}$$

$$\text{Cyclopentene} \xrightarrow{IrH_2S_2L_2^+} CpIrHL_2^+ \qquad (5.41)^{50}$$

$(S = Me_2CO;\ L = PPh_3)$

The paramagnetic metallocenes, such as $NiCp_2$, are very reactive (see Fig. 5.7[51]). Compound **5.31** is an example of a triple-decker sandwich in which the electrons of the center ring are delocalized over the two metal centers. It is rare for a π-bonding carbocyclic ligand to bond to two metals on opposite faces. The reason this happens here is probably that $NiCp_2$ is a 20e compound and so formation of the triple-decker sandwich allows two metals to share the excess electrons.

Two pentahapto ligands that are closely analogous to Cp are cyclohexadienyl **5.32** and pentadienyl **5.33**. In the first, the uncomplexed methylene unit of the ring is bent 30–40° out of the plane of the rest of the ligand, but the ligand is otherwise much like Cp itself. The pentadienyl group on the other hand, is easily able to shuttle back and forth between the η^1, η^3, and η^5 structures.[52] The η^3 form, being a substituted allyl, can have syn and anti

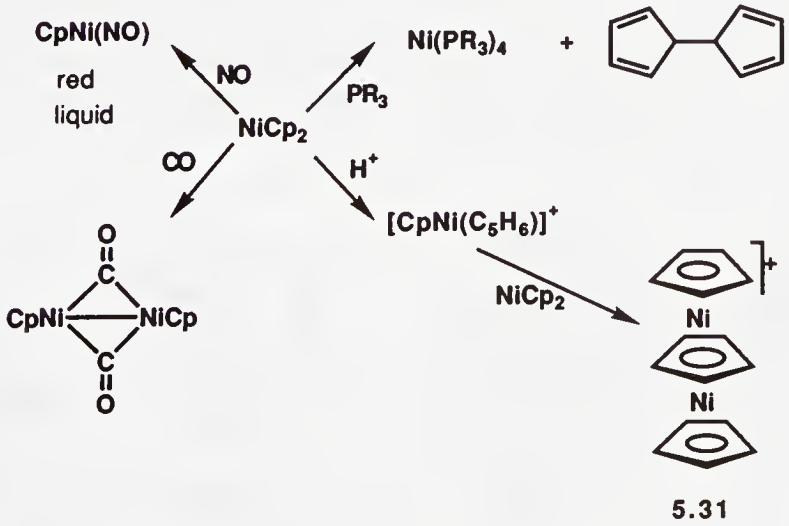
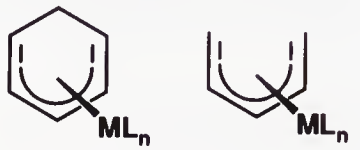
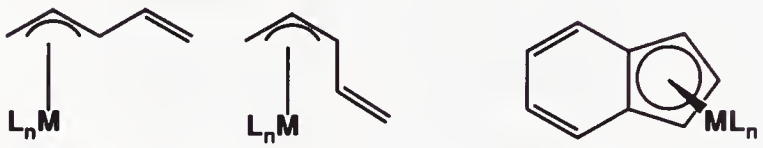


FIGURE 5.7 Some reactions of nickelocene.

isomers (**5.34** and **5.35**), and the η^1 form can have the metal substituted at the 1 or 3 positions along the chain.



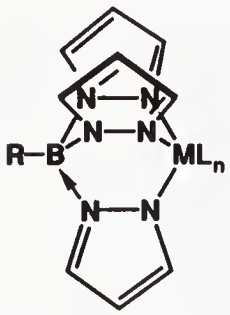
5.32 **5.33**



5.34 **5.35** **5.36**

Ligands Analogous to Cp An interesting Cp analog is indenyl, **5.36**. As we saw in Section 4.5, the tendency of the indenyl to slip from η^5 to η^3 is higher than in Cp because the full aromatic stabilization of the benzo ring is restored in the slipped form. Indenyl is also a better π acceptor than Cp. For example, $[(\eta^5\text{-Ind})IrHL_2]^+$ is deprotonated by NEt_3, but the Cp analog is not deprotonated even by *t*-BuLi. This is probably nothing to do with slip because the η^5-PhC_5H_4 analog is also readily deprotonated.

There is a wide variety of 5e (ionic model: 6e) tridentate L_2X ligands that are more distantly related to Cp, of which tris(pyrazolyl)borate[53a] ($HBpz_3^-$ or Tp) (**5.37**) is perhaps the best known. It has a lower ligand field strength than Cp; the $Fe(HBpz_3)_2$ ferrocene analog is paramagnetic above room temperature. This means that the ligand field-splitting parameter, Δ, is too small to force the d^6 iron to spin-pair. Ligands discovered by Klaüi[53b] (**5.38**) and by Grim[54a] (**5.39**) are useful LX_2 *O*- and *S*-donor ligands. Some of these show interestingly different reactivity patterns than Cp. For example, certain complexes of **5.39** (X = O) are much more active catalysts than their Cp analogs because they readily open one arm to give η^2 complexes and so allow the substrate for the reaction to bind.[54b] Another group of Cp-like ligands are carboranes like $R_2C_2B_4H_4^{2-}$ (**5.40**).[55]



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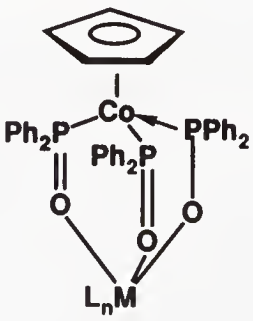

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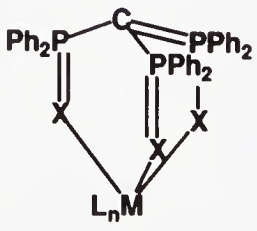
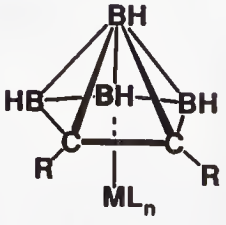


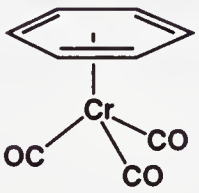
5.39
(X = O or S)



5.40

5.5 COMPLEXES OF ARENES AND OTHER ALICYCLIC LIGANDS

Arenes usually bind to transition metals in the 6e, η^6-form **5.41**, but η^4 (**5.42**), and η^2 (**5.43**) structures are also known.[56a] In the η^4 form the ring is usually strongly folded, while an η^6 arene tends to be flat. The C—C distances are usually essentially equal, but slightly longer than found in the free arene. Arenes are much more reactive than Cp groups, and they are also more easily lost from the metal. This means that arenes cannot be used as inert stabilizing ligands for a whole series of metal complexes as can Cp.



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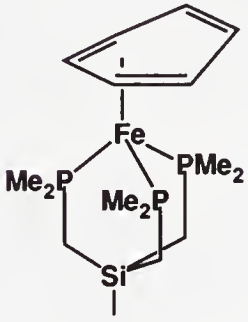
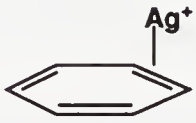


5.42



5.43

The ^{13}C NMR is perhaps the most useful method of characterization, the metal-bound carbons showing a ~25 ppm shift to high field on coordination, due to the increased shielding from the nearby metal.

Synthesis Typical synthetic routes differ little from those used for alkene complexes:

1. From the arene and a complex of a reduced metal:

$$Cr(CO)_6 + C_6H_6 \xrightarrow{n\text{-}Bu_2O} (\eta^6\text{-}C_6H_6)Cr(CO)_3 \qquad (5.42)^{56b}$$

$$Ti(atoms) + PhMe \longrightarrow (\eta^6\text{-}PhMe)_2Ti \qquad (5.43)^{57}$$

$$FeCp_2 + C_6H_6 + AlCl_3 \longrightarrow [CpFe(\eta^6\text{-}C_6H_6)]^+ \qquad (5.44)^{58}$$

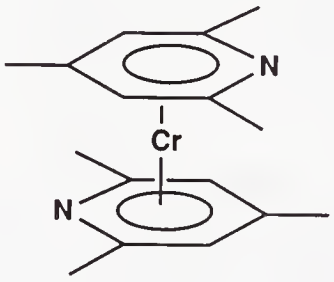
2. From the arene, a metal salt and a reducing agent:

$$CrCl_3 + Al + AlCl_3 + C_6H_6 \longrightarrow [Cr(\eta^6\text{-}C_6H_6)_2]^+ \xrightarrow{\text{reduction}} [Cr(\eta^6\text{-}C_6H_6)_2] \qquad (5.45)^{59}$$

3. From the diene:

$$1,3\text{-cyclohexadiene} + RuCl_3 \longrightarrow [(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2 \qquad (5.46)^{60}$$

The route of Eq. 5.42 is interesting in that the ether solvent may help stabilize the unsaturated Cr complexes that are probably intermediates. Metal vapor synthesis is used to make [Cr(η^6-2,4,6-trimethylpyridine)$_2$] **5.44**, which is not accessible by the usual routes.[61] Note how the steric hindrance of the methyl groups on the pyridine discourage the normally more favored η^1 binding via nitrogen. Arenes bind only to low-valent metals, so metal salts of higher oxidation state are often reduced in the presence of the ligand (method 2 above). In the third route, the diene reduces the metal and in so doing provides the arene ligand by an as yet undefined mechanism.



5.44

The m.o. picture is similar to that for Cp, but the arene ligand is a smaller net donor to the metal. The shift in ν(CO) of only 50 cm^{-1} to lower energy on going from $Cr(CO)_6$ to $(C_6H_6)Cr(CO)_3$ confirms this picture. Binding depletes the electron density on the ring and becomes subject to nucleophilic attack. This makes these complexes very useful for organic synthetic applications (Chapter 14). Apart from nucleophilic attack, the metal encourages deprotonation both at the ring protons, because of the increased positive charge on the ring, and α to the ring (e.g., at the benzylic protons of toluene), because the negative charge of the resulting carbanion can be delocalized on to the metal, where it is stabilized by the CO groups.

Other η^6 Ligands Polycyclic arenes such as naphthalene also bind to low-valent metals. In this case η^6 binding is still common but the tendency to bind η^4 is enhanced because, as we saw for indenyl, this allows the uncomplexed ring to be fully aromatic. If one ring is different in some way from the other, different isomers, called *haptomers,* can exist in which the metal is bound to one or the other ring. The metal can migrate from one ring to the other in a haptomeric equilibrium.

The fullerenes are the most recently discovered polynuclear aromatic compounds.[62] Figure 5.8 shows how the ellipsoidal molecule C_{70} binds[63a] to Vaska's complex. Either only one of the many possible isomers is formed, or more likely, only one crystallized. Free C_{70} itself does not give crystallographically useful crystals, and so this structure confirmed the ellipsoidal structure previously deduced from its NMR spectrum. The junctions between six-membered rings seem to be the most reactive in the fullerenes, and this is where

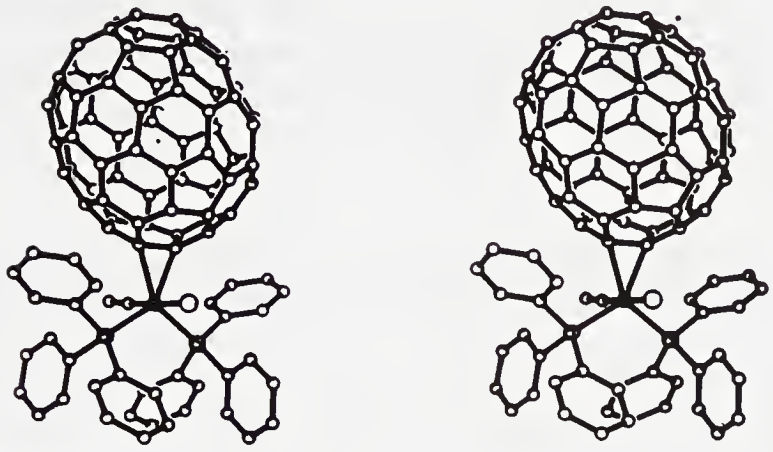


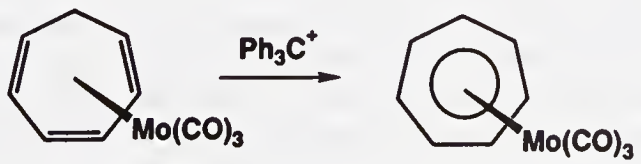
FIGURE 5.8 A stereoscopic drawing of $(\eta^2\text{–}C_{70})Ir(CO)Cl(PPh_3)_2$.[63a]

the metal binds. It is almost always the Cl and CO groups in the planar Vaska's complex that bend back to become cis when an alkene or alkyne binds; here the PPh_3 groups bend back, presumably because of steric repulsion by the C_{70} group. Figure 5.8 is a stereoscopic diagram of a type commonly seen in research papers. With practice, it is possible to relax the eyes so that the two images formed by each eye are fused to give a three-dimensional representation of the molecule. The metal can also be inside the fullerene cavity, in which case the symbol @ is used, as in $Ca@C_{60}$.[63b]

η^7 Ligands η^7-Cycloheptatrienyl ligands are well known. The ring is planar, and the C—C distances are essentially the same; η^5, η^3, and η^1-bonding modes are also known. The tropylium cation $C_7H_7^+$ is stable, and isolable salts, such as the fluoroborate, are often used in the synthesis of the complexes. Although the aromatic $C_7H_7^+$ and not the antiaromatic $C_7H_7^-$ is the stable form of the free ligand, it is still considered as L_3X (or $C_7H_7^-$) for electron counting and oxidation state assignments.

$$\underset{\textbf{17e}}{CpCr(C_6H_6)} + [C_7H_7]BF_4 \longrightarrow \underset{\textbf{17e}}{[CpCr(\eta^7\text{-}C_7H_7)]^+} \xrightarrow{\text{reduction}} \underset{\textbf{18e}}{CpCr(\eta^7\text{-}C_7H_7)} \qquad (5.47)$$

The commonest method is abstraction of H^- from an η^6 cycloheptatriene complex with Ph_3C^+ (Eq. 5.48) or Et_3O^+; the oxonium cation is the reagent of choice, because the by-products, Et_2O and EtH, are both volatile.

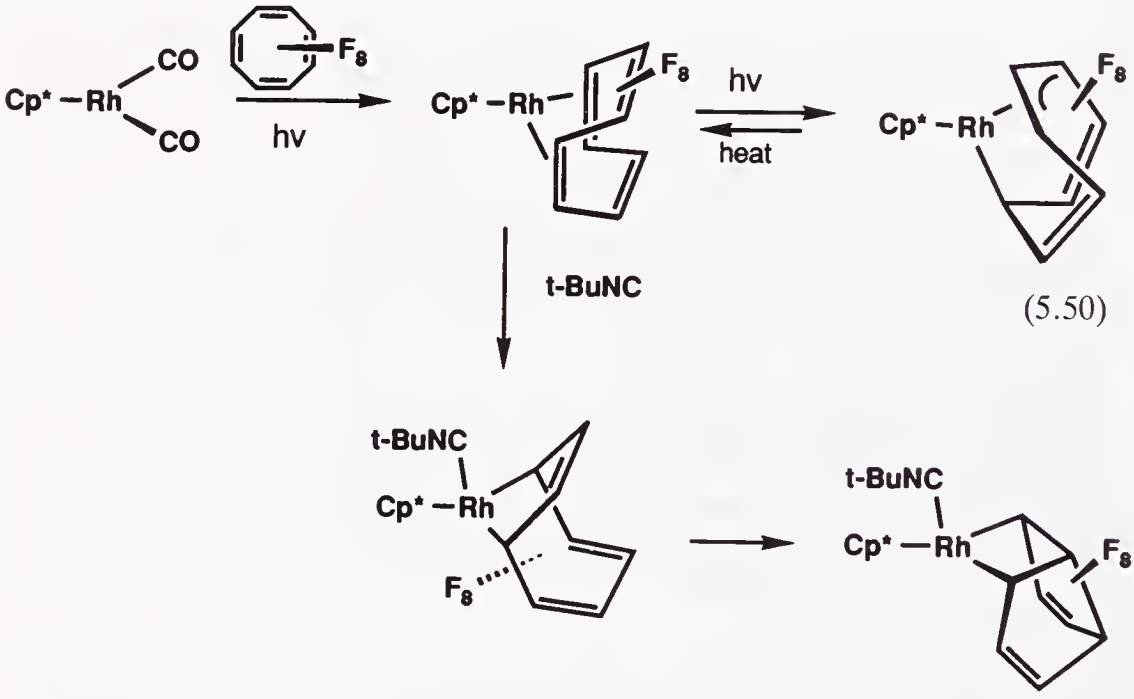


(5.48)

η^8 *Ligands* η^8-Cyclooctatetraene (cot) complexes are usually made from the aromatic cot^{2-} dianion. The classic example is $U(cot)_2$. The large size of U and the fact that it is not limited to 18e (Section 2.7 and Chapter 17) probably gives the complex its special stability.

$$UCl_4 + cot^{2-} \longrightarrow U(cot)_2 \qquad (5.49)$$

Fluorocarbons Perfluorinated polyenes and polyenyls have a chemistry significantly different from that of their hydrocarbon analogs.[64a] Octafluorocyclooctatetraene (ofcot), one of the more extensively studied, has been found to undergo unusual rearrangements and adopt bonding modes unknown for cot (see Eq. 5.50).[64b] Some of the synthetic difficulties are illustrated by the fact that such an apparently simple ligand as (η^5-C_5F_5) has only just been reported in $Cp^*Ru(\eta^5\text{-}C_5F_5)$.[64c]



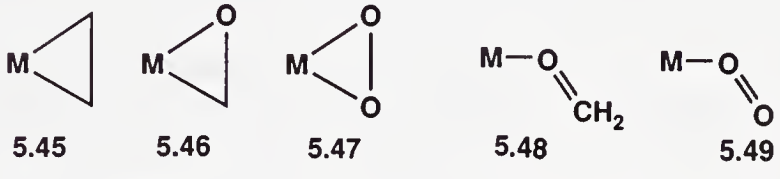
(5.50)

5.6 METALACYCLES AND ISOELECTRONIC AND ISOLOBAL REPLACEMENT

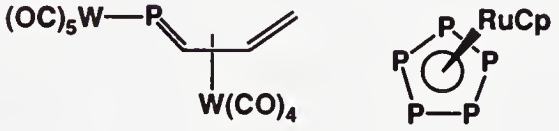
We looked at some metalacycles with saturated rings in Eqs. 3.25–3.26, and we have seen several metalacyclic descriptions of complexes in this chapter (e.g., **5.3**, **5.6**, **5.9**). Isoelectronic replacement is a general strategy for finding new ligand types based on known ones or of drawing comparisons between known types and we illustrate it here with some metalacycles. For example, if one CH_2 in an η^2-alkene complex **5.45** is replaced by O, the result is an η^2-formaldehyde complex **5.46** [e.g., $Cp_2Zr(\eta^2\text{-}CH_2O)$]. In the Zr example, the strong π-donor character of the d^2 metal encourages the η^2-bonding

mode. Thioformaldehyde is not isolable in the free state, but η^2 complexes are known, for example, $Os(CO)_2(PPh_3)_2(\eta^2\text{-}CH_2S)$.[65] Replacing both CH_2 groups by O gives an η^2-dioxygen complex (**5.47**), such as $IrCl(\eta^2\text{-}O_2)(CO)(PPh_3)_2$. The presence of the heteroatom also introduces a lone pair and therefore an alternative mode of binding via that lone pair (e.g., **5.48**, **5.49**).

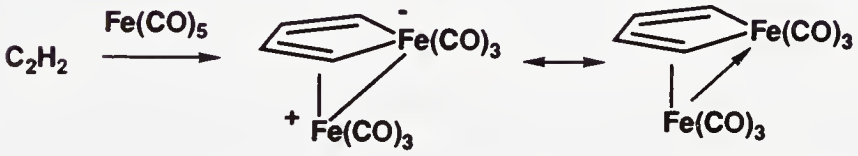
In the unusual heteroatom-substituted species **5.50**, the lone pair of the P is tied up by the $W(CO)_5$ group, leaving the $W(CO)_4$ group to bind the "butadiene" fragment.



5.45 5.46 5.47 5.48 5.49



5.50 5.51

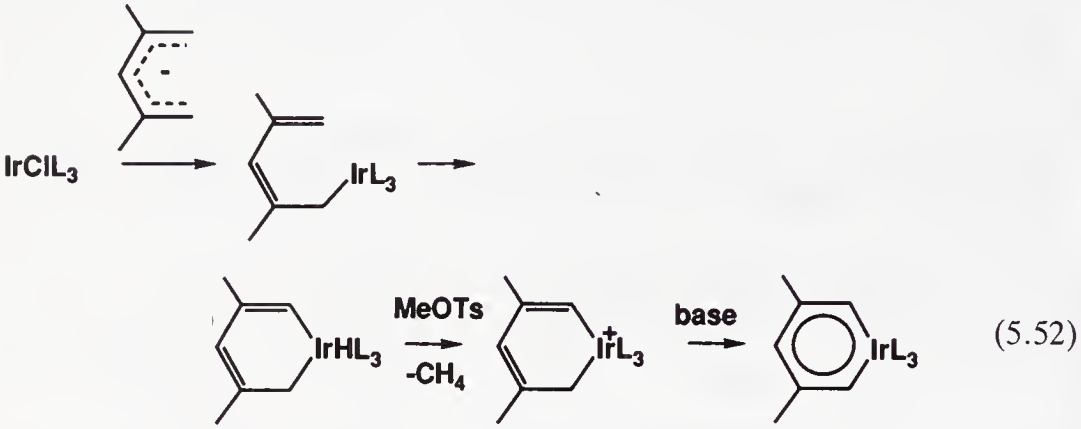


(5.51)

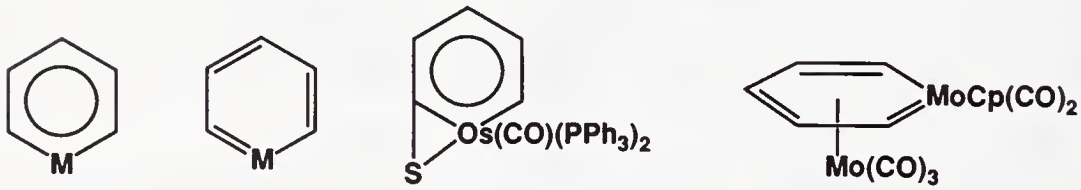
An interesting polyphospha analog of ruthenocene is shown as **5.51**.[66] Among η^5 ligands, a common heteroatom type is a ferrole, or ferracyclopentadiene, shown in Eq. 5.51, where it is not free but bonded to a second $Fe(CO)_3$ group. Note the different canonical forms of the product, one including an Fe → Fe donor metal–metal bond.

An ML_n fragment like $Fe(CO)_4$ is not isoelectronic with C fragments like CH_2, the iron fragment has far more electrons. Hoffmann[67] has pointed out that particular metal fragments can have the same number, occupation, and shape of their orbitals as, say, CH_2, and can replace CH_2 in organic molecules as if they were isoelectronic; he called these fragments *isolobal* with the organic group. For example, $Fe(CO)_4$ is said to be isolobal with CH_2. This concept, which we look at in detail in Section 13.2, has been useful in understanding metallabenzenes (**5.52**). These are species in which we replace on CH of benzene by a metal fragment isolobal with CH.[68] Roper[69] made the first example, **5.52b**, in 1982. The X-ray structure showed a planar OsC_5 ring without the alternating bond lengths that would be expected for the alternative nonaromatic (metalacyclohexatriene) structure **5.52a**. Equation 5.52 shows the sequence used by Bleeke[68] to prepare an iridabenzene. Note the use of methyl triflate (a source of Me^+) to abstract a hydride from Ir and so create the positive charge necessary to remove a proton from a α-CH_2 of

the metalacycle. Structure **5.53** is an example of a complexed metallabenzene.[70a] A 1,3-dimetalabenzene has been isolated recently, but it is strongly nonplanar.[70b]

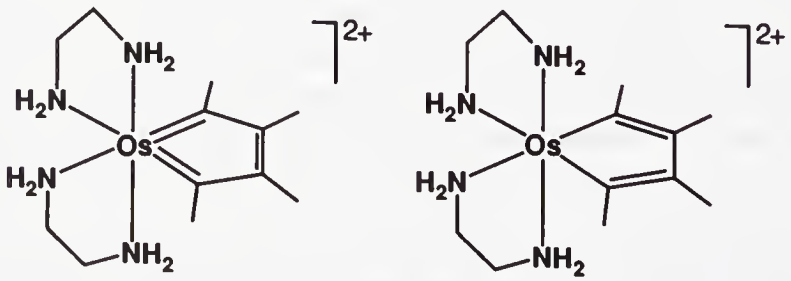


(5.52)



5.52 **5.52a** **5.52b** **5.53**

On a strongly back-donating metal, the normal metallole structure of Eq. 5.51 converts to a second form in which the ligand acts as a bis-carbene. For example,[71] X-ray crystallography shows that **5.54** has the bis-carbene structure **5.54a** and not the usual metallole structure **5.54b**. Note that the metalacycle in **5.54a** is a 4e ligand but in **5.54b** is a 2e ligand, so this conversion can happen only if the metal can accept 2e [on the ionic model both ligands are counted as 4e ligands but the metal is counted as d^6 Os(II) in **5.54a** and d^4 Os(IV) in **5.54b**]; **5.54a** is an 18e complex and **5.54b** is a 16e complex.



5.54a **5.54b**

5.7 STABILITY OF POLYENE AND POLYENYL COMPLEXES

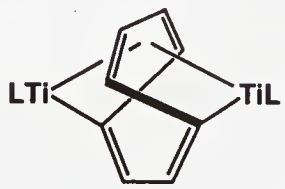
The stability of the polyene complexes L_n toward dissociation is in general less than that of polyenyl complexes L_nX, because the free polyene is usually

a stable species, but the polyenyl must dissociate as an anion, cation, or radical, none of which are likely to be as stable relative to the bound form of the ligand; in addition, ionic dissociation creates a separation of charge, which will generally be unfavorable, especially in the less polar organic solvents. The strongest π-back-bonding, and therefore the most electron-rich, metal fragments will generally bind polyenes and polyenyls most tightly. For example, butadiene complexes of strongly π-basic metal fragments have more LX_2 character than those of less basic fragments and so will less resemble the free ligand and dissociate less easily. Electron withdrawing substituents also tend to encourage back donation and can greatly increase complex stability, as we have seen for C_2F_4 in Section 5.1. Conversely, d^0 metals incapable of back donation, such as Ti(IV) and Nb(V), normally bind L_nX ligands like Cp, but not L_n ligands like CO, C_2H_4, and C_6H_6. The same tendency is seen for the *f*-block lanthanides and actinide elements.

There are many cases in which complexes are known of ligands that are extremely reactive and unstable in the free state. We saw the case of cyclobutadiene in Section 5.3, but alkylidenes [e.g., $Cp_2Ta(=CH_2)Me$, Section 11.2], and benzyne [e.g., $CpTa(\eta^2\text{-}C_6H_4)Me_2$] are also good examples. Cyclic polyene and polyenyl ligands tend to be kinetically more stable to dissociation than their open-chain analogs, because the latter can more easily dissociate in a stepwise manner. The trihapto form of the pentadienyl group is common,[72] but η^3-Cp is very rare. The open chain ligand merely has to undergo a rotation about a C—C bond to become η^3, while a cyclopentadienyl has to fold out of the plane of the ligand to disengage two carbon atoms from the metal. Just as a cyclic ligand can be kinetically slow to depart, they also tend to be slower to bind to a metal. The synthesis of a Cp or a benzene complex is often found to go in lower yield or more slowly than that of related η^3-allyl or ethylene complexes.

As we go to the right in the Periodic Table, the ML_n fragments that are available tend to have a higher electron count simply because the contribution from the metal rises. This means that those polyenes that have a large electron count themselves may not be able to bind because the electron count of the final complex would exceed 18e. As noted above, uranium, with its 32e rule as a result of the presence of *f* orbitals, is able to accept 16e from the two cot ligands in $U(\eta^8\text{-}C_8H_8)_2$. No *d*-block element could do this. Titanium manages to take on one $\eta^8\text{-}C_8H_8$ ring in **5.55** (Eq. 5.53), chromium one $\eta^6\text{-}C_8H_8$ ring in **5.56**, but rhodium does not accept more than 4e from cot in the $\mu\text{-}\eta^4\text{-}C_8H_8$ complex, **5.57**.

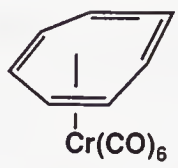
$$Ti(Ot\text{-}Bu)_4 + cot + AlEt_3 \longrightarrow$$



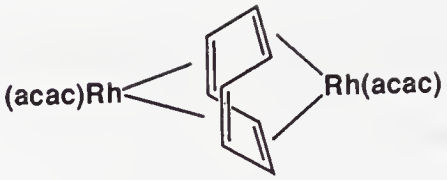
(5.53)

5.55

(L = η^8-cot)



5.56



5.57

Although the problem is less severe for η^5-Cp and (η^6-C_6H_6) complexes, these are notably less stable on the right hand side of the Periodic Table, for example, for Pd and Pt. The η^4-butadiene and η^3-allyl groups do not seem to bind less strongly until we reach Group 11.

Ligands that rely on back donation for stability of binding, notably the L_n polyenes, coordinate much less readily to metals of intermediate oxidation state (II to III) but not at all to high-valent metals. [*Note:* Complexes such as (cod)$ReH_3(PR_3)_2$ are probably more electron-rich than their high formal oxidation state implies; see Sections 2.7, 4.4, and 15.2.] The L_nX polyenyls, especially Cp and Cp*, do bind to high-valent metals (e.g., $CpNbCl_3$, and $CpReO_3$), but in these cases the ligand is a predominant electron donor to the metal.

REFERENCES

1. T. F. Koetzle et al., *Inorg. Chem.*, **14,** 2643, 1975.
2. P. T. Cheng and S. C. Nyburg, *Can. J. Chem.*, **50,** 912, 1972.
3. G. Bombieri et al., *J. Chem. Soc.* A, 1313, 1970.
4. G. L. Geoffroy et al., *Adv. Organometal. Chem.*, **28,** 1, 1988.
5. (a) J. K. Kochi et al., *J. Organometal. Chem.*, **135,** 65, 1977; (b) R. Cramer, *Inorg. Chem.*, **4,** 445, 1965.
6. W. P. Giering and M. Rosenblum, *Chem. Commun.*, 441, 1971.
7. M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton,* 271, 1977.
8. G. Giordano and R. H. Crabtree, *Inorg. Synth.*, **19,** 218, 1979.
9. J. W. Faller and B. V. Johnson, *J. Organometal. Chem.*, **88,** 101, 1975.
10. J. H. Teuben et al, *J. Organometal. Chem.*, **157,** 413, 1978.
11. J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5075, 1962.
12. F. G. A. Stone et al., *J. Chem. Soc.*, Dalton, 102, 1972.
13. M. Green et al., *J. Chem. Res.* (*S*), 206, 1979.
14. H. C. Volger et al., *Rec. Trav. Chim.*, **87,** 229, 1969; M. B. Trost, *Acct. Chem. Res.*, **13,** 385, 1980.
15. (a) R. M. Laine, R. E. Moriarty, and R. Bau, *J. Am. Chem. Soc.*, **94,** 1402, 1972; (b) R. Weiss et al., *J. Am. Chem. Soc.*, **100,** 1318, 1978; (c) J. L. Templeton, *Adv. Organometal. Chem.*, **29,** 1, 1989.
16. (a) R. R. Schrock et al., *J. Am. Chem. Soc.*, **101,** 263, 1979. (b) R. D. Adams et al., ibid., **114,** 10977, 1992.

17. R. Baker, *Chem. Rev.*, **73,** 487, 1973.
18. J. W. Faller et al., *J. Organometal. Chem.*, **187,** 227, 1980.
19. S. F. A. Kettle and R. Mason, *J. Organometal. Chem.*, **5,** 573, 1966.
20. C. Krueger et al., *Organometallics,* **4,** 285, 1985.
21. J. A. Osborn, *J. Am. Chem. Soc.*, **97,** 3871, 1975.
22. E. E. Abel et al., *J. Chem. Soc., Dalton,* 1973, 1706.
23. M. L. H. Green et al., *Adv. Organomet. Chem.*, **2,** 325, 1964.
24. H. A. Martin and F. Jellinek, *J. Organometal. Chem.*, **12,** 169, 1968.
25. H. C. Clark et al., *J. Organometal. Chem.*, **36,** 399, *J. Chem. Soc., Dalton,* 1848, 1973; *Chem. Commun.*, 957, 1971.
26. R. Hoffmann, J. W. Faller, et al. *J. Am Chem. Soc.*, **101,** 592, 2570, 1979.
27. M. Rosenblum, *Acct. Chem. Res.*, **7,** 125, 1974.
28. T. Saegusa et al., *Synth. Commun.*, **9,** 427, 1979.
29. E. J. Corey, M. F. Semmelhack, et al., *J. Am. Chem. Soc.*, **89,** 2755, 1967; **94,** 667, 1972.
30. B. M. Trost et al., *J. Org. Chem.*, **44,** 3448, 1979.
31. J. W. Lauher, *Inorg. Chem.*, **18,** 1687, 1979.
32. (a) R. H. Crabtree, M. F. Mellea, and J. M. Quirk, *J. Am. Chem. Soc.*, **106,** 2913, 1984; (b) J. V. Barinov et al., *J. Organometal. Chem.*, **418,** C24, 1991; (c) T. T. Chen et al., *J. Am. Chem. Soc.*, **115,** 1170, 1993.
33. M. L. H. Green, J. A. K. Howard, et al., *J. Chem. Soc., Dalton,* 2641, 1992.
34. M. L. H. Green et al., *J. Chem. Soc., Dalton,* 1325, 1974; W. R. Roth and J. D. Meier, *Tetrahedron Lett.*, 2053, 1967.
35. L. A. P. Kane-Maguire et al., *J. Chem. Soc., Dalton,* 873, 1979.
36. C. G. Pierpoint et al., *Inorg. Chem.*, **17,** 78, 1976.
37. G. Erker, C. Kruger et al., *J. Am. Chem. Soc.*, **102,** 6344, 1980.
38. J. W. Faller and A. M. Rosan, *J. Am. Chem. Soc.*, **99,** 4858, 1977.
39. R. Pettit et al., *Chem. Commun.*, 1208, 1967.
40. P. M. Maitlis et al., *Can. J. Chem.*, **42,** 183, 1964.
41. M. R. Churchill et al., *Inorg. Chem.*, **8,** 401, 1969.
42. G. G. Emerson and K. Ehrlich, *J. Am. Chem. Soc.*, **94,** 2464, 1972.
43. G. Wilkinson, *J. Organometal. Chem.*, **100,** 273, 1975.
44. A. J. Hart-Davies et al., *Inorg. Chim. Acta,* **4,** 441, 1970.
45. C. P. Casey and W. D. Jones, *J. Am. Chem. Soc.*, **102,** 6156, 1980.
46. G. Wilkinson, *J. Organometal. Chem.*, **100,** 273, 1975; E. O. Fischer et al., *Z. Naturforsch.*, **106,** 665, 1965.
47. P. L. Pauson, *Inorg. Synth.*, **19,** 154, 1979.
48. M. L. H. Green, J. A. McCleverty, J. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4854, 1961.
49. R. G. Sutherland, *Organometal. Chem. Libr.*, **3,** 311, 1977.
50. R. H. Crabtree, M. F. Mellea, J. M. Mihelcic, and J. M. Quirk, *J. Am. Chem. Soc.*, **104,** 107, 1982.

51. P. W. Jolly and G. Wilke, *The Organic Chemistry of Nickel,* Academic Press, New York, 1974.
52. R. D. Ernst, *Acct. Chem. Res.,* **18,** 56, 1985; *Chem. Rev.,* **88,** 1255, 1988; J. R. Bleeke and W.-J. Peng, *Organometallics,* **5,** 635, 1986.
53. (a) S. Trofimenko, *Chem. Rev.,* **93,** 943, 1993; (b) W. Kläui et al., *J. Am. Chem. Soc.,* **109,** 164, 1987.
54. (a) S. O. Grim et al., *Inorg.Chem.,* **25,** 2699, 1986; (b) R. S. Tanke and R. H. Crabtree, *J. Am. Chem. Soc.,* **112,** 7984, 1990.
55. R. N. Grimes, *Pure Appl. Chem.,* **59,** 847, 1987.
56. H. Le Bozec, D. Touchard and P. H. Dixneuf, *Adv. Organometal. Chem.,* **29,** 163, 1989; (b) G. Jaouen et al., *J. Organometal. Chem.,* **182,** 381, 1979.
57. M. L. H. Geen et al., *Chem. Commun.,* 866, 1973.
58. A. N. Nesmeyanov et al., *Tetrahedron Lett.,* 1625, 1963.
59. E. O. Fischer et al., *Z. Anorg. allgem. Chem.,* 286, 146, 1956.
60. M. A. Bennett and A. K. Smith, *J. Chem. Soc., Dalton,* 233, 1974.
61. K. Öfele, *Angew. Chem., Int. Ed.,* **14,** 639, 1975.
62. H. W. Kroto, *Angew. Chem., Int. Ed.,* **31,** 111, 1991.
63. (a) A. L. Balch et al., *J. Am. Chem. Soc.,* **113,** 8953, 1991; (b) K. J. Fisher et al., *Chem. Commun.,* 941, 1993.
64. R. P. Hughes et al.: (a) *Adv. Organometal. Chem.,* **31,** 183, 1990. (b) *Chem Commun.,* 306, 1986, and references cited therein; (c) *J. Am. Chem. Soc.,* **114,** 5895, 1992.
65. W. D. Roper et al., *J. Organometal. Chem.,* **159,** 73, 1978.
66. O. J. Scherer, *Angew. Chem., Int. Ed.,* **26,** 59, 1987.
67. R. Hoffmann, *Angew. Chem., Int. Ed.,* **21,** 711, 1982.
68. J. R. Bleeke, *Acct. Chem. Res.,* **24,** 271, 1991.
69. W. R. Roper et al., *Chem. Commun.,* 811, 1982.
70. (a) R. D. Ernst et al., *Organometallics,* **6,** 2612, 1987; (b) I. P. Rothwell et al., *Angew. Chem., Int. Ed.,* **31,** 1261, 1992.
71. H. Taube et al., *J. Am. Chem. Soc.,* **114,** 7609, 1992.
72. J. R. Bleeke, *Organometallics,* **4,** 194, 1985.

PROBLEMS

1. Rank the following pairs of metal fragments in order of increasing tendency for an attached alkene to undergo nucleophilic attack: (a) $PdCl_2(H_2O)$, $PtCl_2(H_2O)$; (b) $Pd(PPh_3)_2$, $Pd(PPh_3)_2Cl^+$; (c) $CpMo(NO)P(OMe)_3^+$, $CpMo(NO)PMe_3^+$.

2. Although $L_nMCH_2CH_2ML'_n$ can be thought of as a bridging ethylene complex, examples of this type of structure are rarely made from ethylene itself. Propose a general route that does not involve ethylene, and explain how you would know that the complex had the bridging structure, without using crystallography. What might go wrong with the synthesis?

3. Among the products formed from PhC≡CPh and $Fe_2(CO)_9$, is 2,3,4,5,-tetraphenylcyclopentadienone. Propose a mechanism for the formation of this product. Do you think the dienone would be likely to form metal complexes? Suggest a specific example and how you might try to make it.

4. Suggest a synthesis of $Cp_2Mo(C_2H_4)Me^+$ from Cp_2MoCl_2. What orientation would you expect for the ethylene ligand? Given that there is no free rotation of the alkene, how would you show what orientation is adopted?

5. What structural distortions would you expect to occur in the complex $L_nM(\eta^4\text{-butadiene})$ if the ligands L were made more electron-releasing?

6. 1,3-cod (= cyclooctadiene) can be converted into free 1,5-cod by treatment with $[(C_2H_4)IrCl]_2$, followed by $P(OMe)_3$. What do you think is the mechanism? Since 1,5-cod is thermodynamically unstable with respect to 1,3-cod (why is this so?), what provides the driving force for the rearrangement?

7. How many isomers would you expect for $[PtCl_3(propene)]^-$?

8. The complex Fp—CH_2—C≡CH reacts with HPF_6 to give a species $Fp(C_3H_4)$. What do you think is its structure?

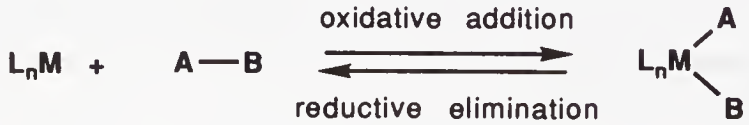
9. $IrH_2(H_2O)_2(PPh_3)_2^+$ reacts with indene, C_9H_8, to give $(C_9H_{10})Ir(PPh_3)_2^+$. On heating, this species rearranges with loss of H_2 to give $(C_9H_7)IrH(PPh_3)_2^+$. Only the first of the two species mentioned reacts with ligands such as CO to displace C_9H_7. What do you think are the structures of these complexes?

10. In attempting to isolate a cationic complex of Rh(I), a student adds the BPh_4^- anion as the potassium salt. A complex that is apparently $[Rh(PPh_3)_2](BPh_4)$ is isolated. The complex does not have the properties expected for a ligand-deficient RhL_2^+ ion; for example, it fails to react with 1,5-cod, and is not an electrical conductor in nitromethane. Suggest more reasonable alternative formulations for the complex and indicate which one you prefer.

CHAPTER 6

OXIDATIVE ADDITION AND REDUCTIVE ELIMINATION

We have seen how various 2e ligands can enter the coordination sphere of a metal by substitution. We will now look at a general method for simultaneously introducing pairs of 1e ligands, A and B, by the oxidative addition of an A—B molecule (Eq. 6.1), a reaction of great importance in both synthesis and catalysis (Chapter 9). The reverse reaction, reductive elimination, leads to the extrusion of A—B from an M(A)(B) complex and is often the product-forming step in a catalytic reaction. In the oxidative direction, we break the A—B bond and form an M—A and an M—B bond. Since A and B are 1e X-type ligands, the oxidation state, electron count, and coordination number all increase by two units during the reaction. It is the change in formal oxidation state that gives the reaction the name *oxidative addition*.



16e 18e (6.1)

$\Delta O.S. = +2$

$\Delta C.N. = +2$

Oxidative additions proceed by a great variety of mechanisms, but the fact that the electron count increases by two units in Eq. 6.1 means that a vacant 2e site is always required on the metal. We can either start with a 16e complex, or a 2e site must be opened up in an 18e complex by the loss of a ligand. The change in oxidation state means that a metal complex of a given oxidation

state must also have a stable oxidation state two units higher to undergo oxidative addition (and vice versa for reductive elimination).

Equation 6.2 shows an example of *binuclear oxidative addition,* in which each of two metals changes its oxidation state, electron count, and coordination number by one unit instead of two. This typically occurs in the case of a 17e complex where the metal has a stable oxidation state more positive by one unit. Table 6.1 systematizes the more common types of oxidative addition reactions by d^n configuration and position in the Periodic Table. In the overall process, whatever the mechanism adopted, there is a net transfer a pair of electrons from the metal into the σ^* orbital of the A—B bond, and of the A—B σ electrons to the metal. This cleaves the A—B bond and makes an M—A and a M—B bond. The reaction is promoted by starting with a metal in a reduced state; only rarely do metals in an oxidation state higher than +2 retain sufficient reducing character to undergo oxidative addition, except with powerful oxidants, like Cl_2. Conversely, a highly oxidized metal is more likely to undergo reductive elimination.

$$\begin{array}{lllll} 2L_nM & (\text{or } L_nM\text{-}ML_n) & \xrightarrow{A—B} & L_nM\text{-}A + & L_nM\text{-}B \\ 17e & 18e & & 18e & 18e \\ & & & \Delta O.S. = +1 & \Delta O.S. = +1 \\ & & & \Delta C.N. = +1 & \Delta C.N. = +1 \end{array} \qquad (6.2)$$

As we have seen, oxidative addition is the inverse of reductive elimination and vice versa. In principle, each reaction is reversible, but in practice the reactions tend to go in the oxidative or reductive direction only. The position of equilibrium in any particular case is governed by the overall thermodynamics; this in turn depends on the relative stabilities of the two oxidation states and the balance of the A—B versus the M—A and M—B bond strengths. Alkyl hydride complexes commonly eliminate alkane, but only rarely do alkanes oxidatively add to a metal. Conversely, alkyl halides commonly add to metal complexes, but the adducts rarely reductively eliminate the alkyl halide. Third-row elements, which tend to have stronger metal–ligand bonds, tend to give more stable adducts. Occasionally, an equilibrium is established in which both the forward and back reactions are observed.

$$[Ir(cod)_2]^+ \underset{}{\overset{H_2,\ \text{fast},\ -80^\circ}{\rightleftharpoons}} \textit{cis}\text{-}[IrH_2(cod)_2]^+ \qquad (6.3)^1$$

It is typical for the two hydrogens to end up cis to one another in the product.

Reaction in the oxidizing direction is usually favored by strongly donor ligands because these stabilize the oxidized state. While the formal oxidation state change is always +2 for Eq. 6.1, the real charge on the metal changes much less than that, because A and B do not end up with pure −1 charges

TABLE 6.1 Common Types of Oxidative Addition Reactions[a]

Change in d^n Configuration	Change in Coordination Geometry	Examples	Group	Remarks
$d^{10} \rightarrow d^8$	Tet. $\xrightarrow{X_2}$ Sq. Pl.	Au(I) → (III)	11	
		Pt, Pd(0) → (II)	10	
$d^8 \rightarrow d^6$	Sq. Pl. $\xrightarrow{X_2}$ Oct.	Pt(II) → (IV)	10	Ni and Pd(IV) are unstable
		Rh, Ir(I) → (III)	9	Very common
		M(0) → (II)	8	Rare
	TBP. $\xrightarrow{-L,\ X_2}$ Oct.	M(I) → (III)	9	
		M(0) → (II)	8	
$d^7 \rightarrow d^6$	2Sq. Pyr. $\xrightarrow{X_2}$ 2Oct.	2Co(III) → (II)	8	Binuclear
	2Oct. $\xrightarrow{-L,\ X_2}$ 2Oct.	2Co(III) → (II)	8	Binuclear
$d^6 \rightarrow d^4$	Oct. $\xrightarrow{X_2}$ 7-c	Re(I) → (III)	7	
		M(0) → (II)	6	
		V(−I) → (I)	5	
$d^4 \rightarrow d^3$	2Sq. Pyr. $\xrightarrow{X_2}$ 2Oct.	2Cr(II) → (III)	6	Binuclear
	2Oct. $\xrightarrow{-L,\ X_2}$ 2Oct.	2Cr(II) → (III)	6	Binuclear
$d^4 \rightarrow d^2$	Oct. $\xrightarrow{X_2}$ 8-c	Mo, W(II) → (IV)	6	
$d^2 \rightarrow d^0$	Various	M(III) → (V)	5	
		M(II) → (IV)	4	

[a]Abbreviations: Tet. = tetrahedral, Oct. = octahedral, Sq. Pl. = square planar, TBP = trigonal bipyramidal, Sq. Pyr. = square pyramidal; 7-c, 8-c = 7- and 8-coordinate.

TABLE 6.2 Carbonyl Stretching Frequencies of the Oxidative Addition Products from Vaska's Complex

Addendum	ν(CO) (cm^{-1})	$\Delta\nu$(CO) (cm^{-1})
None	1967	0
O_2	2015	48
D_2[a]	2034	67
HCl	2046	79
MeI	2047	80
C_2F_4	2052	85
I_2	2067	100
Cl_2	2075	108

[a]The D isotope is used because the Ir–H stretching vibrations have a similar frequency to ν(CO) and so couple with CO stretching and cause ν(CO) to shift for reasons that have nothing to do with the electronic character of the metal (see Chapter 10).

in $L_nM(A)(B)$. The change in real charge depends mostly on the electronegativity of A and B in Eq. 6.1, so that the following addenda are more oxidizing in the order: $H_2 < HCl < Cl_2$. We can estimate the oxidizing power of different addenda experimentally by measuring $\Delta\nu$(CO) on going from $IrCl(CO)L_2$ to $Ir(A)(B)Cl(CO)L_2$ (Table 6.2), because a more oxidizing addendum will reduce M—CO back bonding and make $\Delta\nu$(CO) more negative.

These reactions are not limited to transition metals; perhaps the most familiar oxidative addition is the formation of Grignard reagents (Eq. 6.4), but it can occur whenever an element has two accessible oxidation states two units apart. Equation 6.5 illustrates oxidative addition to P(III).

$$\text{Me—Br} + \text{Mg} \longrightarrow \text{Me—Mg—Br} \tag{6.4}$$

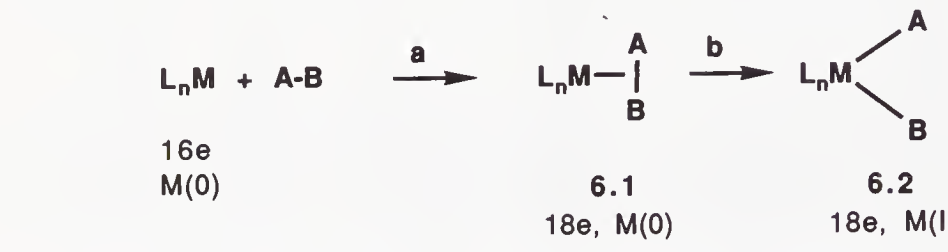
$$\text{Cl—Cl} + \text{PCl}_3 \longrightarrow \text{PCl}_5 \tag{6.5}$$

The unusual feature of oxidative addition reactions of transition metals is the unusually wide range of addends A—B that can be involved, including such normally relatively unreactive molecules as silanes, H_2, and even alkanes. Oxidative additions are a very diverse group of reactions in terms of mechanism, and we shall therefore consider each type separately.

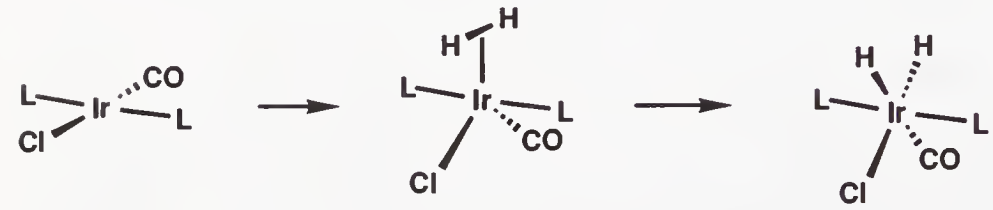
6.1 THREE-CENTER ADDITIONS

Nonpolar addenda, such as H_2, or compounds containing C—H and Si—H bonds, tend to react by a transition state, or more probably an intermediate of the type shown as **6.1** (A = H, B = H, C, or Si). Step *a* of Eq. 6.6 involves formation of a σ-bond complex; sometimes this is stable and the reaction stops here. Step *b* is the oxidative part of the reaction in which metal electrons

are formally transferred to σ^* of A—B. The best-studied case is the addition of H_2 to 16e square planar d^8 species, such as $IrCl(CO)(PPh_3)_2$, *Vaska's complex*.[2] to give 18e d^6 octahedral dihydrides (Eq. 6.6). Normally two ligands that are trans in the Ir(I) complex fold back to give the cis dihydride isomer, but subsequent rearrangement can occur. Conversely, in a reductive elimination such as the loss of H_2 from the dihydride, the two ligands to be eliminated normally have to be cis to one another.

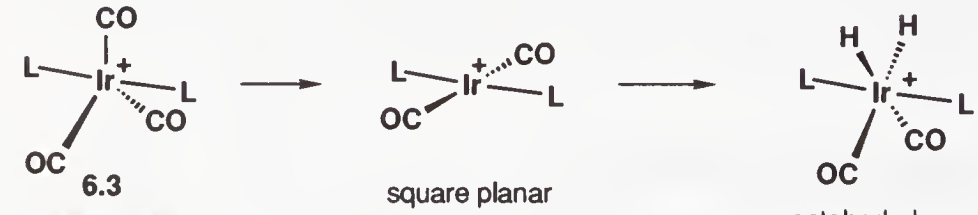


(6.6)



(6.7)

In oxidative addition to Vaska's complex, either the pair of phosphines or the X(CO) set of ligands can fold back, depending on the circumstances.[3,4] The lumo in a d^8 square planar complex has $d_{x^2-y^2}$ character, and so tends to lie in the plane of the ligands. Folding back two of the mutually trans ligands directs an empty orbital in the direction of the incoming H_2 ligand. The transition state may resemble **6.1**. A 2e site must be present on the metal for the reaction to occur, so that in 18e complexes, such as **6.3**, ligand dissociation must take place first. The stereochemistry of the product of Eq. 6.8 can be specified as *cis, cis, trans*-$[IrH_2(CO)_2L_2]^+$.



(6.8)[5]

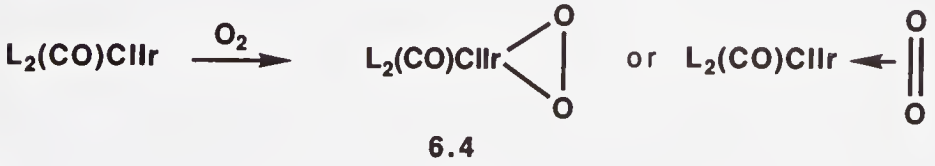
The reactions are usually second-order and show negative entropies of activation (ca. −20 eu) consistent with an ordered transition state such as

6.1. They are little affected by the polarity of the solvent, but may be accelerated to some extent by electron-releasing ligands. The C—H and Si—H bonds of various hydrocarbons and silanes can also oxidatively add to metals. Among different type of C—H bonds, those of arenes are particularly prone to do this because of the high thermodynamic stability of the aryl hydride adduct.

Agostic complexes, σ-bond complexes with C—H—M bridges, can be thought of as lying along the pathway for oxidative addition but arrested at different points. A study[7a] of the structures of a series of these complexes allowed the kinetic pathway for Eq. 6.9 to be mapped out. This is a general strategy[7b] for studying reaction trajectories. The C—H bond seems to approach with the H atom pointing toward the metal and then the C—H bond pivots around the hydrogen to bring the carbon closer to the metal in a side-on arrangement, followed by C—H bond cleavage.[7] The addition goes with retention of stereochemistry at carbon, as expected on this mechanism.

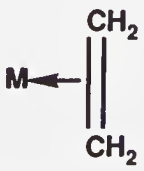
$$\text{C—H} + \text{M} \longrightarrow \text{C—M—H} \tag{6.9}$$

Another ligand that is conventionally considered to undergo a three-center oxidative addition to Vaska's complex is O_2. In this picture, the metal reduces the O_2 to O_2^{2-}, the peroxide ion, which coordinates to the Ir(III) to give **6.4**. Why not envisage the reaction as a ligand addition by regarding O_2 as a 2e donor like ethylene? This is the same problem we looked at in Section 2.7, and is a result of the different formal oxidation states assigned to the L and X_2 extreme pictures of binding. In fact, ethylene is much closer to the L extreme, as shown in **6.5**, while O_2 is very close to the X_2 extreme (**6.6**). This means that the conventional descriptions of ethylene binding as a ligand addition or simple substitution, and of O_2 binding as an oxidative addition are the most appropriate. For ligands, such as $CF_2{=}CH_2$, which bind in a fashion that is approximately equidistant between the two extremes, there is clearly a gray area in which the choice between the two descriptions is arbitrary. This emphasizes that categories such as "oxidative addition" are mental constructs and have their limitations.



(6.10)

6.4

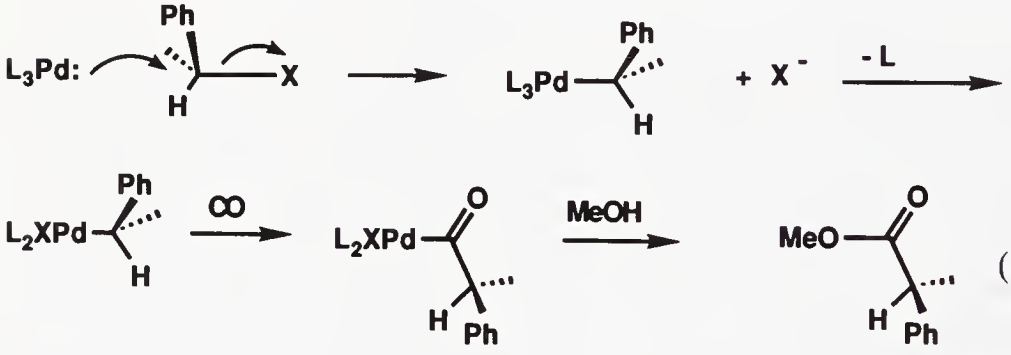


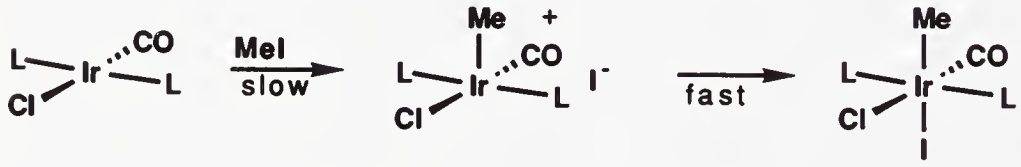
6.5

6.6

6.2 S_N2 REACTIONS

The S_N2 mechanism is often found in the addition of methyl, allyl, acyl, and benzyl halides to species such as Vaska's complex. Like the concerted type, they are second-order reactions, but they are accelerated in polar solvents, and show negative entropies of activation ($\Delta S^{\ddagger} = -40$ to -50 eu).[8] This is consistent with an ordered, polar transition state, as in organic S_N2 reactions. Inversion at carbon has been found in suitably substituted halides. Equation 6.11 shows how the stereochemistry at the carbon of the oxidative addition product was determined by carbonylation to give the metal acyl followed by methanolysis to give the ester. Both of these reactions are known to leave the configuration at carbon unchanged, and the configuration of the ester can be determined unambiguously from the measured optical rotation.[9] R and X may end up cis or trans to one another in the final product, as expected for the recombination of the ion pair formed in the first step. Equation 6.12 shows a case in which the product is trans.





(6.12)

Of the two steps in Eq. 6.12, the first involves oxidation by two units, but no change in the electron count (Me^+ is a 0e reagent), and the second, an increase by 2e in the electron count (Cl^- is a 2e reagent), but no change in the oxidation state. Only the two steps together constitute the full oxidative addition. When an 18e complex is involved, the first step can therefore proceed without the necessity of losing a ligand first. Only the second step requires a vacant 2e site. In some cases the product of the first step is stable and does not lose a ligand to admit the halide anion. This is sometimes loosely called an *oxidative addition*, but it is better considered as an electrophilic attack at the metal, for example:

$$CpIr(CO)L + MeI \longrightarrow [CpIr(CO)LMe]I \qquad (6.13)^{10}$$

The more nucleophilic the metal, the greater its reactivity in S_N2 additions, as illustrated by the reactivity order for some Ni(0) complexes: $Ni(PR_3)_4 > Ni(PAr_3)_4 > Ni(PR_3)_2(alkene) > Ni(PAr_3)_2(alkene) > Ni(cod)_2$ (R = alkyl; Ar = alkyl).[11] Steric hindrance at carbon slows the reaction, so we find the reactivity order: MeI > EtI > *i*-PrI. A better leaving group, X at carbon, accelerates the reaction, which gives rise to the reactivity order $ROSO_2(C_6H_4Me) > RI > RBr > RCl$ for this mechanism.

6.3 RADICAL MECHANISMS

Radical mechanisms in oxidative additions were recognized later than the S_N2 and the concerted processes. A troublesome feature of these reactions is that minor changes in the structure of the substrate, the complex, or in impurities present in the reagents of solvents can sometimes be enough to change the rate, and even the predominant mechanism of a given reaction. Sharp disagreements have turned on questions of repeatability and on what types of experimental evidence should be considered as valid mechanistic criteria. For example, the use of radical traps, such as RNO•, has been critized on the grounds that these may initiate a radical pathway for a reaction that otherwise would have followed a nonradical mechanism in the absence of trap. Much needs to be more firmly established in this difficult area.

Two subtypes of radical process are now distinguished: the nonchain and the chain. The nonchain variant is believed to operate in the additions of certain alkyl halides, RX, to $Pt(PPh_3)_3$ (R = Me, Et; X = I. R = $PhCH_2$, X = Br).[12]

$$PtL_3 \xrightarrow{\text{fast}} PtL_2 \tag{6.14}$$

$$PtL_2 + RX \xrightarrow{\text{slow}} \bullet PtXL_2 + R\bullet \tag{6.15}$$

$$\bullet PtXL_2 + R\bullet \xrightarrow{\text{fast}} RPtXL_2 \tag{6.16}$$

The key feature is one electron oxidation of the metal by RX as a result of X atom transfer from RX to the metal. This produces the pair of radicals shown in Eq. 6.15, which rapidly recombine to give the product before either can escape from the solvent cage. Like the S_N2 process, the radical mechanism is faster the more basic the metal, and the more readily X atom transfer takes place, which gives the reactivity order RI > RBr > RCl. Unlike the S_N2 process, the reaction is very slow for tosylates {e.g., $ROSO_2(C_6H_4Me)$}, and it goes faster as the R radical becomes more stable and so easier to form, giving rise to the order of R group reactivity: 3° > 2° > 1° > Me. In the case of the reaction of NiL_3 with aryl halides, the Ni(I) complex, $NiXL_3$, formed in the first step is sufficiently stable to survive as an observable product of the reaction; the Ar• radical abstracts a hydrogen atom from the solvent to give ArH.[13] There are also cases where the organic radical R• is sufficiently

stable to survive and become a product of the reaction, for example, in the reaction of certain quinones with NiL_3.[14]

The second general kind of reaction is the *radical chain*.[15] This has been identified in the case of the reaction of EtBr and $PhCH_2Br$ with the PMe_3 analogue of Vaska's complex. Equations 6.14 and 6.15 can lead to a chain process if the radicals formed can escape from the solvent cage without recombination. Otherwise, a radical *initiator*, Q•, (e.g., a trace of air) may be required to set the process going (Eq. 6.17 with Q• replacing R•). This can lead to an *induction period* (a period of dead time after which the reaction starts). In either case, a metal-centered radical abstracts X• from the halide (Eq. 6.18), to leave the *chain carrier*, R•. The chain consists of Eq. 6.17–6.18. Chain termination steps such as Eq. 6.19 limit the number of cycles possible per R•. The alkyl group always loses any stereochemistry at the α carbon (because RR′R″C• is planar at the α carbon). Unlike the nonchain case, the reactions slow down or stop in the presence of radical inhibitors, such as the hindered phenol, 2,6-di-*t*-butylphenol; these quench the radical R• to give R—H and the stable, and therefore unreactive aryloxy radical, ArO•.

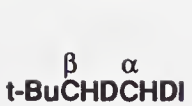
$$R\bullet + Ir^{I}Cl(CO)L_2 \longrightarrow RIr^{II}\bullet Cl(CO)L_2 \qquad (6.17)$$

$$RIr^{II}\bullet Cl(CO)L_2 + RX \longrightarrow RXIr^{III}Cl(CO)L_2 + R\bullet \qquad (6.18)$$

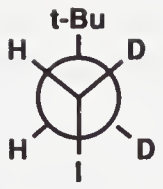
$$2R\bullet \longrightarrow R_2 \qquad (6.19)$$

Certain substrates are particularly useful for determining what happens to the stereochemistry at the α carbon during oxidative addition or in other reactions. For example, **6.7** can be obtained with a defined relative stereochemistry at the α and β carbons. This has the advantage that we do not need to resolve anything, we have both enantiomers of **6.8** present, but we assume that the reaction will do nothing to the stereochemistry at the β carbon, so we can look at the configuration at the α position relative to that at the β. This is easily done by ^1H NMR. The conformation adopted by these substituted ethanes puts the two bulky groups *t*-Bu and ML_n, or *t*-Bu and X anti to one another. This in turn puts the α and β protons gauche or anti to one another according to whether the stereochemistry at the α position has been retained or inverted. By the Karplus relationship, which tells us the HCCH′ dihedral angle from the observed $^3J(H, H')$, the coupling constant between the two hydrogens in the ^1H NMR will be very different in the two cases and this serves to identify the stereochemistry of the product. For example, **6.9** would be the product of an S_N2 reaction.

Other useful tests for radicals rely on the fact that some free radicals are known to rearrange very rapidly (e.g., Eq. 6.20). For example, if hexenyl bromide gives a cyclopentylmethyl metal complex, than a radical intermediate is strongly indicated. Cyclopropylmethyl radicals ($C_3H_5CH_2\bullet$), on the other hand, rearrange by ring opening to give $CH_2{=}CHCH_2CH_2\bullet$. Other common



6.7



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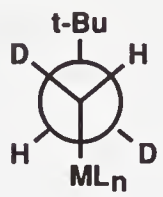
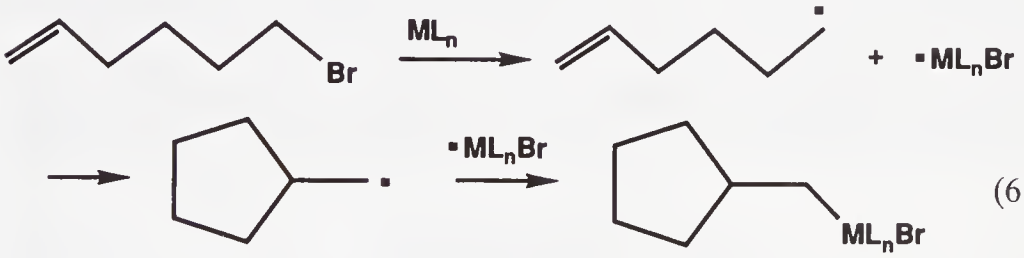


6.9

reactions of radicals are Cl• abstraction from a chlorinated solvent to give RCl, and dimerization to give R—R. An NMR method, called *chemically induced dynamic nuclear polarization* (CIDNP),[16] can be useful in certain cases. The method relies on the fact that the product of a radical recombination can have very unusual distributions of α and β spins. This implies that the ^{1}H NMR *may* show large positive (if α spins are in excess) or negative peaks (if β), if the conditions are right. It is not easy to tell how much of the reaction is going by a radical route, because the intensity of the effect is variable and difficult to predict.



(6.20)

Binuclear oxidative additions, because they involve 1e rather than 2e changes at the metals, often go via radicals. One of the best known examples is shown in Eq. 6.21. The rate determining step is abstraction of a halogen atom from RX by the d^7 Co(II); the resulting R• combines with a second Co(II) center:[17]

$$2[Co(CN)_5]^{3-} + RX \longrightarrow [RCo(CN)_5]^{3-} + [XCo(CN)_5]^{3-} \quad (6.21)$$

$$[Co(CN)_5]^{3-} + RX \xrightarrow{\text{slow}} [XCo(CN)_5]^{3-} + R\bullet \quad (6.22)$$

$$R\bullet + [Co(CN)_5]^{3-} \xrightarrow{\text{fast}} [RCo(CN)_5]^{3-} \quad (6.23)$$

In reactions involving radicals, it is important to use solvents that do not react with R•; alkane, C_6H_6, AcOH, CH_3CN, and water are usually satisfactory.

6.4 IONIC MECHANISMS

Hydrogen halides are often largely dissociated in solution, and the anion and proton tend to add to metal complexes in separate steps. Two variants have been recognized. In the more common one, the complex is basic enough to

protonate, after which the anion binds to give the final product. Rarer is the opposite case in which the halide ion attacks first, followed by protonation of the intermediate. The first route is favored by basic ligands and a low-oxidation-state metal, the second by electron-acceptor ligands and by a net positive charge on the complex. Polar solvents encourage both types; examples are given in Eqs. 6.24 and 6.25:[18]

$$\underset{\text{18e } d^{10} \text{ tetrahedral}}{Pt(PPh_3)_4} + H^+ + Cl^- \xrightarrow{-PPh_3} \underset{\text{16e } d^8 \text{ square planar}}{[HPt(PPh_3)_3]^+} + Cl^- \xrightarrow{-PPh_3} \underset{\text{16e } d^8 \text{ square planar}}{[HPtCl(PPh_3)_2]} \tag{6.24}$$

$$\underset{\text{16e } d^8 \text{ square planar}}{[Ir(cod)L_2]^+} + Cl^- + H^+ \longrightarrow \underset{\text{18e } d^8 \text{ TBP}}{[IrCl(cod)L_2]} + H^+ \longrightarrow \underset{\text{18e } d^6 \text{ octahedral}}{[IrHCl(cod)L_2]^+} \tag{6.25}$$

The rate of the first type generally follows Eq. 6.26, suggesting that protonation is the slow step. This can be carried out independently by using an acid with a noncoordinating anion: HBF_4 and HPF_6 are the most often used. The anion has insufficient nucleophilicity to carry out the second step, and so the intermediate can be isolated. This is an example of a general strategy in which a "noncoordinating" anion is used to isolate reactive cations as stable salts.

$$\text{Rate} = k[\text{complex}][H^+] \tag{6.26}$$

The rate of the second type (Eq. 6.25) usually follows the rate equation shown in Eq. 6.27, suggesting that Cl^- addition is the slow step. This step can be carried out independently with LiCl alone, but no reaction is observed with HBF_4 alone, because the cationic iridium complex is not basic enough to protonate and BF_4^- is a noncoordinating anion.

$$\text{Rate} = k[\text{complex}][Cl^-] \tag{6.27}$$

Other acids (or Lewis acids) which are ionized to some extent in solution, such as RCO_2H and $HgCl_2$ (Eqs. 6.28–6.29), may well react by the same mechanism, but this has not yet been studied in detail.

$$IrCl(CO)L_2 \xrightarrow{RCO_2H} IrH(\eta^1\text{-}OCOR)Cl(CO)L_2 \tag{6.28}[19]$$

$$IrCl(CO)L_2 \xrightarrow{HgCl_2} Ir(HgCl)Cl_2(CO)L_2 \tag{6.29}[20]$$

As we saw in Chapter 3, alkyls $L_nM(R)$ can often be cleaved with acid to give the alkane. In some cases simple protonation of the metal to give $L_nM(R)H^+$ or of the M—R bond to give the σ complex $L_nM(H—R)^+$ is the likely mechanism, but in others (e.g., Eq. 6.30) there is a dependence of the

rate, and in some cases even of the products,[21] on the counterion; in such cases, an oxidative addition–reductive elimination mechanism seems more likely:

$$PtR_2(PR_3)_2 \xrightarrow{HCl} PtHClR_2(PR_3)_2 \xrightarrow{-RH} PtRCl(PR_3)_2 \qquad (6.30)^{22}$$

6.5 REDUCTIVE ELIMINATION

In spite of its great importance, reductive elimination has received less detailed study than oxidative addition. The reaction is most often seen in higher oxidation states, because the formal oxidation state of the metal is reduced by two units in the reaction. The reaction is especially efficient for intermediate oxidation states, such as the d^8 metals, Ni(II), Pd(II), and Au(III), and the d^6 metals, Pt(IV), Pd(IV), Ir(III), and Rh(III). Reductive elimination can also be stimulated by photolysis: the case of photoextrusion of H_2 from dihydrides is the best known (Section 12.3).

Certain groups are more easily eliminated than others, for example, Eqs. 6.31–6.35 often proceed to the right for thermodynamic reasons. Reactions that involve H, such as Eqs. 6.31 and 6.33, are particularly fast, probably because the transition state energy is lowered by the formation of a relatively stable σ-bond complex $L_nM(H—X)$ along the pathway; such complexes are known to be stable only where an H is present.

$$L_nMRH \longrightarrow L_nM + R—H \qquad (6.31)$$

$$L_nMR_2 \longrightarrow L_nM + R—R \qquad (6.32)$$

$$L_nMH(COR) \longrightarrow L_nM + RCHO \qquad (6.33)$$

$$L_nMR(COR) \longrightarrow L_nM + R_2CO \qquad (6.34)$$

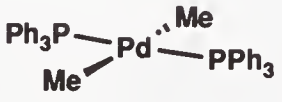
$$L_nMR(SiR_3) \longrightarrow L_nM + R—SiR_3 \qquad (6.35)$$

In discussing the catalysis of organic reactions in Chapter 9, we will see that a reductive elimination is often the last step in a catalytic cycle and that the resulting L_nM fragment must be able to survive long enough to react with the substrates for the organic reaction and so reenter the catalytic cycle. The eliminations of Eqs. 6.31–6.35 are analogous to the three-center oxidative additions in that they are believed to go by a nonpolar, nonradical three-center transition state, such as **6.10**. Retention of stereochemistry at carbon is a characteristic feature of this group of reactions.

6.10

There are differences of detail in the way different metals undergo reductive elimination.[23] In Ni(II) complexes, the 4-coordinate NiR_2L_2 can lose R—R directly (L = 3° phosphine). For PdR_2L_2, one of the phosphine ligands, L, has to be lost first;[24] Au(III) complexes behave similarly.[25] Pt(II) appears to be much more reluctant to eliminate, but prior oxidative addition of RX to give a Pt(IV) complex strongly encourages subsequent elimination.[26] Occasionally, the addition of a fifth ligand to square planar Ni(II) complexes has been found to lead to reductive elimination.[27] Some progress has been made in trying to understand the origin of these differences in m.o. terms.[23]

We will look at elimination from *cis*-PdR_2L_2 in detail only to illustrate how this mechanistic information is obtained. The addition of phosphine retards the rate of the reaction for **6.11**, suggesting that loss of phosphine takes place to give the 3-coordinate intermediate PdR_2L. (The retardation might also have been due to formation of PdR_2L_3, which would have to be less reactive than PdR_2L_2 itself; it can be shown by NMR, that this does not happen, however.) The reactive intermediate may in fact be $Pd(PR_3)(solvent)R_2$, and therefore not really 3-coordinate at all. The chelating diphosphine complex **6.12** loses phosphine much less easily than do the analogs containing monodentate phosphines, and undergoes elimination 100 times more slowly.[24] The "transphos" complex **6.13** does not eliminate ethane under conditions where the corresponding cis derivative **6.12** does so very readily.[24] The groups to be eliminated therefore need to be cis; transphos locks the system in a trans geometry.



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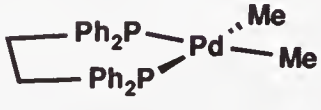

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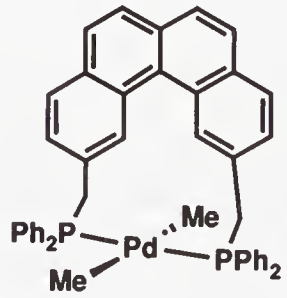

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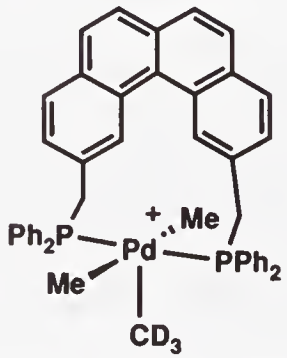


6.14

In an important general mechanistic experiment that is useful for this problem, the *crossover* experiment, a mixture of *cis*-$Pd(CH_3)_2L_2$ and *cis*-$Pd(CD_3)_2L_2$, is thermolyzed. We find that only C_2H_6 and C_2D_6 are formed,

showing that the reaction is *intramolecular;* that is, R groups can couple only within the same molecule of starting complex. This experiment rules out coupling between R groups originating in different molecules of the complex (the *intermolecular* route). The crossover product, CH_3CD_3, would have been formed if, say, free methyl radicals had been involved because they are sufficiently long-lived to migrate through the solution from one molecule of palladium complex to the next. We always need to do proper control experiments; for example, even if CH_3CD_3 is formed, we need to check whether scrambling happens in the reaction or whether the CH_3 and CD_3 groups exchange between the starting materials before reductive elimination takes place or in the analytical method used to detect crossover. This can be done by isolating the starting materials after partial conversion to products to make sure that no $Pd(CH_3)(CD_3)L_2$ is present.

As we saw in Table 6.1, Pd(IV) is not a very stable oxidation state, but it often acts as a transient intermediate in reactions; the transphos complex **6.12** reacts with CD_3I to give CD_3CH_3. This probably goes via the unstable Pd(IV) intermediate **6.14**. Reactions of this type appear to take place with retention of stereochemistry at carbon.

Dialkyls containing β-hydrogens often β-eliminate to give an alkyl hydride and alkene before they reductively eliminate R—H. An interesting case is $PdEt_2(PR_3)_2$: the cis isomer reductively eliminates butane, but in the trans isomer, in which the two R groups are not properly oriented for reductive elimination, the β-elimination–reductive elimination path is followed to give ethylene and ethane.[24]

The stoichiometric decarbonylation of acyl halides with $RhCl(PPh_3)_3$ illustrates the reductive elimination of an alkyl halide from an octahedral Rh(III) intermediate (Eq. 6.36), a reaction that can be useful in organic synthesis:

$$\mathrm{RhClL_3} \xrightarrow{\mathrm{RCOCl}} \mathrm{(RCO)RhCl_2L_3} \xrightarrow{-\mathrm{L,\ retromigratory\ insertion}} \mathrm{RRh(CO)Cl_2L_2} \xrightarrow{\mathrm{red.\ elim.}} \mathrm{RhCl(CO)L_2 + R{-}Cl} \quad (6.36)^{28}$$

Reductive elimination involving acyl groups seems to be easier than for alkyls. For example, the cobalt dimethyl shown in Eq. 6.37 does not lose ethane but undergoes migratory insertion with added CO to give an acyl alkyl complex, which subsequently loses acetone; a crossover experiment with the protonated d_0 and deuterated d_6 dialkyls showed that this reaction is also intramolecular:

$$\mathrm{CpCoMe_2L} \xrightarrow{\mathrm{CO}} \mathrm{CpCO(COMe)MeL} \longrightarrow \mathrm{CpCo(CO)L + Me_2CO} \quad (6.37)^{29}$$

We saw earlier that a binuclear version of oxidative addition is important for those metals that prefer to change their oxidation state by one, rather than two units. The same is true of reductive elimination:

$$MeCH{=}CHCu(PBu_3) \xrightarrow{heat} MeCH{=}CHCH{=}CHMe \quad (6.38)^{30}$$

$$ArCOMn(CO)_5 + HMn(CO)_5 \longrightarrow ArCHO + Mn_2(CO)_{10} \quad (6.39)^{31}$$

Unexpectedly, the binuclear variant can even occur when an intramolecular path looks as if it ought to be available. Norton[32a] has discovered one of the clearest cases for $Os(CO)_4RH$ (R = Me or Et). Alkyl hydrides normally eliminate rapidly to give the alkane, but here the usual intramolecular process (Eq. 6.40) is not observed. The reason seems to be that "$Os(CO)_4$" is a highly unstable species. As a Group 8 element, Os(0) greatly prefers the 5-coordinate geometry over 4-coordinate (d^8 metals of Group 9 tend to prefer, and Group 10 strongly prefer the 4-coordinate geometry). In addition, carbonyls strongly prefer the 18e over the 16e configuration:

$$cis\text{-}Os(CO)_4RH \not\longrightarrow \text{`}Os(CO)_4\text{'} + R{-}H \quad (6.40)$$

Norton's mechanism provides a bimolecular way to eliminate alkane that does not involve 4-coordinate Os(0). The slow step is migratory insertion to give a coordinatively unsaturated 16e acyl. The resulting vacant site is filled by an Os—H bond from a second molecule of the alkyl hydride. Crossover products are seen (e.g., d_1 and d_3 methane from the d_0 and d_4 methyl hydrides), and so the R group of the acyl now appears to eliminate with the hydride from the metal to give a binuclear complex containing an Os—Os bond. A hydride seems to be required for this mechanism to operate, probably because hydrides bridge so easily. The analogous complex *cis*-$Os(CO)_4Me_2$, which clearly does not contain a hydride, is remarkably stable. It decomposes only slowly at 160°C, and even then it does not give an elimination, binuclear or otherwise:

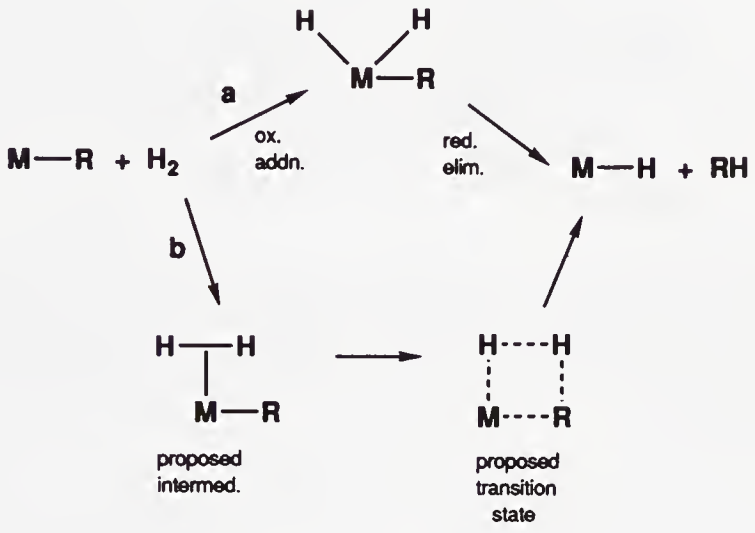
$$cis\text{-}Os(CO)_4RH \xrightarrow[\textbf{6.15}]{} (RCO)Os(CO)_3H \xrightarrow{\textbf{6.15}}$$

$$(RCO)H(CO)_3Os{-}H{-}OsR(CO)_4 \xrightarrow{-RH} H(CO)_4Os{-}OsR(CO)_4 \quad (6.41)$$

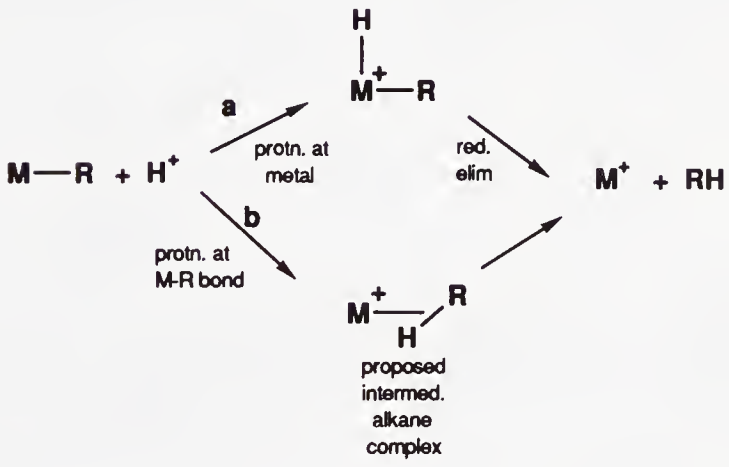
Apparent oxidative addition–reductive elimination sequences can in fact be *σ-bond metathesis* reactions. These are best recognized for d^0 early metal complexes such as Cp_2ZrRCl or WMe_6 because oxidative addition is forbidden in these cases. (The oxidative addition product would unambiguously exceed the maximum permitted oxidation state for the metal.) In a reaction of such a complex with H_2 (Eq. 6.42), the metal therefore cannot follow mechanism a of Eq. 6.43. Instead a concerted process (path b of Eq. 6.43) is believed to operate. Path b probably goes via formation of an intermediate H_2 complex

that is permitted even for d^0 species. The strong proton donor character of $M(H_2)$ species may encourage proton transfer to the R group:[32b]

$$Cp_2ZrRCl + H_2 \longrightarrow Cp_2ZrHCl + RH \tag{6.42}$$



(6.43)



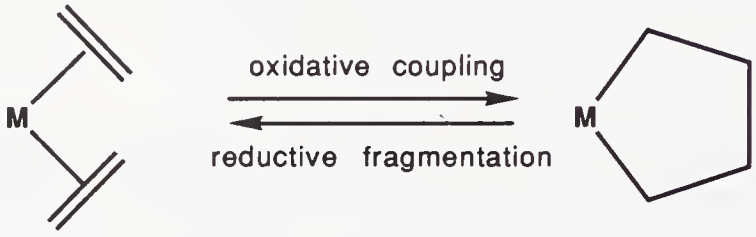
(6.44)

For the same reason, reaction of d^0 alkyls with acids cannot go via initial protonation at the metal (step a in Eq. 6.44) because as a d^0 system, the metal has no lone pairs. Instead, protonation of the M—R bond must take place. Formation of an alkane σ-bond complex then would lead to loss of alkane.

6.6 OXIDATIVE COUPLING AND REDUCTIVE CLEAVAGE

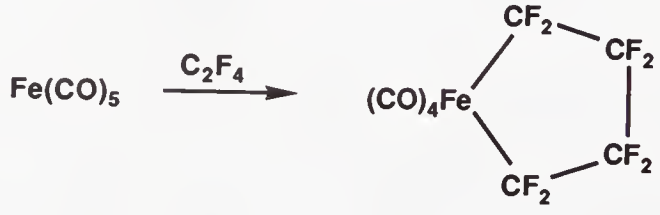
Oxidative coupling is a reaction like that shown in Eq. 6.45 in which the metal induces a coupling reaction between two alkene ligands to give a metalacycle. The formal oxidation state of the metal increases by two units;

hence the "oxidative" part of the name. The electron count decreases by two but the coordination number stays the same. The reverse reaction, which is perhaps best called "reductive cleavage" is more rarely seen. It cleaves a relatively unactivated C—C bond to give back the two unsaturated ligands.

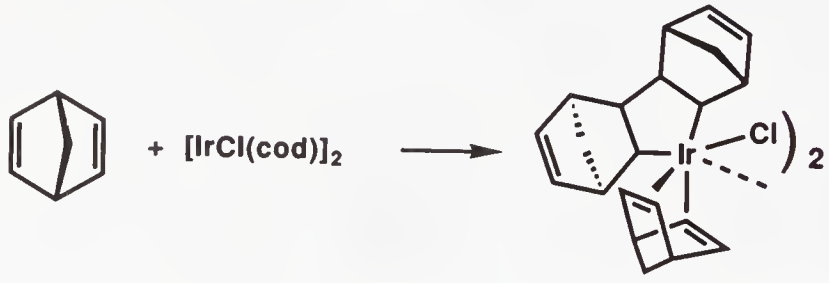


(6.45)

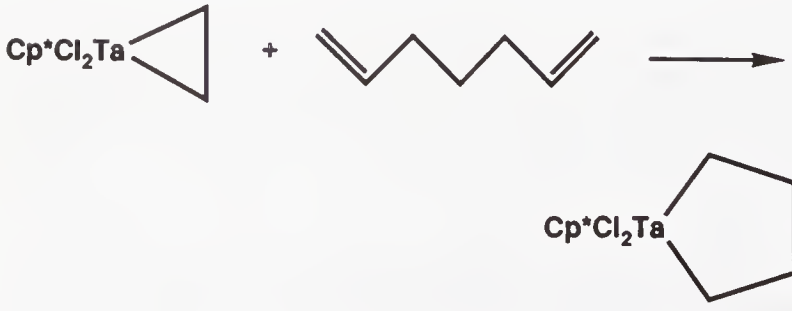
Alkynes undergo the reaction more easily than do alkenes. Alkenes can be activated by electron-withdrawing substituents, or by strain. Simple alkenes will still undergo the reaction if the metal is sufficiently π-basic. Some examples follow:[33–37]



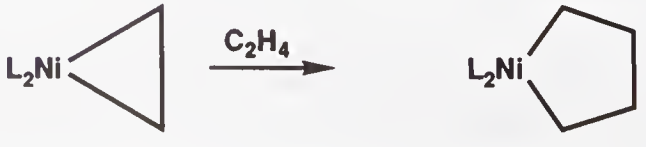
(6.46)



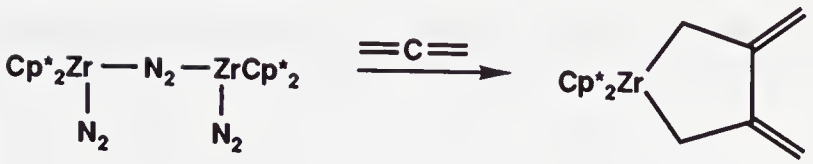
(6.47)



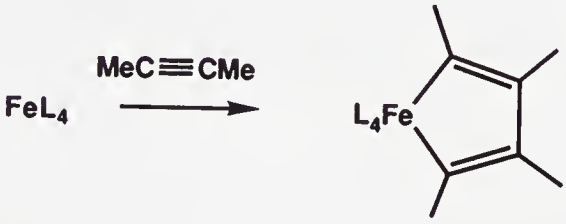
(6.48)



(6.49)



(6.50)



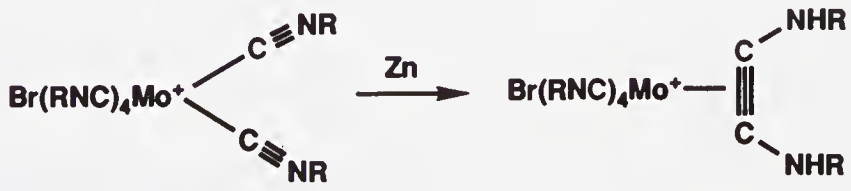
(6.51)

Intermediates with one coordinated alkene are often seen (e.g., Eq. 6.49), but the bis-alkene species is probably the immediate precursor of the coupled product.[38] The products from alkynes are very stable and are known as *metalloles* (Eq. 6.51).

Coupling is not limited to alkenes and alkynes. A particularly interesting case involves carbenes and alkenes going to metalacyclobutanes (Eq. 6.52), the key step of the alkene metathesis reaction (Section 11.3). The reverse reaction constitutes another example of a C—C bond cleavage reaction, as we also saw in Eq. 6.45.

(6.52)

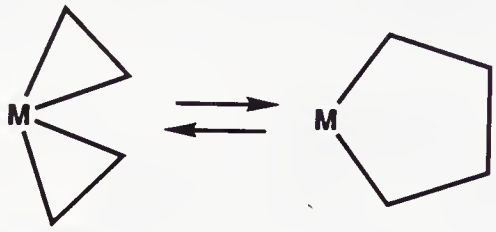
Carbenes, $M{=}CR_2$, can couple to give the alkenes $R_2C{=}CR_2$, (Chapter 11), and the coupling of isonitriles,[39] and more recently, even of carbonyls[39b] has been effected by the reduction of a 7-coordinate Mo complex. Note how the alkyne in Eq. 6.53 behaves as a 4e donor in the product.



(6.53)

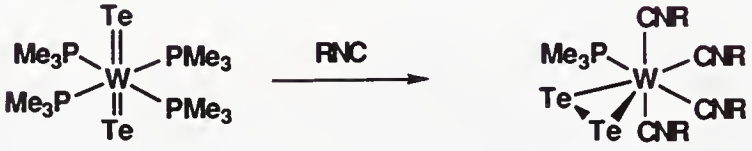
The same oxidation state ambiguity that we have seen several times before also operates here. Equation 6.54 shows that if the alkenes are considered to be in the metalacyclopropane (X_2 or σ_2 form), the coupling reaction proceeds with formal reduction at the metal and resembles a reductive elimination of two alkyl groups. Parkin[40] has a case of a reductive coupling in Eq. 6.55,

which shows how two terminal telluride ligands in a W(IV) precursor can be coupled to give a W(II)η^2Te_2 complex by addition of an isonitrile, *t*-BuNC.



(6.54)

6.16



(6.55)

REFERENCES

1. R. H. Crabtree, H. Felkin, T. Fillebeen-Khan, and G. E. Morris, *J. Organometal. Chem.*, **168,** 183, 1979.
2. L. Vaska, *Acct. Chem. Res.*, **1,** 335, 1968.
3. R. Eisenberg et al., *J. Am. Chem. Soc.*, **105,** 7772, 1983; **107,** 3148, 1985.
4. R. H. Crabtree and R. J. Uriarte, *Inorg. Chem.*, **22,** 4152, 1983.
5. M. J. Mays et al., *J. Chem. Soc. (A),* 2909, 3000, 1970.
6. G. J. Kubas, *J. Am. Chem. Soc.*, **108,** 1339, 1986.
7. (a) R. H. Crabtree, E. M. Holt, M. Lavin, and S. M. Morehouse, *Inorg. Chem.*, **24,** 1986. 1985, (b) H. B. Bürgi and J. D. Dunitz, *Accts. Chem. Res.*, **16,** 153, 1983.
8. P. B. Chock and J. Halpern, *J. Am. Chem. Soc.*, **88,** 3511, 1966.
9. J. K. Stille, *Acct. Chem. Res.*, **10,** 434, 1977; *J. Am. Chem. Soc.*, **100,** 838, 845, 1975.
10. W. A. Graham et al., *Inorg. Chem.*, **9,** 2653, 2658, 1970.
11. E. Uhlig and D. Walton, *Coord. Chem. Rev.*, **33,** 3, 1980.
12. M. F. Lappert and P. W. Lednor, *Chem. Commun., 948, 1973; J. Chem. Soc., Dalton,* 1448, 1980; *Adv. Organometal. Chem.*, **14,** 345, 1976.
13. J. K. Kochi et al., *J. Am. Chem. Soc.*, **101,** 6319, 1979.
14. J. K. Kochi et al., *Frontiers of Free Radical Chemistry,* Pergamon Press, Oxford, 1980, p. 297.
15. J. A. Osborn et al., *Inorg. Chem.*, **19,** 3230, 3236, 1980.
16. R. G. Lawler and H. R. Ward, Chap. 3 in *The Determination of Organic Structures by Physical Methods,* E. A. Braude (ed.), Academic Press, New York, 1973, Vol. 5.
17. J. Halpern, *Pure Appl. Chem.*, **51,** 2171, 1979.

18. W. J. Luow et al., *J. Chem. Soc. Dalton,* 340, 1978; R. H. Crabtree et al., *J. Organometal. Chem.*, **181,** 203, 1979.
19. A. J. Deeming and B. L. Shaw, *J. Chem. Soc. (A),* 1802, 1969.
20. P. D. Brotherton et al., *J. Chem. Soc. Dalton,* 1799, 1976.
21. P. Uguagliati, *J. Organomet. Chem.*, **169,** 115, 1979.
22. R. Romeo et al., *Inorg. Chim. Acta,* **19,** L55, 1976; *Inorg. Chem.*, **17,** 2813, 1978.
23. R. Hoffmann, in *Frontiers in Chemistry,* J. K. Laidler (ed.), Pergamon Press, Oxford, 1982, p. 247.
24. J. K. Stille et al., *J. Am. Chem. Soc.*, **102,** 4933, 1980; **103,** 2143, 1981.
25. R. Hoffmann, J. K. Kochi et al., *J. Am. Chem. Soc.*, **98,** 7255, 1976.
26. G. M. Whitesides, *Pure Appl. Chem.*, **53,** 287, 1981; R. J. Puddephatt et al., *J. Chem. Soc., Dalton,* 2457, 1974.
27. A. Yamamoto et al., *J. Am. Chem. Soc.*, **93,** 3360, 1971.
28. J. K. Stille et al., *J. Am. Chem. Soc.*, **99,** 5664, 1977.
29. R. Bergman, *Acct. Chem. Res.*, **13,** 113, 1980.
30. G. M. Whitesides, C. P. Casey, et al., *J. Am. Chem. Soc.*, **93,** 1379, 1971.
31. J. A. Gladysz, et al., *J. Am. Chem. Soc.*, **101,** 1589, 1979.
32. (a) J. Norton, *Acct. Chem. Res.*, **12,** 139, 1979; (b) this can be the case for methane reactions: T. R. Cundari, *J. Am. Chem. Soc.*, **114,** 10557, 1992.
33. F. G. A. Stone et al., *J. Organometal. Chem.*, **100,** 257, 1975.
34. R. R. Schrock, *J. Am. Chem. Soc.*, **102,** 269, 1980.
35. R. Grubbs et al., *J. Am. Chem. Soc.*, **100,** 7416, 1978.
36. J. E. Bercaw et al., *J. Am. Chem. Soc.*, **100,** 2716, 1978.
37. E. L. Muetterties et al., *J. Am. Chem. Soc.*, **100,** 6966, 1978.
38. R. D. W. Kemmit et al., *J. Organometal. Chem.*, **187,** C1, 1980.
39. (a) S. J. Lippard et al., *J. Am. Chem. Soc.*, ***104,*** 1263, 1982; **114,** 4166, 1992.
40. G. Parkin et al., unpublished data, 1993.

PROBLEMS

1. An oxidative addition to a metal complex **A** is found to take place with $MeOSO_2Me$, but not with *i*-PrI. A second complex, **B**, reacts with *i*-PrI but not with $MeOSO_2Me$. What mechanism(s) do you think is (are) operating in the two cases? Which of the two complexes, **A** or **B**, would be more likely to react with MeI? What further tests could you apply to confirm the mechanism(s)?

2. Suppose we are able to discover that the equilibrium constants for Eq. 6.1 are in the order CH_3—H < Ph—H < H—H < Et_3Si—H for a given square planar Ir(I) complex. Can we say anything about the relative metal–ligand bond strengths in the adducts? Justify any assumptions that you make.

3. A given complex ML_n forms only a dihydrogen complex $(\eta^2\text{-}H_2)ML_n$, not the true oxidative addition product H_2ML_n with H_2. Would the true oxidative addition product be more or less likely to form as we move to (a) more electron-releasing ligands L; (b) from a third- to a first-row metal, M; or (c) to the 1e oxidation product $H_2ML_n^+$? Would you expect the same metal fragment to form an ethylene complex, $(C_2H_4)ML_n$, with predominant Dewar–Chatt, or metalacyclopropane character? Explain.

4. Complexes of the type $Pt(PR_3)_4$ can form $PtCl_2(PR_3)_2$ with HCl. How can we explain this result? The same product can also be formed from *t*-BuCl and $Pt(PR_3)_4$. What do you think is happening here? In each case a different non-metal-containing product is also formed; what do you think they are?

5. A metal complex L_nM is found to react with ethylene to give 1-butene and L_nMH_2. Provide a reasonable mechanism involving oxidative coupling.

6. Predict the order of reactivity of the following in oxidative addition of HCl: **A**, $IrCl(CO)(PPh_3)_2$; **B**, $IrCl(CO)(PMe_3)_2$; **C**, $IrMe(CO)(PMe_3)_2$; **D**, $IrPh(CO)(PMe_3)_2$. Would you expect the $\nu(CO)$ frequencies of **A–D** to (i) be different from one another, or (ii) to change in going to the oxidative addition products? Explain, and justify any assumptions you make.

7. The products from HCl addition to **C** and **D** in problem 6 are unstable, but the addition products to **A** and **B** are stable. Explain, and state how **C** and **D** will decompose.

8. WMe_6 reacts with H_2 and PMe_3 to give $WH_2(PMe_3)_5$. Propose a reasonable mechanism.

9. H_2 adds to Ir(dppe)(CO)Br to give a kinetic product A, in which the cis H ligands are trans to P and CO, and a thermodynamic product in which the cis H ligands are trans to P and Br. Write the structures of **A** and **B**. How would you tell whether the rearrangement of **A** to **B** occurs by initial loss of H_2 or by a simple intramolecular rearrangement of **A**?

10. $Pt(PEt_3)_2$, generated electrochemically, reacts with the PhCN solvent to give $PhPt(CN)(PEt_3)_2$. Oxidative addition of a C—C bond is very rare. Discuss the factors that make it possible in this case.

CHAPTER 7

INSERTION AND ELIMINATION

Oxidative addition and substitution allow us to assemble 1e and 2e ligands on the metal. With insertion, and its reverse reaction, elimination, we can now combine and transform these ligands within the coordination sphere, and ultimately expel these transformed ligands to form free organic compounds. In insertion, a coordinated 2e ligand, AB, can insert itself into an M—X bond to give M—(AB)—X, where ABX is a new 1e ligand in which a bond has been formed between AB and X.

There are two main types of insertion—1,1 and 1,2—as shown in Eqs. 7.1 and 7.2, in which the metal and the X ligand end up bound to the same (1,1) or adjacent (1,2) atoms of the L-type ligand shown as A=B. The type of insertion observed in any given case depends on the nature of the 2e inserting ligand. For example, CO gives only 1,1 insertion: that is, both the M and the X group end up attached to the CO carbon. On the other hand, ethylene gives only 1,2 insertion, in which the M and the X end up on adjacent atoms of what was the 2e ligand. In general, η^1 ligands tend to give 1,1 insertion and η^2 ligands, 1,2 insertion. SO_2 is the only common ligand that can give both types of insertion; as a ligand, SO_2 can be η^1 (S) or η^2 (S, O).

18e 16e (7.1)

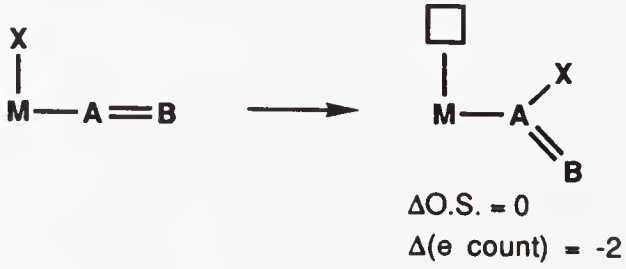
(7.2)

In principle, insertion reactions are reversible, but just as we saw for oxidative addition and reductive elimination in Chapter 6, for many ligands only one of the two possible directions is observed in practice, probably because this direction is strongly favored thermodynamically. For example, SO_2 commonly inserts into M—R bonds to give alkyl sulfinate complexes, but these rarely eliminate SO_2. Conversely, diazoarene complexes readily eliminate N_2, but N_2 has not yet been observed to insert into a metal–aryl bond.

$$M—R + SO_2 \longrightarrow M—SO_2R \tag{7.3}$$

$$M—N{=}N—Ar \longrightarrow M—Ar + N_2 \tag{7.4}$$

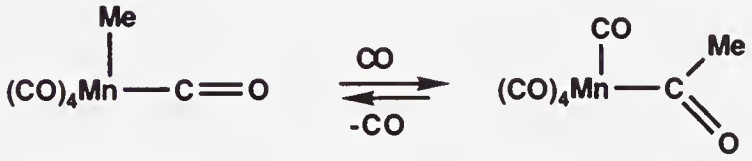
The immediate precursor to the final insertion product usually has both the 1e and 2e ligands coordinated. This means that a net 3e set of ligands is converted to a 1e insertion product (ionic model: 4e → 2e), so that a 2e vacant site is generated by the insertion. This site can be occupied by an external 2e ligand and the insertion product trapped. Conversely, the elimination requires a vacant site, so that an 18e complex will not undergo the reaction unless a ligand first dissociates. The insertion also requires a cis arrangement of the 1e and 2e ligands, while the elimination generates a cis arrangement of these ligands. The formal oxidation state does not change during the reaction:



(7.5)

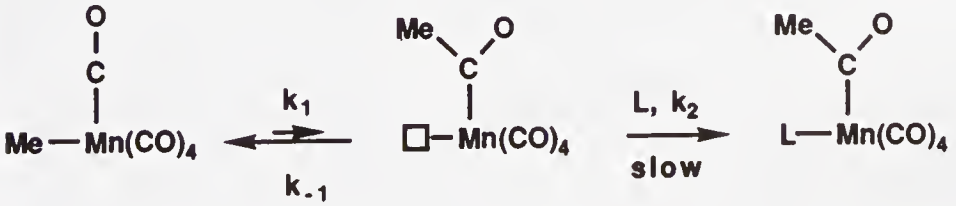
7.1 REACTIONS INVOLVING CO

CO shows a strong tendency to insert into metal alkyl bonds to give metal acyls. The reaction has been carefully studied for a number of systems. Although the details may differ, most follow the pattern set by the best-known case:[1]



(7.6)

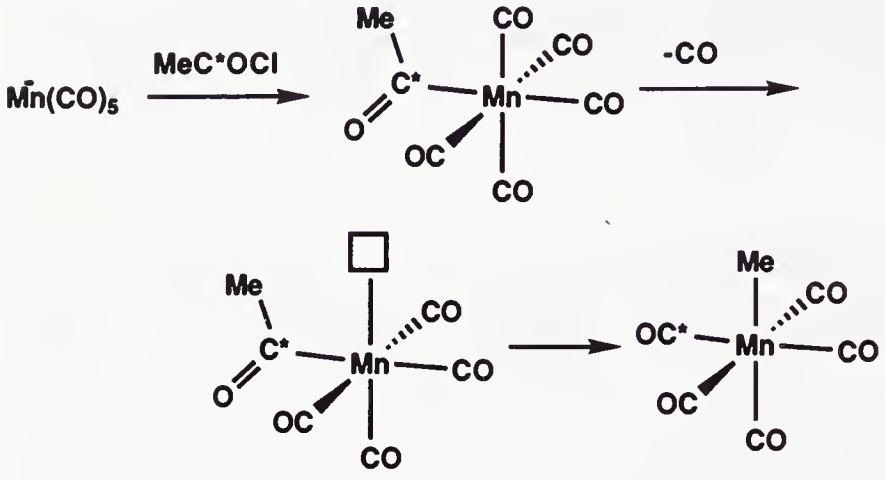
The first step is the migration of the methyl group to a cis CO (hence the alternative name *migratory insertion* for this reaction). This generates a 2e site at the metal, which can be filled by the incoming ligand, typically CO or a phosphine (Eq. 7.7). It is often found that the more nucleophilic the ligand, the faster the reaction, and so it is believed that the first step is rapid and reversible and that trapping with phosphine (k_2) is the rate determining step.[2] When the incoming ligand is ^{13}CO, the product contains only one labeled CO, which is cis to the newly formed acetyl group. This shows that the methyl group migrates to a coordinated CO, rather than free CO attacking the Mn—Me bond. Any stereochemistry at carbon is retained in the insertion as is consistent with the mechanism of Eq. 7.7.[3] We can tell where the labeled CO is located in the product because there is a characteristic shift of the ν(CO) stretching frequency to lower energy in the IR spectrum of the complex as a result of the greater mass of ^{13}C over normal carbon (see Section 10.9).



(7.7)

By studying the reverse reaction (Eq. 7.8), elimination of CO from $Me^{13}COMn(CO)_5$, where we can easily label the acyl carbon with ^{13}C (by reaction of $Mn(CO)_5^-$ with $Me^{13}COCl$), we find that the label ends up in a CO cis to the methyl. This is an example of a general strategy in which we

examine the reverse of a reaction to learn something about the forward process.

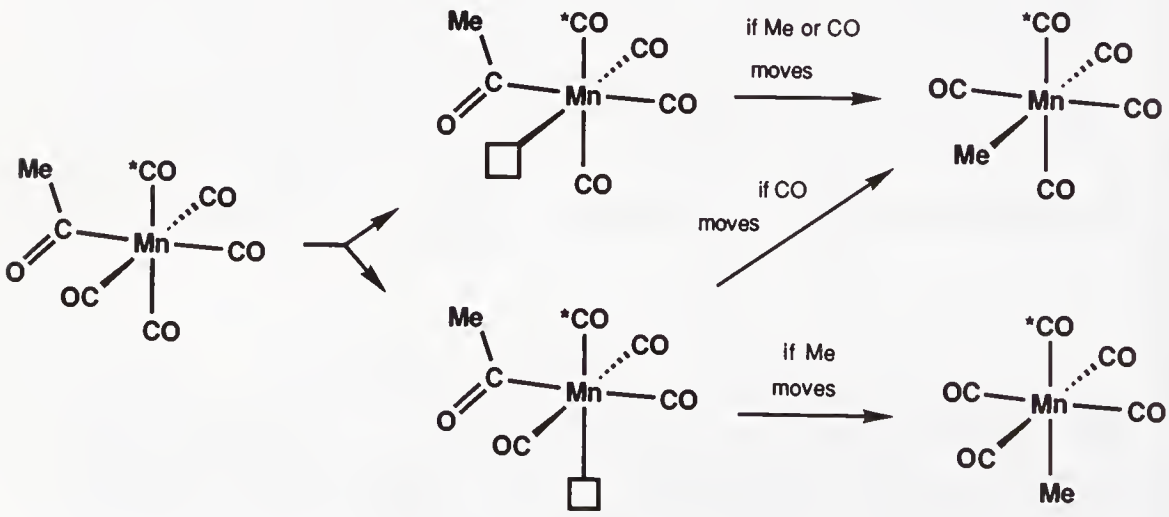


(7.8)

(where C* = ^{13}C).

This relies on *microscopic reversibility,* according to which, the forward and reverse reactions of a thermal process will follow the same path. In this case, if the labeled CO ends up cis to Me, the CO to which a methyl group migrates in the forward reaction, must also be cis to methyl. We are fortunate in seeing the kinetic products of these reactions. If a subsequent scrambling of the COs had been fast, we could have deduced nothing.

It is also possible to use reversibility arguments to show that the acyl ligand in the product is bound at a site cis to the original methyl, rather than anywhere else. To do this we look at CO elimination in *cis*-(MeCO)Mn(CO)$_4$(^{13}CO), in which the label is cis to the acetyl group. If the acetyl CO moves during the elimination, then the methyl in the product will stay where it is and so remain cis to the label. If the methyl moves, then it will end up both cis and trans to the methyl, as is in fact observed:



(7.9)

This observation implies that the methyl also moves when the reaction is carried out in the direction of insertion. The *cis*-$(MeCO)Mn(CO)_4(^{13}CO)$ required for this experiment can be prepared by the photolytic method discussed in Section 4.7, and we again use the IR spectrum to tell where the label has gone in the products. This is the only feature of migratory insertion in $MeMn(CO)_5$ that does not reliably carry over to other systems, where the product acyl is occasionally found at the site originally occupied by the alkyl.[3c]

Double Insertion Given that the methyl group migrates to the CO, why stop there? Why does the resulting acyl group not migrate to another CO to give an MeCOCO ligand? If migration happened repeatedly, we might even get the unknown $R(CO)_mML_n$ polymer, a material that is believed to be thermodynamically unstable with respect to CO itself. The complex that would have been formed in a double insertion can be made by an independent route from MeCOCOCl and $Mn(CO)_5^-$. It easily eliminates CO to give $MeCOMn(CO)_5$, which suggests that the double-insertion product is thermodynamically unstable with respect to $MeCOMn(CO)_5$. The —CHO and CF_3CO— groups share with MeCOCO— the property of eliminating CO irreversibly to give hydride and trifluoromethyl complexes, respectively. The reason is again probably thermodynamic, because the M—COMe, M—H, and M—CF_3 bonds are all distinctly stronger than M—CH_3, the bond formed in CO elimination from the acetyl (Chapter 3). In contrast, isonitriles do undergo repeated migratory insertion to give polymers with as many as 100 isocyanide units inserted:

$$Cl(R_3P)_2Pt—C{\equiv}C—Pt(PR_3)_2Cl + n\text{RNC} \longrightarrow Cl(R_3P)_2Pt—(C{=}NR)_nC{\equiv}C—Pt(PR_3)_2Cl \quad (7.10)$$

Products that *appear* to arise from double migratory insertion of CO have been found by Yamamoto[4b] in the following catalytic reaction:

$$R_2NH + CO + ArI \xrightarrow{\text{Pd catalyst}} R_2NCOCOAr \quad (7.11)$$

In fact, the reaction goes via the cycle shown in Fig. 7.1, in which a reductive elimination reaction, not a migratory insertion, forms the $R_2N(CO)—(CO)Ar$ carbon–carbon bond. In the first step, oxidative addition of ArI forms a Pd—Ar bond. The Ar(CO) ligand is then formed by a conventional migratory insertion, and the $R_2N(CO)$ group arises by a nucleophilic attack of R_2NH on a second CO.

Enhancing Insertion Rates Lewis acids such as $AlCl_3$ or H^+ can increase the rate of migratory insertion by as much as 10^8 fold. Metal acyls (**7.1**) are more basic at oxygen than are the corresponding carbonyls by virtue of the resonance form **7.2**. By binding to the oxygen, the Lewis acid would be

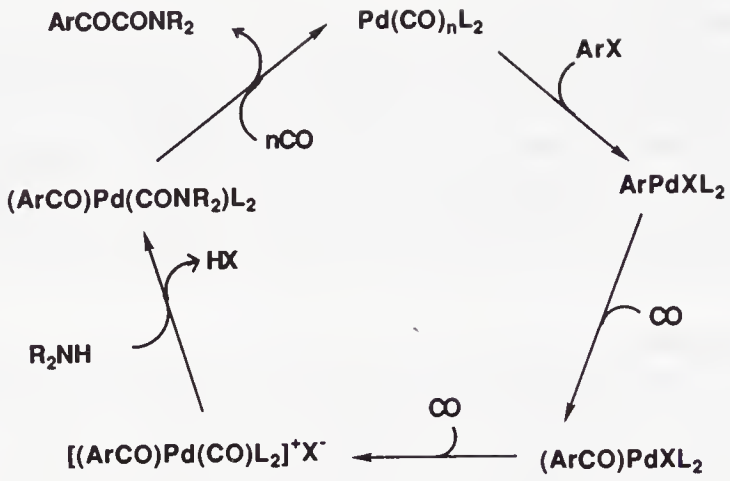


FIGURE 7.1 The catalytic cycle proposed by Yamamoto for the formation of an apparent "double insertion" product.[4b]

expected to stabilize the transition state and speed up trapping by L and therefore speed up the reaction.[5]

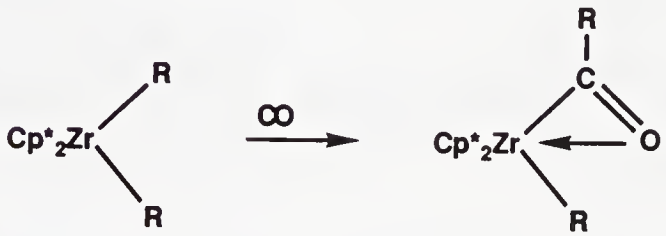
7.1 **7.2**

The second important way of promoting the reaction is oxidation of the metal. $Cp(CO)_2FeMe$ is normally very slow to insert, but 1e oxidation at −78°C in MeCN using Ce(IV) salts (or electrochemically) gives the acyl $[CpFe(MeCN)(CO)(COMe)]^+$, in which the solvent has played the role of incoming ligand.[6] As we saw in Chapter 4, 17e complexes can be very labile, but another factor here may be the increased electrophilicity (decreased π basicity) of the metal, leading to a larger partial positive charge on the CO carbon. The migration of Me^- to an electron deficient CO carbon seems to be a good description of the CO insertion, and so the rate of the reaction may increase in response to the increase in the ∂^+ charge on the CO carbon. Oxidation would also speed up trapping by phosphine, but with Lewis acids or oxidants, this may no longer be the rate determining step.

Under CO, trityl cation, Ph_3C^+, can catalyze migratory insertion in complexes such as $Cp(CO)_2FeMe$, by oxidation to $[Cp(CO)_2FeMe]\cdot^+$. This 17e radical cation then undergoes migratory insertion with CO as the incoming ligand. The trityl radical, formed in the first step, then reduces the 17e insertion product to the 18e $Cp(CO)_2FeCOMe$ and the starting trityl cation.[7]

The rates of insertion are also increased to some extent by using more nucleophilic solvents, suggesting that the solvent may act as a temporary ligand to stabilize an initial, solvated insertion product.[8]

Moving to the early metals has an interesting consequence. These metals are Lewis acids in their own right and tend to bind oxygen ligands (see the discussion of oxophilicity in Section 3.4); they can therefore act as their own Lewis acid catalysts for insertion. The product is an η^2-acyl as shown in Eq. 7.12:[9]



7.3

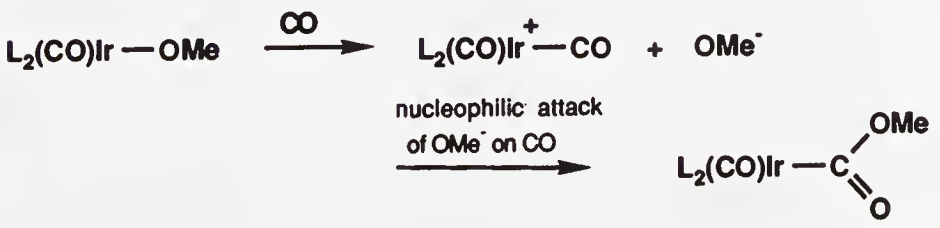
16e, d_0 18e, d_0 (7.12)

By altering the thermodynamics in favor of the adduct, this effect is even sufficient to promote the normally unfavorable CO insertion into an M—H bond, as shown in Eq. 7.13:[10]

(7.13)

In each of these reactions, the formation of an intermediate carbonyl complex is proposed. Zr(IV) and Th(IV) are both poor π bases, and so these intermediates must be very unstable;[11] limited back bonding should make the CO much more reactive toward insertion, however.

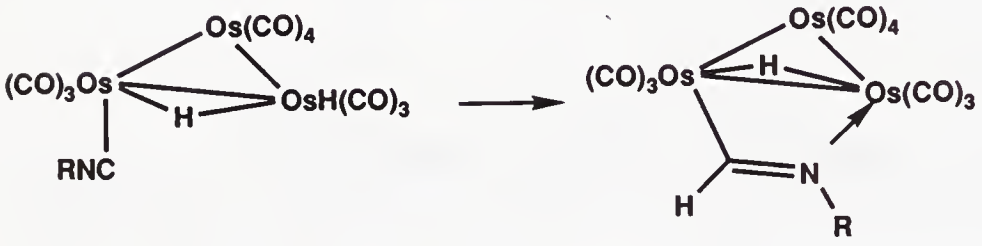
Apparent Insertions Sometimes a reaction that is an apparent insertion can go by an entirely different route. A good example is shown in Eq. 7.14. The late metal alkoxide is unstable (since MeO is a good π donor) and the MeO group dissociates as MeO^- to leave a 2e site at the cationic metal. The CO present then binds to this 2e site, and is strongly activated toward nucleophilic attack at the CO carbon by the positive charge on the metal. The product is the interesting metala-ester complex shown in Eq. 7.14:[12]



(7.14)

Isonitriles Isonitriles insert very readily into M—R and even M—H bonds[13] to give iminoacyls, which can be η^2-bound for the early metals (Eq. 7.15)[14] or in clusters (Eq. 7.16):[15]

(7.15)

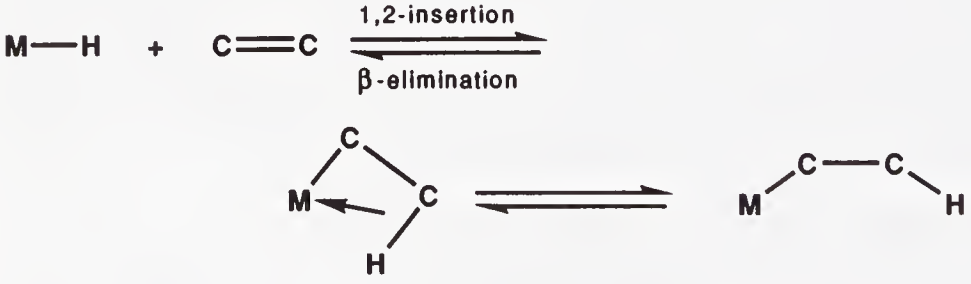


(7.16)

We look at insertions involving carbenes in Chapter 11.

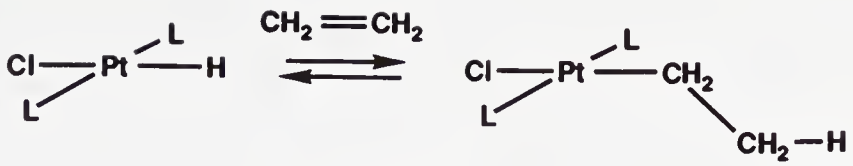
7.2 INSERTIONS INVOLVING ALKENES

The insertion of coordinated alkenes into M—H bonds is a very important reaction because it gives alkyls, and constitutes a key step in a variety of catalytic reactions (see Chapter 9). As η^2-ligands, alkenes give 1,2-insertion. This is the reverse of the familiar β-elimination reaction (Eq. 7.17). Some insertion reactions are known to give agostic (**7.3**) rather than classical alkyls and species of type **7.3** probably lie on the pathway for insertion into M—H bonds.[16a] The position of equilibrium is decided by the thermodynamics of the particular system, and will depend strongly on the alkene. For simple alkenes, such as ethylene (Eq. 7.18),[16b] the equilibrium tends to lie to the left (i.e., the alkyl β-eliminates), but for alkenes with electron-withdrawing ligands (e.g., C_2F_4, Eqs. 7.19 and 7.20), the alkyl is particularly stable and the equilibrium lies entirely to the right; this makes alkyls such as $L_nMCF_2CF_2H$ particularly stable.

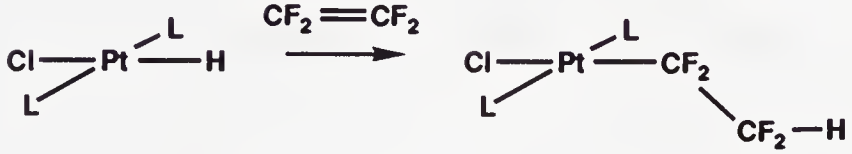


(7.17)

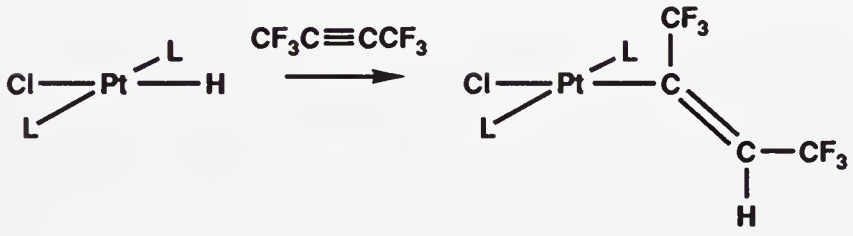
7.3
proposed agostic intermediate



(7.18)[16]

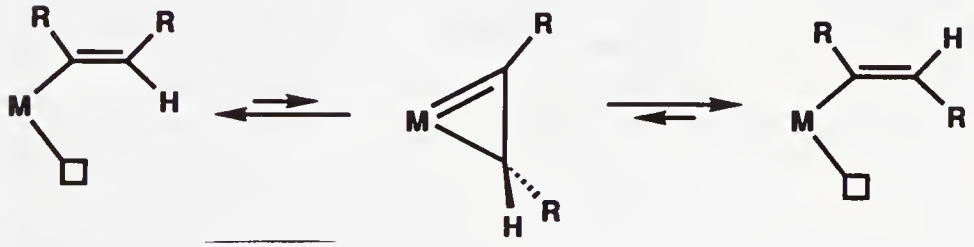


(7.19)

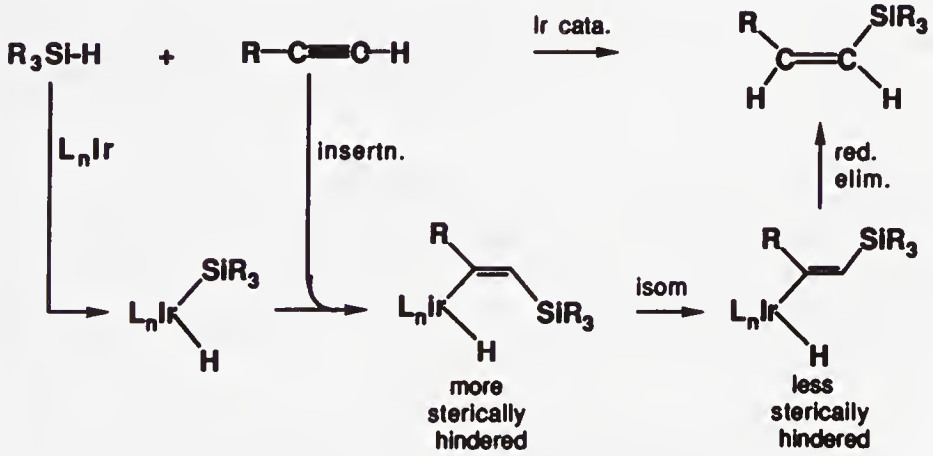


(7.20)[17]

The usual stereochemistry of the insertion is syn, and so the stereochemistry at both carbons is retained, as shown by the alkyne example in Eq. 7.20, but the initially formed *cis*-vinyl complex can sometimes rearrange to the trans isomer,[18a] probably[18b] via an η^2-vinyl (Eq. 7.21). This can lead to a net anti addition of a variety of X—H groups (Eq. 7.22, where X = R_3Si) to alkynes:[18b]



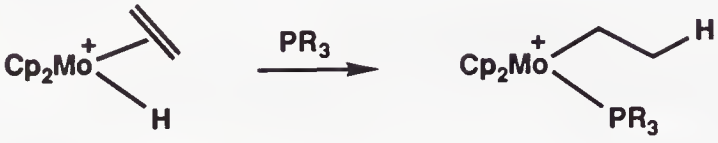
(7.21)



(7.22)

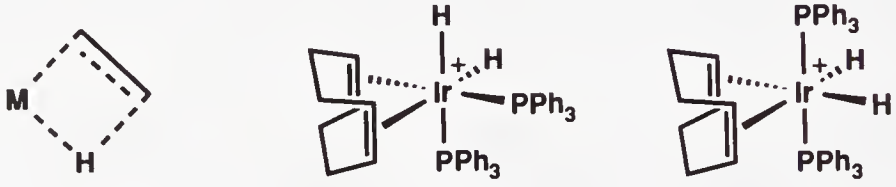
As we saw for CO insertions and eliminations, a 2e vacant site is generated by the insertion (and required for the elimination). The vacant site may be

filled by any suitable ligand, such as the solvent, excess alkene, or a phosphine:[19]



(7.23)

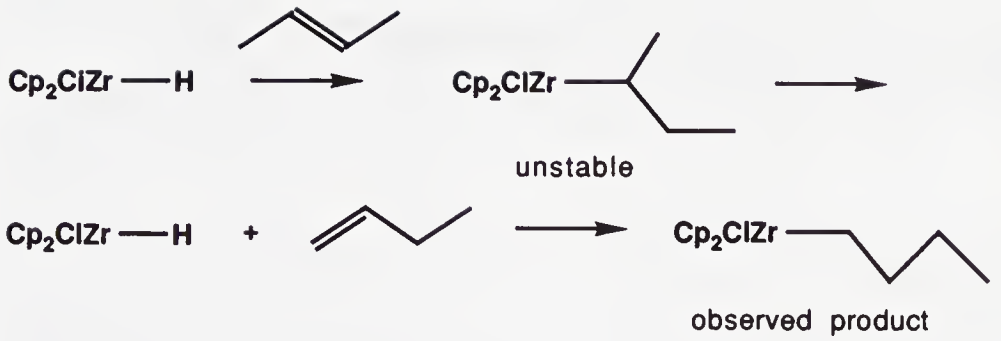
The transition state for insertion, **7.4**, has an essentially coplanar M—C—C—H arrangement, and this implies that both insertion and elimination also require the M—C—C—H system to be capable of becoming coplanar. We have seen in Section 3.1 how we can stabilize alkyls against β elimination by having a noncoplanar M—C—C—H system. The same principles apply to stabilizing alkene hydride complexes. Compound **7.5** undergoes insertion at least 40 times more rapidly than **7.6**, although the alkene and M—H groups are cis in both cases, only in **7.6** is there a noncoplanar M—C—C—H arrangement.[20]



7.4 **7.5** **7.6**

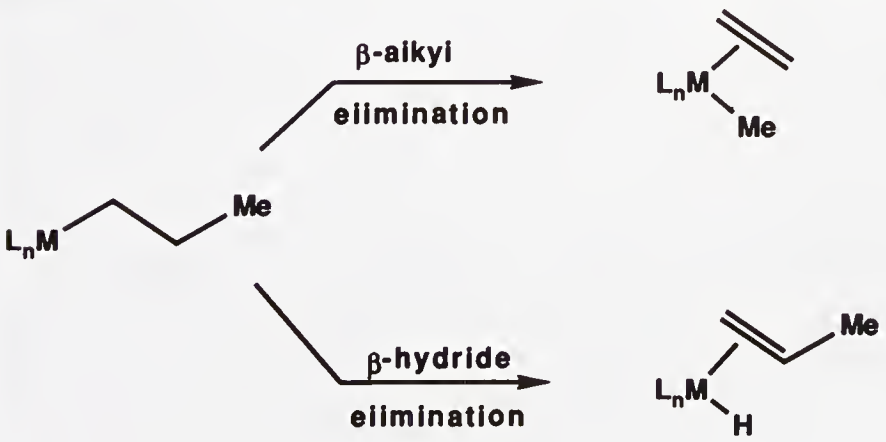
An important application of alkene insertion is hydrozirconation of alkenes by Cp_2ZrHCl.[21] Terminal alkenes insert in the anti-Markownikov direction to give a stable 1° alkyl (Eq. 7.24). Internal alkenes, such as 2-butene, insert to give an unstable 2° alkyl, which is not observed. This intermediate β eliminates to give 1- and 2-butene. The 1-butene can now give the stable 1° alkyl, the observed product (Eq. 7.25). This is a particularly noteworthy reaction because the terminal alkene is less stable than the internal alkene. The insertion goes in the way it does because the 1° alkyl is more stable than any 2° alkyl, probably for steric reasons. The 1° alkyl can now be functionalized in a number of ways as discussed in Chapter 14.

(7.24)[21]



(7.25)[21]

Insertion into M—H versus M—R We saw in the last section that for thermodynamic reasons, CO insertion generally takes place into M—R, but not into M—H bonds. Alkene insertion, in contrast, is common for M—H, but much less common for M—R. Alkene polymerization is a reaction that involves repeated alkene insertion into an M—R bond (Section 11.5). The thermodynamics still favor the reaction with M—R, so its rarity must be due to kinetic factors. Brookhart[22a] has compared the barriers for insertion of ethylene into the M—R bond in $[Cp^*\{(MeO)_3P\}MR(C_2H_4)]^+$, where R is H or Et and M is Rh or Co. The reaction involving M—H is 6–10-kcal/mol easier (Table 7.1). This corresponds to a migratory aptitude ratio k_H/k_{Et} of 10^6–10^8. As we have seen on several occasions, reactions involving M—H are almost always kinetically more facile than reactions of M—R. This means that an alkene probably has less intrinsic kinetic facility for insertion than does CO. Looking at the reverse reaction, elimination, we see that this implies that β-H elimination in an alkyl will be kinetically easier than β-alkyl elimination, and it will also give a thermodynamically more stable product, so it is not surprising that β-alkyl elimination is extremely rare. In those cases where it is observed, there is always some special factor that modifies the thermodynamics or the kinetics or both. For example, for *f*-block metals M—R bonds appear to be comparable in strength, or stronger than M—H bonds and both β-H and β-alkyl elimination can be observed:[22b]



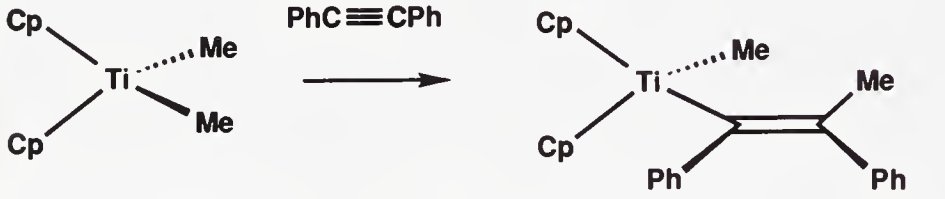
(7.26)

TABLE 7.1 A Comparison of the Barriers (kcal/mol) for Insertion in $[Cp^*\{(MeO)_3P\}MR(C_2H_4)]^+$ for R = H and R = Et[22a]

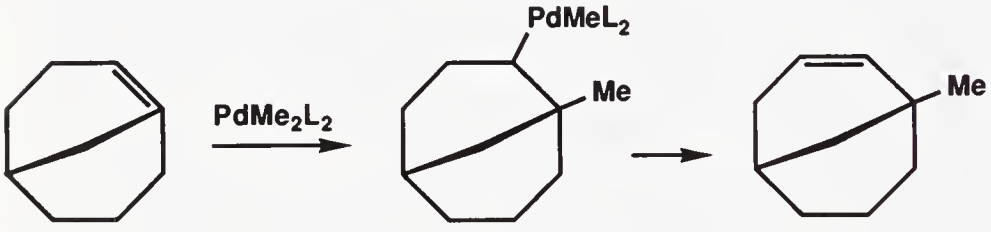
M	R = H[a]	R = Et[b]	Difference
Rh	12.2	22.4	10.2
Co	6–8 (est.)	14.3	6–8 (est.)

[a] ±0.1 kcal/mol.
[b] ±0.2 kcal/mol.

Strain, or the presence of electronegative substituents on the alkene or moving to an alkyne are some of the other factors that can bias both the thermodynamics and the kinetics in favor of insertion, as shown in Eqs. 7.27 and 7.28:[23,24]

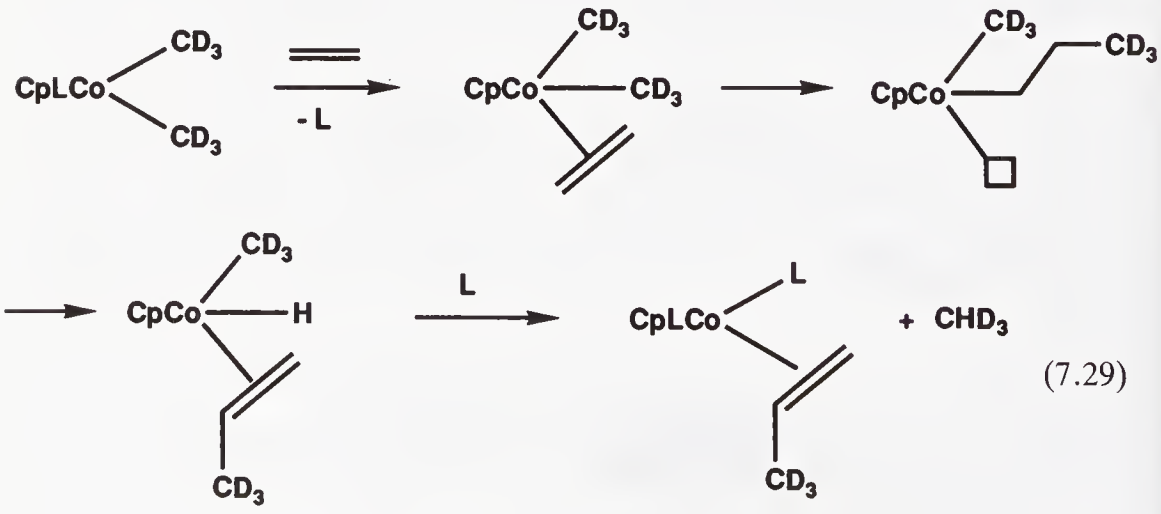


(7.27)

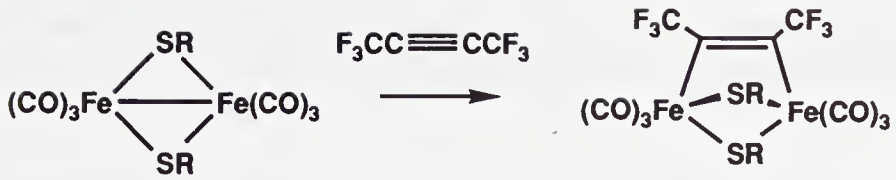


(7.28)

A case in which ethylene inserts into an M—R bond was described by Bergman et al.[25] The insertion mechanism was confirmed by the labeling scheme shown in Eq. 7.29 (L = PPh_3, □ = vacant site). Insertion into M—M bonds is also known, as shown in Eq. 7.30:[26a]



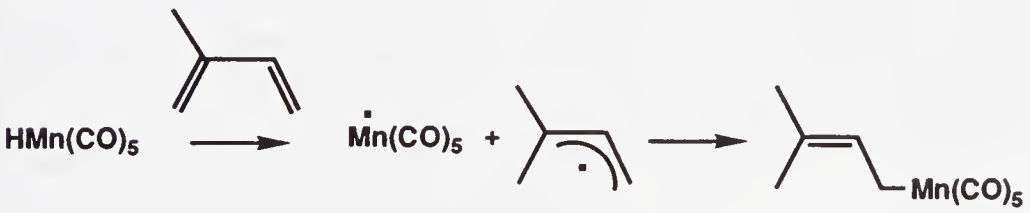
(7.29)



(7.30)

Styrene can insert into the M—M bond of $[Rh(OEP)]_2$ (OEP = octaethylporphyrin). Initial homolysis gives the 15e metalloradical •Rh(OEP), which adds to the alkene to give PhCH•—CH_2Rh(OEP) (the Ph group stabilizes the C-radical) and then (OEP)RhCHPh—CH_2Rh(OEP). $[Rh(OEP)]_2$ also initiates radical photopolymerization of CH_2=CHCOOR, in which case the intermediate C radicals add repetitively to acrylate rather than recombine with the metalloradical as is the case for styrene.[26b]

Dienes As we saw in Sections 5.2–5.3, butadiene and allene react with a variety of hydrides by 1,2 insertion, but butadienes also react with $HMn(CO)_5$ to give an apparent 1,4 insertion. Since this 18e hydride has no vacant site and CO dissociation is slow, a different mechanism must be operating; this is thought to be H atom transfer to give a 1,1-dimethylallyl radical that is subsequently trapped by the metal (Eq. 7.31).[27] Only substrates that form especially stable radicals can react (e.g., 1,3-diene → allyl radical), not simple alkenes.

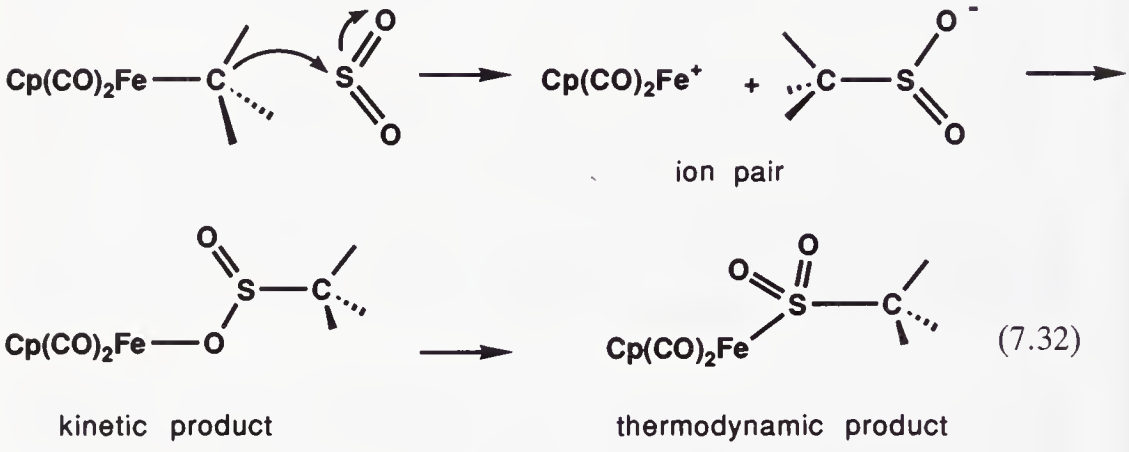


(7.31)

7.3 OTHER INSERTIONS

Sulfur dioxide is a strongly electrophilic species with a vacant orbital on sulfur, which it can use to attack even 18e metal complexes. Wojcicki[28a] has studied these reactions in detail and finds that the SO_2 can give electrophilic attack at the α-carbon of the alkyl from the side opposite the metal, which leads to the formation of an alkyl sulfinate ion (RSO_2^-) with inversion at carbon. Since the anion has much of its negative charge on the oxygens, it is not surprising that the kinetic product of ion recombination is the O-bound sulfinato complex. On the other hand, the thermodynamic product is usually the S-bound sulfinate, as is appropriate for a soft metal (since S is softer than O). This sequence constitutes a 1,2- (if the sulfinate is O-bound in the product) or a 1,1-insertion of SO_2 (if S-bound). A notable feature of this mechanism is that

the SO_2 does not need to bind to the metal, and so a 2e vacant site is not needed, and SO_2 can attack 18e complexes:



(7.32)

As expected for this mechanism, the reactivity falls off as the alkyl group becomes more bulky and as the substituents become more electron-attracting. By carrying out a crossover reaction on a mixture of RS and SR isomers of [CpFe*(CO)L{$CH_2C^*H(Me)Ph$}], which is chiral at both Fe and the carbon shown, very little of the crossover products, the *R*,*R* and *S*,*S* isomers of the sulfinate complex, are seen. This shows that the postulated ion pairs must stay together, and that the intermediate iron cation also has stereochemical stability. Ion pairing is very common in organic solvents, and the ions probably rarely break free from the ion pair.[28b]

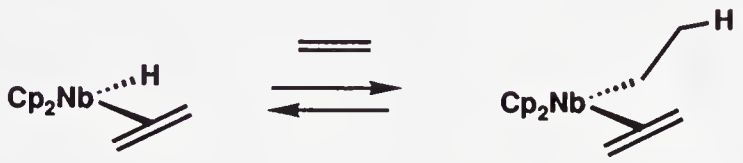
$RCH_2Co^{III}(dmg)_2(py)$ undergoes photochemical insertion with SO_2 to give $RCH_2SO_2Co^{III}L_5$. A radical chain pathway via $RCH_2\bullet$ was proposed because of the induction period and inhibition by galvinoxyl, the radical trap; C-radicals like $RCH_2\bullet$ react very rapidly with SO_2 to give $RCH_2SO_2\bullet$.[29]

We look at insertions involving CO_2 in Section 12.2.

7.4 α, β, γ, AND δ ELIMINATION

β-Elimination As we saw in Chapter 3, β-elimination is the chief decomposition pathway for alkyls that have β-H substituents. A 2e vacant site is required at the metal, and there has to be a roughly coplanar M—C—C—H arrangement that brings the β-H close to the metal. A complicating feature of this process is that the alkene often reinserts into the metal hydride, and this can give rise to isomerisation of the alkene or of the starting alkyl, as we saw for hydrozirconation in Section 7.2. The alkene is rarely coordinated in the final products of a β elimination, because it is usually displaced by the ligand that originally dissociated to open up a 2e vacant site at the metal, or

by some other ligand in the reaction mixture. Rare cases are known in which both the alkyl and the alkene hydride can be observed directly:[30]

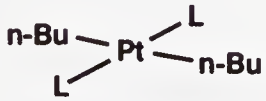


(7.33)

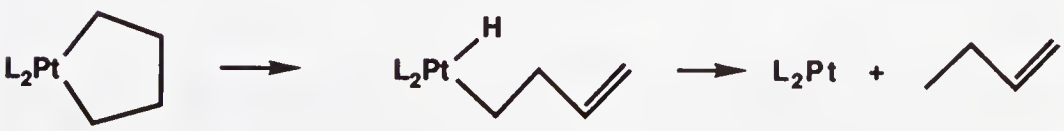
An 18e complex has to lose a ligand to open up a site for elimination (e.g., Eq. 7.34), but this process may[31] or may not[32] be rate limiting. In each case the addition of excess ligand inhibits the reaction by quenching the open site. Only if the elimination itself is rate limiting will we see a kinetic isotope effect for elimination of H over D (e.g., by comparing the rate of elimination of $L_nMC_2H_5$ vs. $L_nMC_2D_5$). The appearance of an isotope effect implies that C—H(D) bond breaking is important in the slow step.

$$\text{Cp(CO)LFe}(n\text{-Bu}) \xrightarrow{-L} \text{Cp(CO)Fe}(n\text{-Bu})(\square) \longrightarrow$$
$$\text{Cp(CO)FeH(1-butene)} \xrightarrow{+L} \text{Cp(CO)LFeH} + \text{1-butene} \quad (7.34)^{32}$$

In 16e complexes, a 2e site is usually available, except for Pd(II), and especially for Pt(II), which tend to avoid the 18e configuration. Yamamoto[33] found that *trans*-$[PdL_2Et_2]$ complexes (L = 3° phosphine), tend to decompose by reductive elimination via an 18e transition state, but Whitesides[34] found that phosphine dissociation is required for β elimination of the corresponding platinum alkyls $[PtL_2Bu_2]$ (**7.7**). The related metalacycle **7.8** β-eliminates 10^4-fold more slowly than **7.7**, presumably because a coplanar M—C—C—H arrangement is harder to achieve:[34]



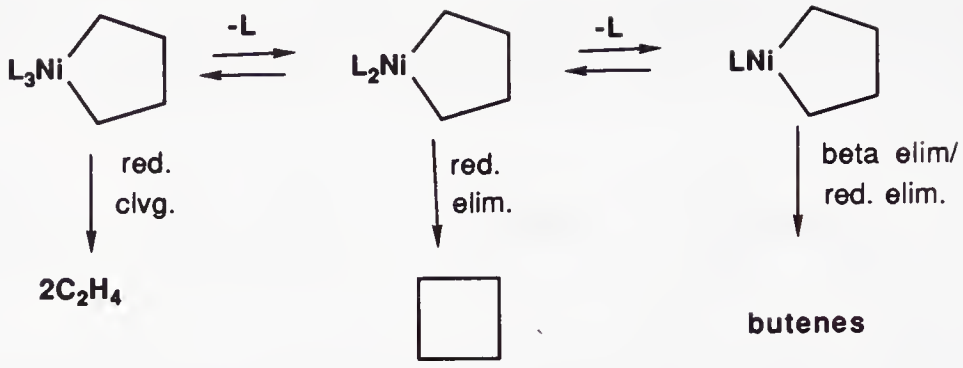
7.7



7.8

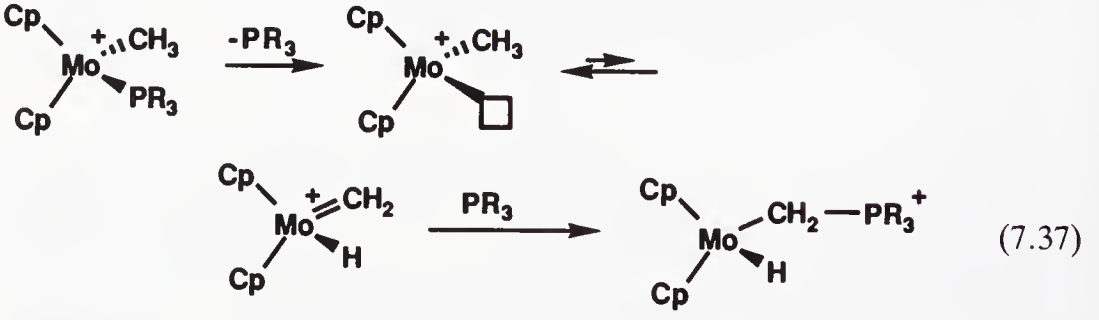
(7.35)

Grubbs[35] has studied the analogous nickel complexes and has found that there are three decomposition pathways, one for each of the different intermediates, 14e, 16e, and 18e, that can be formed (Eq. 7.36). An understanding of the reasons for this diversity has only come with a detailed m.o. study.[36]

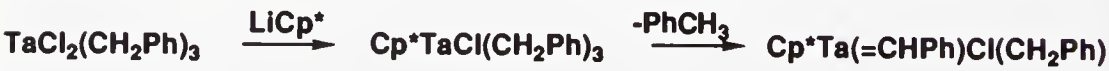


(7.36)

α-*Elimination* If an alkyl has no β hydrogens, it may break a C—H bond in the α, γ, or δ position. The simplest case is a methyl group, which has no β hydrogens and can only undergo α elimination to give the methylene hydride. While the β process gives an alkene, a stable species that can dissociate from the metal, the methylene ligand formed from the α elimination is very unstable in the free state and so does not dissociate. Methylene hydride complexes seem to be unstable with respect to the starting methyl complex, and so the products of α elimination can be intermediates in a reaction, but are seldom seen as isolable species. For this reason, the α-elimination process is far less well characterized than β elimination. Studies of both iridium and tantalum alkyls suggest that α-elimination may be faster than β elimination even in cases in which both α- and β-H substituents are present.[37,38] In some cases, a coordinatively unsaturated methyl complex seems to be in equilibrium with a methylene hydride species, which can sometimes be trapped, either by nucleophilic attack at the carbene carbon (Eq. 7.37)[39] or by removing the hydride by reductive elimination with a second alkyl present on the metal (Eq. 7.38):[40]



(7.37)

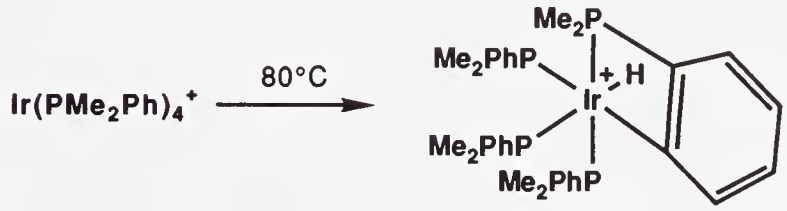


(7.38)

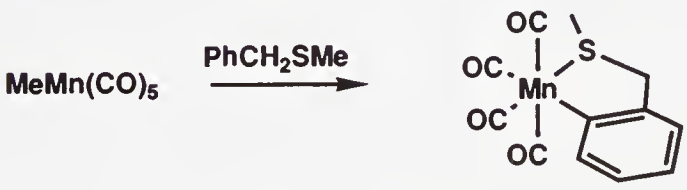
Schrock[41] has found an interesting case of α and β elimination taking place competitively in a tantalum complex, the two tautomers of which can be observed in solution by ^{1}H NMR.

(7.39)

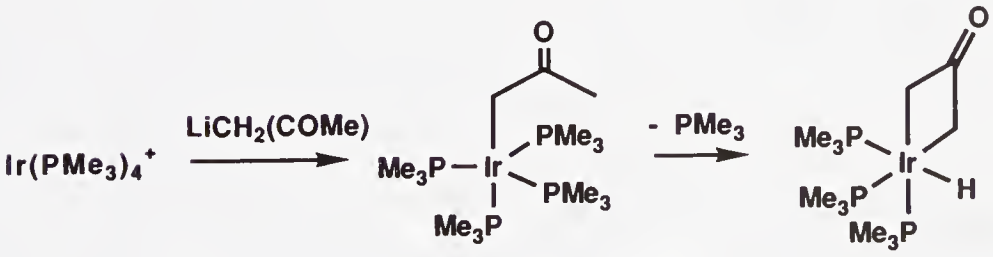
Other Eliminations In addition to alkyls, a great variety of other ligands have no β-H, but do have γ- or δ-H's and can undergo γ or δ elimination to give cyclic products; some examples of these cyclometallation reactions are shown in Eqs. 7.40–7.42:[42–44]



(7.40)



(7.41)



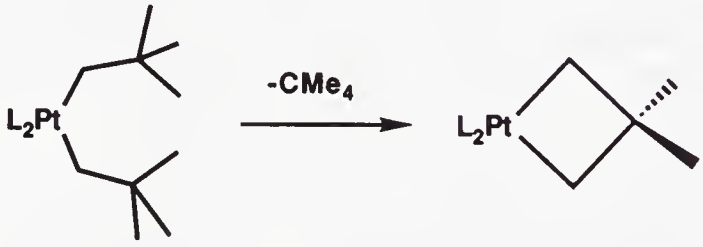
(7.42)

All these elimination reactions can be thought of as analogous to oxidative additions of a C—H bond to the metal. This is seen more clearly for β elimination if we write the metalacyclopropane (X_2) form of the alkene hydride product (Eq. 7.43), and for α elimination if we consider the X_2 form for the product carbene hydride (Eq. 7.44). Both γ and δ elimination are more obvious examples of oxidative addition.

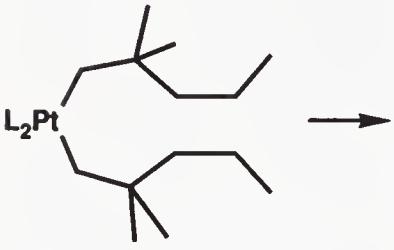
(7.43)

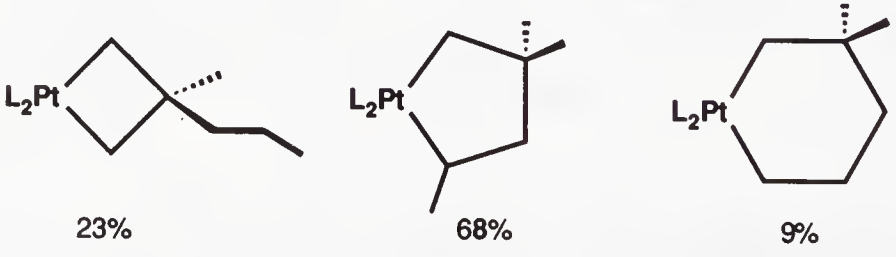
(7.44)

It is interesting that neopentyl platinum compounds tend to decompose by γ elimination (Eq. 7.45), in contrast to the α elimination found for the Ta complexes shown in Eq. 7.39. This may imply that the mechanism in the two cases is different; for example, in the Ta case, a σ bond metathesis is possible in which one alkyl might be deprotonated at the activated α-H by a second alkyl group, rather than undergo an oxidative addition of a C—H bond, which is more favorable for low-valent Pt.[45] Related examples of γ, δ, and ε elimination are shown in Eq. 7.46.



(7.45)





(7.46)

23% 68% 9%

REFERENCES

1. F. Calderazzo, *Angew. Chem., Int. Ed.*, **16,** 299, 1977.
2. I. S. Butler, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **6,** 2074, 1967.
3. (a) F. Calderazzo, *Coord. Chem. Rev.*, **1,** 118, 1966; (b) G. M. Whitesides et al., *J. Am. Chem. Soc.*, **96,** 2814, 1974; (c) H. H. Brunner, I. Bernal, et al., *Organometallics,* **2,** 1595, 1983.

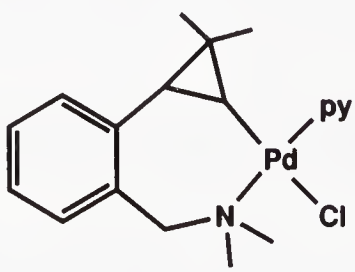
4. (a) S. Takahashi et al., *Angew. Chem., Int. Ed.,* **31,** 851, 1992; (b) A. Yamamoto et al., *J. Am. Chem. Soc.,* **107,** 3235, 1985.
5. D. F. Shriver et al., *J. Am. Chem. Soc.,* **102,** 5093, 5112, 1980; *Inorg. Chem.,* **21,** 1272, 1982; A. Cutler et al., *Organometallics,* **4,** 1247, 1985.
6. W. P. Giering et al., *J. Am. Chem. Soc.,* **102,** 6887, 1980.
7. R. S. Bly, *Organometallics,* **4,** 1247, 1985.
8. R. G. Bergman, *J. Am. Chem. Soc.,* **103,** 7028, 1981.
9. G. Erker et al., *Angew. Chem., Int. Ed.,* **17,** 605, 1978.
10. T. J. Marks et al., *J. Am. Chem. Soc.,* **103,** 6959, 1981.
11. L. Marko et al., *J. Organometal. Chem.,* **199,** C31, 1980.
12. J. D. Atwood et al., *Organometallics,* **4,** 402, 1985.
13. A. Yamamoto, *Coord. Chem. Rev.,* **3,** 193, 1980.
14. A. Dormond, *Chem. Commun.,* 749, 1984.
15. R. D. Adams, *Acct. Chem. Res.,* **16,** 67, 1983.
16. (a) M. Brookhart, M. L. H. Green, and L. L. Wang, *Prog. Inorg. Chem.,* **36,** 1, 1988; (b) J. Chatt and B. L. Shaw, *J. Chem. Soc.,* 5075, 1962.
17. H. C. Clark, *J. Organometal. Chem.,* **200,** 63, 1980.
18. (a) S. Otsuka and A. Nakamura, *Adv. Organomet. Chem.,* **14,** 245, 1976; G. Wilkinson et al., *J. Chem. Soc., Dalton,* 804, 1977; (b) R. S. Tanke and R. H. Crabtree, *J. Am. Chem. Soc.,* **112,** 7984, 1990.
19. M. L. H. Green et al., *Chem. Commun.,* 1324, 1974.
20. R. H. Crabtree, *Acct. Chem. Res.,* **12,** 331, 1979.
21. J. Schwartz, *Pure Appl. Chem.,* **52,** 733, 1980.
22. (a) M. Brookhart et al., *J. Am. Chem. Soc.,* **112,** 5634, 1990; **114,** 10349, 1992; (b) P. L. Watson and D. C. Roe, *J. Am. Chem. Soc.,* **104,** 6471, 1982.
23. W. H. Knoth, *Inorg. Chem.,* **14,** 1566, 1975.
24. S. A. Godleski et al., *Organometallics,* **4,** 296, 1985; R. F. Jordan et al., *J. Am. Chem. Soc.,* **115,** 4902, 1993.
25. R. G. Bergman et al., *J. Am. Chem. Soc.,* **101,** 3973, 1979.
26. (a) J. L. Davidson et al., **46,** C47, 1972; (b) B. B. Wayland et al., *Organometallics,* **11,** 3534, 1992, and references cited therein.
27. V. A. Kormer et al., *J. Organometal. Chem.,* **162,** 343, 1978; *Dokl. Acad. Nauk SSSR,* **246,** 1372, 1979.
28. (a) A. Wojcicki et al., *Inorg. Chem.,* **12,** 717, 1973; *J. Am. Chem. Soc.,* **95,** 6962, 1973; *Inorg. Chim. Acta,* **10,** 229, 1974; (b) K. Fukui et al., *J. Am. Chem. Soc.,* **98,** 4693, 1976.
29. B. D. Gupta, M. Roy, M. Oberoi, and V. Dixit, *J. Organometal. Chem.,* **430,** 197, 1992.
30. F. N. Tebbe and G. W. Parshall, *J. Am. Chem. Soc.,* **93,** 3793, 1971.
31. A. Yamamoto et al., *J. Organometal. Chem.,* **120,** 257, 1976.
32. D. L. Reger and E. C. Culbertson, *J. Am. Chem. Soc.,* **98,** 2789, 1976; M. R. Churchill, R. R. Schrock, et al., *J. Am. Chem. Soc.,* **100,** 647, 1978.
33. A. Yamamoto et al., *J. Am. Chem. Soc.,* **102,** 6457, 1980.

34. G. M. Whitesides et al., *J. Am. Chem. Soc.*, **94,** 5258, 1972.
35. R. H. Grubbs et al., *Chem. Commun.*, 864, 1977; *J. Am. Chem. Soc.*, **99,** 3663, 1977; **100,** 1300, 2418, 7416, 7418, 1978.
36. R. J. McKinney, D. L. Thorn, R. Hoffmann, and A. Stockis, *J. Am. Chem. Soc.*, **103,** 2595, 1981.
37. M. J. Burk and R. H. Crabtree, *J. Am. Chem. Soc.*, **110,** 620, 1988.
38. G. Parkin, J. E. Bercaw, et al., *J. Mol. Catal.*, **41,** 21, 1987.
39. M. L. H. Green, *Pure Appl. Chem.*, **50,** 27, 1978.
40. R. R. Schrock, *Acct. Chem. Res.*, **12,** 98, 1979.
41. R. R. Schrock et al., *Organometallics*, **1,** 481, 1982.
42. R. H. Crabtree, H. Felkin, T. Fillebeen-Khan, C. Pascard, and J. M. Quirk, *J. Organometal. Chem.*, **187,** C32, 1980.
43. M. I. Bruce et al., *J. Organometal. Chem.*, **67,** C72, 1974.
44. T. H. Tulip and D. L. Thorn, *J. Am. Chem. Soc.*, **103,** 2448, 1981.
45. G. M. Whitesides, *J. Am. Chem. Soc.*, **103,** 948, 1981.

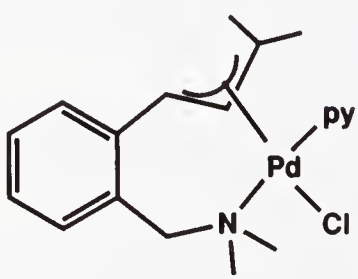
PROBLEMS

1. Predict the structures of the products (if any would be expected) from the following: (a) $CpRu(CO)_2Me + PPh_3$, (b) Cp_2ZrHCl + butadiene, (c) $CpFe(CO)_2Me + SO_2$, (d) $Mn(CO)_5CF_3 + CO$.

2. Me_2NCH_2Ph reacts with $PdCl_2$ to give **A**; then **A** reacts with 2,2-dimethylcyclopropene and pyridine to give a mixture of **C** and **D**. Identify **A** and explain what is happening. Why is it that Me_2NPh does not give a product of type **A**, and that **A** does not react with ethylene.



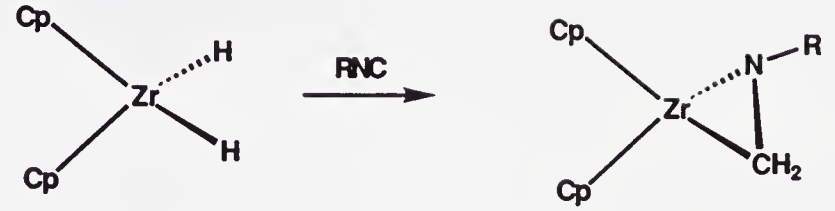
C

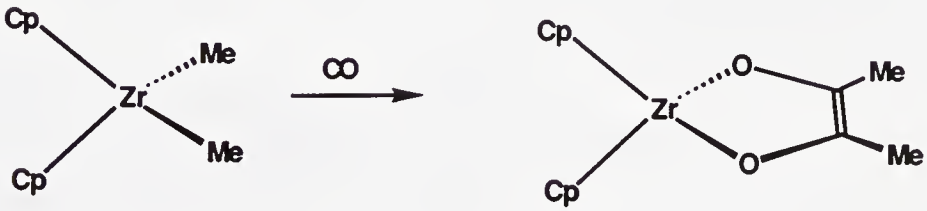


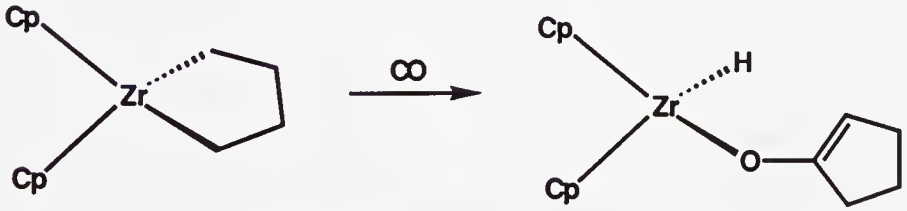
D

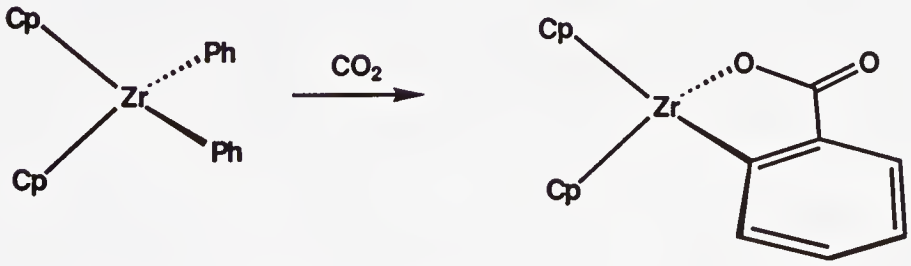
3. In the pyrolysis of $TiMe_4$, both ethylene and methane are observed; explain.

4. Suggest mechanisms for the following:









5. The reaction of *trans*-$PdAr_2L_2$ (**A**, Ar = *m*-tolyl, L = PEt_2Ph) with MeI gives 75% of *o*-xylene (**B**) and 25% of 3,3′-bitolyl (**C**). Explain how these products might be formed, and list the possible Pd-containing products of the reactions. When the reaction was carried out with CD_3I in the presence of d_0-$PdMeIL_2$(**D**), both d_0- and d_3-xylene (**B**) were formed. **A** also reacts with **D** to give **B** and **C**. How does this modify your view of the mechanism?

6. $[Cp^*Co\{P(OMe_3)\}Et]^+$ has an agostic interaction involving the β-H of the ethyl group. Draw the structure. It reacts with ethylene to form polyethylene. How might this reaction proceed? $RhCl_3$/EtOH and other

late metal systems usually only dimerize ethylene to a mixture of butenes. Given that a Rh(I) hydride is the active catalyst in the dimerization, what mechanism would you propose? Try to identify and explain the key difference(s) between the two systems.

7. Design an alkyl ligand that will be resistant to β elimination (but not the ones mentioned in the text; try to be as original as possible). Design a second ligand, which may be an alkyl or an aryl-substituted alkyl, that you would expect to be resistant to β elimination but have a high tendency to undergo β-C—C bond cleavage.

8. Given the existence of the equilibrium

$$L_nM(Me)(CO) \rightleftharpoons L_nM(COMe)(solv)$$

how would you change L, M, and the solvent to favor (a) the right-hand side and (b) the left-hand side of the equation?

9. *trans*-$PtCl(CH_2CMe_3)\{P(C_5H_9)_3\}_2$ gives 1,1-dimethylcyclopropane on heating. What mechanism is most likely, and what Pt-containing product would you expect to be formed? If the neopentyl group is replaced by $—CH_2Nb$ (Nb = 1-norbornyl), then CH_3Nb is formed instead. What metal complex would you expect to find as the other product?

10. In mononuclear metal complexes, β-elimination of ethyl groups is almost always observed, rather than α elimination to the ethylidene hydride $L_nM(=CHCH_3)H$. In cluster compounds, such as $HOs_3(CO)_{10}(Et)$, on the other hand, α elimination to give the bridging ethylidene $H_2Os_3(CO)_{10}(\eta^1,\mu_2\text{-}CHCH_3)$ is observed in preference to β elimination. Suggest reasons for this difference.

CHAPTER 8

NUCLEOPHILIC AND ELECTROPHILIC ADDITION AND ABSTRACTION

For a metal to bring about the reaction of two organic fragments, both of them generally have to be coordinated. Now we see how a metal can activate an unsaturated ligand so that direct attack of an external reagent can take place on the ligand without prior binding of the reagent to the metal.

Types of Reaction The attacking reagent is normally either an electrophile or a nucleophile. Nucleophilic attack is favored when the metal fragment L_nM is a poor π base, but a good σ-acid, for example, if the complex bears a net positive charge or has electron-withdrawing ligands. In such a case, one of the ligands L′, is depleted of electron density to such an extent that the nucleophile, Nu^- (e.g., LiMe, OH^- etc.), can attack L′.

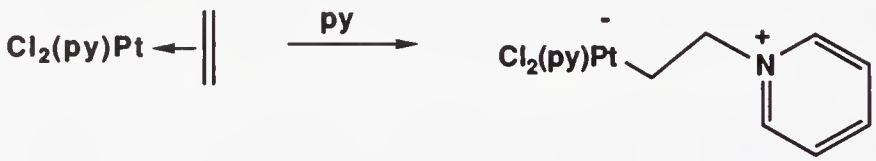
Electrophilic attack is favored when the metal is a weak σ acid but a strong π base, for example, if the complex has a net anionic charge, a low oxidation state, and the ligands L are good donors. The electron density of one of the ligands is enhanced by back donation so that it now becomes susceptible to attack by electrophiles, E^+ (H^+, MeI, etc.).

Two possible modes of nucleophilic or electrophilic attack are found. The reagent can become covalently attached to the ligand L′, so that a bond is formed between the reagent and L′. In this case, the newly modified ligand stays on the metal and we have an *addition*. Alternatively, the reagent can detach a fragment from the ligand L′, or even detach the entire ligand, in which case the modified reagent leaves the coordination sphere of the metal and we have an *abstraction*. A nucleophile will abstract a cationic fragment, such as H^+ or Me^+, while an electrophile will abstract an anionic fragment, such as H^-, or Cl^-. Often, reaction with an electrophile generates a positive

charge on the complex and prepares it for subsequent attack by a nucleophile. We will see examples in Eqs. 8.17, 8.20, and 8.44; the reverse order of addition is seen in Eq. 8.10.

Some examples are shown in Eqs. 8.1–8.9. You can see that the nucleophiles tend to reduce the hapticity of the ligands to which they add because they displace the metal from the carbon to which the addition takes place. In Eq. 8.2, we convert an η^6-L_3 into an η^5-L_2X ligand and make the net ionic charge on the complex one unit more negative, for a net change in the electron count of zero. In general, an L_nX ligand is converted to an L_n ligand and an L_n ligand is converted to an $L_{n-1}X$ ligand. Electrophilic reagents, in contrast, tend to increase the hapticity of the ligand to which they add. Electrophilic attack on a ligand gives rise to a deficiency of electron density on that ligand, which is compensated by the attack of a metal lone pair on the ligand. For instance, in Eq. 8.7, an η^4-L_2 diene ligand becomes an η^5-L_2X pentadienyl ligand. At the same time, a net positive charge is added to the complex, which leaves the overall electron count unchanged. In general, an L_nX ligand is converted to an L_{n+1} ligand and an L_n ligand is converted to an L_nX ligand. Equation 8.3 and 8.4 show nucleophilic abstraction of H^+, which is simply ligand deprotonation.

1. Nucleophilic addition:[1,2]

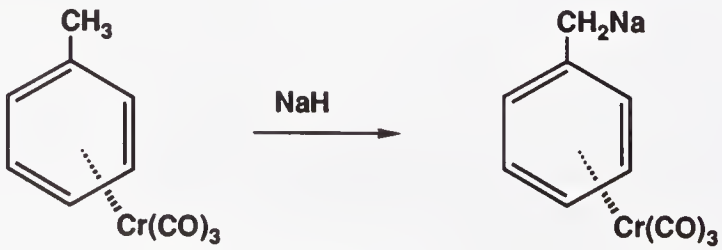


(8.1)

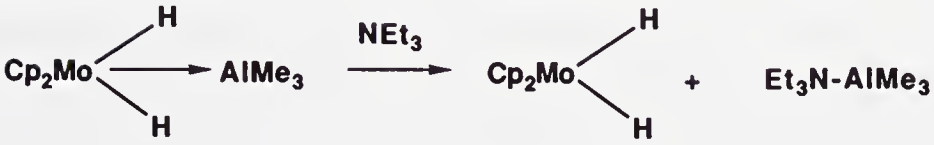
(8.2)

2. Nucleophilic abstraction:[3–5]

$$Cp_2TaMe_2^+ + Me_3PCH_2 \longrightarrow Cp_2Ta(=CH_2)Me + Me_4P^+ \quad (8.3)$$

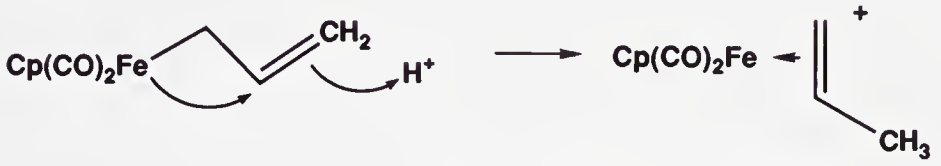


(8.4)

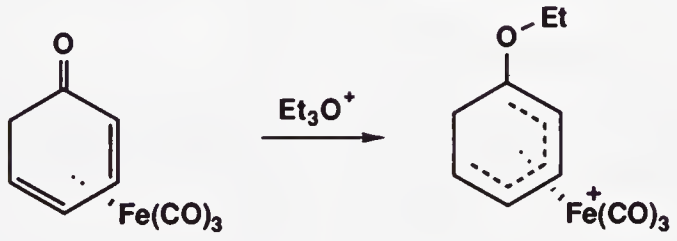


(8.5)

3. Electrophilic addition:[6,7]

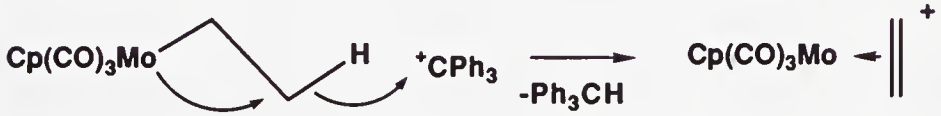


(8.6)

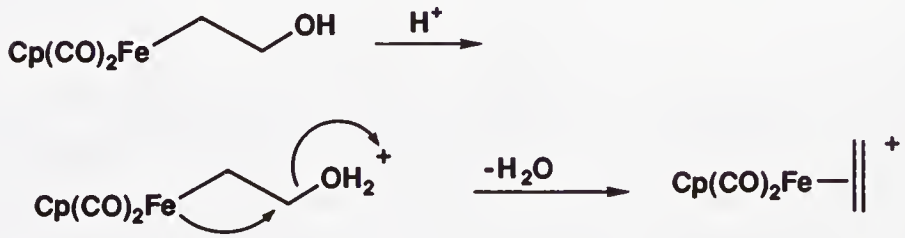


(8.7)

4. Electrophilic abstraction:[8,9]



(8.8)



(8.9)

Attack at the metal, rather than at the ligands, is often observed. In the case of a nucleophile, this is simply associative substitution (Section 4.4) and can lead to the displacement of the polyene. If the original metal complex is 16e, attack may take place directly on the metal, if 18e, a ligand must usually dissociate first. A nucleophile is therefore more likely to attack a ligand, rather than the metal, if the complex is 18e. The pyridine in Eq. 8.1 is a potential 2e ligand, but it does not attack the metal because an 18e config-

uration is not a favorable situation for Pt(II). As we have seen, by attacking the ligand, the nucleophile does not increase the metal electron count.

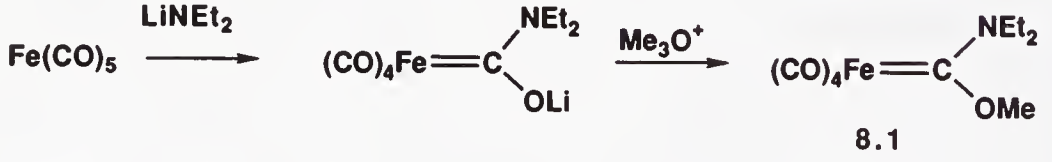
For electrophilic attack, the situation is different. As an 0e ligand, an electrophile does not increase the electron count of the metal whether it attacks at the metal or at the ligand, and so attack at the metal is always a possible alternative pathway even for an 18e complex (except for d^0 complexes that have no metal-based lone pairs). Of course, large electrophiles, such as Ph_3C^+, may have steric problems in attacking the metal directly.

Organic free radicals can also give addition and abstraction reactions, but these reactions are less well understood. Radical addition and abstraction also tends to occur as part of a larger reaction scheme in which radicals are formed and quickly react (e.g., Section 16.4).

The attack of nucleophiles at the metal has been discussed under substitution in Chapter 4; we also looked at the attack of electrophiles and of radicals at the metal in connection with oxidative addition in Chapter 6.

8.1 NUCLEOPHILIC ADDITION TO CO

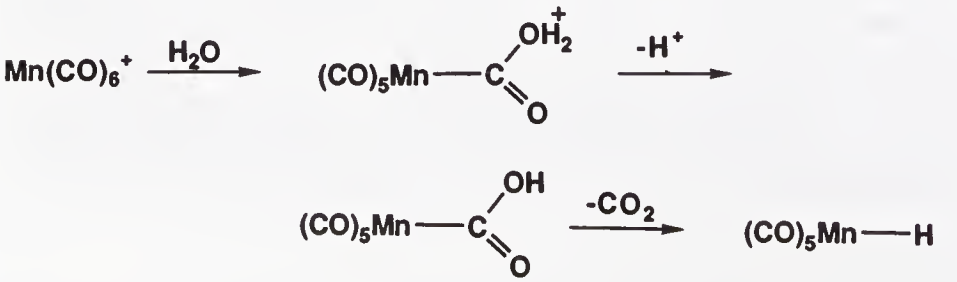
CO is very sensitive to nucleophilic attack when coordinated to metal sites of low π basicity. On such a site, the CO carbon is positively charged because L-to-M σ donation is not matched by L-to-M back donation and the CO π^* orbitals are open to attack by the nucleophile. Alkyllithium reagents convert a number of metal carbonyls to the corresponding anionic acyls. The net negative charge now makes the acyl liable to electrophilic addition to the acyl oxygen to give the Fischer carbene complex, **8.1**.[10]



8.1

(8.10)

The cationic charge on $[Mn(CO)_6]^+$ makes it much more sensitive to nucleophilic attack than is $[Mo(CO)_6]$. In this case, hydroxide, or even water can attack coordinated CO to give an unstable metalacarboxylic acid intermediate. These decompose to CO_2 and the metal hydride by β elimination. This can be synthetically useful as a way of removing a CO from the metal, something that is difficult to do in other ways because CO can be one of the most tightly bound ligands.



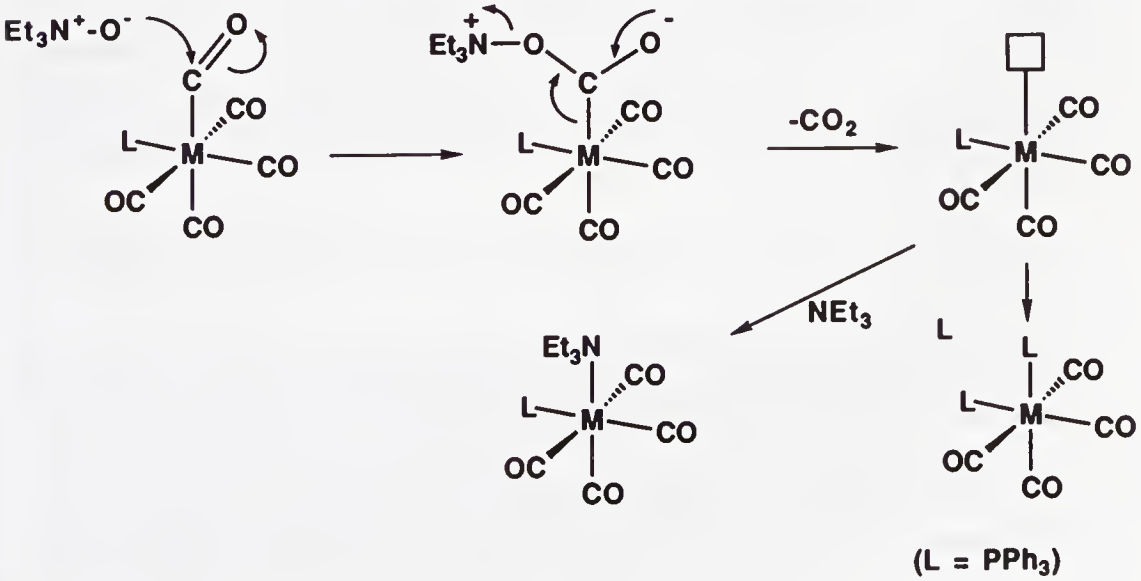
(8.11)

The nucleophilic attack of methanol instead of water can give a metala-ester, $L_nM(COOR)$, which is stable because it has no β-H.

Note how the displacement of Cl^- is favored in the first step of Eq. 8.12 over displacement of PPh_3. This is a consequence of the polar solvent used, and sets the stage for the subsequent nucleophilic attack by putting a positive charge on the complex ion, which activates the CO. Acid can reverse the reaction by protonating the methoxy group, which leads to loss of methanol. This is, of course a methoxide abstraction reaction, and is an example of a nucleophilic addition being reversed by a subsequent electrophilic abstraction. This is common and means that the product of an addition reaction may even decompose via its inverse reaction if unsuitable workup conditions are used. For example, the product of a nucleophilic addition may revert to the starting material if excess acid is added to the reaction mixture with the object of neutralizing the excess nucleophile:

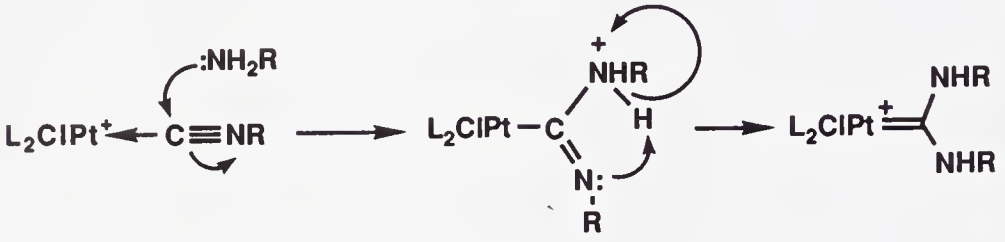
$$(PR_3)_2PtCl_2 \xrightarrow{CO} [(PR_3)_2PtCl(CO)]^+Cl^- \xrightarrow{MeOH,\ Et_3N} [(PR_3)_2PtCl(COOMe)] + (Et_3NH)Cl \quad (8.12)$$

We saw in Chapter 4 that Et_3NO is an excellent reagent for removing coordinated COs from 18e metal complexes.[12] The very nucleophilic oxygen (Et_3N^+-O^-) is capable of attacking the CO carbon to give a species that can break down to Et_3N, CO_2 and the corresponding 16e metal fragment (Eq. 8.13). Note how the cis-disubstituted product is obtained selectively in Eq. 8.13, because a CO trans to another CO has less back donation from the metal and hence is more activated toward nucleophilic attack at carbon than is the CO trans to the weak π-acid PR_3. Unfortunately, the amine formed can sometimes coordinate to the metal if no better ligand is available. A second problem with the method is that successive carbonyls become harder and harder to remove as the back bonding to the remaining CO groups increases, because their sensitivity to nucleophilic attack decreases, and so we are usually unable to remove more than one CO in this way.



(8.13)

Isonitriles are, if anything, more sensitive to attack; the ultimate product is usually a carbene.[13]



(8.14)

8.2 NUCLEOPHILIC ADDITION TO POLYENE AND POLYENYL LIGANDS

Simple polyenes in the free state, such as benzene and ethylene, normally undergo electrophilic, not nucleophilic attack. It is a measure of the power of complexation to alter the chemical character of a group that both of these polyenes, as ligands, become sensitive to nucleophilic, and inert to electrophilic attack (umpolung). If we are interested in inhibiting electrophilic attack, we would regard the metal as a protecting group. On the other hand, if we are interested in promoting nucleophilic attack, we would regard the same metal fragment as an activating group.

In the vast majority of cases, the nucleophile adds to the face of the polyene opposite to the metal. Since the metal is likely to have bound to the least hindered face of the free polyene, we may therefore see a selective attack of the nucleophile on what was the more hindered face in the free polyene; this is often useful in organic synthetic applications.

Green–Davies–Mingos Rules It is not unusual for a single complex to have several polyene or polyenyl ligands, in which case we often see selective attack at one site of one ligand only. Green, Davies and Mingos[14] noticed certain patterns in these reactions and from them devised a set of rules that usually allow us to predict the site of addition.

Rule 1. Polyenes (even or L_n ligands) react before polyenyls (odd or L_nX ligands).

Rule 2. Open ligands react before closed.

Rule 3. Open polyenes: terminal addition in all cases. Open polyenyls: usually terminal attack, but nonterminal if L_nM is electron-donating.

Rule 1 takes precedence over rule 2 whenever they conflict. Polyenes or even ligands are simply ones having an even electron count on the covalent

model (e.g., η^2-C_2H_4, η^6-C_6H_6); odd ligands have an odd electron count (e.g., η^3-C_3H_5, η^5-C_5H_5). Closed ligands are ones like Cp in which the coordinated π system of the polyene or -enyl is conjugated in a ring; in open ligands like allyl, the conjugation is interrupted. Some ligands and their classification according to these rules are illustrated in **8.2–8.5**:

even, open

8.2

odd, open

8.3

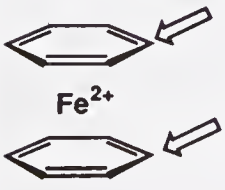
even, closed

8.4

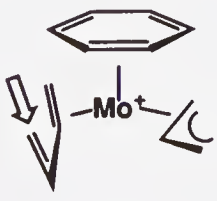
odd, closed

8.5

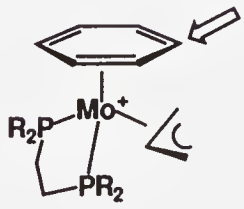
Diagrams **8.6–8.13** show these rules in action. In **8.6**, addition of a variety of nucleophiles takes place at the arene ring (indicated by the arrow in the diagram), as predicted by rule 1. A second nucleophile can also add, but to the other ring, as predicted by rule 1. Diagram **8.7** shows that addition takes place to the even, open butadiene ligand, rather than to the even, closed arene (rule 2) and at the terminal position (rule 3). In **8.8**, we see that the even closed arene is attacked rather than the odd open allyl; we must be careful in a case such as this to apply rule 1 before rule 2. Diagram **8.9** is a rare example of attack at a Cp ring; as an odd closed system, this only happens if there is no other type of ligand present. The utility of Cp as a stabilizing ligand in studies on nucleophilic attack, is that the Cp is usually very resistant to attack and therefore directs addition to other ligands present on the metal.



8.6



8.7



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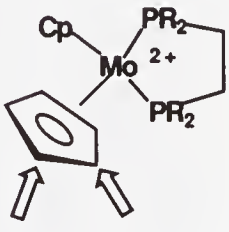
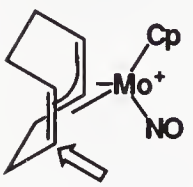


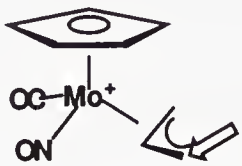
8.9

In **8.10**, we see that we can treat the alkene and the allyl parts of the bicyclooctadienyl as independent entities; the even alkene part is attacked. CO is an even ligand, but it among the least reactive of these, as shown in **8.11** and **8.13**. The examples also illustrate what might be called the "zeroth rule" of nucleophilic addition: a nucleophile usually adds once to a monocation, twice to a dication and so on. **8.12** and **8.13** also show the operation of rule

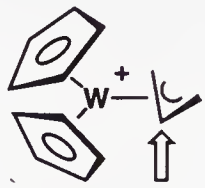
3 in the intermediate cyclohexadienyl species: the second addition takes place at the terminal position in this odd open polyenyl.



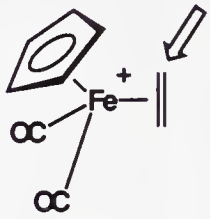
8.10



8.11



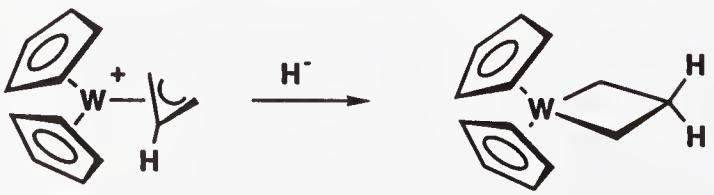
8.12



8.13

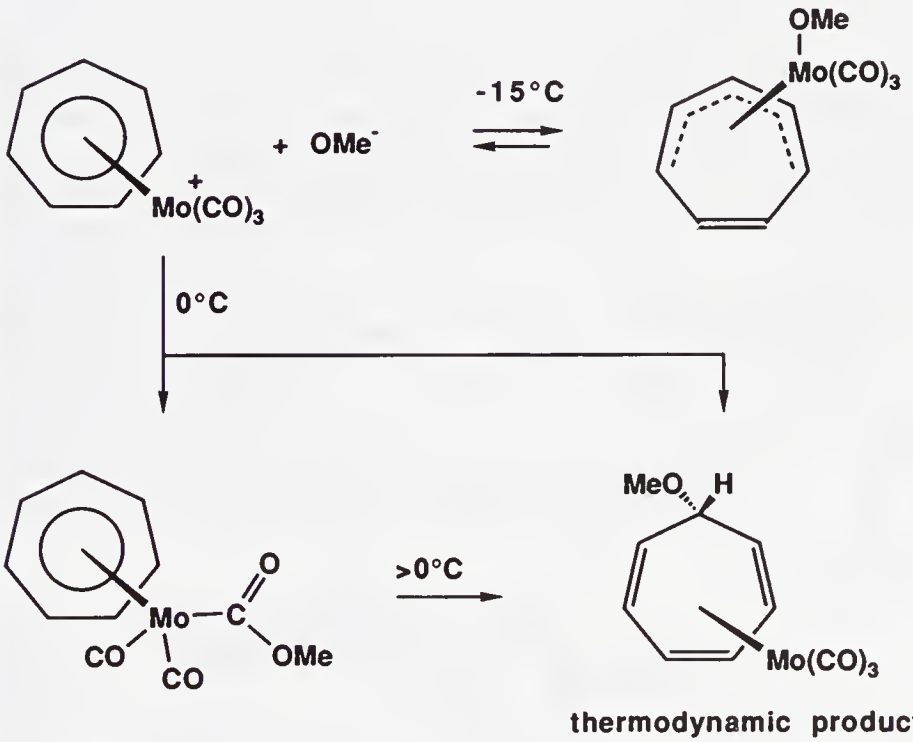
Although the rules were first developed empirically, an m.o. study has shown that they often successfully predict the location of the atom having the highest coefficient of the lumo. Under kinetic control, we would expect addition at the point where this empty acceptor orbital is largest. Qualitatively, we can understand the rules as follows. Ligands having a higher X character will tend to be more negatively charged and therefore will tend to resist nucleophilic attack. The coordinated allyl group, as an L_2X ligand, has more anionic character than ethylene, as an L ligand. This picture even predicts the relative reactivity of different ligands in the same class, a point not covered by the rules. For example, it is found that pentadienyl (L_2X) reacts before allyl (LX); we can understand this, because the former has the lower X character. Ethylene reacts before butadiene; as we saw in Section 5.3, the LX_2 form is always a significant contributor to the structure of butadiene complexes.

The reason the terminal carbons of even open ligands are the sites of addition is that the coefficients of the lumo are larger there. As an example, look at ψ_3 in butadiene as depicted in Fig. 5.2. An odd, open polyenyl gives terminal addition only if the metal is sufficiently electron-withdrawing. Reference to the m.o. picture for the allyl group (Fig. 5.1) will show that the usual lumo, ψ_2, has a large coefficient at the terminus, but ψ_3 has a large coefficient at the central carbon. As we go to a less electron-withdrawing metal, we tend to fill ψ_2 and to the extent that ψ_3 becomes the new lumo, and so we may no longer see terminal attack. An example of nonterminal attack in an allyl is shown by $[Cp_2W(\eta^3\text{-}C_3H_5)]^+$ (Eq. 8.15)—as a d^2 fragment, Cp_2W is strongly electron-donating in character.



(8.15)

It is surprising that these simple rules do so well in most cases. The situation can sometimes be more complicated, however, as shown by Eq. 8.16.[15] Here, the methoxide ion attacks at every possible site, as the mixture is warmed from −80°C to room temperature. Initially addition takes place at the metal (which must be preceded by a decrease in the hapticity of the cycloheptatrienyl to generate an open site), and later at the CO and C_7H_7. Had the reaction been carried out above 0°C, the normal product would have been observed, and the complications would have escaped detection.

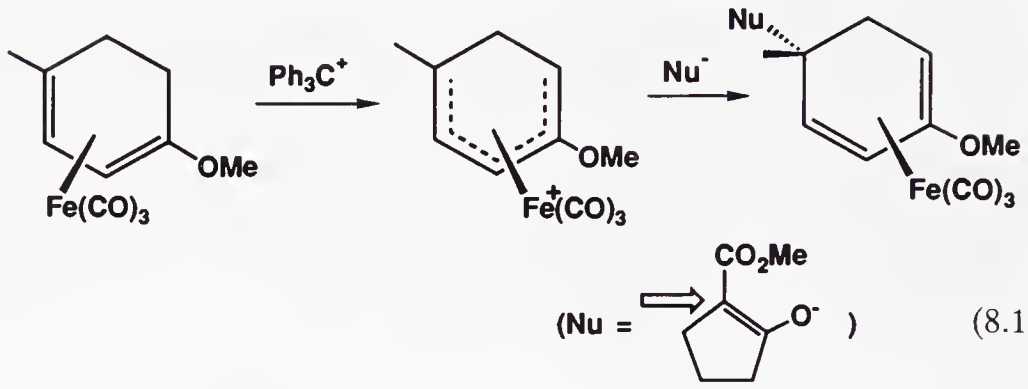


(8.16)

Substituents on an arene tend to direct addition in the way one might expect. Electron-releasing substituents, Q, usually direct attack meta, and electron-attracting ones ortho rather than para, perhaps because that puts Q at the terminus of the conjugated system of the resulting open polyenyl.

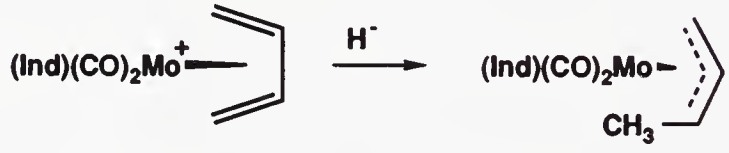
The arene chromium tricarbonyls have been studied intensively[2,4] with regard to their reactions with nucleophiles, and we will look at these in more detail in Chapter 14.

Cyclohexadienyl complexes react with nucleophiles to give 1,3-diene complexes.[16] An example is shown in Eq. 8.17; the arrow refers to the point of attachment of the nucleophile to the polyene ligand. The synthesis of the starting complex by an electrophilic abstraction is also shown; this activates the ligand for nucleophilic attack. Once again, directing effects can be used to advantage: a 2-OMe substituent directs attack to the C-5 position of the cyclohexadienyl, for example.[17]

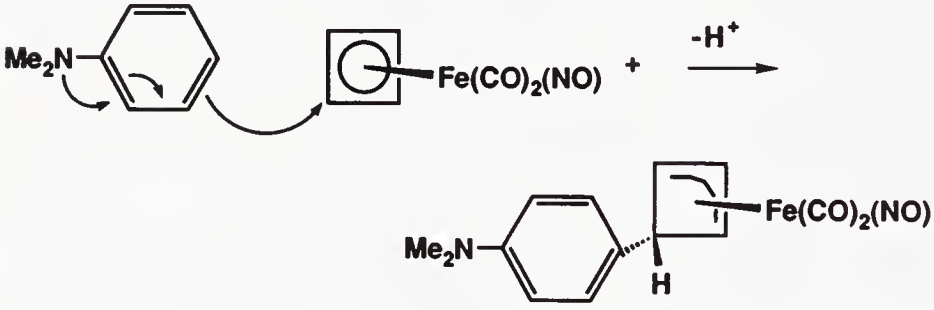


(8.17)

Diene complexes give allyls on nucleophilic attack. Note how the cisoid conformation of the butadiene in Eq. 8.18 gives rise to an anti methylallyl (in the nomenclature of allyl complexes, a substituent is considered as syn or anti with respect to the central CH proton).[18] Equation 8.19 is interesting in that the amine acts in this case as a carbon, not as a nitrogen nucleophile.[19]

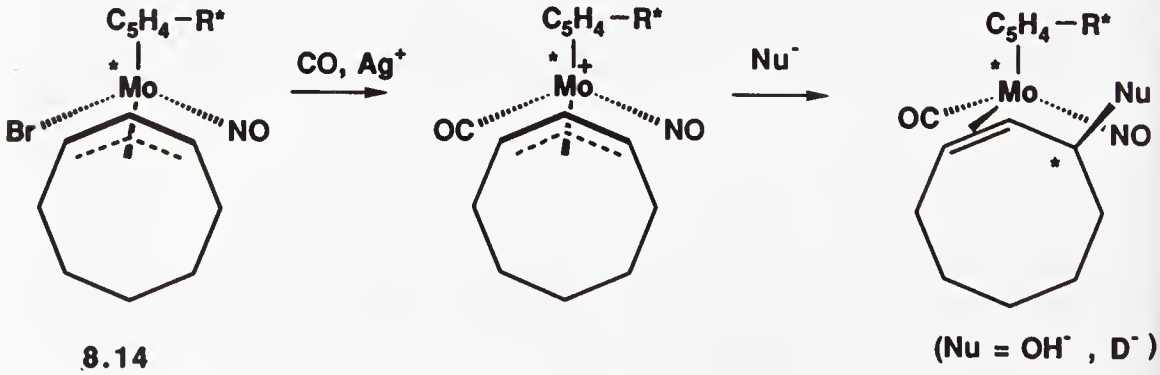


(8.18)



(8.19)

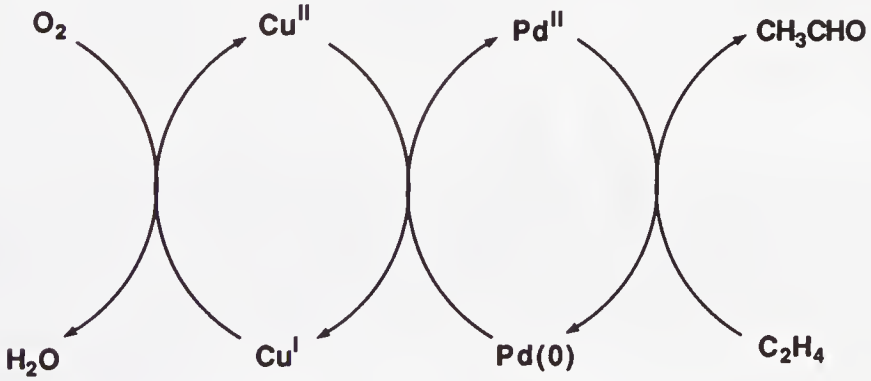
η^3-Allyls are also readily attacked. Note how **8.14** in Eq. 8.20 is activated toward nucleophilic attack by substituting the bromide ion with CO.[20] This not only gives the complex a net positive charge but also makes the metal chiral. The nucleophile adds selectively on the end of the allyl cis to NO.



(8.20)

This gives control over the stereochemistry of the product, because **8.14** can be resolved, thanks to the presence of the optically active group (R*) on the Cp ring, in which case carrying out the addition with one enantiomer of the metal complex means that the new asymmetric center on the ligand is formed with very high asymmetric induction. This reaction therefore constitutes a chiral synthesis of the alkenes shown.

Wacker Process Alkene complexes undergo nucleophilic attack to give metal alkyls, which can often rearrange to give other products. This is the basis of an important industrial process, the Wacker process, now used to make about 4 million tons a year of aldehydes from alkenes. The fact that aqueous $PdCl_2$ oxidizes ethylene to acetaldehyde had been known[21] (although not understood) since the nineteenth century; the reaction consumes the $PdCl_2$ and deposits metallic Pd(0). It took considerable imagination to see that such a reaction might be useful on the industrial scale, because $PdCl_2$ is far too expensive to use as a stoichiometric reagent in the synthesis. The key is catalysis, which allows the Pd to be recycled almost indefinitely. J. Smidt[22] of Wacker Chemie realized in the late 1950s that it is possible to intercept the Pd(0) before it has a chance to precipitate, by using $CuCl_2$, which reoxidizes the palladium and is itself reduced to cuprous chloride. This is air-sensitive and is reoxidized back to Cu(II). The resulting set of reactions (Eq. 8.21) are an elegantly simple solution to the problem and resemble the coupled reactions of biochemical catalysis.



(8.21)

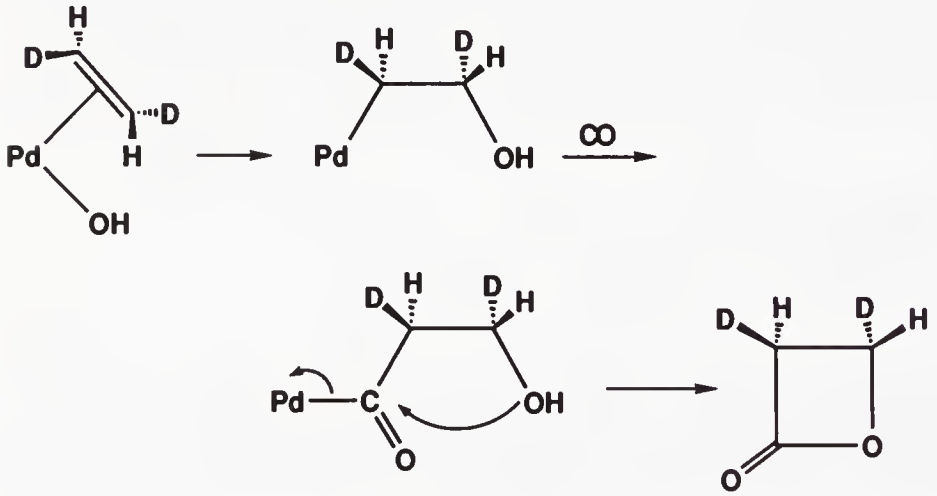
Later mechanistic work revealed the following rate equation:

$$\text{Rate} = \frac{k[PdCl_4^{2-}][C_2H_4]}{[Cl^-]^2[H^+]} \tag{8.22}$$

Equation 8.22 implies that the complex, in going from its normal state in solution, $PdCl_4^{2-}$, to the transition state of the slow step of the reaction has to gain a C_2H_4 and lose two Cl^- ions and a proton. It was originally argued that the proton must be lost from a coordinated water, and so $[Pd(OH)(C_2H_4)Cl_2]^-$ was invoked as the key intermediate; it was assumed

that this might undergo olefin insertion into the Pd—OH bond, or the OH might attack the coordinated ethylene as a nucleophile. The resulting hydroxyethyl palladium complex might β-eliminate to give vinyl alcohol, CH_2=CHOH, which is known to tautomerize to acetaldehyde.

In fact, this mechanism is wrong, something that was only discovered 20 years after the discovery of the Wacker process, as a result of stereochemical work by Bäckvall[23] and by Stille.[24a] According to the original intramolecular mechanism, whether the reaction goes by insertion or by nucleophilic addition from a coordinated OH, the stereochemistry at each carbon of the ethylene should remain unchanged. This can be tested if we use *cis*- or *trans*-CHD=CHD as the alkene and trap the intermediate alkyl. We have to trap the alkyl because the rearrangement to acetaldehyde destroys the stereochemical information. Equation 8.23 shows one way of trapping the alkyl, using CO. You can see that if the hydroxyethyl is carbonylated, the OH group can curl back and effect a nucleophilic abstraction on the acyl to give a free lactone, the stereochemistry of which can be determined by a number of methods, including NMR and microwave spectroscopy. In fact, the stereochemistry of the two carbons in the product is not the same as that of the starting material, which rules out the older mechanisms.



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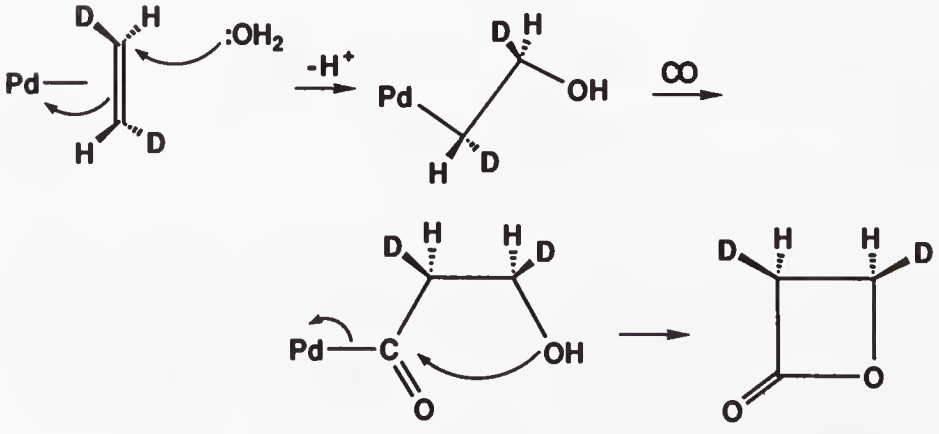
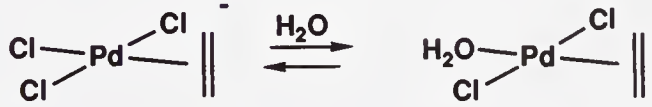


(8.24)

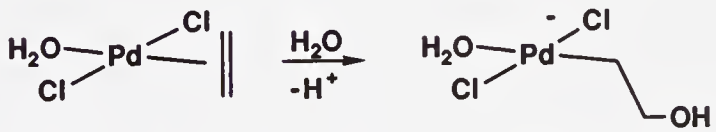
The currently accepted mechanism involves attack of a free water molecule from the solvent on the coordinated ethylene. Equation 8.24 shows how this inverts the stereochemistry at one of the carbons, as opposed to the old insertion mechanism (Eq. 8.23).

The loss of two Cl^- ions removes the anionic charge from the metal, which would otherwise prevent the nucleophilic attack from taking place. Equations 8.25–8.28 show the sequence of events as now understood. This mechanism implies that an $[H_2O]^2$ term should be present in the rate equation, and if it could have been seen, the mechanistic problem would have been solved earlier, but one cannot normally alter the concentration of a solvent and get meaningful rate data, because changing the solvent composition leads to unpredictable solvent effects on the rate.

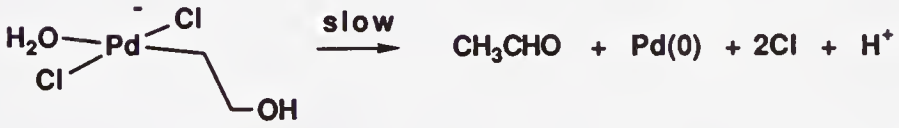
(8.25)



(8.26)

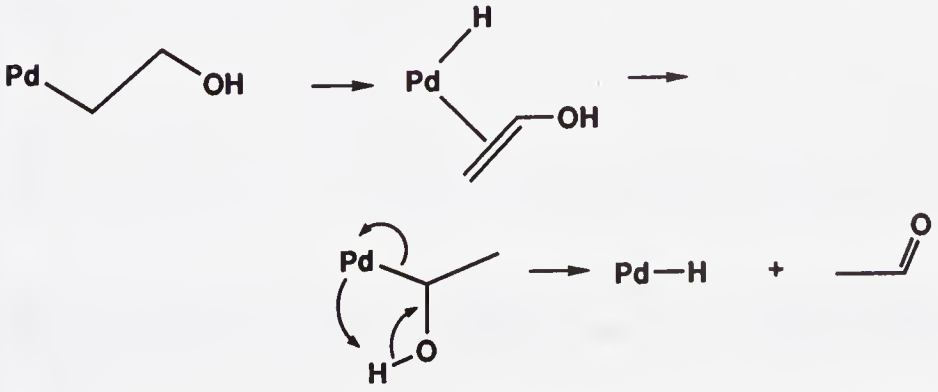


(8.27)



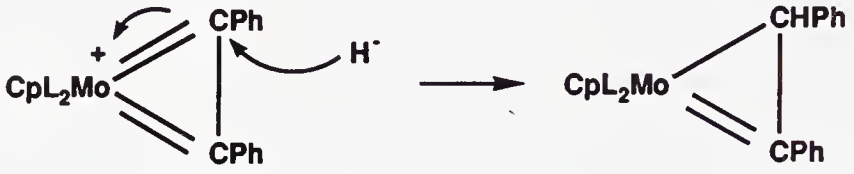
(8.28)

An additional feature revealed by labeling studies is that no deuterium is incorporated into the acetaldehyde when the reaction is carried out in D_2O, which would happen if vinyl alcohol were released. This must be another case in which the β-elimination product never leaves the coordination sphere of the metal until it has had time to rearrange on the metal by multiple insertion–elimination steps:



(8.29)

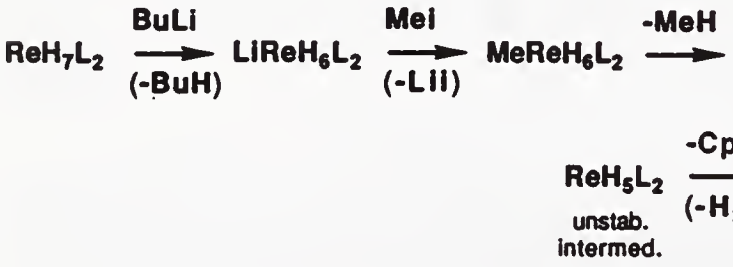
Nucleophilic addition to alkyne complexes gives vinylmetal species. A particularly interesting variant of this reaction is addition to an 18e complex containing a 4e alkyne (see Section 5.1). If the product were a η^1-vinyl, then the complex would be 16e, and so a 3e η^2-vinyl is usually found:[24b]



4e alkyne dihapto-vinyl (8.30)

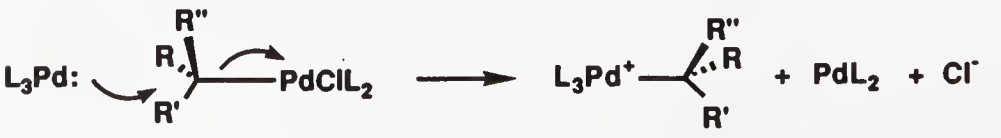
8.3 NUCLEOPHILIC ABSTRACTION IN HYDRIDES, ALKYLS, AND ACYLS

Hydrides Deprotonation of a metal hydride can produce a nucleophilic metal anion. For example, ReH_7L_2 (L_2 = dppe) does not lose H_2 easily like the L = PPh_3 complex. To generate the ReH_5L_2 fragment for the dppe case, Ephritikhine and Felkin first formed the anion with BuLi, and made the intermediate methyl hydride with MeI (Eq. 8.31). The driving force for methane loss is higher than for H_2 loss and the required fragment was formed and intercepted with cyclopentadiene to give the unusual polyhydride $CpReH_2L_2$.



(8.31)

Alkyls and Acyls Alkyl groups can be exchanged between metals with inversion at carbon. This reaction provides a route for the racemization of a metal alkyl during the early stages of an oxidative addition reaction, while there is still some of the low-valent metal left in the reaction mixture. In the case shown in Eq. 8.32, exchange of a $(CR_3)^+$ fragment between the metals oxidizes the Pd(0) nucleophile to Pd(II), and reduces the Pd(II) complex to Pd(0). Mechanistic interpretation of the stereochemical outcome of an oxidative addition can be clouded by exchange reactions such as the one shown. Nucleophilic abstraction of acyls is particularly useful in organic synthetic applications, as we shall see in Chapter 14.



(8.32)

The recurrence of Pd(II) in this section is no accident. It has a very high tendency to encourage nucleophilic attack at the ligands in its complexes. As an element on the far-right-hand side of the transition metal block, it is very electronegative (Pauling electronegativity: 2.2) and its *d* orbitals are very stable. This means that polyene to metal electron donation is more important than metal d_π to polyene π^* back donation, and so the polyene is left with a net positive charge.

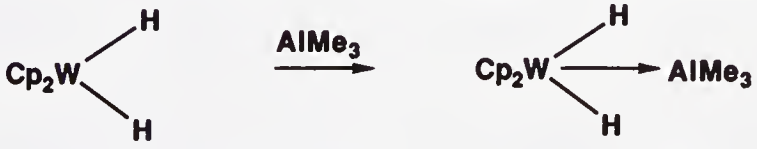
8.4 ELECTROPHILIC ADDITION TO THE METAL

Oxidative addition by the S_N2 or by the ionic mechanisms involves electrophilic attack at the metal (Eq. 8.33 and Sections 6.2 and 6.4):

$$L_nM + MeI \xrightarrow{\text{electrophilic addition}} [L_nMMe]^+I^- \xrightarrow{-L} [L_{(n-1)}MMeI] \quad (8.33)$$

In some cases the second step does not take place, and the counterion never binds to the metal. This makes the reaction an electrophilic addition, rather than an oxidative addition to the metal, although the latter term is sometimes seen in the literature to describe this type of reaction. An example is the reaction of the highly nucleophilic Co(I) anion, cobaloxime, with an alkyl triflate, a reaction known to go with inversion.[25] Protonation of metal complexes to give metal hydrides is also very common (Eqs. 3.30–3.31).

The addition of any zero-electron ligand to the metal can be regarded as an electrophilic addition: $AlMe_3$, BF_3, $HgCl_2$, Cu^+ and even CO_2, when it binds in an η^1 fashion via carbon, can all act in this way. Each of these reagents has an empty orbital by which it can accept a *d*-type lone pair from the metal. Since the acceptor atoms of these ligands are generally more electronegative than the metal, the metal is conventionally regarded as being oxidized by two units for each 0e ligand that binds. So, for example, $Cp_2H_2W \rightarrow AlMe_3$ is conventionally a W(VI) complex because $AlMe_3$ is formally removed as the closed-shell $AlMe_3^{2-}$. Complex formation of this type is more likely the more basic the starting complex, and the more powerful the Lewis acid.

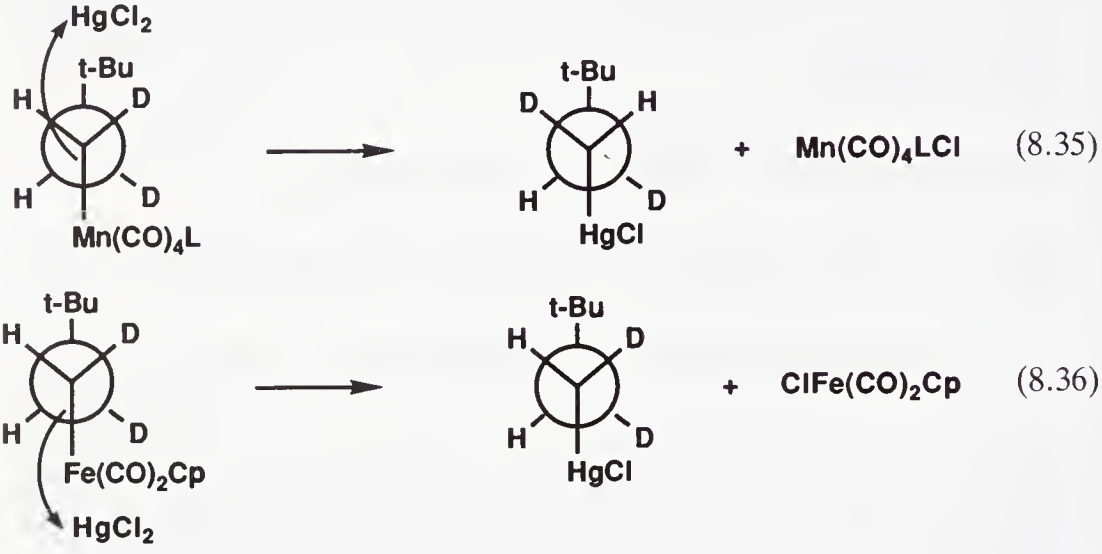


(8.34)

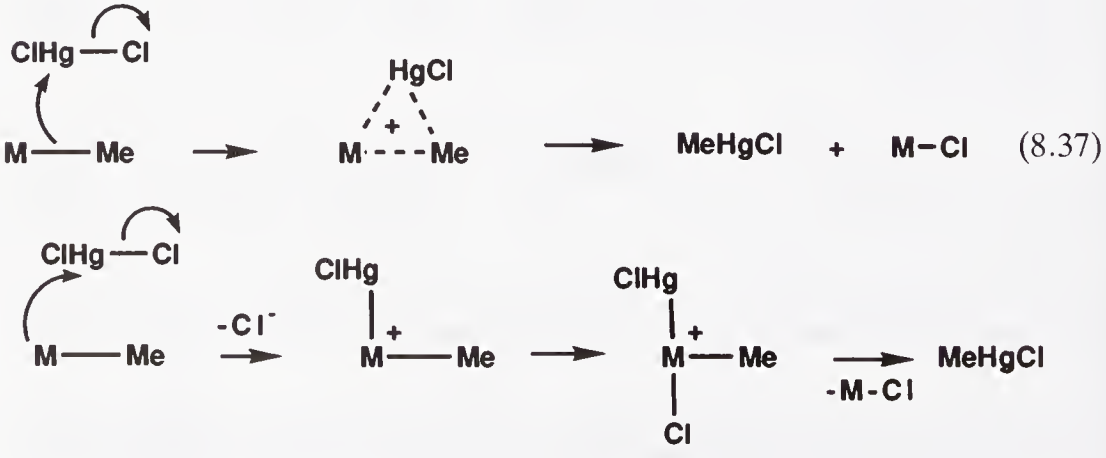
8.5 ELECTROPHILIC ABSTRACTION OF ALKYL GROUPS

Electrophilic metal ions, notably, Hg^{2+} can cleave transition metal alkyl bonds relatively easily. Two main pathways have been identified, one of which is attack at the α carbon of the alkyl, which can lead to inversion of configuration

at that carbon (Eq. 8.35). In the other, attack occurs at the metal or at the M—C bond and retention of configuration is found (Eq. 8.36). The difference has been ascribed to the greater basicity of the metal in the iron case.[26,27]



As a 0e ligand, $HgCl_2$, or more likely, $HgCl^+$, can bind to an 18e metal exactly in the same way as can a proton. It is not yet clear whether the electrophilic attack takes place at the M—C bond or at the metal. The first pathway can give RHgCl directly (Eq. 8.37), the second gives an alkylmetal mercuric chloride, which can reductively eliminate to give the same product (Eq. 8.38). In the absence of an isolable intermediate it is very difficult to tell the two paths apart. This is an important process: as we will see in Chapter 16, electrophilic attack by Hg(II) on the methyl derivative of coenzyme B_{12} is the route by which mercuric ion from various sources is converted into the toxic methylmercury cation in natural waters.



The proton is often able to cleave metal alkyls. This happens most readily for the electropositive metals, where the alkyl has a higher negative charge. Even water is a good enough source of protons for RLi, RMgBr, and many of the early metal alkyls. The later metals need stronger acids and more vigorous conditions.[28]

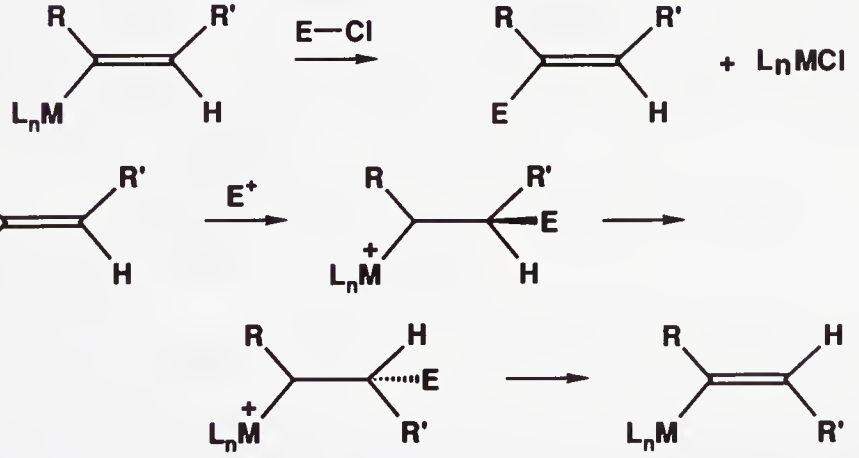
$$CpL_2FeMe + CF_3COOH \longrightarrow [CpL_2FeMeH]^+(CF_3COO)^- \xrightarrow{-CH_4} [CpL_2Fe(OCOCF_3)] \quad (8.39)$$

Other electrophiles are known to abstract transition metal alkyls, as shown below:

$$Cp_2TaMe_3 + Ph_3C^+ \longrightarrow [Cp_2TaMe_2]^+ + Ph_3CMe \quad (8.40)^3$$

$$[Co(CN)_5(CH_2Ph)]^{3-} + NO^+ \longrightarrow [Co(CN)_5(H_2O)]^{2-} + PhCH_2NO\bullet \longrightarrow PhCH{=}NOH + \text{other products} \quad (8.41)^{29}$$

Retention of configuration is not always observed in the electrophilic abstraction of vinyl groups, because the electrophile sometimes gives an initial reversible addition to the β carbon (Eq. 8.43). Free rotation about a C—C single bond in the carbene intermediate then leads to loss of stereochemistry.



(8.42)

(8.43)

Halogens are electrophilic reagents and can readily cleave many metal alkyls to give the free alkyl halides. One common mechanism involves oxidation of the metal. This increases the electrophilic character of the alkyl group and generates halide ion, so that, paradoxically, it is *nucleophilic* abstraction of the alkyl group by halide ion that leads to the final products. Co(III) alkyls are known to behave in the same way, and the intermediate Co(IV) species are stable enough to be detected by EPR at −50°C.[32]

$$Cp(CO)_2Fe{-}R + \tfrac{1}{2}Br_2 \longrightarrow Cp(CO)_2Fe^{\cdot+}{-}R + Br^- \longrightarrow Cp(CO)_2Fe\cdot + R{-}Br \xrightarrow{1/2Br_2} Cp(CO)_2FeBr + RBr \quad (8.44)$$

As we saw in Section 7.3, some reactions that lead to overall insertion into an M—R bond go by the electrophilic abstraction of an alkyl as the first step. SO_2 insertion is the best known, but it is thought that SO_3, $(CN)_2C{=}C(CN)_2$, and $CF_3C{\equiv}CCF_3$, may be able to react in the same way.

An alternative pathway for the reaction of a metal alkyl with an electrophile is the abstraction of a substituent at the α carbon to form a carbene.

$$Cp(CO)_2LMo{-}CH_2OMe + Ph_3C^+ \longrightarrow [Cp(CO)_2LMo{=}CHOMe]^+ \quad (8.45)^{33}$$

$$Cp(CO)_2Fe{-}CF_3 + BF_3 \longrightarrow [Cp(CO)_2Fe{=}CF_2]^+BF_4^- \quad (8.46)^{34}$$

8.6 SINGLE-ELECTRON TRANSFER PATHWAYS

It is sometimes difficult to tell the difference between a true electrophilic abstraction or addition, a one step process in which a pair of electrons is implicated, and a two step process involving a single-electron transfer (SET) step to give radical intermediates.

$$L_nM{-}R \xrightarrow[\text{electrophilic abstraction}]{E^+} L_nM^+{-}\square + E{-}R \quad (8.47)$$

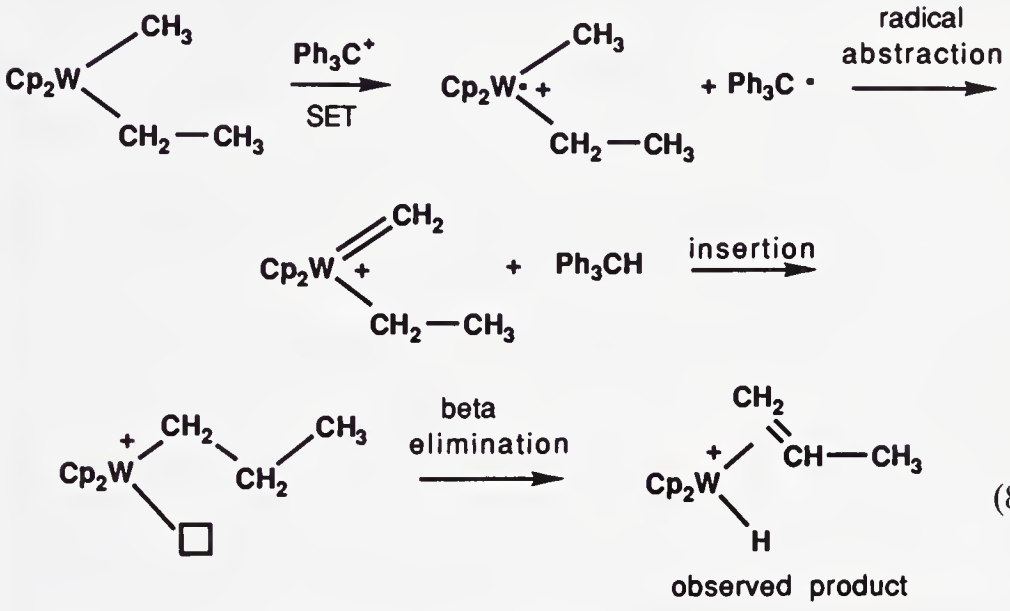
$$L_nM{-}R + E^+ \xrightarrow{SET} L_nM^{\bullet+}{-}R + E^{\bullet} \xrightarrow[\text{radical abstraction}]{} L_nM^+{-}\square + E{-}R \quad (8.48)$$

(SET = single electron transfer)

An analogous ambiguity holds for nucleophilic reactions. We have already seen one facet of this problem in the oxidative addition of alkyl halides to metals (Section 6.3), which can go either by an electrophilic addition to the metal, the S_N2 process, or by SET and the intermediacy of radicals. The two processes can often give the same products. Other related cases we have seen are the promotion of migratory insertion and nucleophilic abstraction by SET oxidation of the metal (Sec. 7.1), and electrophilic abstraction of alkyl groups by halogen (Section 8.5).

Cooper[35a] has described abstraction reactions from a metal alkyl by an electrophilic reagent that goes by an SET route. Instead of the normal β abstraction from an ethyl group, which occurs in the usual electrophilic abstraction, he finds a preference for α abstraction from a methyl group. Since

H atom abstraction usually takes place at the weakest C—H bond, the metal substituent presumably weakens the α- more than the β-C—H bonds of the alkyl.



(8.49)

Nucleophiles can also give SET reactions. Lapinte[35b] has shown that $[Cp^*Mo(CO)_3(PMe_3)]^+$ reacts with $LiAlH_4$ to give $[Cp^*Mo(CO)_3(PMe_3)]$, observed by epr. Loss of CO, easy in this 19e species, leads to $Cp^*Mo(CO)_2(PMe_3)$, which abstracts H•, probably from the thf solvent, to give the final product, $Cp^*MoH(CO)_2(PMe_3)$.

8.7 REACTIONS OF ORGANIC FREE RADICALS WITH METAL COMPLEXES

The reactions of organic free radicals with metal complexes is much less well understood than the attack of electrophiles and nucleophiles. If the starting material is an 18e complex, the product will be a 17e or 19e species and therefore reactive, so the nature of the initial reaction product may have to be inferred from the final products. Addition to the metal is well recognized and is easiest to detect when the starting complex is 17e, so that the product becomes 18e. For example, organic radicals are known to react very rapidly with $[Co^{II}(dmg)_2py]$ as follows:

$$[Co^{II}(dmg)_2py] + R\bullet \longrightarrow [RCo^{III}(dmg)_2py] \qquad (8.50)$$

We saw an example of this process as part of larger mechanistic schemes in the radical-based oxidative additions of Section 6.3. We also saw typical radical rearrangements used to detect the presence of radical intermediates (e.g., Eq. 6.20).

Since organic radicals react rapidly by the pathways shown in Eq. 8.51, only a rapid reaction with a metal complex can successfully compete.

$$\underset{}{RCH{\bullet}CH_3} \longrightarrow \underset{\text{recombination product}}{R(CH_3)HC{-}CH(CH_3)R} + \underset{}{RCH{=}CH_2} + \underset{\text{disproportionation products}}{RCH_2CH_3} \quad (8.51)$$

$$R{\bullet} + solvH \longrightarrow RH + solv{\bullet} \quad (8.52)$$

The reaction of Eq. 8.52 means that the solvent has to be chosen with care or solvent derived radicals may attack the metal complex. Solvents with strong C—H bonds, such as water, *t*-BuOH, *n*-alkane, benzene, and acetic acid, are resistant to loss of an H atom via Eq. 8.52.

Radical abstraction is still uncommon, but it constitutes one step of Eq. 8.49 (above) and it has been proposed to explain the acceleration in the rate of substitution of $Cp_2Fe_2(CO)_4$ caused by O_2/BEt_3. In this case Et• radicals, formed from BEt_3 and O_2, are thought to abstract CO from the complex to give EtCO• and a coordinatively unsaturated 17e Fe species, which undergoes substitution.[36] A related radical addition to a CO group of $IrCl(CO)_2(PMe_3)_2$ has been proposed by Goldman,[37] who generated $C_6H_{11}{\bullet}$ (= Cy•) by photolysis of benzophenone in cyclohexane and saw CyCHO as the organic product:

$$Ph_2CO \xrightarrow{h\nu} Ph_2CO^* \xrightarrow{CyH} Ph_2C{\bullet}{-}OH + Cy{\bullet} \quad (8.53)$$

$$Cy{\bullet} \xrightarrow{M(CO)_n} (CyCO)M{\bullet}(CO)_{n-1} \xrightarrow{Ph_2C.{-}OH\ CO}$$

$$CyCHO + M(CO)_n + Ph_2CO \quad (8.54)$$

REFERENCES

1. G. Natile et al., *J. Chem. Soc., Dalton,* 651, 1977.
2. M. F. Semmelhack, *Ann. N.Y. Acad Sci.,* 36, 1977.
3. R. R. Schrock, *Acct. Chem. Res.,* **97,** 6577, 1975.
4. G. Jaouen et al., *Tetrahedron,* **35,** 2249, 1979.
5. C. P. Casey, R. L. Anderson, et al., *J. Am. Chem. Soc.,* **94,** 8947, 1972; **96,** 1230, 1974.
6. J. W. Faller et al., *J. Organometal. Chem.,* **88,** 101, 1975.
7. A. J. Birch et al., *Tetrahedron Lett.,* 115, 1975.
8. M. L. H. Green et al., *J. Chem. Soc.,* 889, 1963.
9. M. Rosenblum, W. P. Giering, et al., *J. Am. Chem. Soc.,* **94,** 7170, 1972.
10. E. O. Fischer, *Adv. Organometal. Chem.,* **14,** 1, 1976.
11. H. C. Clark, et al., *Synth. React. Inorg. Met.-Org. Chem.,* **4,** 355, 1974.
12. Y. Shvo, *Chem. Commun.,* 336, 1974; T. L. Brown et al., *J. Organometal. Chem.,* **71,** 173, 1975.
13. R. L. Richards et al., *J. Chem. Soc., Dalton,* 1800, 1972.

14. S. G. Davies, M. L. H. Green, and D. M. P. Mingos, *Tetrahedron,* **34,** 3047, 1978.
15. D. A. Brown et al., *Organometallics,* **5,** 158, 1986.
16. A. J. Birch et al., *J. Chem. Soc., Perkin I,* 1882, 1900, 1973; *Tetrahedron Lett.,* 871, 979, 2455, 1980.
17. A. J. Pearson, *J. Chem. Soc., Perkin I,* 1980, 395.
18. J. W. Faller and A. M. Rosan, *J. Am. Chem. Soc.,* **99,** 4858, 1977.
19. J. C. Calabrese, S. D. Ittel, S. G. Davies, and D. A. Sweigert, *Organometallics,* **2,** 226, 1983.
20. J. W. Faller et al., *Organometallics,* **3,** 927, 1231, 1984.
21. F. C. Phillips, *Am. Chem. J.,* **16,** 255, 1894.
22. J. Smidt et al., *Angew. Chem.,* **71,** 176, 1959; **74,** 93, 1962.
23. J. E. Bäckvall, B. Åkermark, et al., *J. Am. Chem. Soc.,* **101,** 2411, 1979.
24. (a) J. K. Stille et al., *J. Organometal. Chem.,* **169,** 239, 1979. (b) M. Mori et al., *J. Am. Chem. Soc.,* **93,** 1529, 1971.
25. P. L. Bock and G. M. Whitesides, *J. Am.Chem. Soc.,* **96,** 2826, 1974.
26. M. C. Baird et al., *Inorg. Chem.,* **18,** 188, 1979.
27. G. M. Whitesides et al., *J. Am. Chem. Soc.,* **96,** 2814, 2826, 1974.
28. A. Wojcicki et al., *J. Organometal. Chem.,* **193,** 359, 1980.
29. M. D. Johnson, et al., *J. Chem. Soc., (A),* 177, 1966.
30. J. Schwartz et al., *J. Am. Chem. Soc.,* **99,** 638, 1977.
31. M. D. Johnson, et al., *J. Chem. Soc., Perkin II,* 1262, 1976.
32. J. Halpern, M. E. Vol'pin, et al., *Chem. Commun.,* 44, 1978.
33. G. M. Whitesides et al., *J. Am. Chem. Soc.,* **93,** 1529, 1971; S. E. Kegley, M. Brookhart, et al., *Organometallics,* **1,** 760, 1982.
34. A. Crespi and D. F. Shriver, *Organometallics,* **4,** 1830, 1985.
35. (a) J. C. Hayes and N. J. Cooper, *J. Am. Chem. Soc.,* **104,** 5570, 1982; (b) C. Lapinte et al., *Organometallics,* **11,** 1419, 1992.
36. S. Nakanishi et al., *Chem. Commun.,* 709, 1993.
37. W. T. Boese and A. S. Goldman, *J. Am. Chem. Soc.,* **114,** 350, 1992.

PROBLEMS

1. Where would hydride ion attack each of the following?

$[(\eta^5\text{-cyclohexadienyl})(\eta^5\text{-Cp})(C_2H_4)MoMe]^+$

$[(\eta^5\text{-cyclohexadienyl})(CO)_3Fe]^+$

$[(\eta^4\text{-}C_4H_4)(\eta^4\text{-butadiene})(\eta^3\text{-allyl})MoMe]^+$

2. Predict the outcome of the reaction of $CpFe(PPh_3)(CO)Me$ with HCl, Cl_2, $HgCl_2$, and HBF_4/thf.

3. Explain the outcome of the reaction shown below:

$$\text{Butadiene} + \text{PhI} + \text{R}_2\text{NH} \xrightarrow{\text{Pd(OAc)}_2,\ \text{PPh}_3} \text{PhCH}_2\text{CH=CHCH}_2\text{NR}_2 + \text{PhCH=CHCH=CH}_2 \quad (8.55)$$

4. $[CpCo(dppe)(CO)]^{2+}$ (A) reacts with 1° alcohols, ROH, to give $[CpCo(dppe)(COOR)]^{+}$, a reaction known for very few CO complexes. The ν(CO) frequency for A is 2100 cm^{-1}, extremely high for a CO complex. Br^- does not usually displace CO from a carbonyl complex, but it does so with A. Why is A so reactive?

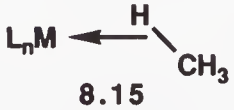
5. Nucleophilic addition of MeO^- to free PhCl is negligible slow under conditions for which the reaction with $(\eta^6\text{-}C_6H_5Cl)Cr(CO)_3$ is fast. What product would you expect, and why is the reaction accelerated by coordination?

6. Given a stereochemically defined starting material (either erythro or threo), what stereochemistry would you expect for the products of the following electrophilic abstraction reaction:

$$CpFe(CO)_2(CHDCHDCMe_3) + Ph_3C^+ \longrightarrow CHD{=}CHCMe_3 + CHD{=}CDCMe_3 \quad (8.56)$$

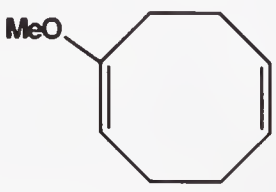
Let us say that for a related 16e complex $L_nM(CHDCHDCMe_3)$ gave precisely the same products, but of opposite stereochemistries, what mechanism would you suspect for the reaction?

7. You are trying to make a methane complex $L_nM(\eta^1\text{-H—CH}_3)^+$ (**8.15**, unknown as a stable species at the time of writing), by protonation of a methyl complex L_nMMe with an acid HA. Identify three things that might go wrong and suggest ways to guard against each. (If you try this and it works, send me a reprint.)



8.15

8. (cod)$PtCl_2$ reacts with MeOH/NaOAc to give a species $[\{C_8H_{12}(OMe)\}PtCl]_2$. This in turn reacts with PR_3 to give 1-methoxy cyclooctadiene (**8.16**) and $PtHCl(PR_3)_2$. How do you think this might go?



8.16

9. $CpFe(CO)(PPh_3)(MeC{\equiv}CMe)$ reacts with (i) $LiMe_2Cu$ (a source of Me^-) and (ii) I_2 to give compound **8.17**; explain this reaction. What product do you think might be formed from $LiEt_2Cu$?

8.17

10. Me_3NO is a good reagent for removing CO from a metal, but why does Me_3PO not work? Why does Me_3NO not work in the case of $Mo(dppe)_2(CO)_2$? Can you suggest an O-donor reagent that might be more reactive than Me_3NO?

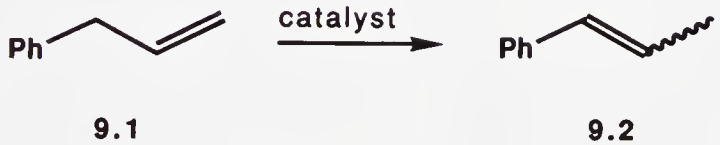
CHAPTER 9

HOMOGENEOUS CATALYSIS

The catalysis of organic reactions[1–4] is one of the most important applications of organometallic chemistry and has been a significant factor in the rapid development of the whole field. The catalysts we shall look at are soluble complexes, which act as *homogeneous catalysts,* as opposed to catalysts such as palladium on carbon, which are called *heterogeneous catalysts.*[4] These names are used because the catalyst and substrates for the reaction are in the same phase in the homogeneous, but not in the heterogeneous type, where catalysis takes place at the surface of a solid catalyst. Some reactions, such as hydrogenation, are amenable to both types of catalysis, but others are currently limited to one or the other, for example, O_2 oxidation of ethylene to the epoxide over a heterogeneous silver catalyst or Wacker air oxidation of ethylene to acetaldehyde with homogeneous Pd(II) catalysts.

The term *homogeneous catalysis* also covers such things as simple acid catalysts and nonorganometallic catalysis, such as the decomposition of H_2O_2 by Fe^{2+}. Catalytic mechanisms are considerably easier to study in homogeneous systems, where such powerful methods as NMR can be used both to assign structures and follow reaction kinetics. Homogeneous catalysts can also be chemically grafted on to solid supports for greater ease of separation of the catalyst from the reaction products. Although the catalyst is now technically heterogeneous, it often retains the characteristic reactivity pattern that it showed as a homogeneous catalyst, and its properties are usually distinct from those of any of the classical heterogeneous catalysts—these are sometimes called "heterogenized" homogeneous catalysts. The mechanistic ideas developed in homogeneous catalysis are also becoming more influential in the field of classical heterogeneous catalysis by suggesting structures for intermediates and mechanisms for reactions steps.

The effect of a catalyst is to change the rate of conversion of a substrate into products in some reaction. Sometimes, the thermal and catalyzed reactions can give different products—in this case the catalyst has accelerated a reaction that is normally kinetically unfavorable. Here, we look at catalysts that increase the reaction rate, but *inhibitors,* catalysts that reduce the rate of reaction, are also of great practical importance (e.g., inhibitors of oxidation: flame retardants, anticorrosion and antiknock additives). A typical reaction (Eq. 9.1) that is catalyzed by many transition metal complexes is the isomerization of allylbenzene (the substrate) into propenylbenzene (the product). Normally, the substrate for the reaction will coordinate to the metal complex that serves as catalyst. The metal then brings about the rearrangement, and the product dissociates, leaving the metal fragment free to bind a new molecule of substrate and undergo the catalytic cycle again and again. It is this feature of a catalyst that distinguishes it from a simple reagent: a mole of catalyst will convert many (typically, 10^2 to 10^6 or more) moles of substrate into products.



(9.1)

9.1 **9.2**

Before setting out to find a catalyst for a given reaction, say the one shown in Eq. 9.1, the first consideration is thermodynamic: whether the reaction is favorable. If the desired reaction were thermodynamically strongly disfavored, as is the conversion of H_2O to H_2 and O_2, for example, then no catalyst, however efficient, could *on its own* bring about the reaction. If we wanted to bring about an unfavorable reaction of this sort, we would have to provide the necessary driving force in some way. There are ways of doing this, such as coupling a strongly favorable process to the unfavorable one you want to drive, as Nature commonly does with the hydrolysis of ATP (adenosine triphosphate), or we could use the energy of a light photon, as in photosynthesis or we can selectively remove the products (e.g., by distillation).

Normally, the catalyst only increases the rate of a process but does not alter its position of equilibrium, which is decided by the relative thermodynamic stabilities of substrate and products (we discuss ways of getting around this restriction in Section 12.4). Fig. 9.1a illustrates this point: the substrate S is slightly less stable than the product, P, so the reaction will eventually reach an equilibrium favoring P. In the case of **9.1** going to **9.2**, the additional conjugation present in **9.2** is sufficient to ensure that the product is thermodynamically more stable than the starting material and so the reaction is indeed favorable. Normally, the substrate binds to the metal before it undergoes the rearrangement. This substrate-catalyst complex is represented as

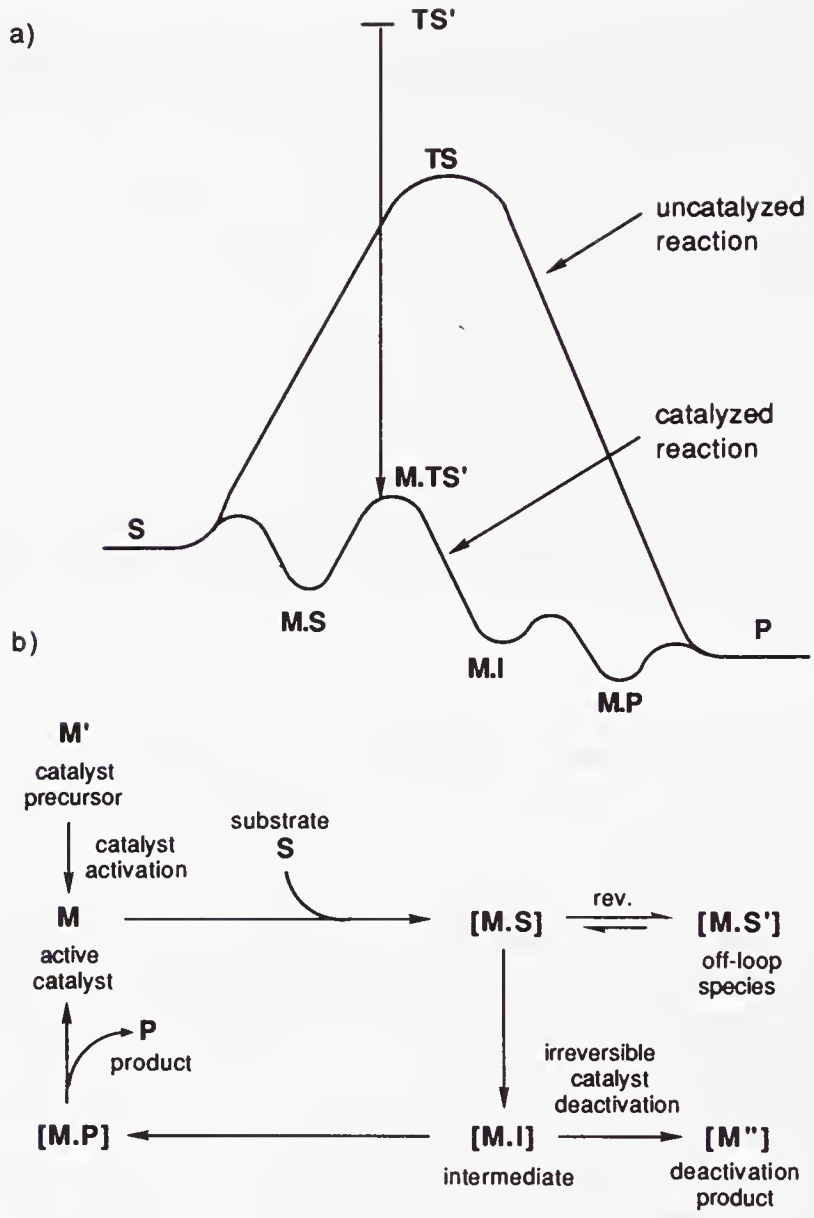


FIGURE 9.1 A catalyst lowers the activation energy for a chemical reaction. Here the uncatalyzed conversion of substrate S to product P passes by way of the high-energy transition state TS. In this case the metal-catalyzed version goes via a different transition state TS′, which is very unstable in the free state but becomes viable on binding to the catalyst as M.TS′. The arrow represents the M—TS′ binding energy. The uncatalyzed and catalyzed processes do not necessarily lead to the same product as is the case here.

"M.S" in Fig. 9.1. It might be thought that strong binding would be needed. A moment's reflection will show why this is not so. If the binding is too strong, M.S will be too stable, and the activation energy to get to "M.TS" will be just as large as it was in going from S to TS in the uncatalyzed reaction. S cannot bind too weakly, because it may otherwise be excluded from the metal

and fail to be activated by the metal at all. Similarly, the product P will normally be formed as the complex M.P. Product P must be the least strongly bound of all, because if it is not then S will not be able to displace P, and the catalyst will be effectively poisoned by the products of the reaction. Many of these ideas also apply to the chemistry of Nature's homogeneous catalysts, enzymes.[5a]

For most transition metal catalysts, the catalyzed pathway is completely changed from the pathway of the uncatalyzed reaction, as shown in Fig. 9.1*a*. Instead of passing by way of the high-energy uncatalyzed transition state TS, the catalyzed reaction normally goes by a multistep mechanism in which the metal stabilizes intermediates that are stable only when bound to the metal. One new transition state M.TS′ is shown in Fig. 9.1. The TS′ structure in the absence of the metal would be extremely unstable, but the energy of binding is so high that M.TS′ is now much more favorable than TS and the reaction all passes through the catalyzed route. Different metal species may be able to stabilize other transition states TS″—which may lead to entirely different products—hence different catalysts can give different products.

In a stoichiometric reaction, the passage through M.TS′ would be the slow, or rate determining, step. In a catalytic reaction the cyclic nature of the system means that the rates of all steps are identical. On a circular track, on average the same number of trains must pass each point per unit time.The slow step in a catalytic process is called the *turnover limiting step.* Any change that lowers the barrier for this step will increase the *turnover frequency* (TOF) or number of moles of product formed per mole of catalyst per unit time. Changes in other barriers will not affect the TOF. For a high TOF, we require that none of the intermediates be bound too strongly (otherwise they may be too stable and not react further), and that none of the transition states be prohibitively high in energy. Indeed, the whole reaction profile must not stray from a rather narrow range of free energies, accessible at the reaction temperature. Even if all this is arranged, a catalyst may undergo a catalytic cycle only a few times and then "die." This happens if undesired deactivation reactions are faster than the productive reactions of the catalytic cycle itself. There are many ways in which a catalyst can fail, and for success it is often necessary to look hard for the right metal, ligand set, solvent, temperature range, and other conditions. Many of the reactions that occupied the attention of the early workers were relatively forgiving in terms of the range of possible catalysts and conditions. Some of the problems that are under study today, notably alkane conversions, constitute more searching tests of the efficiency of homogeneous catalysts.

Figure 9.1*b* shows a schematic catalytic cycle. The *active catalyst,* M is often rather unstable and is only formed in situ from the *catalyst precursor* (or precatalyst), M′. If during the reaction we observe the system, for example, by NMR, we normally see only the disappearance of S and the appearance of P. Decreasing the substrate concentration [S] and increasing the metal concentration [M] may allow us to see the complex. We may still see only

M′ because only a small fraction of the metal is likely to be on the loop at any given time. Even if a species appears to be an intermediate we still cannot be sure it is not M.S′, an off-loop species. If a species builds up steadily during the reaction it might be a *catalyst deactivation product* M″, in which case the catalytic rate will fall as [M″] rises. Two excellent reviews are available on the determination of mechanism in catalytic reactions.[3a,5b]

9.1 ALKENE ISOMERIZATION

Many transition metal complexes are capable of catalyzing the 1,3-migration of hydrogen substituents in alkenes, a reaction that has the net effect of moving the C=C group along the chain of the molecule (e.g., Eq. 9.1). This is often a side reaction in other types of catalytic alkene reaction, desired or not according to circumstances. Two mechanisms are most commonly found: the first goes via alkyl intermediates (Fig. 9.2*a*); the second, by η^3-allyls (Fig. 9.2*b*). Note that in each cycle, all the steps are reversible, so that the substrates and products are in equilibrium, and therefore although a nonthermodynamic ratio of alkenes can be formed at early reaction times, the thermodynamic ratio is eventually formed if the catalyst remains active long enough. In other catalytic reactions, we sometimes find that the last step is irreversible. As we shall see later, this distinction has important practical consequences in allowing the formation of grossly non-thermodynamic ratios (e.g., in asymmetric catalysis).

Alkyl Mechanism In the alkyl route, we require an M—H bond and a vacant site. The alkene binds and undergoes insertion to give the alkyl. For 1-butene, the alkyl might be the 1° or the 2°, according to the regiochemistry of the insertion. If the 1° alkyl is formed, β elimination can give back only 1-butene, but β elimination in the 2° alkyl, often faster, can give both 1- and *cis*- and *trans*-2-butene. Since insertion to give the 1° alkyl is favored for many catalysts, nonproductive cycling of the 1-butene back to 1-butene is common, and productive isomerization may be slower. The *initial* cis/trans ratio in the 2-butenes formed depends on the catalyst; the cis isomer is often favored. The final ratio depends only on the thermodynamics, and the trans isomer is preferred. A typical isomerization catalyst is $RhH(CO)L_3$ ($L = PPh_3$).[6] As this is a *coordinatively saturated* 18e species it must lose a ligand, PPh_3 in this case, to form a *coordinatively unsaturated* intermediate (<18e), able to bind the alkene.

Allyl Mechanism The second common mechanism involves allyl intermediates and is adopted by those metal fragments that have two 2e vacant sites but no hydrides. It has been established for the case of $Fe_3(CO)_{12}$ as catalyst, a system in which "$Fe(CO)_3$," formed by fragmentation of the cluster on heating, is believed to be the active species.[7] The cluster itself is an example of a catalyst precursor. As a 14e species, $Fe(CO)_3$ may not have an indepen-

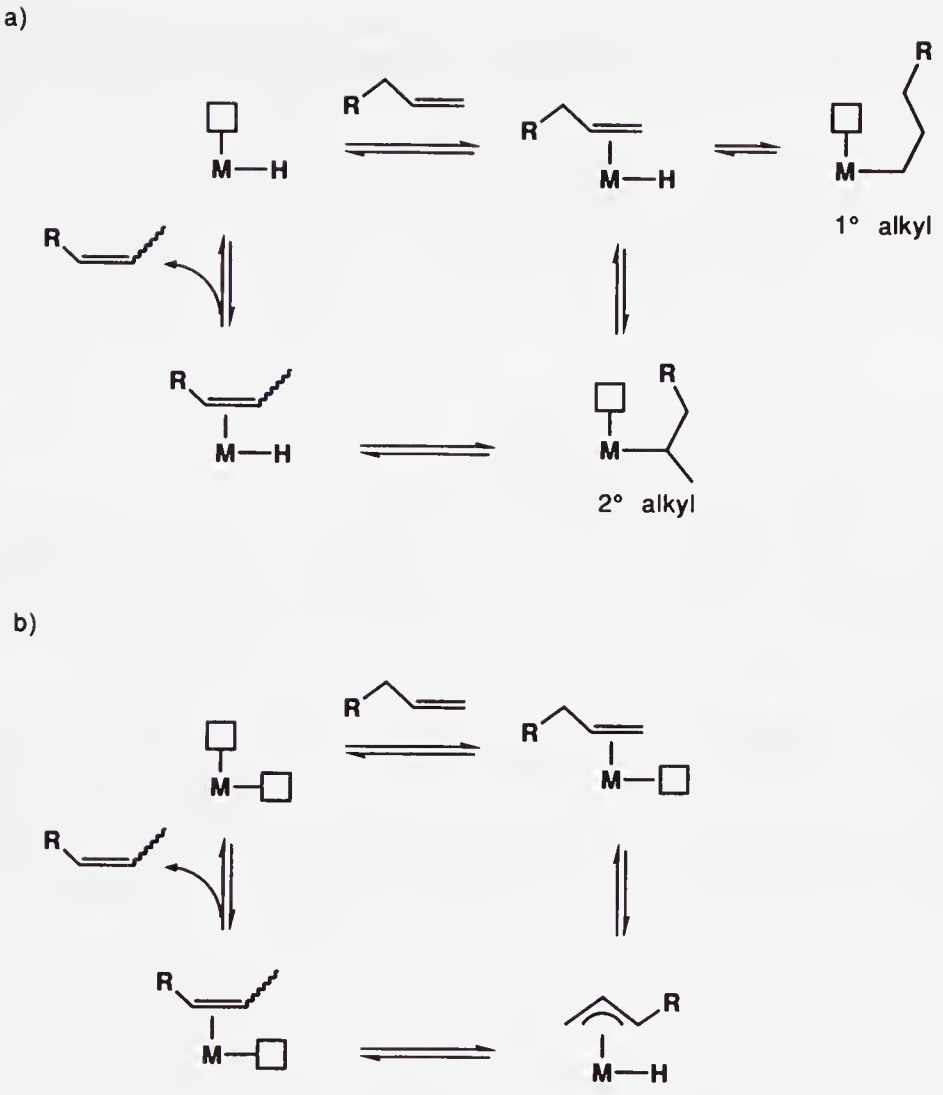
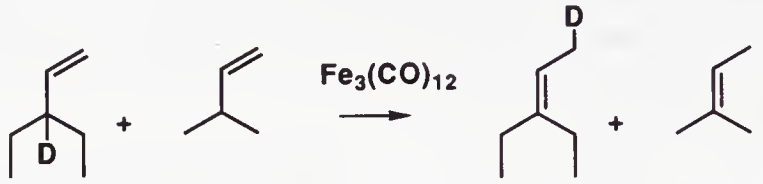


FIGURE 9.2 The hydride (*a*) and allyl (*b*) mechanisms of alkene isomerization. The open box represents a 2e vacancy or potential vacancy in the form of a labile 2e ligand.

dent existence in solution, but may always be tied up with substrate or product. The open box in Fig. 9.2 represents a vacant site or a labile ligand. In this mechanism the C—H bond at the activated allylic position of the alkene undergoes an oxidative addition to the metal. The product is an η^3-allyl hydride. Now, we only need a reductive elimination to give back the alkene. Again, we can have nonproductive cycling if the H returns to the same site it left, rather than to the opposite end of the allyl group.

An experimental distinction[7] can be made between the two routes with a crossover experiment (Section 6.5) using the mixture of C_5 and C_7 alkenes of Eq. 9.2. For the allyl mechanism, we expect the D in **9.3a** to end up only in the corresponding product **9.3b** having undergone an intramolecular 1,3 shift.

For the hydride mechanism, the D will be transferred to the catalyst that can in turn transfer it by crossover to the C_5 product.



9.3a 9.3b (9.2)

9.2 ALKENE HYDROGENATION

Hydrogenation catalysts[3] add molecular hydrogen to the C=C group of an alkene to give an alkane. Three general types have been distinguished, according to the way each type activates H_2. This can happen by (1) oxidative addition, (2) heterolytic activation, and (3) homolytic activation.

Oxidative Addition Perhaps the most important group employs oxidative addition, of which $RhCl(PPh_3)_3$ (**9.4**, Wilkinson's catalyst) is the best known. A catalytic cycle that is important under certain conditions is shown in Fig. 9.3. Hydrogen addition to give a dihydride leads to labilization of one of the PPh_3 ligands (high trans effect of H) to give a site at which the alkene binds.

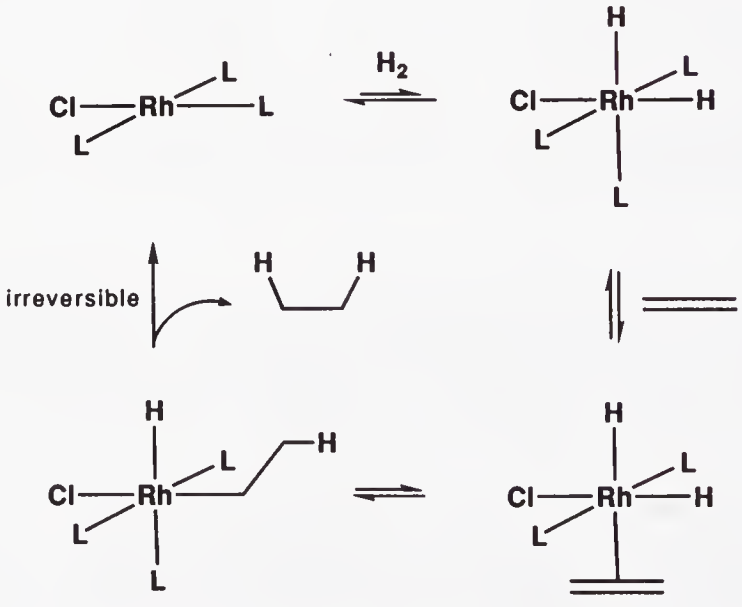
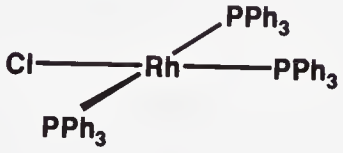


FIGURE 9.3 A mechanism for the hydrogenation of alkenes by Wilkinson's catalyst. Other pathways also operate in this system, however.

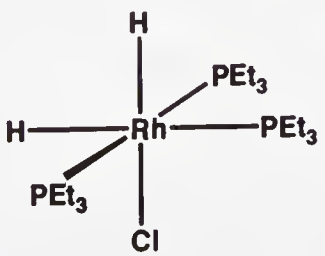
The alkene inserts, as in isomerization, but the intermediate alkyl is irreversibly trapped by reductive elimination with the second hydride to give an alkane. This is an idealized mechanism.[3] In fact, **9.4** can also solvate to give $RhCl(PPh_3)_2(solv)$, and dimerize via halide bridges and each of these species have their own separate catalytic cycles[3c] that can be important under different conditions, but they all resemble Fig. 9.3. In a key study by Tolman, the dihydride was directly seen by ^{31}P NMR under H_2 and the reversible loss of the PPh_3 trans to a hydride detected from a broadening of the appropriate resonance, as discussed in Section 10.5.[3d]



9.4

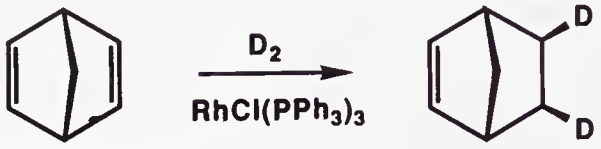
Figure 9.3 represents the *hydride mechanism* in which H_2 adds before the olefin. Sometimes the olefin adds first (the *olefin mechanism*) as is found for $[Rh(dpe)(MeOH)_2]BF_4$.[3e]

Since we need to bind two hydrides and the alkene, for a total electron count of 4e, the 16e catalyst $RhCl(PPh_3)_3$ needs to dissociate a ligand, PPh_3 in this case, to do this. The PEt_3 analog of **9.4** reacts with H_2 to give a stable and catalytically inactive dihydride $RhH_2Cl(PEt_3)_3$, **9.5**. The smaller PEt_3 ligand does not dissociate and so **9.5** is not an active catalyst. All we have to do to make the PEt_3 analog active is artificially arrange to generate the desired RhH_2ClL_2 intermediate by forming it in situ by starting with 0.5 equiv of $[(nbd)Rh(\mu\text{-}Cl)]_2$ and adding 2 equiv of PEt_3, for a final P/Rh ratio of 2. Under H_2, the norbornadiene (nbd) is removed by hydrogenation, and we get $RhH_2Cl(PEt_3)_2$, which is an active hydrogenation catalyst under these conditions.[8] A key prerequisite for catalysis in many systems is coordinative unsaturation, that is, an open site at the metal.



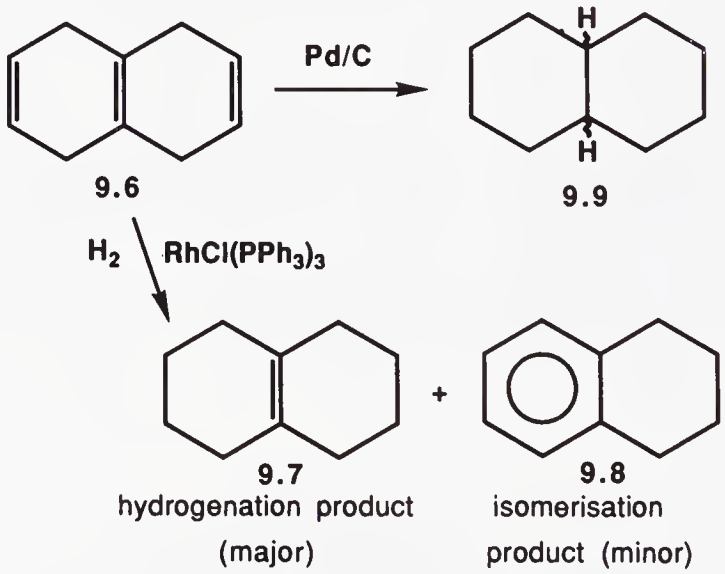
9.5

As predicted by the mechanism of Fig. 9.3, the hydrogen gives syn addition to the alkene, although it is possible to tell only this in certain cases. For example:



(9.3)

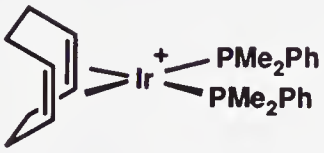
Isomerization is often a minor pathway in a hydrogenation catalyst, because the intermediate alkyl may β-eliminate before it has a chance to reductively eliminate. The more desirable catalysts, such as **9.4**, tend to give little isomerization. The selectivity for different alkenes (the hydrogenation rates change in the order: monosubstituted > disubstituted > trisubstituted > tetrasubstituted = 0) is determined by how easily they can bind to the metal, the poorer ligands among them being reduced slowly, if at all. This means that **9.4** reduces the triene **9.6** largely to the octalin **9.7** (Eq. 9.4). Heterogeneous catalysts give none of this product, but only the fully saturated decalin (**9.9**), and the isomerization product, tetralin (**9.8**) (Eq. 9.4). The C=O and C=N double bonds of ketones and imines are successfully reduced only by certain catalysts. Other functional groups which can be reduced by heterogeneous catalysts, such as —CN, —NO_2, —Ph, and —CO_2Me are not reduced by the usual homogeneous catalysts.



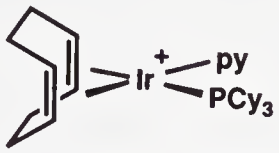
(9.4)

$IrCl(PPh_3)_3$, the iridium analog of **9.4**, is inactive because of the failure of the dihydride $IrH_2Cl(PPh_3)_3$ to lose phosphine; this is a result of the stronger metal-ligand bond strengths usually found for the third-row metals. Using the same general strategy we saw for Rh, $[(cod)Ir(\mu\text{-}Cl)]_2$ is active if only 2 mol of phosphine are added per metal. A more useful catalyst is obtained

by replacing the chloride with a "noncoordinating" anion and changing the ligands to give the precursors $[(cod)Ir(PMePh_2)_2]^+PF_6^-$, **9.10**, and $[(cod)Ir(py)(PCy_3)]^+PF_6^-$, **9.11**.[8] These catalysts tend to bind a solvent, such



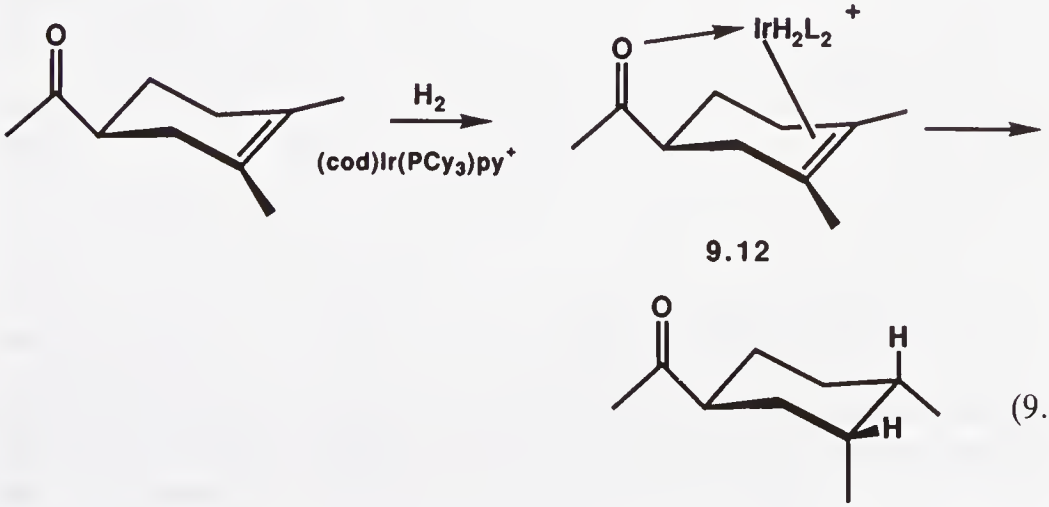
9.10



9.11

as EtOH, much more firmly than do such uncharged catalysts as **9.4**, for example, to give the isolable species $[IrH_2(solv)_2(PMePh_2)_2]^+PF_6^-$ (solv = acetone, ethanol, or water). This seems to be a result of the net cationic charge, which tends to make the metal a harder Lewis acid. Unlike many noncationic catalysts, these species are also air-stable and even tolerate halocarbons. As a result, the catalyst can be used in CH_2Cl_2, a much more weakly coordinating solvent than EtOH. Compound **9.11** has the unusual feature that it can reduce even highly hindered alkenes like $Me_2C{=}CMe_2$. This is probably because these alkenes do not have to compete with dissociated phosphine or a coordinating solvent for a site on the metal, and perhaps also because the $\{Ir(py)(PCy_3)\}^+$ fragment is not very bulky.

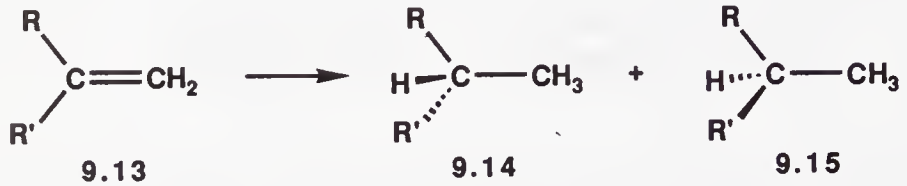
Directing Effects The catalyst **9.11** shows strong directing effects, which can be very useful in organic synthetic applications (see Section 14.8).[9] This means that H_2 is added to one face of the substrate, if there is a coordinating group (e.g., —OH, —COMe, —OMe) on that face (Eq. 9.5). The net positive ionic charge makes the metal hard enough to bind to the directing group and, as IrL_2^+ is a 12e fragment, it still has enough vacant sites left to bind both H_2 and the alkene to give the key intermediate **9.12**. Of the four possible geometrical isomers of the saturated ketone, only one is formed, H_2 having been added cis to the directing group.



9.12

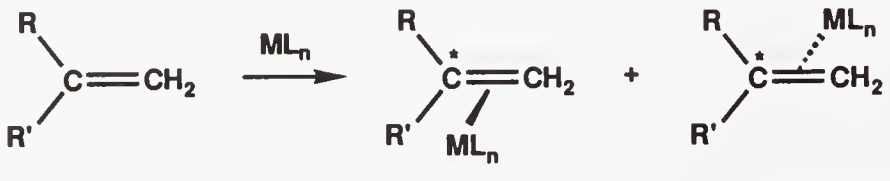
(9.5)

Asymmetric Catalysis The corresponding "RhL_2^+" catalysts were developed by Schrock and Osborn.[10a] Their most important application is asymmetric catalysis.[10b] Eq. 9.6 shows how the achiral alkene **9.13** can give two enantiomers **9.14**, and **9.15** on hydrogenation.



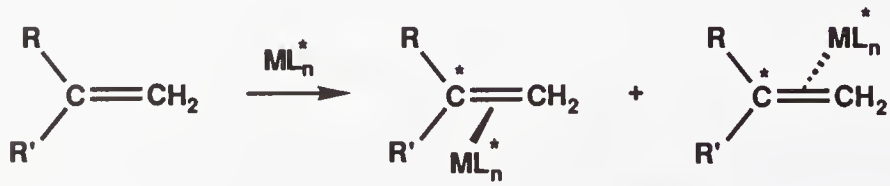
(9.6)

Any alkene having this property is called *prochiral,* which implies that the two faces of the molecule are different. In **9.13**, one face has a clockwise arrangement of R, R′, and $=CH_2$ about the central carbon; the other face has an anticlockwise arrangement of these groups. If the H_2 is added from one face, one enantiomer is formed, if from the other face, the other enantiomer is the product. If we were to bias the addition of H_2 to one face, then we would have an asymmetric synthesis. As shown in Eq. 9.7, when a prochiral alkene binds to an achiral metal, two enantiomers are formed; that is, the complex is chiral even though neither the ligand nor the metal were chiral before the complex was formed. One way of thinking about this is to regard the carbon indicated by the asterisk as having four different substituents, one of which is the metal.



(9.7)

enantiomers



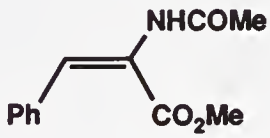
(9.8)

diastereomers

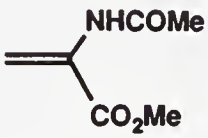
The key point is that if the ML_n catalyst fragment can also be made chiral (say because a ligand L has an asymmetric carbon), then we can use one resolved enantiomer of the chiral complex as catalyst. In Eq. 9.8, instead of forming two enantiomeric complexes such as **9.16** and **9.17**, we will have diastereomeric alkene–catalyst complexes, **9.18** and **9.19**, because we now

have two asymmetric centers present, C* in the coordinated alkene and the asymmetric ML_n^* fragment. Since diastereomers generally have different chemical properties, **9.18** and **9.19** normally have different rates of hydrogenation. This bias on the rates of hydrogenation can give us one of the pair of enantiomers **9.14** or **9.15** over the other. In summary, one enantiomer of the catalyst should preferentially give one enantiomer of the hydrogenated alkene, and the other enantiomer give the other product. This is an extremely valuable method, because we can obtain a large amount of one enantiomeric product from a small amount of resolved material (the catalyst). This is precisely the method Nature uses to make pure enantiomers, enzymes are such efficient asymmetric catalysts that essentially only one enantiomer is normally formed in most enzymatic processes.

In asymmetric hydrogenation, 95–99% enantiomeric excess [e.e. = 100 × {amount of major isomer − amount of minor isomer}/{total of both isomers}] can be obtained in favorable cases. The first alkenes to be reduced with high asymmetric induction contained a coordinating group, examples of which are shown as **9.20** and **9.21**.



9.20

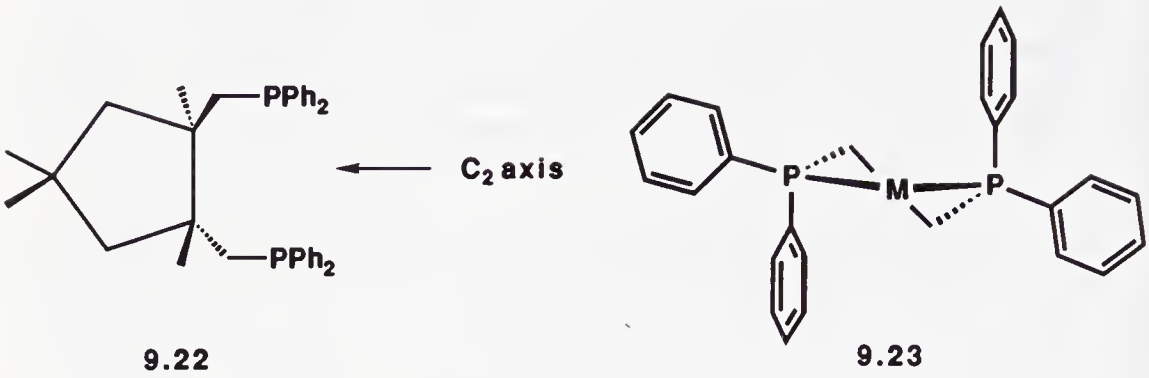


9.21

These are believed to bind to the metal via the amide carbonyl just as we saw happen in directed hydrogenation. This improves the rigidity of the alkene–catalyst complex, which in turn increases the chiral discrimination of the system. As in directed hydrogenation, a 12e catalyst fragment, such as that formed from the Schrock–Osborn catalyst is required.

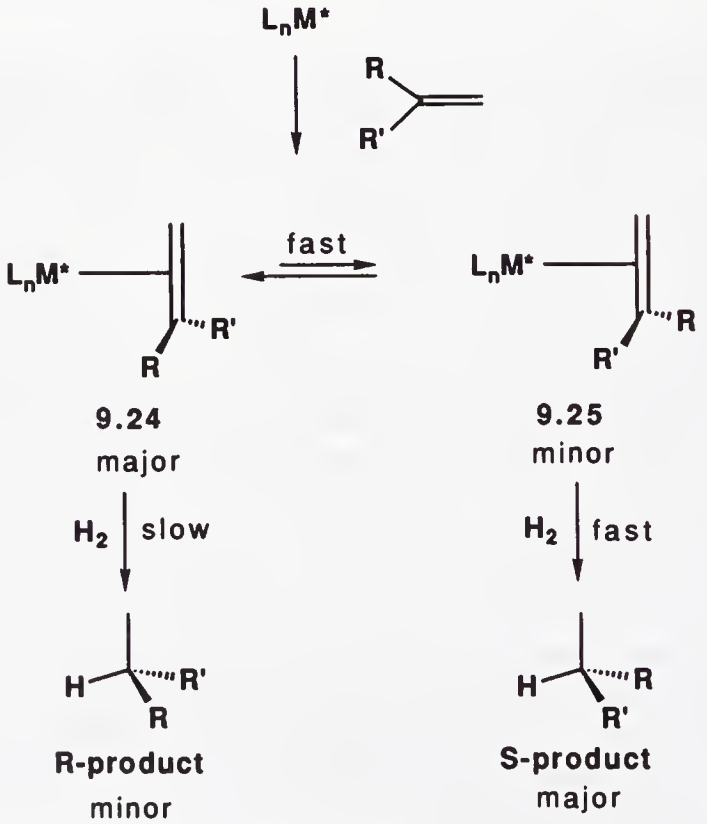
One of the best ways of making the metal chiral is to use the ligand shown as **9.22**, called "diop." This ligand contains two chiral centers and has a so-called C_2 axis; this simply means that it has the symmetry of a helical bolt, which can, of course, either have a left-handed or a right-handed thread. The chiral centers impose a twist on the conformation of the diop–metal complex which in turn leads to a chiral, propeller-like arrangement of the phenyl groups on phosphorus (**9.23**). These phenyl groups can be thought of as transmitting the chiral information from the asymmetric centers to the binding site for the alkene. The advantage of a C_2 symmetry is that the substrate sees the same chirality however it binds; we can think of the substrate as being analogous to a nut with a left hand thread which will mate with a left-handed (but not a right-handed) bolt, whichever face of the nut is tried.

In the simplest case, one face of the substrate binds better to the catalyst than does the other. Let us say that if H_2 were added to this face we would get the *S* hydrogenation product. It was once thought that this preferential



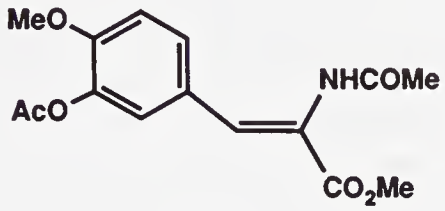
9.22 **9.23**

binding of the substrate always determines the sense of asymmetric induction. Halpern[11] showed that in a system that gives the *R* product in good yield, the metal is bound to the "wrong" face in the major diastereomer (**9.24**), the face that would be expected to give the *S* product, and so it is the minor isomer of the catalyst–alkene complex that gives rise to most of the product. This in turn means that the minor isomer must react at about 10^3 times the rate of the major isomer (Eq. 9.9). Since **9.24** and **9.25** interconvert rapidly, **9.24** is continually converting into **9.25** because the faster hydrogenation of **9.25** continually depletes the concentration of this minor isomer. Note that Eq. 9.9 is an example of the "olefin mechanism."



(9.9)

This reaction was used in the highly successful commercial production of the drug L-DOPA by hydrogenation of the alkene **9.26**. L-DOPA is effective against Parkinson's disease. Another commercial process is the asymmetric synthesis of the pain reliever, naproxen.[12]



9.26

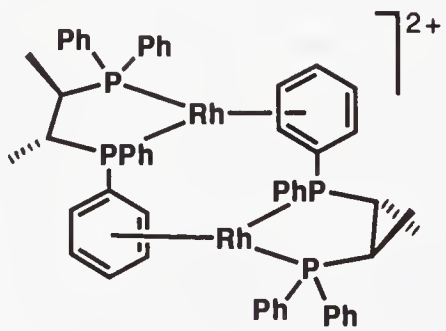
Kinetic Competence A useful general point emerges from this work: catalysis is a kinetic phenomenon, and so the activity of a system may rely on a minor, even miniscule, component of a catalyst. This emphasizes the danger on relying too heavily on spectroscopic methods in studying catalysts. The fact that a series of plausible intermediates can all be seen by, say, NMR in the catalytic mixtures does not mean these are the true intermediates. What we need to do is to show that each of the proposed intermediates reacts sufficiently fast to account for the formation of products, that is, that they are *kinetically competent* to do the reaction.

A particularly unpleasant variation of this situation is the decomposition of some or all of the complex to give a highly reactive form of the free metal, which now acts as a heterogeneous catalyst. Organometallic chemists like to find examples of homogeneous catalysts that catalyze reactions previously known to be catalyzed heterogeneously only. The Fischer–Tropsch reaction (Section 12.1) and alkane activation (Section 9.6) are examples. It is therefore embarrassing to discover that your unique "homogeneous" catalyst is just a well-known hetereogeneous catalyst in disguise. Many of the "homogeneous" hydrogenation catalysts reported in the early days of the development of the field contained a platinum metal halide in a polar solvent under H_2. Viewed with the jaundiced eye of the modern observer, many of these look like preparations of colloidal, and therefore heterogeneous, platinum group metal. (The platinum group metals are Ru, Os, Rh, Ir, Pd, and Pt.) The standard test is the addition of liquid Hg, which selectively poisons any heterogeneous Pt group metal catalyst by absorbtion of Hg onto the active sites.[13a–d]

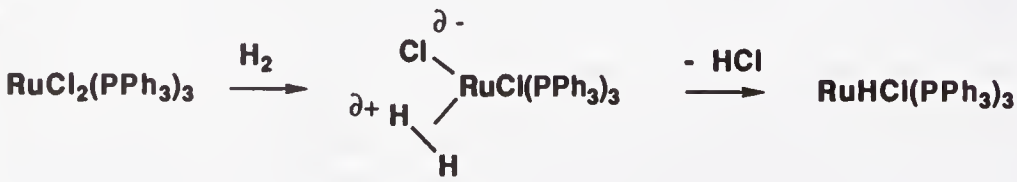
Reversibility A second general point about hydrogenation is that the final step, the reductive elimination of the product, is *irreversible.* This contrasts with the situation in alkene isomerization. In a reversible cycle the products can equilibrate among themselves, and a thermodynamic mixture is always obtained if we wait long enough and if the catalyst retains its activity. This is not the case in hydrogenation, if it were, the *R* and *S* products would eventually come to equilibrium and the e.e. would go to zero with time in

an asymmetric hydrogenation. Only an irreversible catalytic cycle (i.e., one in which the last step is irreversible) can give a nonthermodynamic final product ratio. This is very useful because it means we can obtain different (kinetic) product ratios by using different catalysts, and we do not need to be concerned that the products will equilibrate if we leave them in contact with the catalyst. A reversible catalyst can give a nonthermodynamic product ratio initially, but the final ratio will be thermodynamic.

Chiral Poisoning A new method that can be useful in asymmetric catalysis is *chiral poisoning,* in which an enantiomerically pure compound, P*, selectively binds to and poisons one enantiomer of a racemic catalyst. An e.e of 49% has been achieved using racemic $[(\text{chiraphos})\text{Rh}]_2(\text{BF}_4)_2$ and (*S*)-$[\text{Ph}_2\text{POCH}_2\text{CH}(\text{NMe}_2)\text{CH}_2\text{CH}_2\text{SMe}]$ as poison with a Rh:P* ratio of 0.7. An advantage is that P* can be easily made from methionine, itself easily available optically pure.[13e] A related result is seen with partially resolved $[(\text{chiraphos})\text{Rh}]_2(\text{BF}_4)_2$, where the minor enantiomer prefers to form an inactive dimer with the other, leaving the major enantiomer predominating in the pool of catalytically active free monomers. In such a *chiral amplification,*[13f] the product of the catalytic reaction has a higher e.e than one would expect from the optical purity of the starting catalyst because the major enantiomer of the catalyst acts as a chiral poison for the minor enantiomer. The structure of the dimer is shown below; its 18e configuration makes it catalytically inactive until it dissociates.



Heterolytic H_2 Activation We now look at the second mechanistic class of hydrogenation catalyst. $RuCl_2(PPh_3)_3$[14a] is believed to activate H_2 heterolytically, a reaction accelerated by bases, such as NEt_3.[14b] The base may either be external or one of the ligands on the metal abstracts a proton from H_2, leaving an H^- bound to the metal (Eq. 9.10).

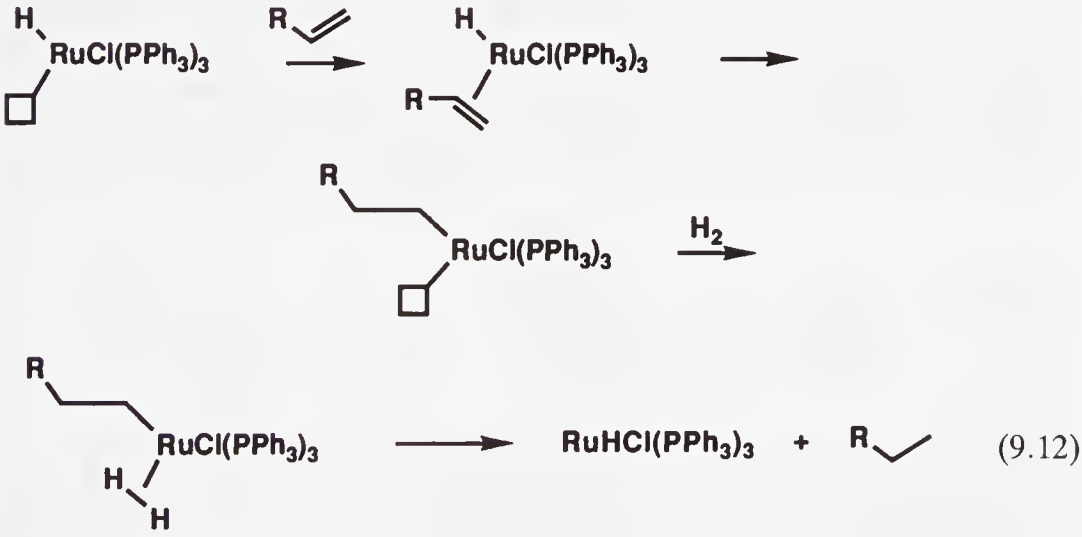


(9.10)

Equation 9.10 is a simple example of a *σ-bond metathesis,*[15] a reaction that has the general form of Eq. 9.11, and in which Y is often a hydrogen atom.

$$X—Y + M—Z \longrightarrow M—X + Y—Z \qquad (9.11)$$

It now seems very likely that the intermediate in the heterolytic activation of H_2 is a dihydrogen complex (Section 3.4). The protons of a dihydrogen ligand are known to be more acidic than those of free H_2, and many H_2 complexes can be deprotonated by NEt_3.[16a] In this way the metal gives the same products that would have been obtained by an oxidative addition–reductive elimination pathway, but by avoiding the oxidative addition, the metal avoids becoming Ru(IV), not a very stable state for ruthenium; even $RuH_4(PPh_3)_3$, long thought to be Ru(IV), is now known to have the structure $Ru(H_2)H_2(PPh_3)_3$.[16b] Other than in their method of activating H_2, these catalysts act very similarly to the oxidative addition group. As a 16e hydride complex, $RuCl_2(PPh_3)_3$ can coordinate the alkene, undergo insertion to give the alkyl, then liberate the alkyl by a heterolytic activation of H_2, in which the alkyl group takes the proton and the H^- goes to the metal to regenerate the catalyst.



(9.12)

Homolytic H_2 Activation Iguchi's[17] paramagnetic d^7 $Co(CN)_5^{3-}$ system was a very early (1942) example of a homogeneous hydrogenation catalyst. It is an example of the third and rarest group of catalysts, which activate hydrogen homolytically. Another way of looking at this is to say the cobalt system activates H_2 by a binuclear oxidative addition. This is not unreasonable for this Co(II) complex ion, a metal centered radical which has a very stable oxidation state, Co(III), one unit more positive. Once $CoH(CN)_5^{3-}$ has been formed, a hydrogen atom is transferred to the substrate in the second step, a reaction that does not require a vacant site at the metal, but does require the resulting organic radical to be moderately stable—hence the fact that the

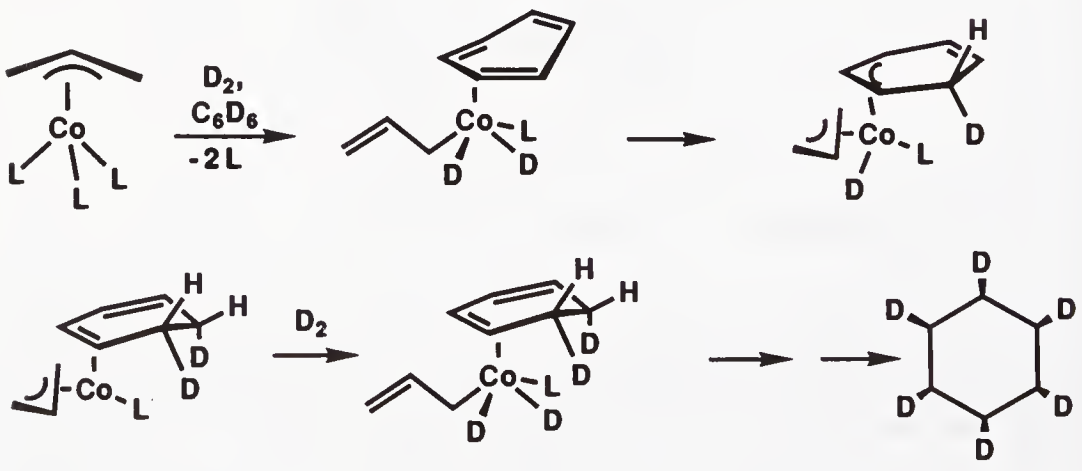
Iguchi catalyst will reduce only activated alkenes, such as cinnamate ion, in which the radical is benzylic. Finally, the organic radical abstracts H• from a second molecule of the cobalt hydride to give the final product.

(9.13)

(9.14)

(9.15)

Arene Hydrogenation Although heterogeneous hydrogenation catalysts such as Rh/C readily reduce arenes, none of the homogeneous catalysts discussed up to now are effective for this reaction. A few homogeneous catalysts have been found, however, of which (η^3-allyl)Co{P(OMe)$_3$}$_3$ is the best known.[18] When benzene is reduced with this catalyst using D_2, the all-cis isomer of $C_6H_6D_6$ is obtained, and no propane or propane is formed. This suggests that the role of the allyl group may be to open up to the η^1 form to allow the arene to bind in the η^4 form. Phosphite dissociation is still required to allow the H_2 to bind; plausible first steps of the reduction are as follow:



(9.16)

Transfer Hydrogenation[19a] In this important variant of hydrogenation, the source of the hydrogen is not free H_2 but an easily reducible substrate, such as isopropanol.

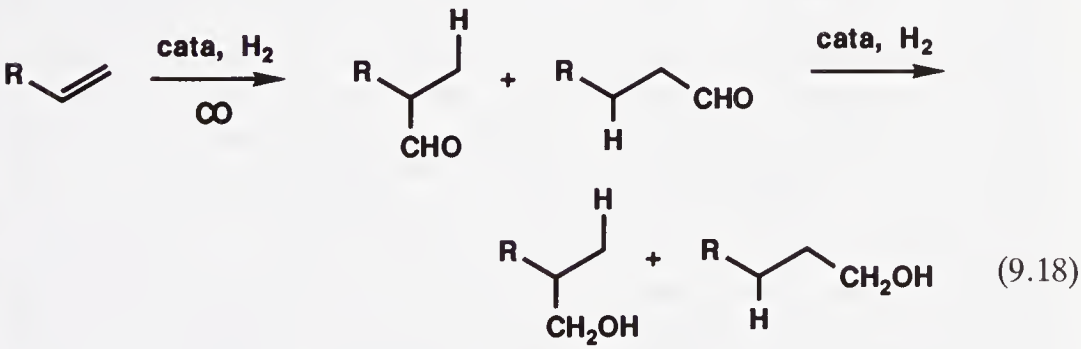
$$Me_2CHOH + RCH{=}CH_2 \longrightarrow Me_2C{=}O + RCH_2CH_3 \qquad (9.17)$$

Transfer hydrogenation is particularly good for the reduction of ketones and imines that are somewhat more difficult to reduce with H_2 than are C=C bonds. Bäckvall has shown how $RuCl_2(PPh_3)_3$ is effective at 80°C with added base as catalyst promoter. The role of the base is no doubt to form the isopropoxide ion, which presumably coordinates to Ru and by β elimination forms a hydride and acetone.

In ionic hydrogenation, the substrate is protonated and the resulting carbonium ion quenched with a hydride, such as $CpW(CO)_3H$. This is effective for ketones and hindered alkenes, but has not yet been made catalytic.[19b]

9.3 ALKENE HYDROFORMYLATION

In the late 1930s, Otto Roelen at Ruhrchemie discovered hydroformylation, sometimes called the *oxo* process, one of the first commercially important reactions to use a homogeneous catalyst. He found that an alkene can be converted to the homologous aldehyde by the addition of H_2 and CO, catalyzed by $Co_2(CO)_8$; further reduction to the alcohol is observed under some conditions (Eq. 9.18). Four million tons of aldehydes are made annually in this way.



(9.18)

A schematic mechanism of this reaction is shown in Fig. 9.4. The $Co_2(CO)_8$ first reacts with H_2 via a binuclear oxidative addition to give $HCo(CO)_4$, which is the active catalyst. The proposed catalytic cycle[20a] is shown in Fig. 9.4: CO dissociation generates the vacant sites required for the alkene and H_2. The first steps resemble hydrogenation in that an alkyl is formed by alkene insertion. Note that at this stage there is no hydride on the metal, so that instead of being trapped by reductive elimination with a hydride, as happens in hydrogenation, the alkyl undergoes a migratory insertion to give the corresponding acyl. H_2 probably binds to give an H_2 complex, followed by a heterolytic H_2 cleavage (e.g., Eq. 9.10) to give the product aldehyde and regenerate the catalyst.[20a] This route avoids oxidative addition of H_2, which has a high activation energy in this system. $HCo(CO)_4$ can also cleave the acyl to give the aldehyde by a binuclear reductive elimination but this is probably a minor pathway in the catalytic cycle.

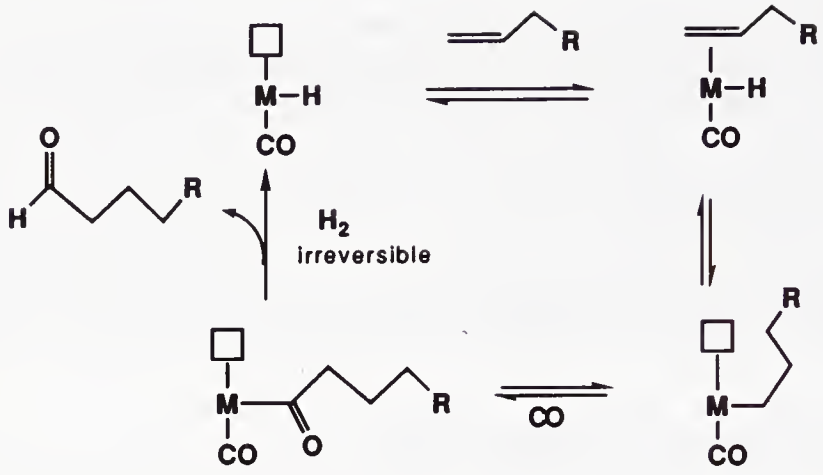


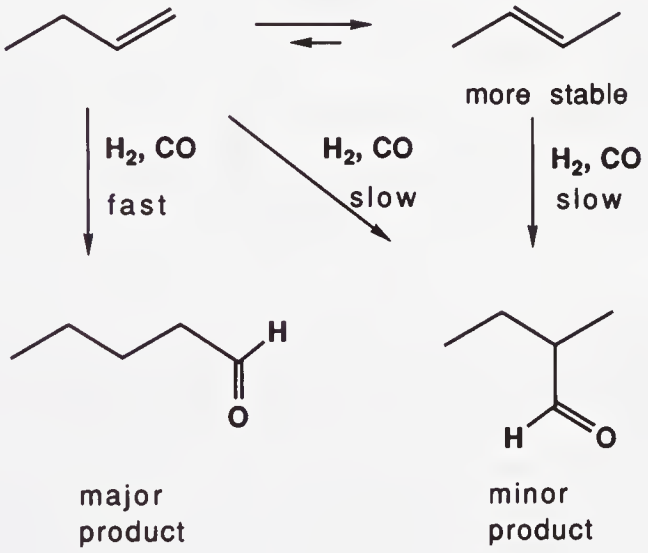
FIGURE 9.4 A catalytic cycle proposed for hydroformylation with $HCo(CO)_4$ as catalyst. Alkene insertion also takes place in the opposite direction to give the 2° alkyl, which goes on to the branched aldehyde RCH(Me)CHO, but this parallel and usually less important cycle is not shown.

Either 1° or 2° aldehydes can be formed from an alkene such as propene; the linear 1° material is much more valuable commercially. Since this is an irreversible cycle, the 1° and 2° products do not come to equilibrium, the kinetic ratio of products being retained. It is not so much the regiochemistry of alkene insertion that decides this ratio, but the rate at which the 1° and 2° alkyls are trapped by migration to CO. Slaugh and Mullineaux[20b] made the commercially important discovery that the addition of phosphines, such as $P(n\text{-}Bu)_3$, gives a catalyst that is not only much more active (5–10 atm pressure are required vs. 100–300 atm for the unmodified catalyst)[1], but which also favors the 1° over the 2° aldehyde to a greater extent (8:1 vs. 4:1). It is believed that the steric bulk of the phosphine both encourages the formation of the less hindered 1° alkyl and speeds up migratory insertion.

With some substrates, $HCo(CO)_4$ is thought to transfer H• to the alkene. This tends to happen when the substrate radical is specially stabilized (e.g., $PhCH•—CH_3$ from $PhCH{=}CH_2$). The radical may then recombine with the Co to give an alkyl. This accounts for the preferential formation of the 2° aldehyde from styrene.

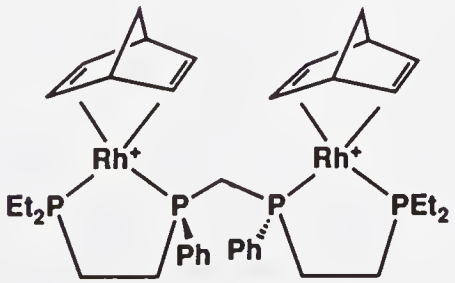
The more highly phosphine substituted rhodium species $RhH(CO)(PPh_3)_3$ is an even more active catalyst, 1 atm pressure and 25°C being sufficient, and it is even more selective for the 1° product.[21a] $Rh_4(CO)_{12}$ is also very active but has very poor selectivity, so once again, the presence of phosphine improves the selectivity. The mechanism is broadly similar to the Co-catalyzed process. In practice, excess PPh_3 is added to the reaction mixture to prevent the formation of the less selective $HRh(CO)_4$ and $HRhL(CO)_3$ species by phosphine dissociation. The system is also an active isomerization catalyst, because much the same mixture of aldehydes is formed from any of the

possible isomers of the starting alkene. This is a very useful property of the catalyst, because internal isomers of an alkene are easier to obtain than the terminal one. The commercially valuable terminal aldehydes can still be obtained from these internal alkenes. The catalyst first converts the internal alkene, such as 2-butene, to a mixture of isomers including the terminal one. The latter is hydroformylated much more rapidly than the internal ones, accounting for the predominant 1° aldehyde product. Since the terminal alkene can only ever be a minor constituent of the alkene mixture (because it is thermodynamically less stable than the other isomers), this reaction provides another example of a catalytic process in which the major product is formed from a minor intermediate:



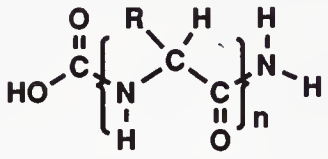
(9.19)

Binuclear Catalysts Stanley[21b] et al. have shown how a rhodium complex that is a poor catalyst in monomeric form becomes very active and selective when connected in a binuclear system with a methylene bridge as shown below. Linear to branched ratios as high as 27 to 1 can be achieved. A rhodium hydride is believed to attack a RhCOR group at the neighboring site in the product forming step. This shows how the proximity of two metals can provide useful chemical effects *without* their being permanently connected by a metal-metal bond.

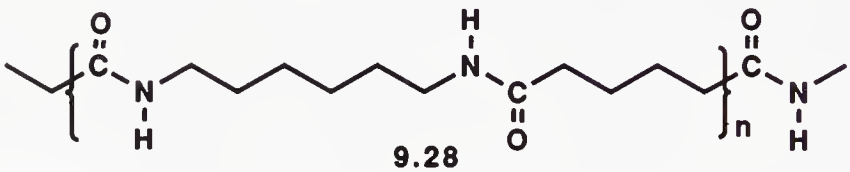


9.4 THE HYDROCYANATION OF BUTADIENE[22]

The existence of proteins (**9.27**) suggested to Carothers at du Pont that the peptide link, —NHCO—, might be useful for making artificial polymers. Out of this work came Nylon-6,6 (**9.28**), one of the first useful petroleum-based polymers.



9.27



9.28
Nylon-6,6

Now that the original patents have long expired, the key to making this material commercially is having the least expensive source of adiponitrile. The polymer itself is made from adipoyl chloride and hexamethylene diamine, both of which are made from adiponitrile. This nitrile was originally made by the chlorination of butadiene (Eqs. 9.20–9.22). This route involves Cl_2, which leads to corrosion difficulties, only to give NaCl as a by-product, which involves disposal problems. All large commercial concerns defend their key intermediates by trying to find better routes to them before their competitors do. The advent of homogeneous catalysis provided an opportunity to improve the synthesis of adiponitrile very considerably. Fortunately for du Pont it was in their laboratories that the new route was discovered by Drinkard.

$$CH_2{=}CHCH{=}CH_2 \xrightarrow{Cl_2} ClCH_2CH{=}CHCH_2Cl \xrightarrow{NaCN}$$

$$NCCH_2CH{=}CHCH_2CN \xrightarrow{H_2,\ catal.} \underset{\text{adiponitrile}}{NC(CH_2)_4CN} \quad (9.20)$$

$$\underset{\text{hexamethylene diamine}}{H_2NCH_2(CH_2)_4CH_2NH_2} \xleftarrow{H_2,\ catal.} \underset{\text{adiponitrile}}{NC(CH_2)_4CN} \xrightarrow{(i)\ H_2O,\ (ii)\ PCl_3}$$

$$\underset{\text{adipoyl chloride}}{ClCO(CH_2)_4COCl} \quad (9.21)$$

$$H_2NCH_2(CH_2)_4CH_2NH_2 + ClCO(CH_2)_4COCl \longrightarrow \text{nylon} \quad (9.22)$$

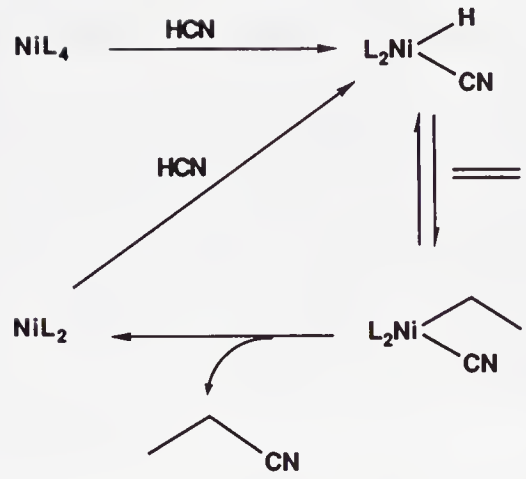


FIGURE 9.5 The hydrocyanation of ethylene by NiL_4 [L = P(O*o*-tolyl)$_3$].

In the hydrocyanation of butadiene, 2 mol of HCN are added to butadiene with a nickel complex as catalyst to obtain adiponitrile directly.

$$CH_2{=}CHCH{=}CH_2 \xrightarrow{2HCN,\ NiL_4} NC(CH_2)_4CN \qquad (9.23)$$

For simplicity, we will first look at the hydrocyanation of ethylene, for which the cycle shown in Fig. 9.5 is believed to operate. The oxidative addition of HCN to the metal gives a 16e nickel hydride that undergoes ethylene insertion to give an ethyl complex. Reductive elimination of EtCN gives the product. The reaction with butadiene is more complex. In the alkene insertion, the product is an allyl complex (Fig. 9.6); reductive elimination now gives 3-pentene nitrile. This internal alkene cannot be directly hydrocyanated to give adiponitrile, but has to be isomerized first. $HNiL_3^+$, present in the reaction mixtures, is a very active isomerization catalyst by the hydride mechanism. The internal alkene is therefore isomerized to the terminal alkene and hydrocyanated to give adiponitrile. One remarkable feature of the isomerization is that the most stable alkene, 2-pentene nitrile, is formed only at a negligible rate. This is fortunate, because once it is formed it cannot revert to the 3- and 4-isomers, nor is it hydrocyanated, so remains as a contaminating by-product. The terminal alkene, 4-pentene nitrile, once formed, is rapidly hydrocyanated selectively to the linear adiponitrile product; all the other possible dinitriles are formed at a much slower rate.

An important step at several points in the catalytic cycle is loss of L to open up a vacant site at the metal. The rate and equilibrium constant for these dissociative steps are controlled largely by the bulk of the ligand. Electron-withdrawing ligands are required to facilitate the other steps in the cycle, so that one of the best is *o*-tolyl phosphite, which combines steric bulk with a strongly electron-withdrawing character.

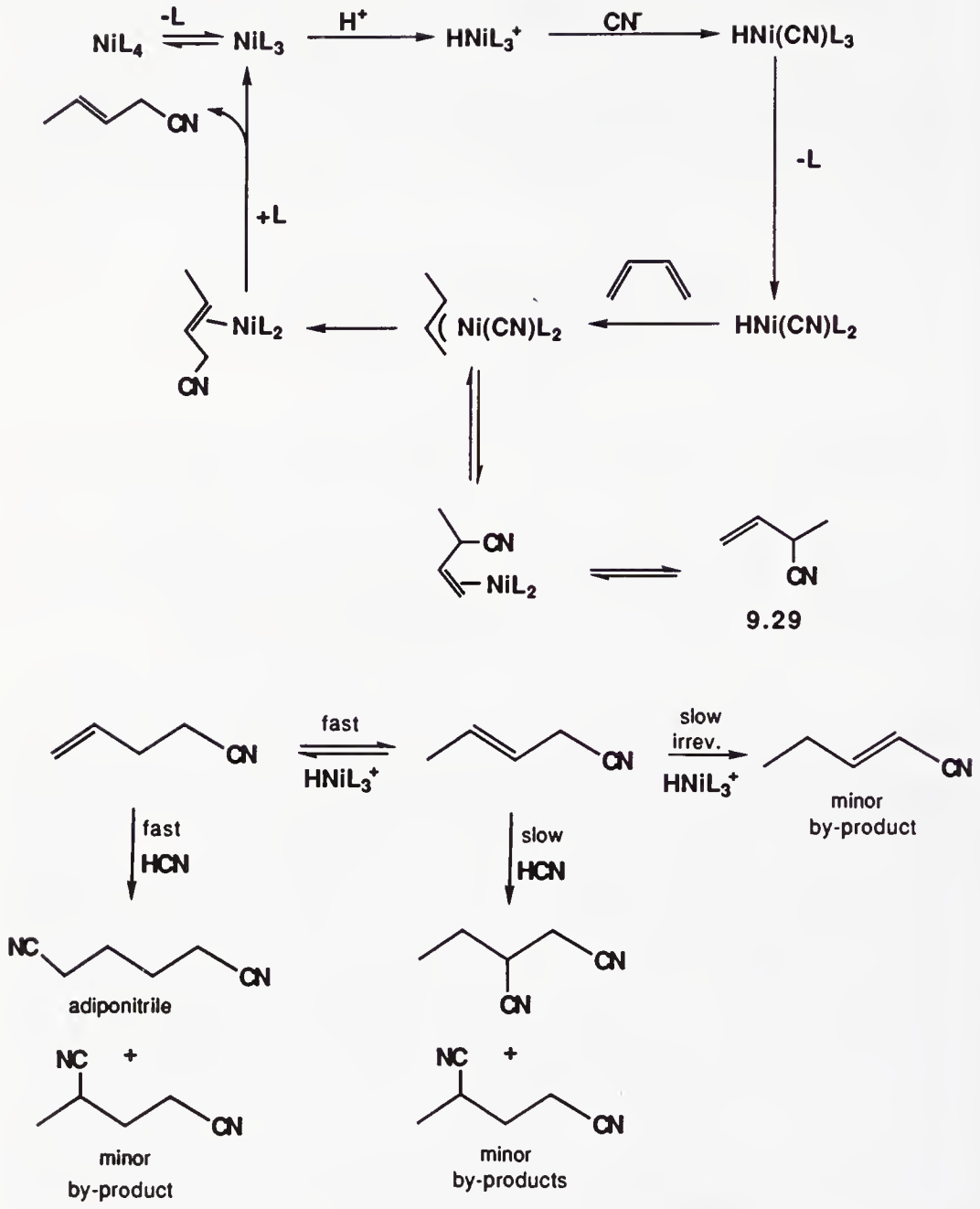


FIGURE 9.6 The hydrocyanation of butadiene by NiL_4 [L = P(O*o*-tolyl)$_3$].

When the first HCN adds to butadiene, some undesired branched 2-methyl-3-butenenitrile, **9.29** in Figure 9.6, is formed along with the desired linear 3-butenenitrile. Interestingly, the first HCN addition to butadiene is reversible, because the branched nitrile can be isomerized to the linear form with NiL_4. This means that **9.29**, which is an activated allylic nitrile, can oxidatively add to the nickel to give back the η^3-allyl nickel cyanide. Labelling studies suggest that this intermediate goes back to HCN and butadiene, before readdition

to give the linear nitrile. The formation of the saturated dinitriles is irreversible, however.

The Lewis acid BPh_3 is a useful cocatalyst for the reaction. Such additives are often termed *promoters*. In this case the promoter improves the selectivity of the system for linear product (it is not clear exactly why) and improves the life of the catalyst. A catalyst deactivates when it loses some or all of its activity by going down an irreversible path that leads to an inactive form of the metal complex. In this case, the formation of the inactive $Ni(CN)_2$ is the principal deactivation step. This can happen in several ways; an example is shown here:

$$HNiL_2(CN) \xrightarrow{HCN} \{H_2NiL_2(CN)\}^+CN^- \xrightarrow{-H_2} \{NiL_2(CN)\}^+CN^- \xrightarrow{-L} Ni(CN)_2 \quad (9.24)$$

The promoter is believed to inhibit the reaction in Eq. 9.24 by binding to the NiCN groups by the lone pair on nitrogen. This lowers the basicity of the metal and makes it less likely to protonate. Binding of the promoter to the CN group can be detected by IR spectroscopy: on adding BPh_3 to a solution of $HNiL_2(CN)$, the ν(CN) stretching vibration moves 56 cm^{-1} to higher frequency and the intensity increases. This is because the lone pair on nitrogen has some C—N antibonding character, so depleting the electron density in this orbital by transfer of some of the electron density to boron strengthens the C—N bond and moves the corresponding vibration to higher frequency. The intensity of IR bands is controlled by the change in dipole moment during the vibration ($d\mu/dr$); by polarizing the ligand, the Lewis acid increases $d\mu/dr$.

9.5 ALKENE HYDROSILATION AND HYDROBORATION

Hydrosilation This is the addition of a silane $R_3Si—H$ across a C=C double bond as illustrated in Eq. 9.25. It is a reaction of some commercial importance for the synthesis of silicon-containing monomers, for use in such products as the self-curing silicone rubber formulations sold for domestic use.

$$Cl_3Si—H + H_2C{=}CH_2 \longrightarrow Cl_3Si—CH_2—CH_3 \quad (9.25)$$

One of the earliest catalysts (1957), H_2PtCl_6, or Speier's catalyst,[23] is extremely active; 0.1 ppm of catalyst is effective. Commercially, the catalyst is normally not even recovered from the product, even though Pt is a precious metal. There is an induction period before hydrosilation begins, which is attributed to reduction of H_2PtCl_6 to the active catalyst, which was taken to be a Pt(II) species. The mechanism of Chalk and Harrod,[24] shown in Fig. 9.7*a*, was accepted for many years. Only recently has it been suggested[13d,25]

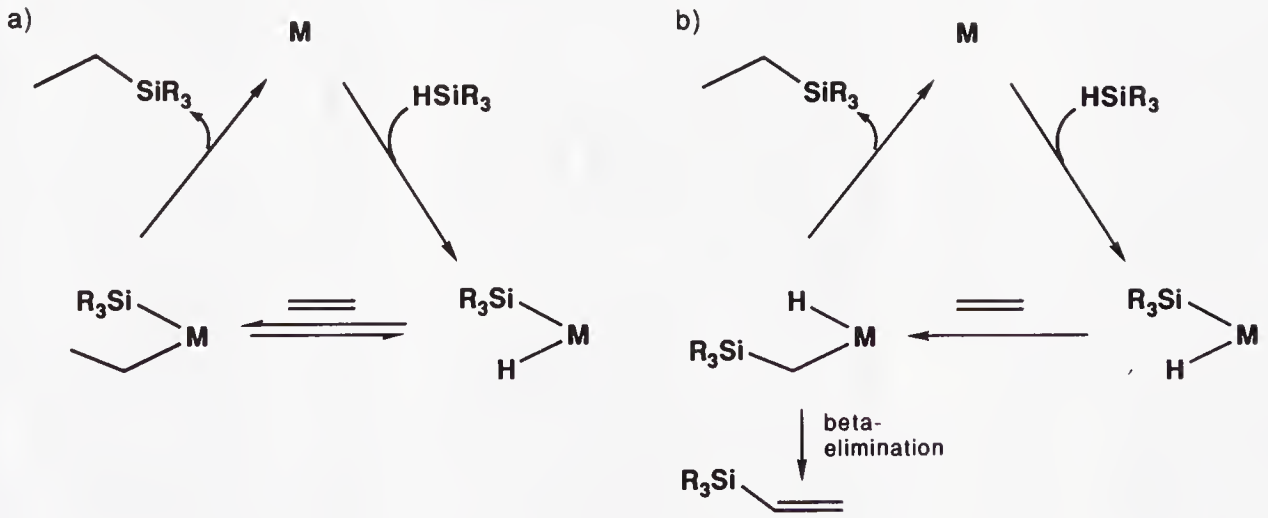


FIGURE 9.7 (*a*) The Chalk–Harrod mechanism for alkene hydrosilation. (*b*) An alternative mechanism in which insertion takes place into the M—Si bond. This accounts for the formation of vinylsilane, sometimes seen as a by-product in hydrosilation.

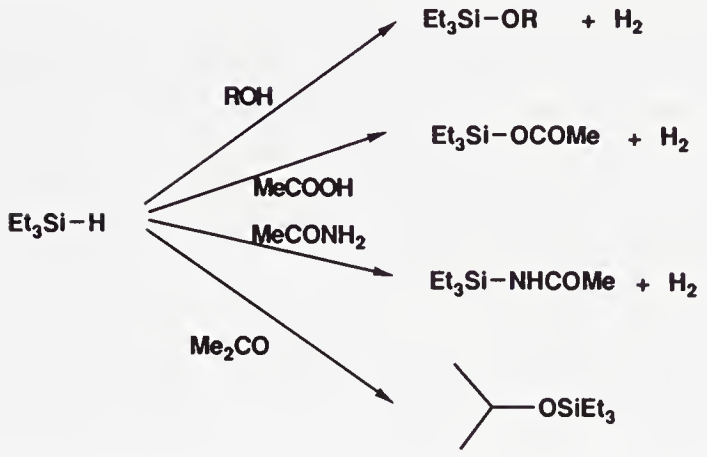


FIGURE 9.8 Other metal-catalyzed reactions of silanes.

that the true catalyst is colloidal platinum metal. A colloid of this type is a suspension of very fine particles (ca. 10–1000 Å radius) of metal in a liquid, which will not settle out of the liquid even on prolonged standing. This implies that in its active form of Speier's catalyst is a heterogeneous catalyst. In spite of this new development, other hydrosilation catalysts, such as $Co(CO)_8$, $Ni(cod)_2$, $NiCl_2(PPh_3)_2$, and $RhCl(PPh_3)_3$, do seem likely to be authentically homogeneous and may well operate by the Chalk–Harrod mechanism.

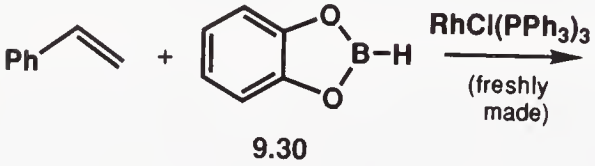
As in hydroformylation, both linear and branched products can be obtained from a substituted alkene like $RCH{=}CH_2$:

$$RCH{=}CH_2 + R'_3Si{-}H \xrightarrow{\text{catal.}} RCH_2CH_2SiR'_3 + RCH(Me)SiR'_3 \quad (9.26)$$

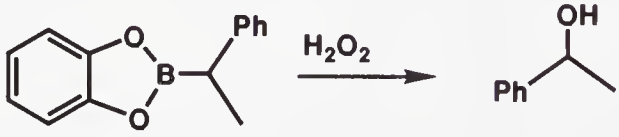
The amount of each product obtained depends on the catalyst and the nature of R and R′, but the linear form generally tends to predominate. The unsaturated vinylsilane, $RCH{=}CHSiR'_3$, is also a product. Although minor in most cases, conditions can be found in which it predominates. The Chalk–Harrod mechanism cannot explain the formation of this *dehydrogenative silation* product, but the alternate mechanism of Fig. 9.7*b* in which the alkene inserts into the M—Si bond first does explain it because β elimination of the intermediate alkyl leads directly to the vinylsilane. As in hydrogenation, syn addition is generally observed. Apparent anti addition is due to isomerization of the intermediate metal vinyl, as we saw in Eqs. 7.21 and 7.22, a reaction in which initial insertion of alkyne into the M—Si bond must predominate (>99%).[26] $Co_2(CO)_8$ also catalyzes a number of other reactions of silanes, as shown in Fig. 9.8.

Hydroboration $RhCl(PPh_3)_3$ catalyzes the addition of the B—H bond in catecholborane (**9.30**) to alkenes (eq. 9.27). This reaction also goes without catalyst, but the catalytic reaction has usefully different chemo-, regio-, and stereoselectivities.[27] Oxidative workup of the alkylboron product normally

gives the corresponding alcohol. The catalytic cycle may be complex, with more than one species contributing to activity, and the results depend on whether aged or freshly prepared catalyst is used. For example, fresh catalyst (or aged catalyst with excess PPh_3) gives >99% branched product, PhCHOHMe, from styrene, while aged catalyst gives approximately 1:4 branched:linear alcohol. The uncatalyzed reaction gives linear alcohol. In certain cases, dehydrogenative hydroboration is seen and the vinylboron product appears as an aldehyde or ketone on oxidative workup. As in hydrosilation this may be the result of C=C insertion into Rh—X (X = B or Si) bonds,[28] followed by β elimination. In the stoichiometric reaction of catecholborane with $RhCl(PPh_3)_3$, one product is the B—H oxidation product, $RhHCl(BR_2)(PPh_3)$.



9.30



(9.27)

Future Prospects An area in which we may expect future developments is in the imaginative application of currently known catalytic reactions to the commercial and laboratory synthesis of new classes of compounds.[2] Our understanding of the catalysis of oxidation is still in a much more primitive state than is the case for the reductive reactions discussed in this chapter, and this remains a great challenge. The current interest in developing environmentally sound synthetic routes in the chemical industry will also provide important new goals for homogeneous catalysis for the future.

REFERENCES

1. C. Masters, *Homogeneous Transition-Metal Catalysis,* Chapman, Hall, London, 1981.
2. G. W. Parshall, *Homogeneous Catalysis,* Wiley-Interscience, New York, 1980.
3. (a) R. B. Jordan, *Reaction Mechanisms of Inorganic and Organometallic Systems,* Oxford University Press, Oxford, 1991; (b) B. R. James, *Adv. Organometal. Chem.*, **17,** 319, 1979; (c) J. Halpern and S. Wong, *J. Chem. Soc., Chem Commun.*, 629, 1973; (d) P. Meakin, J. P. Jesson, and C. A. Tolman, *J. Am. Chem. Soc.*, **94,** 3240, 1972; (e) J. Halpern et al., *J. Am. Chem. Soc.*, **99,** 8055, 1977.
4. G. A. Somorjai, *Chemistry in Two Dimensions,* Cornell Univ. Press, Ithaca, N.Y., 1981.

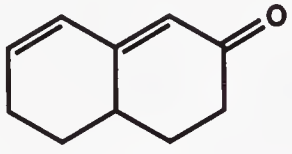
5. C. Walsh, *Enzymatic Reaction Mechanisms,* Freeman, San Francisco, 1979.
6. D. Evans, J. Osborn, and G. Wilkinson, *J. Chem. Soc.* (*A*), 3133, 1968.
7. C. P. Casey and C. R. Cyr, *J. Am. Chem. Soc.,* **95,** 2248, 1973.
8. R. H. Crabtree, *Acct. Chem.Res.,* **12,** 331, 1979.
9. J. M. Brown et al., *Chem. Commun.,* 348, 1982; *Tetrahedron Lett.,* **25,** 1393, 1984; R. H. Crabtree and M. W. Davis, *Organometallics,* **2,** 681, 1983; G. Stork et al., *J. Am. Chem. Soc.,* **105,** 1072, 1983; D. A. Evans et al., ibid, **106,** 3866, 1984.
10. (a) R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.,* **98,** 2134, 2143 and 4450, 1976. (b) W. A. Nugent, T. V. RajanBabu, and M. J. Burk, *Science,* **259,** 479, 1993, and refs. cited.
11. J. Halpern et al., *J. Am. Chem. Soc.,* **102,** 5954, 1980.
12. R. D. Larsen et al., *J. Am. Chem. Soc.,* **111,** 7650, 1989.
13. (a) P. Maitlis et al., *J. Mol. Catal.,* **7,** 543, 1980; (b) D. R. Anton and R. H. Crabtree, *Organometallics,* **2,** 855, 1983; (d) J. P. Collman et al., *J. Am. Chem. Soc.,* **106,** 2569, 1984; (d) L. N. Lewis and N. Lewis, *J. Am. Chem. Soc.,* **108,** 7228, 1986; (e) J. W. Faller and J. Parr, *J. Am. Chem. Soc.,* **115,** 804, 1993; (f) H. B. Kagan et al., *J. Am. Chem. Soc.,* **108,** 2353, 1986; R. Noyori, *Angew. Chem., Int. Ed.,* **30,** 49, 1991.
14. (a) D. Evans, J. Osborn, J. A. Jardine, and G. Wilkinson, *Nature,* **208,** 1203, 1965; (b) P. Brothers, *Prog. Inorg. Chem.,* **28,** 1, 1981.
15. J. E. Bercaw et al., *J. Am. Chem. Soc.,* **109,** 203, 1987.
16. (a) R. H. Crabtree, M. Lavin, and L. Bonneviot, *J. Am. Chem. Soc.,* **108,** 4032, 1986; (b) R. H. Crabtree and D. G. Hamilton, *J. Am. Chem. Soc.,* **106,** 3124, 1986.
17. J. Iguchi, *J. Chem. Soc. Jpn.,* **60,** 1287, 1939; R. Mason and D. W. Meek, *Angew. Chem., Int. Ed.,* **17,** 183, 1978.
18. L. S. Stuhl, M. Rakowski-Dubois, F. J. Hirsekorn, J. R. Bleeke, A. Z. Stevens, and E. L. Muetterties, *J. Am. Chem. Soc.,* **97,** 237, 1975; E. L. Muetterties and J. R. Bleeke, *Acct. Chem. Res.,* **12,** 324, 1979; see also K. Jonas, *J. Organometal. Chem.,* **400,** 165, 1990.
19. (a) J. E. Bäckvall et al., *Chem. Commun.,* 1063, 1991; 337, 980, 1992; (b) R. M. Bullock, J. R. Norton, et al., *Angew Chem., Int. Ed.,* **31,** 1233, 1992.
20. (a) T. Ziegler and L. Versluis, *Adv. Chem. Ser.,* **230,** 75, 1992; (b) L. H. Slaugh and R. D. Mullineaux, *J. Organometal. Chem.,* **13,** 469, 1968.
21. (a) I. Tkatchenko, in *Comprehensive Organometallic Chemistry,* G. Wilkinson (ed.), **8,** 101, 1982. (b) G. B. Stanley et al., *Science,* **260,** 1784. 1993.
22. W. C. Siedel and C. A. Tolman, *Ann. N.Y. Acad. Sci.,* **415,** 201, 1983.
23. J. S. Speier, *Adv. Organometal. Chem.,* **17,** 407, 1979.
24. J. F. Harrod and A. J. Chalk, *J. Am. Chem. Soc.,* **88,** 3491, 1966.
25. (a) In 1961,[25b] it was suggested that the Speier catalyst was heterogeneous, but that view was later reversed;[25c] (b) R. A. Benkeser et al., *J. Am. Chem. Soc.,* **83,** 4385, 1961; (c) R. A. Benkeser et al., *J. Am. Chem. Soc.,* **90,** 1871, 1968.
26. R. S. Tanke and R. H. Crabtree, *J. Am. Chem. Soc.,* **112,** 7984, 1990.

27. D. A. Evans and G. C. Fu, *J. Org. Chem.*, **55,** 2280, 1990; K. Burgess, R. T. Baker, et al., *J. Am. Chem. Soc.*, **114,** 9350, 1992; K. Burgess, *Chem. Rev.*, **91,** 1179, 1991.

28. R. T. Baker, T. B. Marder, et al., *J. Am. Chem. Soc.*, **115,** 4367, 1993.

PROBLEMS

1. Compound **9.31** is hydrogenated with a number of homogeneous catalysts. The major product in all cases is a ketone, $C_{10}H_{16}O$, but small amounts of an acidic compound $C_{10}H_{12}O$, **9.32**, are also formed. What is the most reasonable structure for **9.32**, and how is it formed?



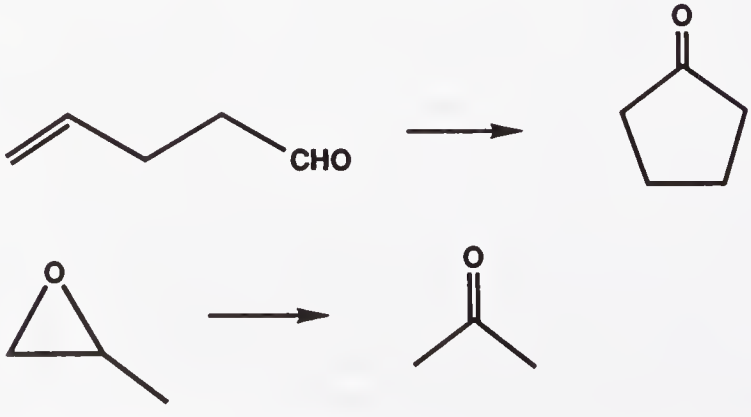
9.31

2. Would you expect Rh(triphos)Cl to be a hydrogenation catalyst for alkenes (triphos = $Ph_2PCH_2CH_2CH_2PPhCH_2CH_2CH_2PPh_2$)? How might the addition of BF_3 or $TlPF_6$ affect the result?

3. Predict what you would expect to happen in the hydrocyanation of 1,3-pentadiene with HCN and $Ni\{P(OR)_3\}_4$?

4. Write out a mechanism for arene hydrogenation with (η^3-allyl)$Co\{P(OMe)_3\}_3$, invoking the first steps shown in Eq. 9.14. Why do you think arene hydrogenation is so rare for homogeneous catalysts? Do you think that diphenyl or naphthalene would be more or less easy to reduce than benzene? Explain your answer.

5. Suggest plausible mechanisms for the reactions shown below, which are catalyzed by a Rh(I) complex, such as $RhCl(PPh_3)_3$.



6. Comment on the possibility of finding catalysts for each of the following:

$$\text{Propane} \longrightarrow \text{cyclopropane} + H_2$$

$$CO_2 \longrightarrow CO + \tfrac{1}{2}O_2$$

$$CH_4 + \tfrac{1}{2}O_2 \longrightarrow CH_3OH$$

7. What do you think is the proper formulation for H_2PtCl_6? Why do you think the compound is commonly called chloroplatinic *acid*? Make sure your formulation gives a reasonable electron count and oxidation state.

8. In some homogeneous alkyne hydrosilations, a second product (B) is sometimes found in addition to the usual one (A). How do you think B is formed? Try to write a balanced equation for the reaction, assuming an A/B ratio of 1:1 and you will see that A and B cannot be the only products. Suggest the most likely identity for a third *organic* product C, which is always formed in equimolar amounts with B.

$$RC{\equiv}CH + R_3SiH = \underset{A}{RCH{=}CHSiR_3} + \underset{B}{RC{\equiv}CSiR_3}$$

9. The reaction

$$2CH_2{=}CHCO_2Et = EtOOCCH{=}CHCH_2CH_2COOEt$$

catalyzed by $(\eta^6\text{-}C_6H_6)Ru(CH_2{=}CHCO_2Et)_2/Na[C_{10}H_8]$ has been studied by workers at du Pont as a possible route to adipic acid, an important precursor for nylon. Suggest a mechanism. How might you use a slightly modified substrate to test your suggestion? ($Na[C_{10}H_8]$ is simply a reducing agent.)

10. $(\eta^6\text{-}C_6H_6)Mo(CO)_3$ is a catalyst for the reduction of 1,3-dienes to cis monoenes with H_2; suggest how this might work, why the cis product is formed, and why the alkene is not subsequently reduced to alkane.

$$RCH{=}CH{-}CH{=}CHR + H_2 = \textit{cis}\text{-}[RCH_2{-}CH{=}CH{-}CH_2R]$$

CHAPTER 10

CHARACTERIZATION OF ORGANOMETALLIC COMPOUNDS*

We now look at some of the main methods of identifying a new complex, assigning its stereochemistry, and learning something about its properties. We will look at some applications of the most commonly used spectroscopic and crystallographic methods to organometallic chemistry. Citations to both introductory and more advanced treatments of the methods themselves are also included.

10.1 ISOLATION

Before we can study the complexes, we have to isolate them in a pure form. The methods used resemble those of organic chemistry. Most organometallic complexes are involatile crystalline materials, although some are liquids [e.g., $CH_3C_5H_4Mn(CO)_3$], or even vapors [e.g., $Ni(CO)_4$] at room temperature and pressure. They normally have solubilities similar to those of organic compounds. The main difference from organic chemistry is that many organometallic compounds are "air-sensitive," which usually means that they react with O_2 and sometimes with water. The electropositive *f*-block, and early *d*-block metals are the most reactive. Crystalline material is usually stabler than are solutions, but in many cases both must be kept under dry N_2 or Ar, and air and water must be completely removed from all the solvents used. One general method involves using flasks and filter devices fitted with ground joints

*Undergraduates taking this course may not have had a physical chemistry course. The material on spectroscopy has therefore been gathered together here, so that instructors have the option of omitting all or part of it without losing the narrative flow of the rest of the book.

for making connections and vacuum taps for removing air or admitting nitrogen. This so-called Schlenk glassware allows all operations to be carried out under an inert atmosphere on an ordinary benchtop. In an alternative setup, operations are carried out in a N_2-filled inert atmosphere box. This sounds more formidable than it is, and the details of the techniques used are available in an excellent monograph.[1a]

10.2 ^{1}H NMR SPECTROSCOPY

A variety of spectroscopic techniques are also available for structure determination.[1b] Organometallic chemists tend to rely heavily, perhaps too heavily, on NMR. The ^{1}H NMR technique[2] is perhaps most useful for metal hydrides, which resonate in an otherwise empty region of the spectrum (0 to -40δ) to high field of TMS.[3] This unusual chemical shift is ascribed to shielding by the metal *d* electrons, and the observed shifts generally become more negative on going to higher d^n configurations. The number of hydrides present may be determined by integration, or if phosphines are also present, from ^2J(P,H) coupling seen in the ^{31}P NMR (Section 10.4).[4] When we refer to ^nJ(X,Y) coupling, we mean the coupling of nucleus X and Y; *n* indicates the number of bonds that connect X and Y by the shortest route. ^2J(P,H) coupling to the phosphorus nuclei of cis or trans phosphines to the hydride proton in phosphine hydride complexes can also be seen in the ^{1}H spectrum. Trans couplings (90–160 Hz) are larger than cis ones (10–30 Hz), and this can be very useful in determining the stereochemistry of the molecule. Figure 10.1 shows the spectra of some octahedral iridium hydrides that illustrate how the stereochemistries can be deduced. 5-, 7-, 8-, and 9-coordinate hydrides are often *fluxional.* That is to say the molecules are nonrigid, so that the ligands exchange positions within the complex fast enough to become equivalent on the NMR timescale ($\sim 10^{-2}$ sec). We will look at the consequences of fluxionality in more detail later (Section 10.5).

Virtual Coupling Alkyl phosphines, such as PMe_3 or PMe_2Ph, also give important stereochemical information in the ^{1}H NMR. If two such phosphines are cis, they behave independently, and we usually see a doublet for the methyl groups, due to coupling to the $I = \frac{1}{2}$ ^{31}P nucleus. If the two phosphines are trans, the phosphorus–phosphorus coupling becomes so large that the ^{1}H NMR of the methyl substituents is affected. Instead of a simple doublet, we see a distorted triplet with a broad central peak. This behavior is called *virtual coupling,*[3] and means that the methyl group appears to be coupled to both its own and the trans phosphorus nucleus about equally, giving rise to the virtual triplet (Fig. 10.2*a*). This happens when ^2J(P,P) between equivalent P nuclei becomes large, as it is when the phosphines in question are trans. Intermediate values of the phosphorus–phosphorus coupling constant, which

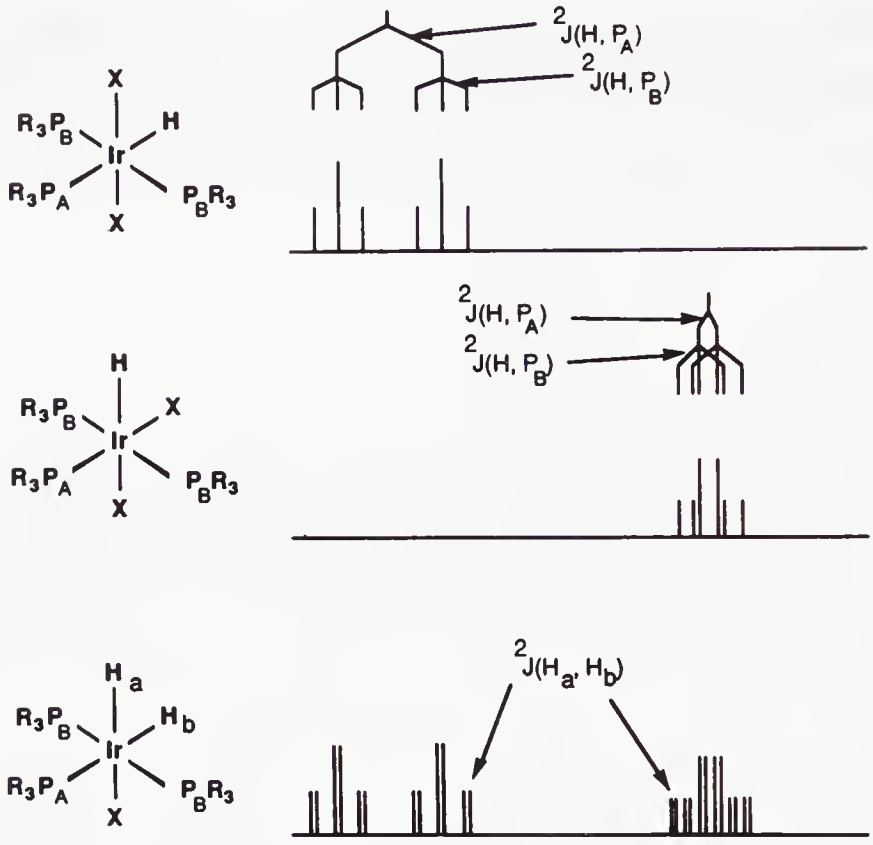


FIGURE 10.1 The ^1H NMR spectra of some iridium hydrides (hydride region). Each stereochemistry gives a characteristic coupling pattern.

may occur for P—M—P angles between 90° and 180°, give patterns intermediate between a doublet and a virtually coupled triplet (Fig. 10.2*b*,*c*).

Diastereotopy The ^1H NMR spectrum of PMe_2Ph ligand in a metal complex gives useful information about the symmetry of the complex. Suppose we want to distinguish between **10.1** and **10.2** (Fig. 10.3) from the NMR alone. **10.1** has a plane of symmetry (shown in the figure) containing X, Y, the PMe_2Ph phosphorus atom, and the metal. Note that in the rotamer of PMe_2Ph in which the Ph group also lies in the plane of symmetry, the mirror plane reflects one P—Me group into the other and makes them equivalent. In **10.2**, on the other hand, there is no such plane of symmetry and Me′ and Me″ are inequivalent. When this happens the two methyls are called *diastereotopic* groups.[2a] In general, two groups will be inequivalent if no symmetry element of the molecule relates the two groups. By far the most common situation is the presence of a plane of symmetry that contains the M—P bond; the presence of such a plane makes the two methyls equivalent. Diastereotopic groups are inequivalent and will generally resonate at different chemical shifts. We will therefore see a simple doublet (due to coupling to phosphorus) for **10.1**, and a pair of doublets for **10.2**. Because each doublet comes at a different

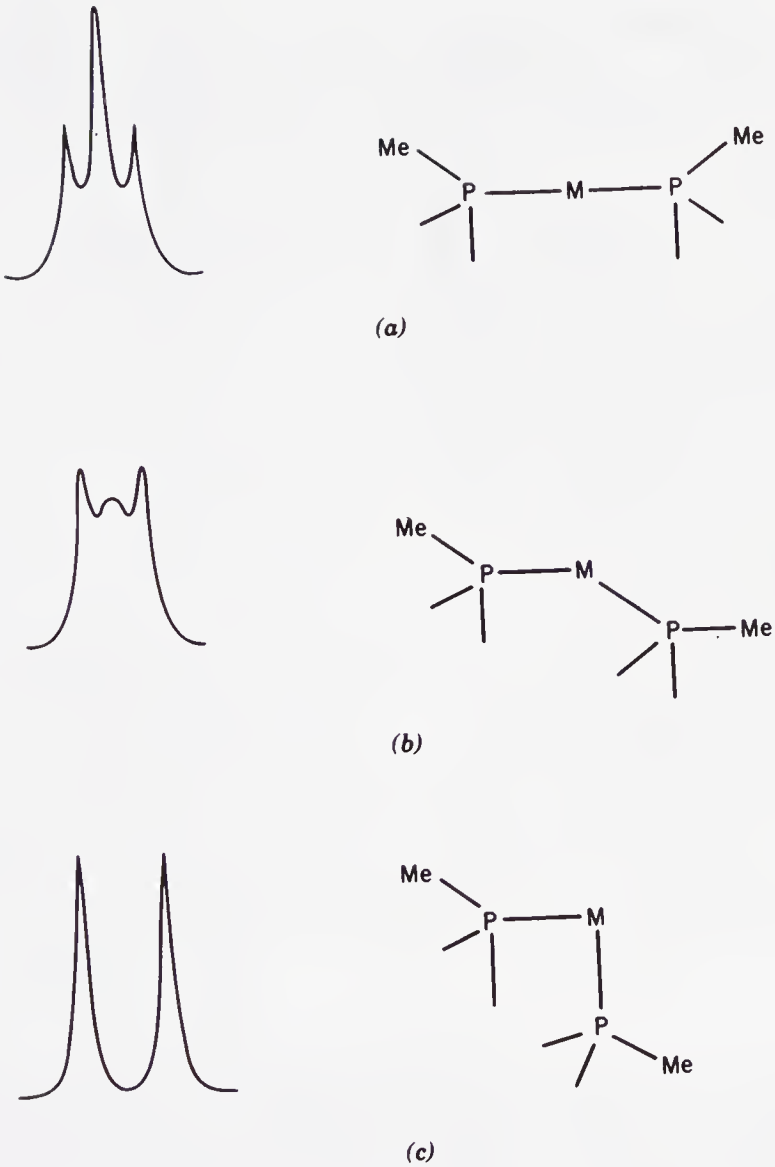
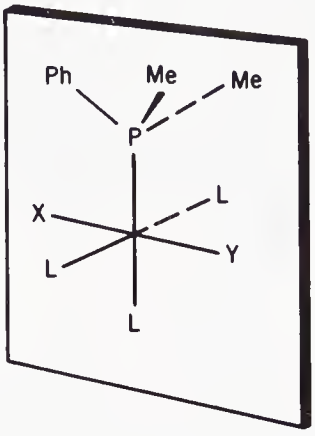
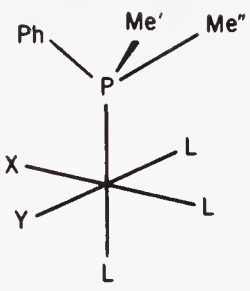


FIGURE 10.2 Virtual coupling in the P*Me* proton resonance of methylphosphine complexes. Each methyl group shows coupling both to its own phosphorus nucleus and to that of the second phosphine as long as ^2J(P, P′) is large enough. As the P—M—P angle decreases from 180°, the virtual coupling decreases, until at an angle of 90°, the appearance of the spectrum is a simple doublet, owing to coupling of the phosphorus methyl protons only to their own phosphorus nucleus, not that of the second phosphine.

chemical shift, the appearance of the spectrum will be different at a different magnetic field, as shown in Fig. 10.3. The resonances for the diastereotopic groups differ by a certain chemical shift; the pattern therefore changes at higher field (also shown in Fig. 10.3), where there are more hertz per ppm (parts per million).[2a] The same inequivalence is found for any compound



10.1



10.2

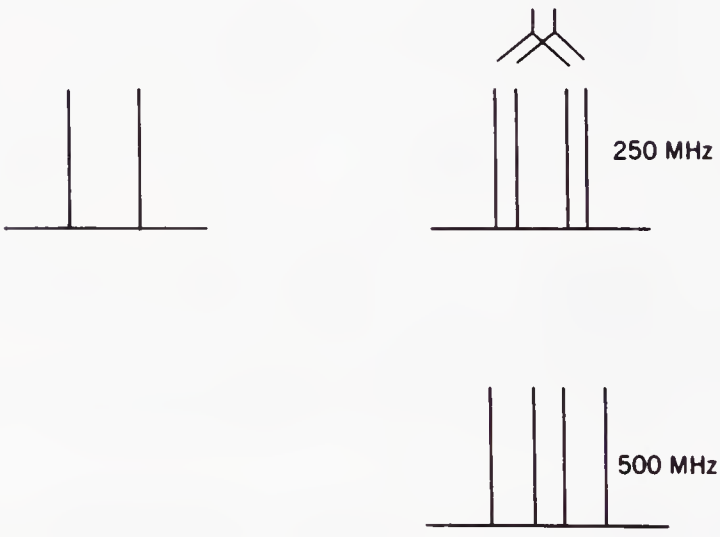
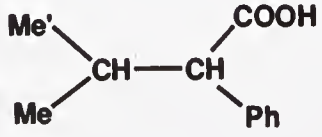


FIGURE 10.3 The methyl groups in **10.1** are equivalent in the proton NMR because of the presence of a mirror plane that contains the M—P bond; they appear as a single doublet due to ^2J(P, H) coupling. The methyl groups in **10.2** are inequivalent (diastereotopic) and so resonate at different frequencies. The two distinct doublets that result do not appear the same at a higher field and so are distinguishable from a doublet of doublets due to coupling, the appearance of which would be essentially invariant with field.

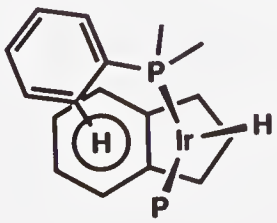
(e.g., **10.3**) in which no element of symmetry exists that will transform one of the two otherwise identical groups into the other. Structures **10.2** and **10.3** show inequivalent Me groups, whether the M—P or C—C bonds are freely rotating or not.



10.3

Chemical Shifts In organic compounds, we are used to thinking of certain ranges of chemical shift values as being diagnostic for certain groups. We have to be more cautious in organometallic chemistry, because the shifts are much more variable. For example, the vinyl protons of a coordinated alkene can resonate anywhere from 2 to 5δ (free alkene: 5–7δ). In the metalacyclopropane (X_2) extreme, the shifts are at the high-field end of the range, closer to those in cyclopropane itself and in the opposite L extreme, they are closer to those in the free alkene, near 5δ. Hydride resonances are even more variable. In Ir(III) complexes, they tend to depend on the nature of the trans ligand and can range from −10δ, for high-trans-effect ligands, (e.g., H) to −40δ, for low-trans-effect ligands, (e.g., H_2O).[4a] Structural assignments based on the value of a coupling constant tend to be more secure than ones based on the value of a chemical shift, although the shifts can be valuable in cases where their reliability has been well established, such as in the Ir(III) hydrides mentioned above. In general, protons attached to carbons bound to a metal show a coordination shift of 1–4 ppm to low field on binding; more remote protons usually show small coordination shifts (<0.5 ppm).

There are also special circumstances in which shifts can be affected by neighboring groups in predictable ways. In indenyl complexes, for example, the aromatic ring current of the benzo group induces high-field shifts in the protons of other ligands on the metal that spend a substantial amount of their time directly above the benzo ring. The ortho protons of the PPh_3 groups of **10.4** experience a shift of −0.27 ppm relative to those of the analogous complex $CpIrHL_2^+$, which lacks the benzo ring. The preferred conformation of **10.4** in solution, shown below, was deduced from this evidence.[5]

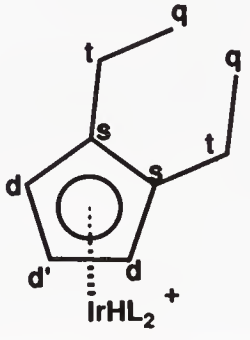


10.4

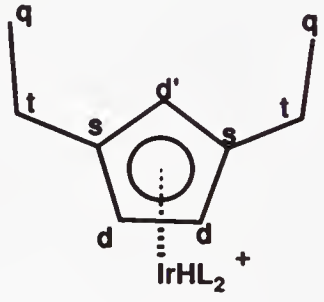
Paramagnetic Complexes It is important to bear in mind that metal complexes can be paramagnetic and that this can lead to large shifts in the NMR resonances;[2d] for instance, $(\eta^6\text{-}C_6H_6)_2V$ has a ^{1}H NMR resonance at 290δ. More commonly, these resonances are broadened to such an extent that they become effectively unobservable. As we shall see in Section 10.5, other processes can also broaden resonances in diamagnetic molecules. A featureless NMR spectrum does not necessarily mean that no organometallic complexes are present.

10.3 ^{13}C NMR SPECTROSCOPY[2c]

Although ^{13}C ($I = \frac{1}{2}$) constitutes only 1% of natural carbon, it is usually possible to get good proton decoupled ^{13}C NMR spectra from most organometallic complexes in a reasonable time. It is helpful to run an off-resonance decoupled spectrum as well; this introduces only 1-bond C,H couplings and reveals the number of protons to which each carbon is bound (CH_3 gives a quartet, CH_2 a triplet, etc.). The resulting spectra often allow the structure of a complex to be deduced, even in cases in which the proton NMR spectrum is too complex to decipher. The structures of **10.5** and **10.6**, which could be obtained only in an inseparable mixture, were deduced in this way.[6] After accounting for the PPh_3 resonances, each complex showed two quartets, two triplets, two doublets, and a singlet in the off-resonance decoupled spectrum. These were assigned as shown, ruling out any of the possible alternative structures that had been envisaged for the complexes.



10.5



10.6

Certain groups are found in characteristic resonance positions, for example, alkyls from -40 to $+20\delta$, π-bonded carbon ligands such as alkenes, Cp, and arenes from $+40$ to $+120\delta$, carbonyls around 150–220δ (terminal) and 230–290δ (bridging) and carbenes in the range 200–400δ. Relaxation (Section 10.7) of the ^{13}C nuclei, especially of carbonyls, may be slow, which makes them difficult to observe unless a relaxation reagent such as $Cr(acac)_3$ is added to the sample. Since the dynamic range of the method greatly exceeds that of ^1H NMR, the ^{13}C peaks for different carbons in a complex will normally be farther apart in frequency (hertz) than the corresponding ^1H peaks. This means that the spectra of complicated molecules are much easier to assign because overlapping of peaks is less likely and also that slower fluxional processes (Section 10.5) can be studied. Coupling is transmitted by the σ bonds of a molecule—the higher the *s* character of a bond, the higher is the coupling. This is the reason that $^1J(C,H)$ values depend on the hybridization of the C—H bond: sp^3, ~125 Hz, sp^2, ~160 Hz, and sp, ~250 Hz. As in ^1H NMR of hydrides, trans couplings, for example, of methyl carbons to phosphorus are larger (~100 Hz) than cis couplings (~10 Hz).

Unfortunately, integration of carbon spectra is rarely reliable, in part because of the wide range of relaxation times encountered. Relaxation times of carbonyls and other carbons lacking proton substituents are especially long. This means that the nuclei are easily saturated and intensities are low; sometimes a paramagnetic complex, such as Cr(acetylacetonate)$_3$, is added to help relax these carbons.

In polyene and polyenyl complexes, those carbons directly attached to the metal tend to be more shielded on binding, and a coordination shift (i.e., shift relative to the free ligand) of ~25 ppm to high field is observed. If the metal has a $\frac{1}{2}$ spin, coupling to the metal is also seen. This is very useful for determining the hapticity of the ligand. Coupling to other ligands is sometimes seen, but this is not reliable. The phenomenon of diastereotopy discussed in the last section also applies to carbon NMR, and is shown by the diastereotopic P—Me carbons in complexes **10.1** and **10.2**.

10.4 ^{31}P NMR SPECTROSCOPY

Phosphorus-31 NMR spectroscopy[2c,7] is very useful in studying phosphine complexes. Normally all the ligand protons are decoupled so as to simplify the spectra. The only common exception is the determination of n in $H_nM(PR_3)_m$. This can be done by decoupling only the PR_3 protons, while leaving the hydride protons undecoupled.[4] The phosphorus resonance will then appear as an $n + 1$ multiplet. $MoH_6(PR_3)_3$ could be identified only in this way, because it could only be obtained in an impure form.[4b]

Different types of phosphorus ligand will normally resonate within different chemical shift ranges, so that phosphines and phosphites can be reliably distinguished, for example. Free and bound phosphorus ligands also show large coordination shifts. Of even more use is the chelation shift that is observed in chelating phosphines. If the phosphorus is part of a 4-, 5-, or 6-membered ring, then it will resonate at a position shifted by -50, $+35$, and -15 ppm relative to a coordinated but nonchelating ligand having chemically similar R groups around phosphorus.[8] The origin of this shift is not yet understood, but it probably results from changing the hybridization at phosphorus as a consequence of changing the bond angles at phosphorus in different ways in rings of different sizes. This is useful for the detection of such species as cyclometallated phosphines and monodentate diphosphines, both of which are very difficult to characterize in any other way, except by crystallography.

Mechanistic Study of Wilkinson Hydrogenation Tolman et al.[9] were able to deduce the initial events in the mechanism of Wilkinson hydrogenation (Eq. 10.1 and Section 9.2) from the ^{31}P NMR data shown in Fig. 10.4. Spectrum A shows the proton-decoupled ^{31}P NMR of $RhCl(PPh_3)_3$ itself. Two types of phosphorus are seen in a 2:1 ratio, P_a and P_b in **10.7**, each showing coupling to Rh ($I = \frac{1}{2}$, 100% abundance). P_a also shows a cis coupling to P_b

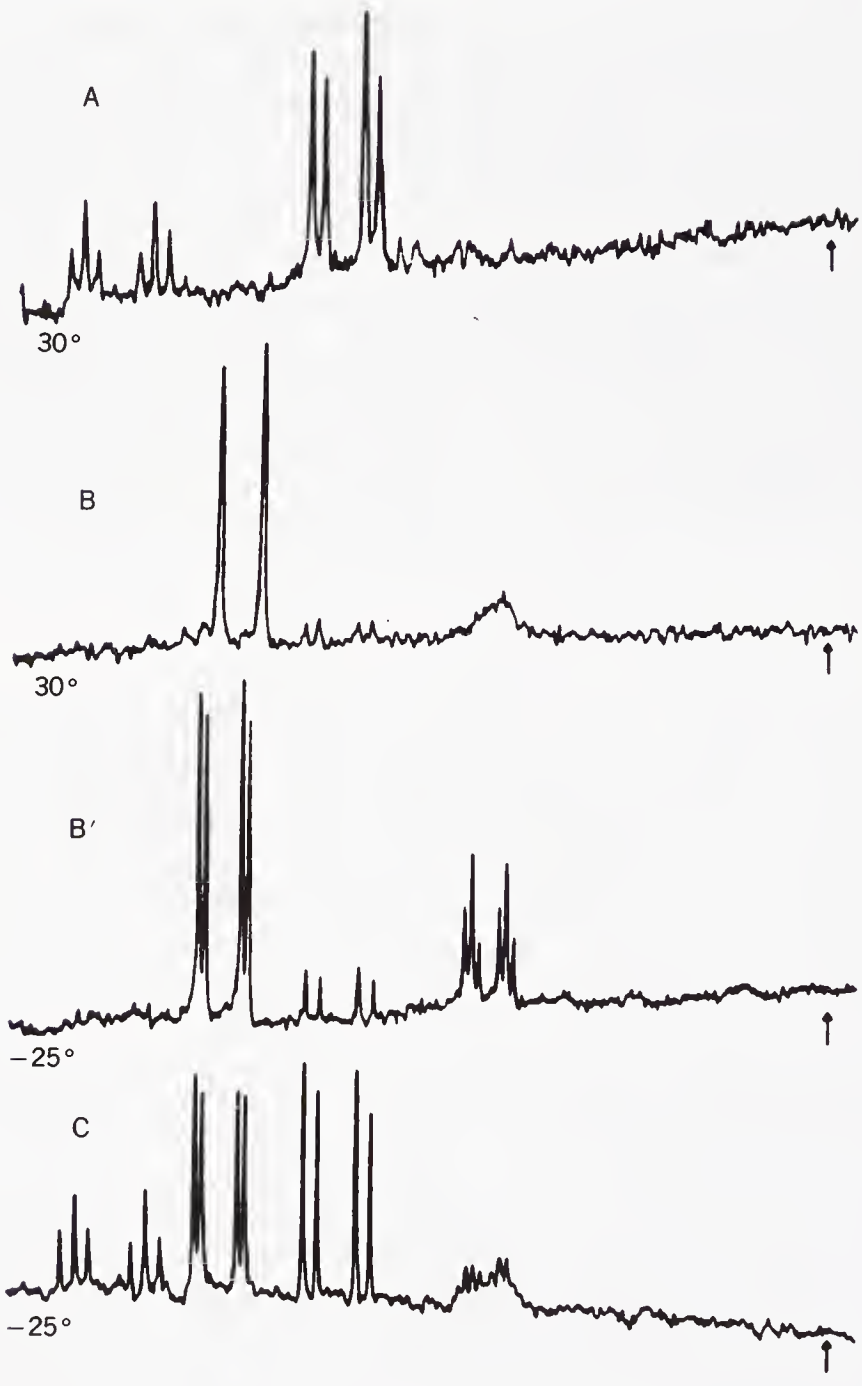
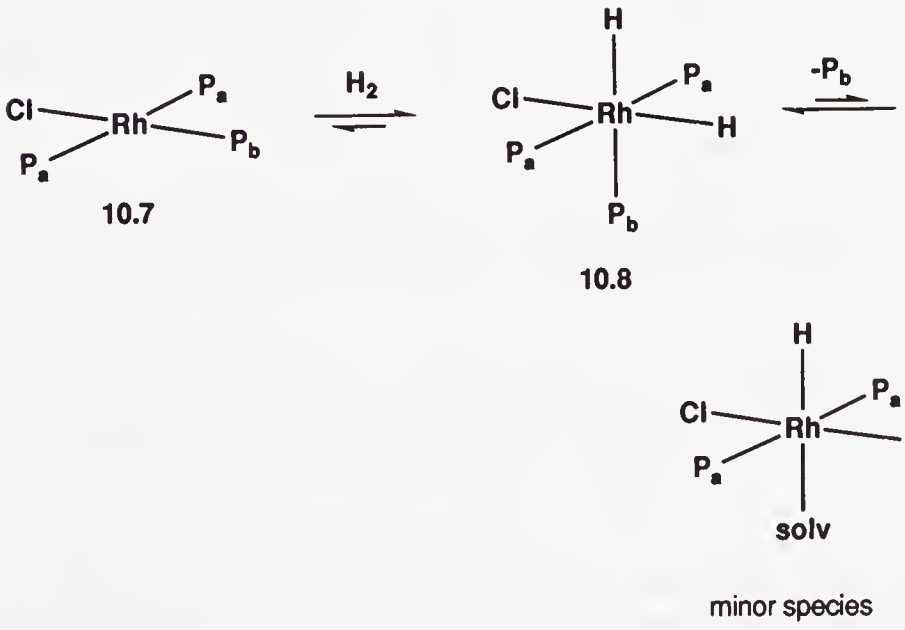


FIGURE 10.4 Proton decoupled ^{31}P NMR data for $RhCl(PPh_3)_3$: (*A*) dissolved in CH_2Cl_2; (*B*) after addition of H_2 at 30°; (*B′*) after addition of H_2 and cooling to −25°; (*C*) after sweeping solution *B* with nitrogen. The different P nuclei in the complex are seen, together with coupling to Rh (large) and couplings to other phosphines (small). In spectrum *B*, the loss of coupling to Rh and P for one of the two P resonances indicates that this ligand is reversibly dissociating. The most intense peaks are assigned to P_a. Free PPh_3 (arrow) is absent. (Reproduced from ref. 7b with permission.)

and P_b shows two cis couplings to the two P_as. On adding H_2 (spectrum B), the starting material almost disappears and is replaced by a new species, **10.8**, in which only P_a now shows coupling to Rh and P_b is a broad hump. Cooling to $-30°$ (spectrum B′) restores the coupling pattern expected for the static molecule **10.8**. The change from B to B′ is the result of P_b dissociating at a rate which is slow at $-30°$ but comparable with the NMR timescale at 30° (Section 10.5). In a fluxional process in which two coupled nuclei always stay in the same molecule, couplings are retained in the NMR, but when dissociation of a ligand takes place we have crossover between molecules and couplings to that ligand are lost. In spectrum B, P_a retains full coupling to Rh, while P_b does not, so it is P_b which is dissociating. (The reason is that each of the two peaks of P_a doublet in spectrum B comes from a different population of molecules, one with the Rh spin α and the other with β spin. When P_b moves from molecule to molecule it samples α and β Rh spins equally and so ends up resonating at an averaged chemical shift.) The amount of *free* PPh_3 always remains very small—the arrows show where free PPh_3 would appear. Passing nitrogen partially reverses the reaction and a mixture of **10.7** and **10.8** results (spectrum C).



10.7 10.8

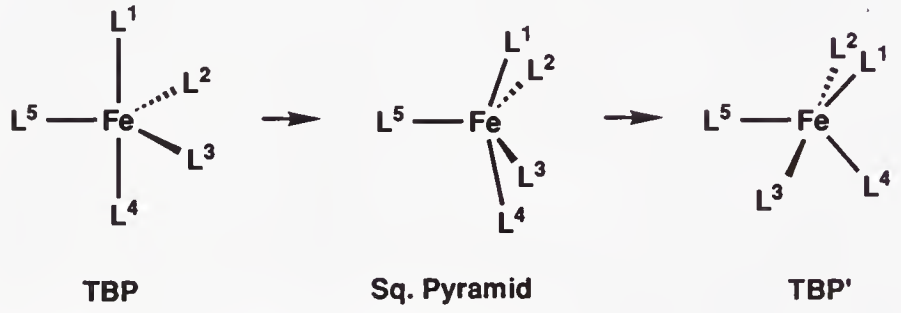
minor species (10.1)

NMR spectra can even be obtained from a number of the common transition metal nuclei,[2e] but this is not yet a routine procedure.

10.5 DYNAMIC NMR

Many organometallic species give fewer NMR resonances than would be predicted from their static structures. This is usually because the molecules are nonrigid,[10] and the nuclei concerned are exchanging places at a rate faster

than the NMR timescale ($\sim 10^{-1}$ to 10^{-6} sec).[2a] For example, $Fe(CO)_5$ gives only one carbon resonance at 25°, and yet its IR spectrum (a technique with the much faster timescale of $\sim 10^{-12}$ sec) indicates a TBP structure with two types of carbonyl. The reason, proposed by Berry, is that the axial and equatorial carbonyls are exchanging by the *Berry pseudorotation* mechanism shown in Eq. 10.2. Ligands 1–4 become equivalent in the square pyramidal intermediate and 1 and 4, which were axial in TBP become equatorial in TBP′.



(10.2)

Rate of Fluxionality Sometimes the exchange takes place at a rate which is comparable with the NMR timescale. When this happens we can usually slow the exchange down by cooling the sample until we see the static spectrum; this is called the *low-temperature limit.* On the other hand, if we warm the sample, the rate of exchange may rise to the extent that the fully averaged spectrum is observed (the *high-temperature limit*). In between these two extremes, broadened resonances are usually seen. For example, if we take a molecule with two sites A and B that are equally populated, on warming we will see the sequence of spectra illustrated in Fig. 10.5. The two sharp peaks broaden as the temperature rises. If we measure this initial broading at half peak height in units of hertz, and subtract out the natural linewidth that was present before broadening set in, then we have $W_{1/2}$, a measure by Eq. 10.3 of the rate at which the nuclei leave the site during the exchange process.

$$\text{Rate} = \pi(W_{1/2}) \tag{10.3}$$

As we continue to warm the sample, the broadening increases until the two peaks *coalesce.* The exchange rate required to do this depends on how far apart the two peaks were initially; the appropriate equation is shown as Eq. 10.4, where $\Delta\nu$ is the separation of the two resonances of the static structure.

$$\text{Rate} = \pi\Delta\nu/\sqrt{2} \tag{10.4}$$

On further warming, the now single peak gets narrower according to Eq. 10.5, and we finally reach a point at which the signal is sharp once more.

$$\text{Rate} \approx \frac{\pi(\Delta\nu)^2}{2(W_{1/2})} \tag{10.5}$$

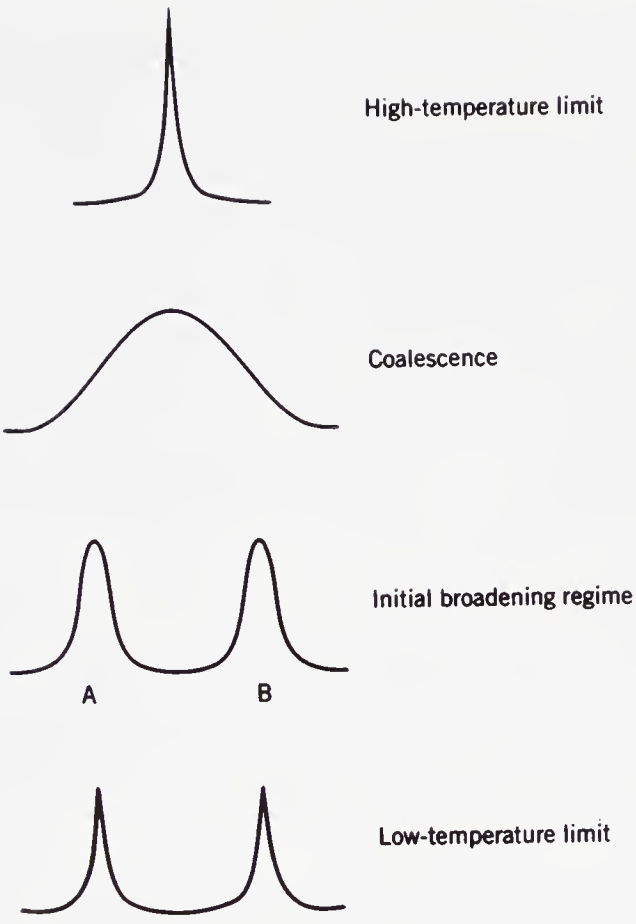


FIGURE 10.5 The changes in the ^{1}H NMR spectrum of a two-site system on warming as the H_A and H_B protons begin to exchange at rates comparable with the NMR timescale.

This happens because the exchange is now much faster than the NMR timescale and only an averaged resonance is seen. Note that Eqs. 10.4 and 10.5 contain $\Delta\nu$, the separation of the two resonances measured in hertz. Since this will be different at different magnetic fields (two resonances 1 ppm apart will be 60 Hz apart as observed on a 60-MHz spectrometer, but 100 Hz apart as observed at 100 MHz), the coalescence temperature and the high-temperature limit are field-dependent. On cooling the sample, the same changes occur in reverse, a process known as *decoalescence*. The position of the averaged resonance at the high-temperature limit is simply the weighted average of the resonance positions at the low-temperature limit. For example, if we have n_1 nuclei resonating at δ_1 and n_2 at δ_2, then at the high-temperature limit, the resonance position will be the weighted average δ_{av}, given by

$$\delta_{av} \approx \frac{n_1\delta_1 + n_2\delta_2}{n_1 + n_2} \tag{10.6}$$

Dynamic NMR is a very powerful method for obtaining kinetic information about processes which occur at a suitable rate.[11]

Mechanism of Fluxionality Fluxionality is very common for 5-coordinate TBP complexes, as it is for 7-, 8-, and 9-coordination; 4-, and 6-coordinate complexes, on the other hand, tend to be rigid. There is also a second type of fluxionality that takes place irrespective of coordination number.[12] An example is $CpFe(CO)_2(\eta^1\text{-}C_5H_5)$ (Fig. 10.6), which shows only two proton resonances at room temperature, one for the $\eta^5\text{-}C_5H_5$, and one for the $\eta^1\text{-}C_5H_5$. The explanation is that the iron atom is migrating around the $\eta^1\text{-}C_5H_5$ ring at a sufficient rate to average all the proton resonances from the $\eta^1\text{-}C_5H_5$ ring. On going to lower temperature, separate resonances can be distinguished for the three different types of proton in the static $\eta^1\text{-}C_5H_5$ group. If we warm the sample from the low-temperature limit, there will be a different degree of initial broadening of the different proton resonances of the $\eta^1\text{-}C_5H_5$ group if the fluxionality involves 1,2 shifts rather than 1,3 shifts. This is because the H_Cs are next to one another and so a 1,2 shift (which is indistinguishable

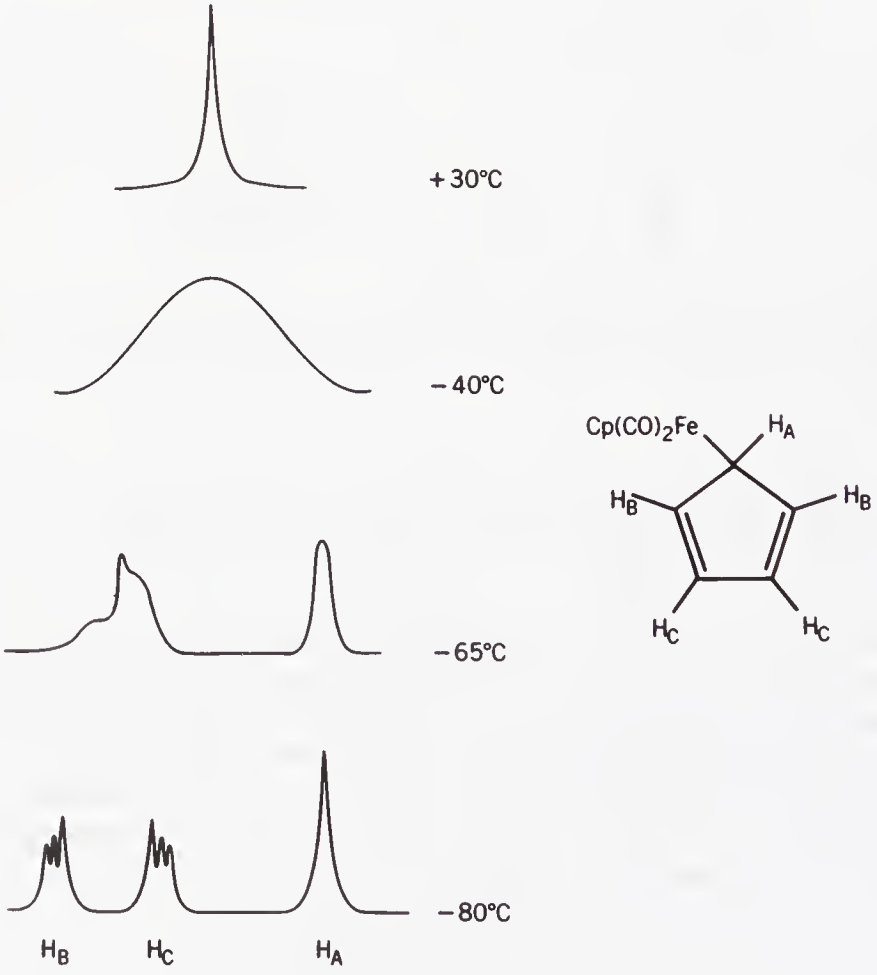
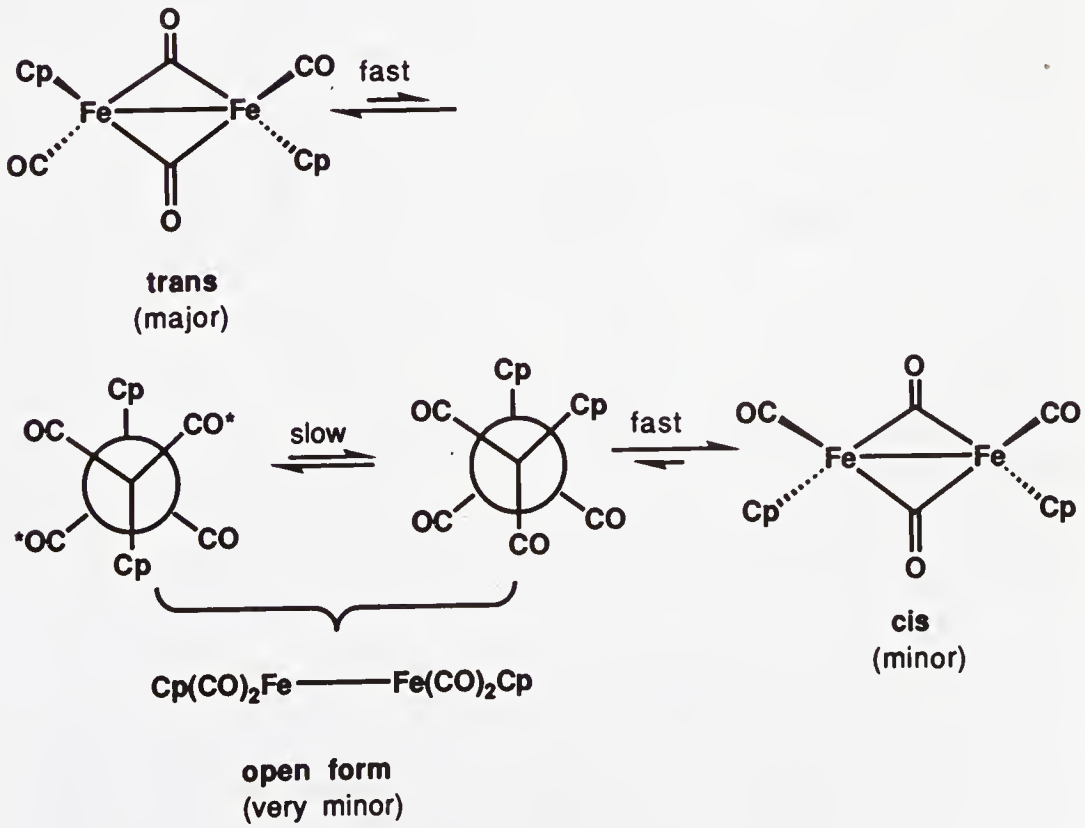


FIGURE 10.6 The fluxionality of $CpFe(CO)_2(\eta^1\text{-}Cp)$, showing the faster collapse of the H_B resonance, indicating the operation of a 1,2, rather than a 1,3 shift. Only the resonances for the η^1 Cp group is shown, for greater simplicity.

from a 1,5 shift) will mean that one of the H_Cs will still end up in an H_C site after a 1,2 shift. On the other hand, all the H_Bs will end up in non-H_B sites. The exchange rate for H_Cs will therefore appear to be one-half of the exchange rate for H_Bs, and the resonance for H_C will show less initial broadening. Conversely, H_Bs are three carbons apart and so 1,3 shifts will lead to the H_Bs showing less initial broadening. Experimentally, it is found that a 1,2 shift is taking place.[13a] Note that we need to assign the spectrum correctly to obtain the correct mechanism and this is often the most difficult step.

In the case of the Cp ligand it is impossible to distinguish between a Woodward–Hoffmann allowed 1,5 shift, and a least-motion 1,2 shift, because they both give the same final observable result. In an η^1-C_7H_7 system, the two cases are distinguishable, Woodward–Hoffman giving a 1,4, and least motion a 1,2 shift. The appropriate compounds are difficult to make, but Graham and Heinekey were able to show that $(\eta^1\text{-}C_7H_7)Re(CO)_5$ follows a least motion, and η^1-$C_7H_7SnMe_3$ a Woodward–Hoffmann path.[13b]

Another important case of fluxionality is bridge-terminal exchange in carbonyl complexes. The classic example is $[CpFe(CO)_2]_2$, which shows separate Cp resonances for cis and trans CO-bridged isomers in the proton NMR below −50°C, but one resonance at room temperature. The Adams–Cotton mechanism of exchange (Eq. 10.7) invokes concerted opening of both CO bridges at once; indeed 1% of the resulting nonbridged isomer has been detected in

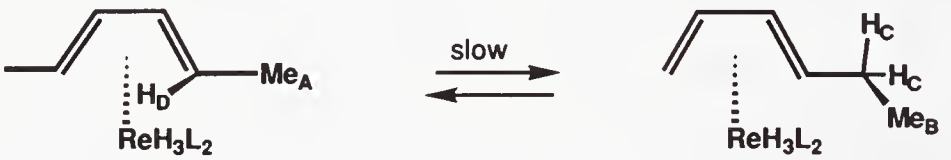


(10.7)

solution. The trans compound gives much faster exchange between bridging and terminal COs by ^{13}C NMR. This is because only the nonbridged form of the trans compound, shown on the left in Eq. 10.7, has a choice of COs for re-forming the bridge. For example, if the starred COs were originally bridging, the compound can choose the unstarred pair to re-form the new bridge. In the open form of the cis compound, also shown, there is only one pair of trans COs, and the same ones that opened up also have to re-form the bridge unless a rotation takes place, which is thought to be slow.[14]

10.6 SPIN SATURATION TRANSFER

It sometimes happens that a fluxional exchange process is suspected on chemical grounds but the low-temperature spectrum is seen at all accessible temperatures, and so the exchange is slow on the NMR timescale. An example is shown in Eq. 10.8, where we have to postulate exchange to account for the chemistry of the system, but it is too slow to affect the NMR lineshapes. In such circumstances, we can sometimes use *spin saturation transfer.*[15] The principle of the method is to irradiate one of the resonances in the spectrum of one of the two species and watch for the effects on the spectrum of the other species. If we irradiate the Me_A protons in **10.9a**, we see a diminution in the intensity of the resonance for Me_B in **10.9b**. This shows that Me_A in **10.9a** becomes Me_B in **10.9b** in the course of the exchange; likewise, irradiation at the frequency of H_C affects the intensity of the H_D. In this way we can obtain mechanistic information about the fluxional process.



(10.8)

10.9a **10.9b**

The method works because by irradiating the Me_A protons we equalize the spin population in the α (lower-energy) and β (higher-energy) states. If the Me_A protons now become Me_B protons as a result of the exchange, then they carry with them the memory of the equalized populations. Since we need *un*equal α and β populations in order to observe a spectrum, the newly arrived Me_B protons do not contribute their normal amount to the intensity of the resonance. Now, a very important point is that the Me_A protons begin to lose their memory of the original, artificially equalized α- and β-spin populations by a process known as *relaxation.* There are several mechanisms for relaxation, one of which we will go into in detail in a moment. We need only recognize for now that the initially equal populations in the newly arriving protons relax back to the equilibrium population ratio with a rate $1/T_1(B)$, where $T_1(B)$ is

the so-called spin lattice relaxation time, or T_1, of the Me_B site. This is commonly of the order of a few seconds, and must be measured independently. The exchange rate has to be faster than about 10 times the T_1, or $>0.1\ sec^{-1}$, in order to give a measurable spin saturation transfer effect. This means that the exchange process must be taking place at a rate in the range of ~ 0.1–$1\ sec^{-1}$ for useful information to be obtained; if the exchange is faster than this, line broadening measurements usually give better rate data. If the initial intensity of the B resonance is I_0, the relaxation time of the B protons is $T_1(B)$, and the final intensity of the B resonance on irradiating the A resonance is I_f, then the exchange rate k is as given by Eq. 10.9.

$$\frac{I_0}{I_f} = \frac{\{T_1(B)\}^{-1}}{k + \{T_1(B)\}^{-1}} \tag{10.9}$$

The most useful feature of the method is not so much the rate data, but that it tells us which protons are exchanging with which, and so allows us to solve some difficult mechanistic problems. In certain circumstances the nuclear Overhauser effect (NOE) (Section 10.7) can affect the experiment, and must also be taken into account.[15]

10.7 T_1 AND NOE

We now need to look at how we can determine the T_1 for any signal, something that we need to do in the spin saturation transfer experiment. If we imagine the sample in the magnetic field, the z direction being the direction of the applied magnetic field, then the nuclei will line up with and against the field. The difference in energy between these two states is small, and so the excess of the more stable α spins is very slight. This excess we can consider as constituting a net magnetization of the sample pointing in the $+z$ direction (Fig. 10.7). The application of an r.f. (radio-frequency) pulse to the sample has the effect of rotating this vector out of the z direction into the xy plane, where it can be measured by sensitive detectors. A pulse that is of just the right strength to rotate the vector precisely into the xy plane is called a "90° pulse," because it has caused the vector to move through 90°. The reason we can measure it only in the xy plane is that the vector will now be rotating around the z axis at the Larmor frequency; this moving magnetic field generates a signal in the receiver coil of the instrument. This is the conventional FT NMR experiment.

One way to measure T_1 is to apply to the sample a pulse that precisely inverts the spins. This requires a so-called 180° pulse, which is twice the strength of the 90° pulse and rotates the vector from the $+z$ to the $-z$ direction. Originally, there was a slight excess of α spins, because these are in a slightly more stable energy level in the magnetic field. A 180° pulse will now give us a slight excess of β spins. We now wait for relaxation to convert

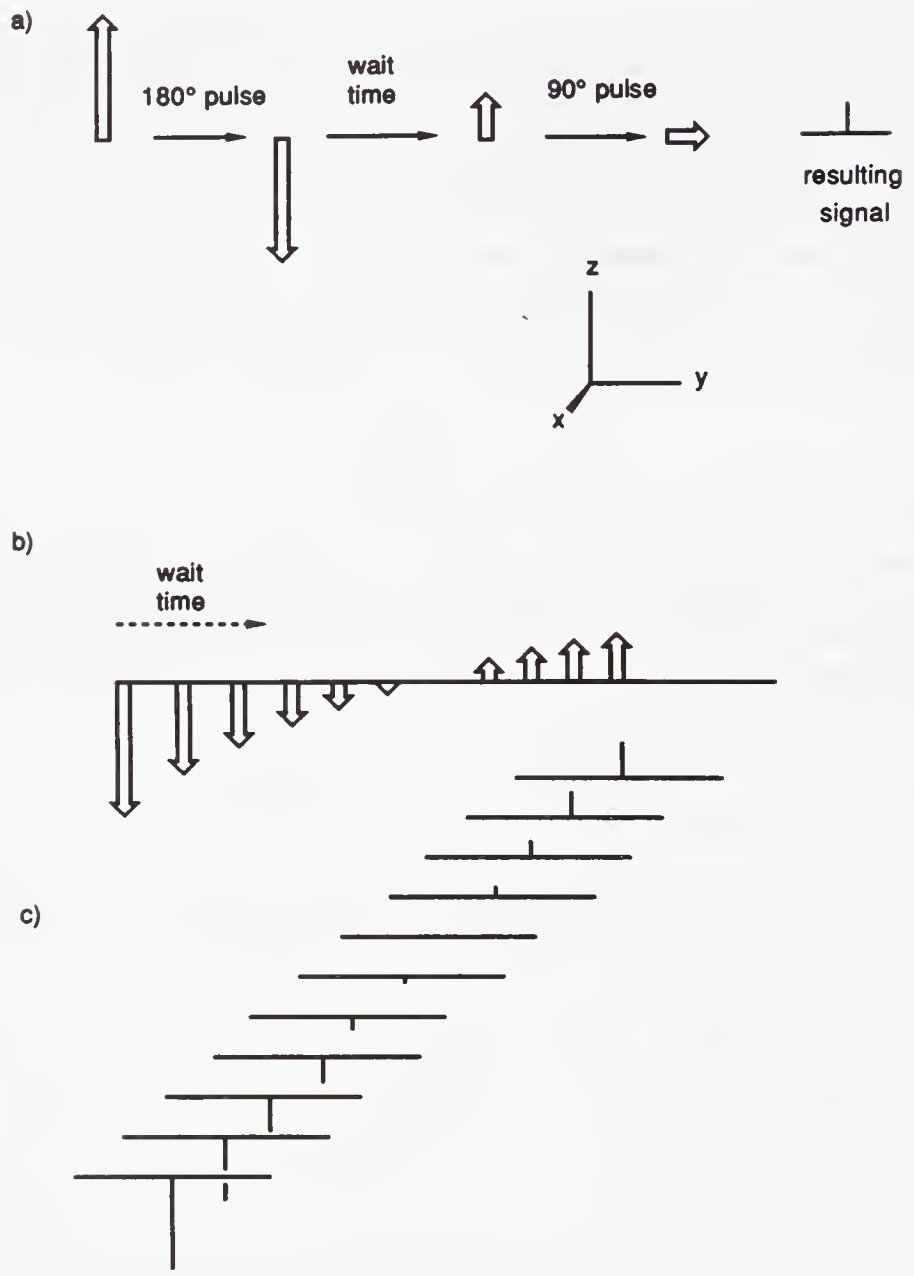
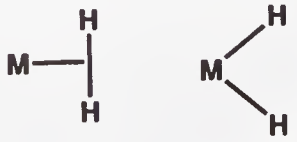


FIGURE 10.7 The inversion recovery method for determining T_1. (*a*) A 180° pulse inverts the spins. They partially recover during the wait time and are sampled by a 90° pulse. (*b*) Varying the wait time allows us to follow the time course of the recovery process, as seen in a stacked plot of the resulting spectra (*c*).

the new nonequilibrium distribution favoring β spins back to the old one favoring α. In separate experiments, we can sample the spins after, say, 0.1 sec, then after 0.2 sec and so on, to see how far they are along the path to recovery. Sampling simply requires a further 90° pulse to bring the spins back into the *xy* plane to be measured. This gives us the sort of result shown in Fig. 10.7. The negative peaks at short times are due to the inverted spin

population at that time; after a sufficiently long time the resonances are all positive and the populations have therefore recovered. Relaxation is normally a first-order process with rate constant $1/T_1$.

T_1 and H_2 Complexes A useful application of T_1 measurements is the distinction between molecular hydrogen complexes, **10.10**, and classical dihydrides, **10.11**. The reason is that two protons that are very close together can relax one another very efficiently by the so-called dipole–dipole mechanism. Dipole–dipole couplings are several orders of magnitude larger than the usual J couplings we see as splitting in the normal NMR spectrum. The reason we do not see the dipole–dipole splittings in the normal spectrum is that they average exactly to zero with the tumbling of the molecule in solution. Although we cannot see the effects of dipole–dipole coupling directly, the random tumbling of the molecule in solution causes one nucleus, say, H_A, to experience a randomly fluctuating magnetic field due to the magnetic field of a nearby nucleus, H_B. If the fluctuations happen to occur at the Larmor frequency, then H_A can undergo a spin flip by this means, and the α and β spins are eventually brought to thermal equilibrium, or relaxed, in this way. Relaxation is important because to see an NMR signal we need a difference in the populations of α and β spins—when the populations are equal in Fig. 10.7, there is no signal. Observing the signal pumps energy into the spins and tends to equalize their populations—relaxation drains energy from the spins and tends to reestablish the population difference.



10.10 **10.11**

The rate of relaxation is given by Eq. 10.10, in which h is Planck's constant, γ is the gyromagnetic ratio of the nuclei involved, τ_c is the rotational correlation time (a measure of the rate of molecular tumbling in solution), z is the Larmor frequency, I is the nuclear spin, and r is the distance between the two nuclei:

$$\text{Rate} = \frac{1}{T_1} = 0.4\left(\frac{h^2}{2\pi}\right)\gamma^2\{I(I+1)\}r^{-6}\left[\frac{\tau_c}{1+\omega^2\tau_c^2} + \frac{4\tau_c}{1+4\omega^2\tau_c^2}\right] \quad (10.10)$$

The r^{-6} term makes the relaxation rate very sensitive to the distance r. In classical dihydrides, this distance would never be shorter than ~1.6 Å, leading to a relaxation time on the order of half a second. On the other hand, in unstretched molecular hydrogen complexes, this distance is ~0.85 Å and the relaxation time is tens of milliseconds at −80°C. Figure 10.8 shows how the

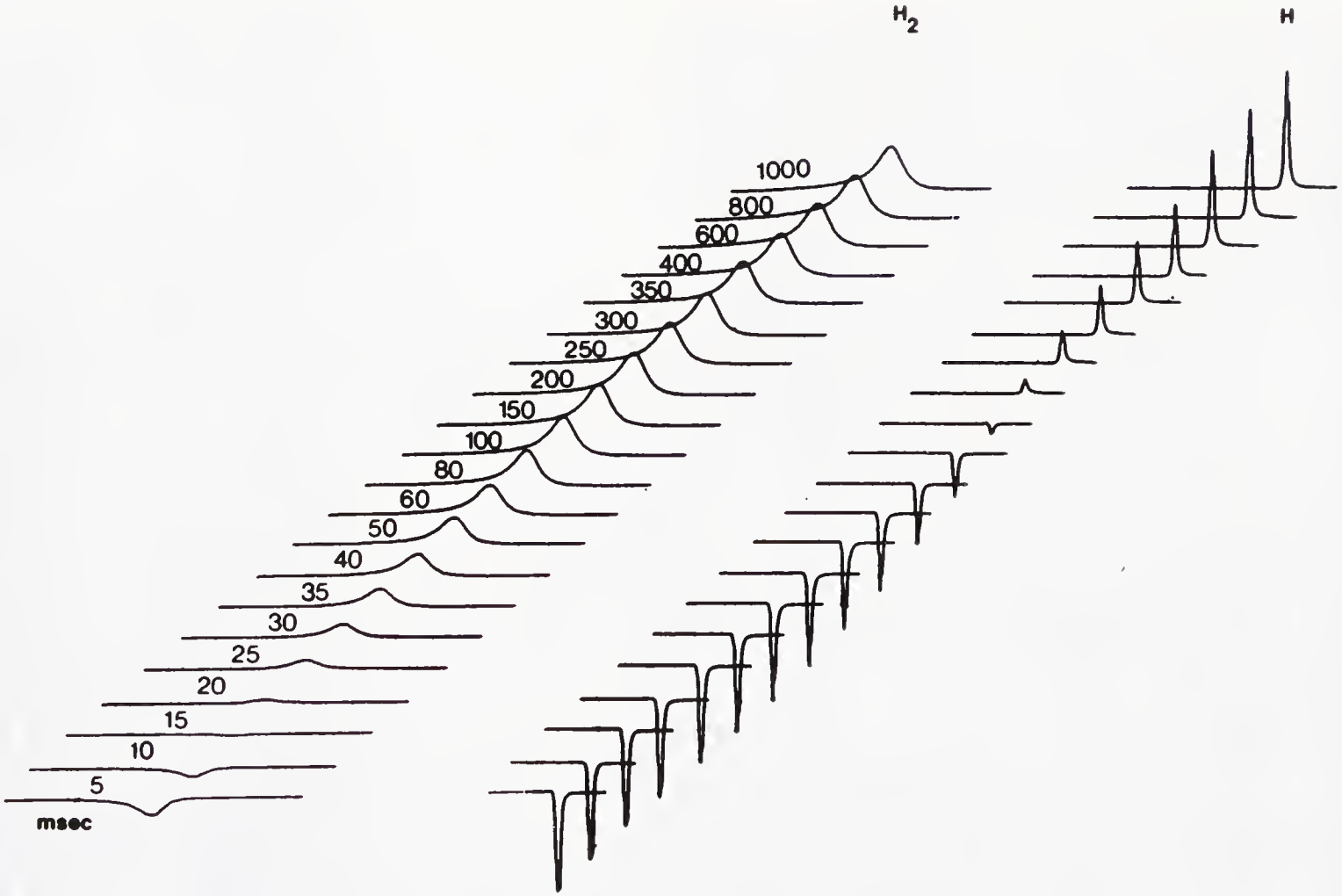
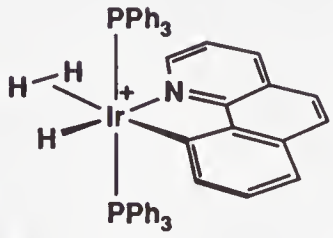


FIGURE 10.8 The differential relaxation of $M(H_2)$ and M—H resonances in **10.12**. The wait times in milliseconds are shown to the left. (We thank the American Chemical Society for permission to reproduce this figure from ref. 16a.)

method distinguishes between the classical and nonclassical hydride resonances in **10.12**.[16a]



10.12

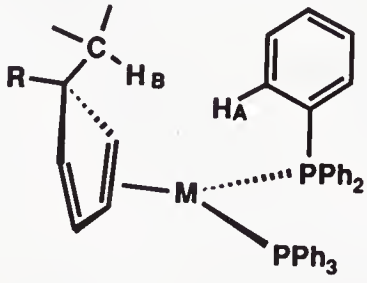
Unfortunately, we do not know τ_c in Eq. 10.10. If we did, we could calculate the H—H distance. It turns out that on cooling the sample, T_1 passes through a minimum value. Equation 10.10 predicts that this should happen when $\tau_c = 0.62/\omega$. Since we know ω, we can calculate τ_c at the minimum and so estimate the H—H distance directly. A number of precautions need to be taken because rotation of the H_2 about the M—(H_2) bond reduces the relaxation rate,[16c] and certain metals, notably Re, Nb, V, Mn, Co, and Ta, cause a substantial, but easily calculable, dipole–dipole relaxation of attached protons because both γ and I are high.[16d] We also assume isotropic (random) motion of the molecule, which is not the case for such systems as IrH_5L_2 and Cp^*ReH_6, where the MH_x unit has a low moment of inertia and so spins rapidly.

PHIP A related phenomenon is PHIP,[17a] or para-hydrogen-induced polarization. On cooling a sample of H_2 in the presence of a suitable catalyst, the H_2 becomes enriched in p-H_2 in which the two nuclear spins are aligned. If a hydrogenation reaction is now carried out in an NMR tube under p-H_2, the two hydrogens may be transferred together to a substrate. Their spins are initially aligned in the product but the alignment decays with a rate of $1/T_1$. If decay is not too fast, this results in an extremely nonthermal distribution of spins in the product, and this in turn leads to very large enhancements of the resonances. Traces of a metal dihydride in equilibrium with H_2 are normally undetectable by NMR but can be seen using PHIP.[17b]

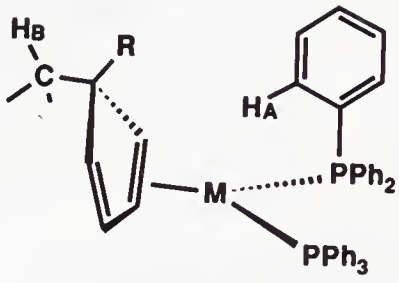
NOE A valuable technique for determining the conformation of a molecule in solution is NOE (nuclear Overhauser effect). This is observed for any two nuclei in a molecule, say, H_A and H_B, that relax each other by the dipole–dipole mechanism. For this to be effective, the two nuclei need to be <2 Å apart, again as a result of the r^{-6} dependence shown in Eq. 10.10. Distance is the only criterion; the two nuclei do not have to have a bond between them.

The experiment consists of irradiating H_A, while observing H_B. NOE can lead to an increase in the intensity of the H_B resonance by as much as 50%,

but usually the increase is 5–10%. In a typical application, NOE is observed in one isomer but not in the other. For example, H_A and H_B in **10.13**, but not **10.14**, show the NOE effect, leading to the assignments shown, which were later confirmed crystallographically.[6]



10.13



10.14

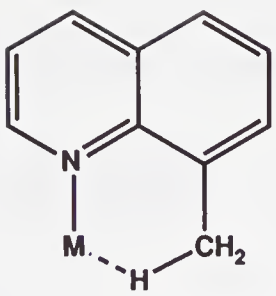
The origin of the effect is described in ref. 17c, but in essence by irradiating H_A, we equalize the α- and β-spin populations for this nucleus. Dipole–dipole relaxation then transfers some of the increased spin population in the upper β state of H_A to the lower α state of H_B, and consequently increases the intensity of the H_B resonance. The enhancement is measured by the NOE factor, η, given by Eq. 10.10, where I_0 and I_f are the initial and NOE enhanced intensities, respectively.

$$\eta = \frac{I_f - I_0}{I_0} \tag{10.11}$$

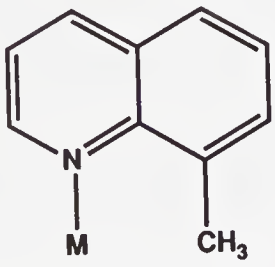
10.8 ISOTOPIC PERTURBATION OF RESONANCE

The isotopic perturbation of resonance (IPR) technique, originally developed by Saunders,[18] was first applied to organometallic chemistry by Shapley.[19] IPR is useful where we are in the fast exchange limit of a fluxional system at all accessible temperatures. We might think that in such a case, we could never obtain information about what the spectrum would be at the low-temperature limit. For example, suppose we want to know whether the methyl group in a complex of 8-methylquinoline is agostic (**10.15**) or not (**10.16**). The usual ^{1}H NMR experiment does not help us, because a singlet is expected for both structures. This is so because agostic methyl groups are fluxional, so that the terminal and bridging hydrogens are exchanging rapidly even at −100°C.

The IPR experiment consists of taking the proton spectrum of a mixture of isotopomers of the complex in which the methyl group has been partially substituted with deuterium. In the d_0 isotopomer (i.e., the isotomer containing zero deuterium atoms), the observed chemical shift, δ_0, is the average of the shifts for the bridging and terminal positions, weighted by the fact that any



10.15



10.16

given proton will spend twice as much time in terminal sites, as there are two of them, than in the bridging one.

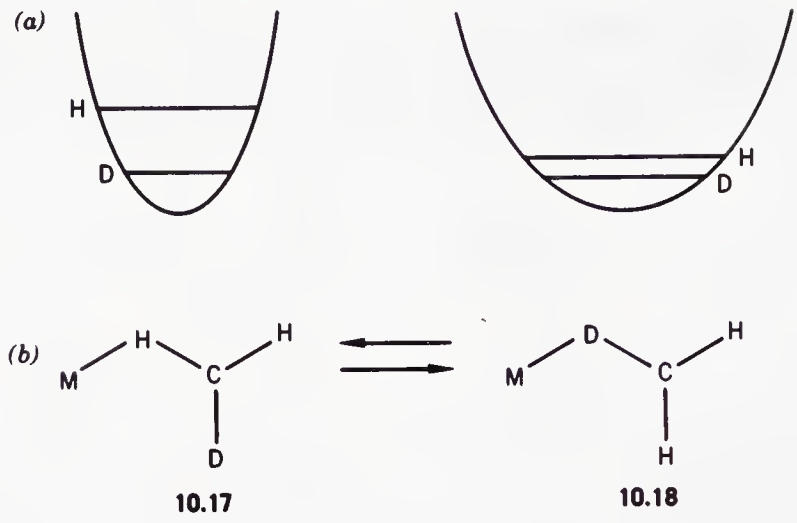
In the d_1 isotopomer, there will be an isotopic preference for H to occupy the bridging sites. The reason is that the zero point energy of H is greater than that of D, and the stability difference depends on the strength of the C—(H,D) bond. The H/D zero-point energy difference is greater for the terminal C—$(H,D)_t$ than for the weaker bridging C—$(H,D)_b$ bond, and so there is an energy advantage for a hydrogen atom to be in a C—H_b site. This population shift translates into a chemical shift in the ^1H NMR resonance of the methyl group. δ_1, the shift for the d_1 complex, will be an average that we can calculate by looking at the equilibrium shown in Fig. 10.9*b*. First we calculate the average shift that would be observed for each form in the absence of IPR. For example, **10.17** has one terminal and one bridging H and so the required average is $(\delta_t + \delta_b)/2$. We next apply a Boltzmann weighting, A, to the stabler form, **10.18**, with D in the bridge. Here, A is $\exp(-\Delta E/RT)$, and therefore always less than one, and ΔE is the energetic preference for D being in the bridge (this is usually about 150 cal/mol, but the exact value is extracted from the data), and T is the absolute temperature. Finally, we need a statistical weighting for **10.17** because there are two ways of having D terminal, since there are two terminal positions. Equation 10.13 gives the appropriate average. We can test that we have not made a mistake, by putting $A = 1$, which should make the IPR go to zero and $\delta_0 = \delta_1 = \delta_2$:

$$\delta_0 = \frac{2\delta_t + \delta_b}{3} \tag{10.12}$$

$$\delta_1 = \frac{\delta_b + \delta_t + A\delta_t}{2 + A} \tag{10.13}$$

$$\delta_2 = \frac{\delta_b + 2A\delta_t}{2A + 1} \tag{10.14}$$

The best way to measure the shifts involved is to have all the isotopomers present in the same NMR tube. The shifts should be measured at different



10.17 **10.18**

	10.17	10.18
Chemical shift:	$(\delta_t + \delta_b)/2$	δ_t
Boltzmann weighting:	1	A
Statistical weighting:	2	1
Overall weighting:	2	A
Final calculated shift:	$\delta_1 = (\delta_b + \delta_t + A\delta_t)/(2 + A)$	

FIGURE 10.9 The origin of "isotopic perturbation of resonance." Zero-point energy differences between C—H and C—D bonds make H prefer the bridging position. A is the Boltzmann factor (exp $-\Delta E/RT$). (*a*) Zero-point energies are larger in the steeper well corresponding to the stronger terminal C—H(D) bond (left) as compared to the weaker bridging C—H(D) (right). (*b*) Calculation of the shifts and relative weightings for **10.17** and **10.18**.

temperatures to confirm that they change in accordance with Eqs. 10.12–10.14. The mere fact of observing IPR only tells us the static structure is unsymmetric, but the results allow us to calculate δ_b, δ_t, and ΔE, and these values may help us find out what the static structure is.

10.9 IR SPECTROSCOPY

Bands in the IR spectrum[1b,20] correspond to vibrational modes of a molecule. The position of the band, ν, depends (Eq. 10.15) on the strength of the bond(s) involved as measured by a force constant k, and on the reduced mass of the

system, m_r. Equation 10.16 shows the reduced mass calculated for a simple diatomic molecule, where m_1 and m_2 are the atomic weights of the two atoms:

$$\nu = \frac{1}{2\pi c\{\sqrt{(k/m_r)}\}} \tag{10.15}$$

(where c = the velocity of light)

$$m_r = \frac{m_1 m_2}{m_1 + m_2} \tag{10.16}$$

Carbonyl Complexes IR spectroscopy is especially useful for carbonyl complexes because the C=O stretching vibration appears at 1700–2100 cm^{-1}, a region that is usually free of other ligand vibrations. The intensity is large because $d\mu/dr$, the dipole moment change during the vibration, is large, thanks to the polarization of the CO on binding to the metal. In complexes with more than one CO, the carbonyls do not usually vibrate independently, but instead vibrate in concert, and are therefore said to be coupled together in a way that depends on the symmetry of the $M(CO)_n$ fragment.[21]

The simplest case is an octahedral dicarbonyl, which may have the carbonyls cis or trans. If the carbonyls are trans, then coupling leads to the situation shown in Fig. 10.10. The COs may vibrate in phase, in which case both the carbonyls reach their maximum C—O extension at the same time (Fig. 10.10*a*), or they may vibrate out of phase (10.10b), in which case one carbonyl is at the maximum when the other is at the minimum C—O extension.

The in-phase, or symmetric vibration, ν_s, appears at higher frequency because it is harder to stretch both COs at once. The reason is that on stretching, each CO becomes a better π acceptor; this is easier for the metal to satisfy if each CO stretches alternately, rather than at once. The intensity of the in-phase vibration is low because the dipoles of the two COs are opposed to each other. One might think that the absorbtion should have zero intensity, but there is usually enough mixing with other, allowed vibrations in the molecule to lend it enough intensity to make it observable. The out-of-phase, or asymmetric, vibration, ν_{as}, has a very high intensity because the two opposed dipoles alternate in their stretching. The final spectrum, Fig. 10.10*c*, with an intense band at lower energy, and a weak band at higher energy, is characteristic for a trans dicarbonyl. A cis dicarbonyl shows the same two bands, but now of approximately equal intensity, because ν_s now has a large $d\mu/dr$. The relationship between the ratio of the intensities and θ, the angle between the two COs, is shown in Eq. 10.17:

$$\frac{I(\text{sym})}{I(\text{asym})} = \cot^2 \theta \tag{10.17}$$

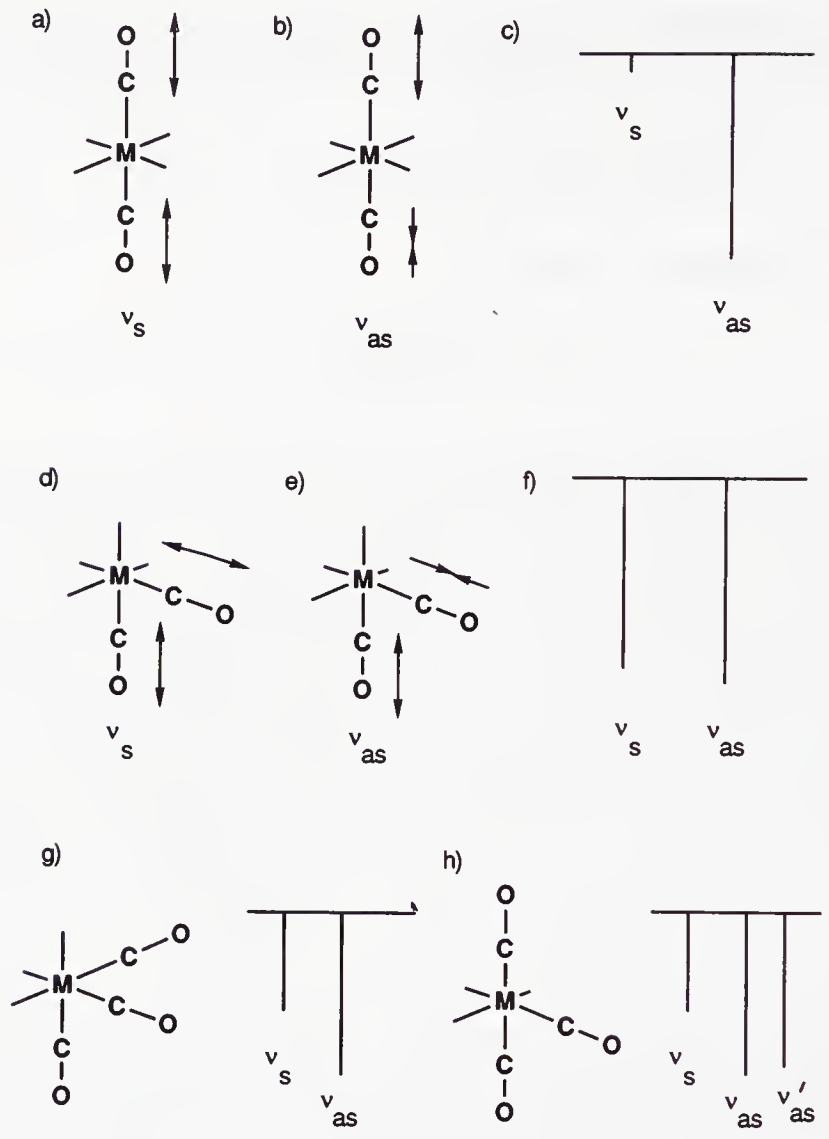


FIGURE 10.10 Effect of the structure of a metal carbonyl on the IR absorption pattern observed.

Octahedral tricarbonyls can be facial (fac), or meridional (mer); tetracarbonyls can be cis or trans (the labels refer to the orientation of the noncarbonyl ligands); but there are only single isomers of penta- and hexacarbonyls. In each case there is a characteristic pattern of IR bands that allow us to identify each type; Fig. 10.10 shows the spectra expected for the two tricarbonyl isomers.

The pattern will be displaced to higher or lower frequency as the net ionic charge, or the noncarbonyl ligands, or the metal is changed. For example, a net negative charge, or more strongly donor ligands, or a more π-basic metal will give rise to more back bonding and so to a weaker C=O bond. This will shift the IR frequencies to lower energy, which means to lower wavenumber (Table 1.2).

Other Ligands The IR spectrum is also helpful in the identification of other ligands. Hydrides often show ν(M—H) bands, but the intensities can be very low if the polarity of the bond is small. Carboxylates can be chelating or nonchelating, and the IR data usually serves to distinguish the two cases. Complexes of CO_2, SO_2, NO, and other oxygen containing ligands give intense bands that are often useful in their identification. Oxo ligands give very intense bands around 500–1000 cm^{-1}, but the usual polyenes and polyenyls do not give very characteristic absorbtions. In an agostic C—H system, the bond is sometimes sufficiently weakened to give a band at ~2800 cm^{-1}. Dihydrogen complexes sometimes give a similar band at 2300–2700 cm^{-1}, but in this case we again rely on mixing to obtain any intensity at all and indeed the band is completely absent in some cases. Metal–halogen stretching vibrations can be seen in the far IR at 200–450 cm^{-1}, but since few spectrometers cover this range, they are rarely observed.

Identification of Bands A common problem in IR work is the identification of a given absorbtion band as arising from a given ligand, rather than from some other vibration in the molecule. For example, a weak band at 2000 cm^{-1} might be a metal hydride, or there might be a small amount of a CO complex present. This kind of problem is solved by isotopic substitution. If we repeat the preparation with deuterated materials, then we will either see a shift of the band to lower frequency, in which case it can be identified as the M—(H,D) stretch, or it will not, in which case the CO complex becomes a more likely alternative. If we can obtain the ^{13}CO analog, then the band should shift appropriately if it is due to CO stretching. The shift can be estimated by calculating the reduced masses of the normal and isotopically substituted systems from Eq. 10.16 (it is usual to assume that L_nM can be assigned infinite mass), and deducing the shift from Eq. 10.15. In the case cited above of an M—H band at 2000 cm^{-1}, the M—D band will come at about $2000/\sqrt{2} = 1414$ cm^{-1}.

Raman Spectroscopy This is rarely applied to organometallic species, but the method is in principle useful for detecting nonpolar bonds, which do not absorb, or absorb only weakly in the IR. The intensity of the Raman spectrum depends on the change of polarizability of the bond during the vibration. It was used very early in its history to detect the Hg—Hg bond in the mercurous ion [ν(Hg—Hg) = 570 cm^{-1}], for example.

10.10 CYSTALLOGRAPHY

Structure determination[1b,22] in the solid state is an extremely important part of organometallic chemistry. Two methods are generally used: X-ray and neutron diffraction. The whole three-dimensional structure of the crystal can be described in terms of a repetitive arrangement of the simplest unit of the structure called the *unit cell,* just as a single tile is often a unit cell for a two-

dimensional repetitive pattern such as one might find in an Arabian courtyard. According to the space group of the three-dimensional arrangement of the unit cell of the structure, then Bragg's law will be satisfied at certain orientations of the crystal, and a beam of X rays will flash out from the crystal at a certain angle to the incident beam. Bragg's law (Eq. 10.18, where λ is the wavelength of the radiation, 2θ is the angle between the incident and diffracted ray, n is an integer, and d is the spacing of the cells) requires that the diffracted radiation from different layers of unit cells be in phase.

$$2d \sin \theta = n\lambda \tag{10.18}$$

In the X-ray method, a beam of monochromatic X rays is passed through a single crystal of the sample. The incident beam is diffracted at various angles; a photograph, for example, will show a pattern of spots. The intensity of this set of diffracted beams will depend on the nature and arrangement of the atoms in the unit cell. In short, the intensities carry the information about the locations of the atoms in the unit cell, while the relative positions of the spots on the film carry the information about the arrangement of the unit cells in space. The positions and intensities are seldom measured by film methods today, but by a computer-controlled device known as a *diffractometer.*

Limitations of the Method The X rays are diffracted by the electron clouds around each atom. This means that the diffraction pattern is often dominated by the metal in a complex, because it usually has a greater number of electrons than the other atoms present. Conversely, hydrogen atoms are very hard to find because they have few electrons. Where it is important to know the hydrogen positions (e.g., metal hydrides, dihydrogen complexes, or in determining the bond angles at carbon in ethylene complexes), neutron diffraction is used. Neutrons are diffracted from the nuclei of the atoms. All elements have broadly similar ability to diffract neutrons, so that the resulting intensities are not dominated by any one atom, and the positions of all the atoms can therefore be obtained. There are only a few laboratories around the world that are equipped to carry out neutron work; an added inconvenience is the much larger crystal size that has been required to obtain sufficient intensities of diffraction. In contrast, many large chemistry departments have an X-ray facility, and a substantial fraction of papers in organometallic chemistry include one or more X-ray structures.

The results of an X-ray structural determination are often represented as a diagram showing the positions of all the atoms in the molecule (e.g. Fig. 5.8). These have a deceptively persuasive appearance. As in all experimental methods, we have to be aware of the pitfalls. The first question is whether the crystal is representative of the bulk. It is not unusual to have several other compounds as minor impurities in a crystallizing sample, if only because the sample may be slowly decomposing. X-Ray diffraction results are often based

on work on one crystal. How do we know the rest of the material was the same? Usually it is possible to obtain an IR spectrum of the crystal on which the structural data were collected to check that it is the same material as the bulk of the sample. The more difficult question is whether the structure in the solid state is really the same as the structure of the same material in solution, to which the solution NMR data will correspond. Several organometallic complexes exist as one tautomer in solution but as another in the solid state. If several isomers are interconverting in solution, then any crystals that form will generally consist of the *least soluble* (not the most stable) tautomer. A different tautomer may crystallize from a different solvent. Surprisingly large forces are present within the lattices, especially of ionic crystals; these may change the details of the structure compared with the solution state, in which most reactions take place. This is why it is so useful to have the NMR methods of structure determination in solution to compare with the X-ray results. IR spectroscopy is also very useful, because we can obtain a spectrum both in solution and in the solid state. Recently, it has become possible to obtain sharp-line NMR spectra on solid-state samples by the technique of "magic angle" spinning. This can allow us to see how the NMR of the molecule under study changes on going from the solution to the solid state, and therefore is a further check on the interpretation of any X-ray results.

Interpreting the Results In organic structures, it is generally always possible to describe the final structure obtained from X-ray work in simple valence bond terms. We know whether atom A is bonded to atom B, and we can make a very good estimate of the bond order, given the observed A—B distance. In organometallic structures, a similar interpretation of the results is not always easy. There are many examples of metal–ligand interactions that do not amount to a full bond and that are longer than the normal M···L covalent distance. We have seen agostic C—H bonds in Section 3.3; the M···H distance can be up to 1 Å longer than the sum of the covalent radii. Semibridging carbonyls can have the M···C distance 0.7 Å longer than the sum of the covalent radii. Binuclear bridged complexes are known which have almost all the possible M···M distances between the shorter ones appropriate for M—M bonding and the very long ones that unambiguously imply no bonding; in the midrange, of course, no clear-cut distinction is possible.

10.11 OTHER METHODS

Many other methods can be useful for the characterization of metal complexes, and we will briefly discuss some of them here. Microanalysis of the products is standard practice, and the values found for C and H are normally acceptable if they fall within ±0.03% of the calculated figure. Solvent of crystallization can be present in the lattice and can alter the percentages

observed; the presence of this solvent should be confirmed by another method such as NMR or IR. The molecular weight of a complex can be obtained by a method such as osmometry.

Conductivity measurements[23] in solution are useful for telling whether a given complex is ionic, and the measurements can also give the electrolyte type (A^+B^-, $A_2^+B^{2-}$, etc.).

The UV–visible spectrum of an organometallic complex is most commonly obtained when photochemical experiments are carried out, to help decide at which wavelength to irradiate (see Section 4.7). A detailed interpretation of the spectrum has been carried out for few organometallic complexes, a situation that contrasts with that in coordination chemistry, where UV–visible spectroscopy and the ligand field interpretation of the results has always been a major focus of attention.[24]

One other diffraction method that has proved useful for sufficiently volatile organometallic compounds is electron diffraction.[25] In this technique the organometallic compound is introduced into a vacuum chamber through a nozzle, and an electron beam is passed through the stream of molecules. The resulting diffraction pattern contains much less information than does an X-ray diffraction pattern, but by making simple assumptions about the structure of the molecule, valuable data can be obtained. A useful feature of the results is that they refer to the molecule in an isolated state in a vacuum, so solvation or crystal packing effects are absent.

Paramagnetic Organometallic Complexes Once rare, these are much more commonly studied today.[26a] The magnetic moment is most conveniently determined by Evans's[26b] method. This involves measuring the chemical shift of a solvent resonance on going from the pure solvent (often present in the form of a sealed capillary tube placed in the sample) to a solution of the paramagnetic complex. A paramagnetic complex may give an EPR[1b,27] spectrum, which may be useful in characterizing the complex, particularly its symmetry, and in determing how the unpaired electron is delocalized. Paramagnetic complexes may give usable NMR spectra, but the resonance positions may be strongly shifted and broadened compared to a diamagnetic complex. If we oxidize a Ni(II) complex, LNi, we may make a paramagnetic species LNi^+. Sometimes the EPR of the product gives a resonance near $g = 2$ (the g scale is the equivalent of chemical shift in NMR) appropriate for an organic radical, in which case we assign the complex as $Ni(II)(L^{\bullet+})$ with the oxidation having taken place at the ligand. In other cases the epr shows $g \neq 2$ in which case a Ni(III)L formulation may be considered more appropriate. Assignment of the oxidation or reduction to M or L can be a contentious issue, however, because the real structure may not be purely $Ni(II)(L^{\bullet+})$ or Ni(III)L. Electrochemical methods, especially cyclic voltammetry, are invaluable for studies on redox-active complexes. With this method the redox potentials and lifetimes of the oxidized or reduced species can be determined.[26a]

Volatile Species Sufficiently volatile organometallic compounds can also be studied by mass spectrometry,[1b,28] photoelectron spectroscopy,[1b,29] and very occasionally, by microwave spectroscopy.[30] Mass spectrometry often allows the molecular weight of a complex to be measured directly, if the molecular ion can be seen. Some ligands such as CO easily dissociate in the spectrometer and give false molecular ions.[28b] In addition, the isotopic pattern for many of the heavier elements (e.g., Mo, Cl, Br, Pd, Ru) is distinctive, and so the nature and number of these elements can usually be unambiguously identified in the molecular ion and in other fragments. Finally, thermodynamic data about the strength of bonds within the complex can sometimes be approximately estimated from the appearance potentials of certain fragments in the spectrum.[31,32] In another variant of the method, called *ion cyclotron resonance spectroscopy,*[33] the vapor-phase reactions of metal ions or of metal fragment ions with organic molecules can be studied. For example, it has been found that bare Fe^+ ions react readily with alkanes to break both C—H and C—C bonds.[34]

Photoelectron spectroscopy (PES)[35] is important because it gives us experimental data about the molecular energy levels within the complex. A solid sample is irradiated with X rays of a given frequency. If the X rays are of an appropriate energy, they can ionize even the core levels of the atoms; this is the electron spectroscopy for chemical analysis (ESCA) experiment. The photoelectrons emitted from the sample are detected and their energies analyzed. Each element in the sample emits at a characteristic energy, and so we have an elemental analysis. In addition, the energy observed shifts very slightly according to the charge on the particular element in the molecule; if the element is more positively charged in complex A than in complex B, the energy levels will be slightly stabilized and the photoelectron will be emitted with a slightly lower kinetic energy in complex A. Unfortunately, the data are not always sufficiently good to distinguish the small, chemically interesting differences between the charges on a metal in different environments. If the exciting radiation is less energetic [e.g., the He(I) lines at 21.22 or 40.8 eV], photoelectrons only from the valence orbitals of the molecule are observed. In this PES experiment, chemically interesting differences are found between different complexes. Each band can often be associated with a particular m.o., and the effect of different substitution patterns on the m.o. energies can be studied. Vibrational fine structure can be seen in certain cases and this helps in assigning the bands.

Computational Methods Molecular orbital theory,[36a] at both the extended Hückel and ab initio levels, has played an indispensable role in clarifying the structure and reactivity of a wide range of organometallic compounds. Such studies are particularly useful when they are interpreted so that the important interactions are explicitly identified. The results of some of these studies are incorporated into the discussion in other chapters of this book.

Molecular mechanics[36b] is a method that has been very useful in organic chemistry by which the strain energy of a given structure can be evaluated by summing all the relevant interactions such as steric repulsions. By minimizing the strain energy, favored conformations can be located. The method is beginning to be used in organometallic chemistry.

Interpretation of Results Care always needs to be taken with interpreting physical data because Nature has a thousand ways to mislead. An approach to test your conclusion is to ask if there is any combination of events that could falsify it.

REFERENCES

1. (a) D. F. Shriver, *The Handling of Air-Sensitive Compounds,* McGraw-Hill, New York, 1969. (b) E. A. V. Ebsworth, D. W. H. Rankin, and S. Cradock, *Structural Methods in Inorganic Chemistry,* Blackwell, Oxford, 1987.
2. (a) W. Kemp, *NMR in Chemistry,* 1st ed., Macmillan, London, 1986, is a good nonmathematical introduction; a more rigorous treatment is given in (b) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance,* Pergamon Press, Oxford, 1966, K. A. McLaughlan, *Magnetic Resonance,* Clarendon Press, Oxford, 1982, or J. A. Pople, W. G. Schneider, and H. J. Bernstein, *High Resolution Nuclear Magnetic Resonance Spectroscopy,* McGraw-Hill, New York, 1959; (c) P. S. Pregosin and R. W. Kunz, *^{31}P and ^{13}C NMR Spectroscopy of Transition Metal Complexes,* Springer-Verlag, Heidelberg, 1979; (d) G. N. Lamar, W. D. Horrocks, and R. H. Holm, *NMR of Paramagnetic Molecules,* Academic Press, New York, 1973; (e) W. v. Philipsborn, *Pure Appl. Chem.,* **58,** 513, 1986; D. Rehder, *Chimia,* **40,** 186, 1986.
3. J. C. and M. L. H. Green, Chap. 48 in *Comprehensive Organometallic Chemistry,* J. Bailar et al. (eds.), Pergamon Press, Oxford, 1973, p. 355.
4. (a) J. Chatt, R. S. Coffey, and B. L. Shaw, *J. Chem. Soc.,* 7391, 1965; (b) R. H. Crabtree and G. G. Hlatky, *Inorg. Chem.,* **23,** 2388, 1984.
5. J. W. Faller, R. H. Crabtree, and A. Habib, *Organometallics,* **4,** 929, 1985.
6. R. H. Crabtree, D. Gibboni, and E. M. Holt, *J. Am. Chem. Soc.,* **108,** 7222, 1986.
7. D. G. Gorenstein, *Prog. NMR Spectrosc.,* **16,** 1, 1983.
8. P. Garrou, *Chem. Rev.,* **81,** 229, 1981.
9. P. Meakin, J. P. Jesson, and C. A. Tolman, *J. Am. Chem. Soc.,* **94,** 3240, 1972.
10. J. W. Faller, *Adv. Organometal. Chem.,* **16,** 211, 1977.
11. R. S. Drago, *Physical Methods in Chemistry,* Saunders, Philadelphia, 1977.
12. M. A. McKinney and M. A. Howarth, *J. Chem. Educ.,* **57,** 110, 1980.
13. (a) F. A. Cotton, *J. Organometal. Chem.,* **100,** 29, 1975; (b) D. Heinekey and W. A. G. Graham, *J. Am. Chem. Soc.,* **101,** 6115, 1979.
14. L. J. Farrugia, *Organometallics,* **11,** 2941, 1992, and references cited therein.

15. J. W. Faller, in *The Determination of Organic Structures by Physical Methods,* F. C. Nachod and J. J. Zuckerman (eds.), Academic Press, New York, 1973, Vol. 5, Chap. 2.
16. (a) R. H. Crabtree, M. Lavin, et al., *J. Am. Chem. Soc.,* **108,** 4032, 1986; (b) R. H. Crabtree and D. G. Hamilton, ibid., **108,** 3124, 1986; (c) R. H. Morris et al., ibid., **113,** 3027, 1991; (d) J. Halpern et al., ibid., **13,** 4173, 1991; X. L. Luo, H. Liu, and R. H. Crabtree, *Inorg. Chem.,* **30,** 4740, 1991.
17. (a) R. Eisenberg et al., *J. Am. Chem. Soc.,* **109,** 8089, 1987; *Acct. Chem. Res.,* **24,** 110, 1991; (b) R. Eisenberg et al., *J. Am. Chem. Soc.,* **115,** 5292, 1993; (c) J. H. Noggle and R. E. Shirmer, *The Nuclear Overhauser Effect,* Academic Press, New York, 1971.
18. M. Saunders et al., *J. Am. Chem. Soc.,* **99,** 8070, 1977.
19. J. Shapley et al., *J. Am. Chem. Soc.,* **100,** 7726, 1978.
20. Chap. 6 in ref. 11, and Chap. 5 in ref. 1b.
21. F. A. Cotton, *Chemical Applications of Group Theory,* Wiley-Interscience, New York, 1967.
22. G. H. Stout and L. H. Jensen, *X-Ray Structure Determination,* Macmillan, New York, 1968, and Chap. 8 in ref. 1b.
23. W. J. Geary, *Coord. Chem. Rev.,* **7,** 81, 1971.
24. Chap. 6 in ref. 1b, and B. N. Figgis, *An Introduction to Ligand Fields,* Wiley-Interscience, Chichester (UK), 1966.
25. Chap. 8 in ref. 1b, and J. C. Brand and J. C. Speakman, *Molecular Structure,* Arnold, London, 1960, Chap. 9.
26. (a) M. Chanon et al. (eds.), *Paramagnetic Organometallic Species,* Kluwer, Dordrecht, 1987; (b) J. Evans, *J. Chem. Soc.,* 2003, 1960.
27. Chap. 13 in ref. 11, and Chap. 3 in ref. 1b.
28. (a) Chap. 9 in ref. 1b, J. R. Chapman, *Practical Organic Mass Spectrometry,* Wiley, New York, 1985; (b) W. A. Graham et al., *J. Am. Chem. Soc.,* **95,** 1684, 1973.
29. Chap. 6 in ref. 1b, and C. R. Brundle and A. D. Baker (eds.), *Electron Spectroscopy, Theory, Techniques and Applications,* Academic Press, New York, 1977; J. L. Hubbard and D. L. Lichtenberger, *J. Am. Chem. Soc.,* **104,** 2132, 1982; J. C. Green, D. M. P. Mingos, and E. A. Seddon, *Inorg. Chem.,* **20,** 2595, 1981.
30. E. N. diCarlo, *J. Am. Chem. Soc.,* **102,** 2205, 1980.
31. Chap. 4 in ref. 1b.
32. T. R. Spalding, *J. Organometal. Chem.,* **149,** 371, 1978.
33. H. Hartmann and K. P. Wanczek, *Ion Cyclotron Resonance Spectroscopy,* Springer-Verlag, Berlin, 1978, 1982.
34. D. P. Ridge et al., *J. Am. Chem. Soc.,* **101,** 1332, 1979; J. L. Beauchamp et al., *Organometallics,* **1,** 963, 1982.
35. D. L. Lichtenberger et al., *J. Am. Chem. Soc.,* **108,** 2560, 1986.
36. (a) T. A. Albright, J. K. Burdett, and M.-H. Whangbo, *Orbital Interactions in Chemistry,* Wiley, New York, 1985; (b) M. C. Baird, *Organometallics,* **11,** 3712, 3724, 1992.

PROBLEMS

1. Sketch the ^{1}H NMR spectrum of (i) *cis*- and (ii) *trans*-$OsH_2(PMe_3)_4$. How could we go about finding the value of a trans $2J$(H,H) coupling by looking at the spectra of an isotopic modification of one of these complexes?

2. *trans*-$OsH_2(PMe_3)_4$ reacts with HBF_4 to give $[OsH_3(PMe_3)_4]^+$. What structures should we consider for this species, and how might ^{1}H NMR spectroscopy help you decide which structure is in fact adopted?

3. $(Indenyl)_2W(CO)_2$ is formally a 20e species. How might it achieve a more reasonable 18e configuration, and how could you use ^{13}C NMR spectroscopy to test your suggestion?

4. How could we distinguish between an [(η^6-benzene)ML_n] and an [(η^4-benzene)ML_n] structure for a given diamagnetic complex by ^{1}H NMR? Note that the observation of a single-benzene resonance does not prove the η^6-benzene structure, because the η^4-benzene form might be fluxional at all accessible temperatures.

5. Two chemically inequivalent hydrides, H_a and H_b in a metal dihydride complex at 50°C, resonate at -5δ and -10δ, respectively, and are exchanging so that each resonance shows an initial broadening of 10 Hz at a field corresponding to 500 MHz. What is the rate of exchange? At 80°C, we observe coalescence; what is the new rate of exchange?

6. Which of the methods (a) to (e) would be suitable for solving problems 1–6 mentioned below? (a) X-ray crystallography; (b) ^{1}H NMR spectroscopy; (c) ^{31}P NMR spectroscopy; (d) IR spectroscopy; (e) magnetic moment determination; (1) Characterizing a cyclometallated $Ph_2PC_6H_4$ complex; (2) characterizing a dihydrogen complex; (3) characterizing a CO_2 complex; (4) determining the stereochemistry of $M(CO)_2(dppe)_2$; (5) comparing the relative donor properties of a series of ligands L in $LNi(CO)_3$; (6) finding out whether a given complex $NiCl_2L_2$ were square planar or tetrahedral in solution. If you cite more than one method, be sure to state which method you would use first as being the simplest way to obtain a definitive result.

7. $IrCl(CO)_2(PMe_3)_2$ has two solution IR bands in the CO region, for which I_{sym}/I_{asym} is 0.33. What is the preferred geometry of this complex in solution?

8. Why are the CO stretching bands of a bridging carbonyl at lower frequency in the IR spectrum than those of a terminal CO? What would you expect for a μ_3-CO?

9. How can a complex having an apparent formulation $[IrHCl(CO)(acetate)(PR_3)_2]$, as judged from analytical and NMR measurements, be formulated with (a) an η^1-acetate, (b) an η^2-acetate in solution? For each of your suggested formulations, state what methods of characterization would be useful to test your suggestions.

10. $[Ir(cod)(PMe_2Ph)(2\text{-methylpyridine})]^+$ shows a *pair* of doublets for the PMePh protons in the ^1H NMR; explain. (Coupling to the metal is not responsible; Ir does not have an $I = \frac{1}{2}$ nucleus.)

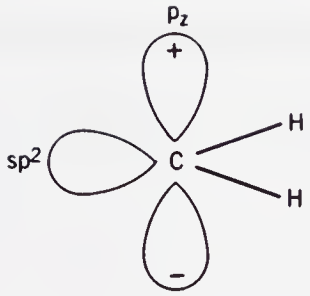
CHAPTER 11

CARBENES, METATHESIS, AND POLYMERIZATION

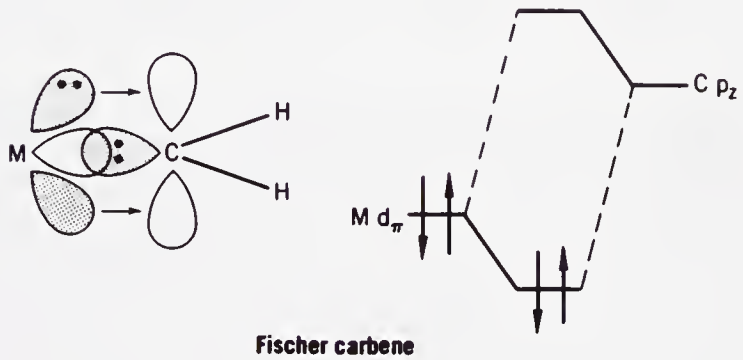
We now look in detail at compounds with multiple bonds between metal and ligand. We are chiefly concerned with multiple bonds to carbon, as in metal–carbene complexes $L_nM{=}CR_2$, which have a trigonal planar carbon and at least formally contain an M=C double bond, and metal–carbyne complexes, $L_nM{\equiv}CR$, which are linear and contain an M≡C triple bond, but we also look at complexes with multiple bonds to O and N.

The simplest carbene is methylene, CH_2, which has an sp^2 hybrid orbital and a p orbital in addition to the two C—H bonds. As a 6e species, CH_2 has 4e in the two C—H bonds and therefore two electrons remain to be placed in the sp^2 and p orbitals on carbon. We will consider that both electrons are placed in the lower-lying sp^2 orbital to give a singlet carbene, leaving the p orbital empty (see Fig. 11.1*a*). In the free carbene, the triplet state, where the two unpaired electrons have parallel spins, is also important, however.

Fischer versus Schrock Carbenes and Carbynes Two extreme types of coordinated carbene can be distinguished: the Fischer[1] and the Schrock[2] type. Each represents a different formulation of the bonding of the CR_2 group to the metal. Carbenes, $L_nM{=}CR_2$, have Fischer character for low oxidation state, late transition metals, having π-acceptor ligands L, and π-donor substituents, R, such as —OMe or —NMe_2, on the carbene carbon. Such a carbene behaves as if it carries a ∂^+ charge, that is to say it is electrophilic. Schrock character is shown by carbenes bound to higher oxidation state, early transition metals, having non-π-acceptor ligands, and non-π-donor R groups. In this case, the carbene behaves as a nucleophile, having a ∂^- carbon. Cases intermediate between the two extremes are especially common for

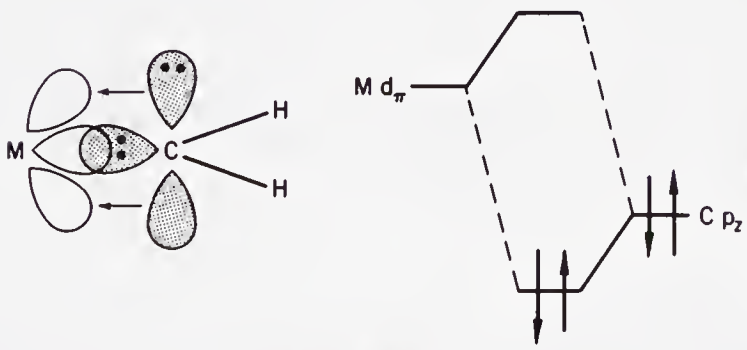


(a)



Fischer carbene

(b)



Schrock carbene

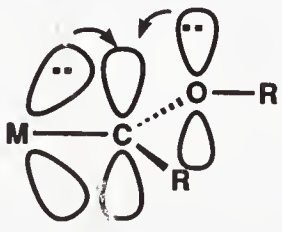
(c)

FIGURE 11.1 The relative energies of the M(d_π) and the C(p_z) orbitals control the electrophilic or nucleophilic character of the carbene. (*a*) The orbitals of free CH_2. (*b*) If the M(d_π) levels are lower in energy, a Fischer carbene will result. (*c*) If the M(d_π) levels are higher in energy, a Schrock carbene will result. Shading represents occupied orbitals.

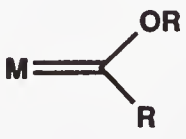
$M{=}C(Hal)_2$ because the halide has intermediate π-donor strength between H and —OMe.[3a]

The charge on the carbene carbon is in part controlled by the energy of the $M(d_\pi)$ orbitals, as shown in Fig. 11.1. The late metals, being more electronegative, have stabler $M(d_\pi)$ orbitals. The presence of π-acceptor ligands L stabilizes the $M(d_\pi)$ levels even more, by the mechanism shown in Fig. 1.7. The early metals, which are more electropositive, have less stable $M(d_\pi)$ levels (greater electropositive character implies that electron loss is easier, which in turn implies that the corresponding orbitals are less stable); d^2 metals are especially strong π donors. A change in oxidation state can alter the situation; for example, $RuCl_2COL_2(=CF_2)$ is predominantly Fischer type and $Ru(CO)_2L_2(=CF_2)$, with its higher-energy $M(d_\pi)$ orbitals, is predominantly Schrock-type.[3a]

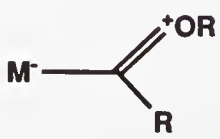
In forming the $M—CR_2$ σ bond, the ligand lone pair [$C(sp^2)$] donates to the metal in the conventional way in both Fischer and Schrock types. The π bond in the Fischer type is best described as a $M(d_\pi)$ to $C(p_z)$ back donation. The electron pair remains largely on the metal because the $M(d_\pi)$ level is considerably more stable than the $C(p_z)$. The electron-deficient carbene carbon is affected by the presence of the lone pair(s) of its π-donor substituents, which I will call OR(l.p.) and which causes the energy of $C(p_z)$ to rise, favoring Fischer character. Structure **11.1** shows how the $M(d_\pi)$ and OR(l.p.) orbitals can be thought of as competing for the stabilization of the carbene carbon. This can be described in v.b. (valence bond) language by resonance between **11.2** and **11.3**. The real structure often resembles **11.3** rather than **11.2** as shown by the long M—C and short C—O bonds found by X-ray studies. For electron counting purposes we use **11.2** and regard the Fischer carbene as an L-type ligand like CO. Note that the true M=C bond order is less than 2, thanks to the contribution of **11.3**.



11.1



11.2



11.3

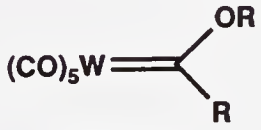
The π bond in the Schrock case is polarized in the $M^+—C^-$ direction, because the $M(d_\pi)$ levels now lie above the $C(p_z)$ level. One way of looking at this is to say that the two electrons originally in $M(d_\pi)$ transfer to the more stable $C(p_z)$ orbital, oxidizing the metal by two units and giving a CR_2^{2-} ligand. The system can therefore be seen as a metal-stabilized carbanion acting as both a σ donor and a π donor to the metal, not unlike phosphorus ylids such as $Ph_3P^+—CH_2^-$. This oxidation of the metal translates into the Schrock

TABLE 11.1 Fischer and Schrock Carbenes $L_nM{=}CR_2$

Property	Fischer	Schrock
Nature of carbene carbon	Electrophilic	Nucleophilic
Typical R groups	π Donor (e.g., —OR)	Alkyl, H
Typical metal	Mo(0), Fe(0)	Ta(V), W(VI)
Typical ligands	Good π-acceptor (e.g., CO)	Cl, Cp, alkyl
Electron count (covalent model)	2e	2e
Electron count (ionic model)	2e	4e
Oxidation state change on addition of CR_2 to L_nM	0	+2

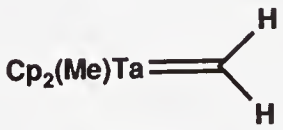
carbene acting as an X_2 ligand, just as the oxo group acts as O^{2-} in a complex such as $Re(=O)Cl_3(PPh_3)_2$ or $Re(=O)Me_4$.

In summary, we can think of the Fischer and Schrock extreme formulations as being L and X_2 models, respectively. This is not unlike the situation we saw in alkene complexes that are also 2e donors, but can adopt either the L (alkene complex), or the X_2 (metalacyclopropane) extreme. In the latter case we also oxidize the metal by two units. In both cases, we expect all possible intermediate structures to exist. Table 11.1 summarizes the differences. Structures **11.4** and **11.5** show typical Fischer (**11.4**) and Schrock (**11.5**) carbenes.



W(0), 18e

11.4

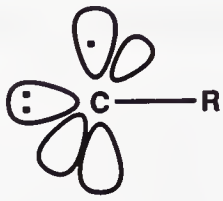


Ta(V), 18e

11.5

The term *alkylidene* refers to carbenes, CR_2 with alkyl substituents; for example, $MeCH{=}ML_n$ is an ethylidene complex but "alkylidene" is sometimes used as a synonym for "Schrock carbene" in the older literature because the first alkylidenes were of the Schrock type. There are electrophilic Fischer alkylidenes as well as nucleophilic Schrock ones, however, so the terms should be kept separate. For example, $[Cp_2W(=CH_2)Me]^+$, and $Cp_2Ta(=CH_2)Me$ are isoelectronic, but the former is electrophilic and the latter nucleophilic at the carbene carbon;[3b] the net positive charge on the tungsten complex must stabilize the $M(d_\pi)$ levels and is therefore probably the main reason for the difference.

Carbyne complexes contain an M≡CR triple bond and are also known for both low and high oxidation states. We can regard the carbyne fragment as having an *sp* lone pair and a single electron in one of the two *p* orbitals (**11.6**).

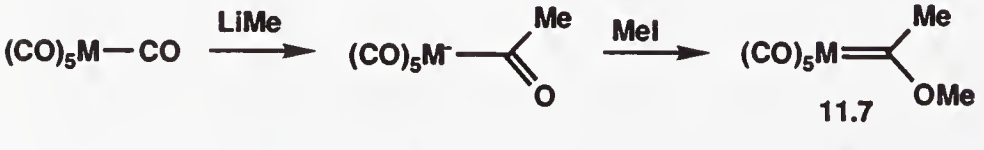


11.6

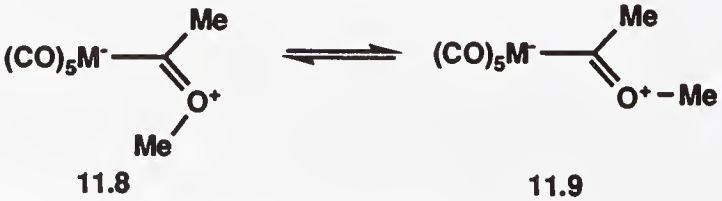
In the Fischer bonding scheme, we can consider that in forming its three bonds to the metal, the carbyne (1) acts as a σ donor via the C(*sp*) lone pair, (2) forms a normal π covalency by the combination of its singly occupied C(*p*) orbital with a singly occupied M(*d*) orbital, and (3) accepts back bonding from a filled M(*d*) orbital into its empty C(*p*) orbital. In the Schrock carbene, the pair of electrons that were M-to-L back bonding in the Fischer case are moved completely on to the C(*p*) orbital of the ligand. In both cases we have a 3e donor ligand on the covalent model (ionic model: Fischer, 4e; Schrock, 6e), but of LX type in the Fischer and X_3 type in the Schrock case, so that the ligand makes the oxidation state of the metal more positive by one or three units, respectively, in the two cases. Oxidation states are usually counted as follows: $L_nM{=}CR_2$ is M(0) for a Fischer and M(II) for a Schrock case; in intermediate cases both assignments can be found.

11.1 METAL CARBENES

Fischer Carbenes Fischer recognized the first carbene complexes in 1964.[4] They were formed by the attack of an alkyllithium on a metal carbonyl followed by methylation (Eq. 11.1). Going back to the bonding picture mentioned above, we saw that the methoxy substituent will also help stabilize the empty *p* orbital on the carbene carbon by π donation from one of the lone pairs on oxygen. Resonance form **11.3**, which is probably the dominant one in the heteroatom stabilized Fischer carbenes, shows the multiple character of this bond. This effect is responsible for the restricted rotation often observed for the heteroatom–carbene carbon bond in NMR studies. For example cis and trans isomers **11.8** and **11.9** of methoxymethyl carbenes are rapidly interconverting at room temperature (Eq. 11.2), but can be frozen out in the proton NMR at $-40°C$.[5]

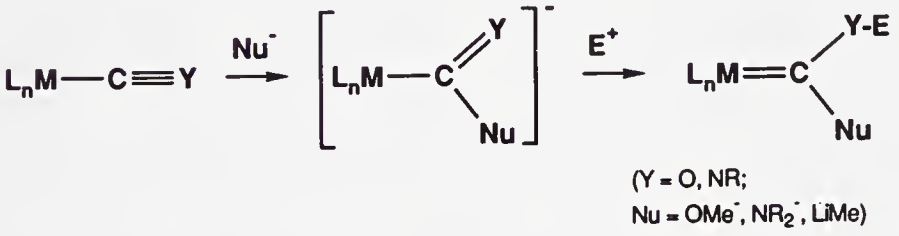


11.7 (11.1)

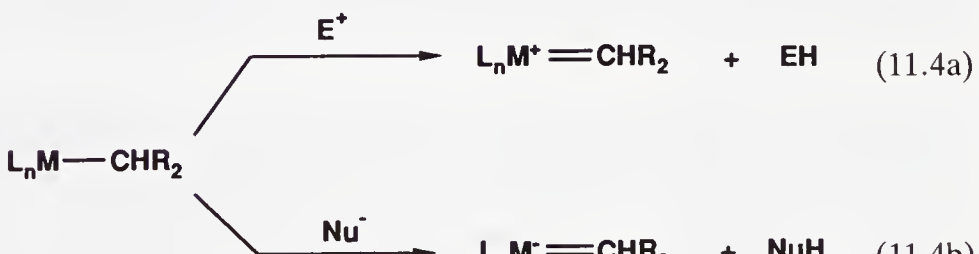


11.8 **11.9** (11.2)

Preparation The key synthetic routes tend to fall into one of three general categories, illustrated by Eqs. 11.3–11.5. In Eq. 11.3, an acyl or similar species (often but not always formed by a nucleophilic attack on a CO or a similar ligand) is treated with an electrophile to give a Fischer carbene. In Eq. 11.4 an H^- (Fischer case) or an H^+ (Schrock case) is abstracted from the α position of an alkyl, and in Eq. 10.5 a carbene source is used. In Eqs. 11.4b and 11.5 the L_nM fragment must be able to accept an extra pair of electrons during the reaction, and so the starting material must have <18e or be able to lose a ligand. Examples of Eqs. 11.3 and 11.4a are shown below, and examples of 11.4b and 11.5 are shown in the section on Schrock carbenes.

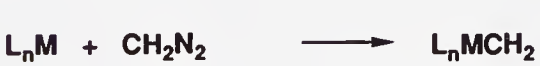


(11.3)



(11.4a)

(11.4b)

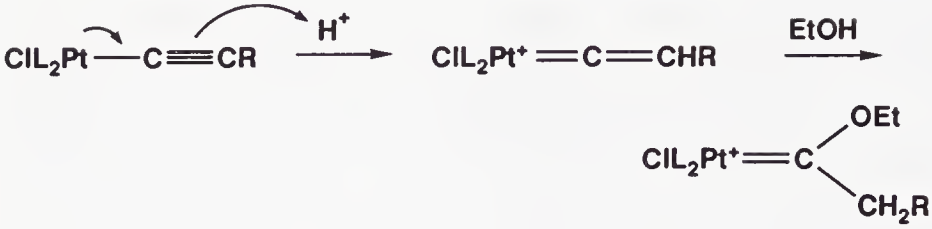


(11.5)

Isonitriles are very sensitive to nucleophilic attack, and a wide range of bis-heteroatom-stabilized carbenes can be obtained:[6]

(11.6)

Chugaev[7] obtained carbene complexes very similar to these as early as 1915, but was not able to assign the right structure, given the methods available at that time. Acetylides $L_nM—C{\equiv}CR$ are unexpectedly good bases[8a] via their canonical form $L_nM^+{=}C{=}C^-R$. They can react with acid in alcohol solution to give the carbenes shown in Eq. 11.7. An intermediate vinylidene cation probably undergoes nucleophilic attack by the alcohol.[8b] In this case the usual order of attack shown in Eq. 11.3 (Nu^-, then E^+) is inverted.



(11.7)

Electrophilic abstraction from an alkyl complex (Eq. 11.4a) is illustrated in the reactions of Eqs. 11.8 and 11.9; Eq. 11.9 is driven by the high Si—F bond strength.

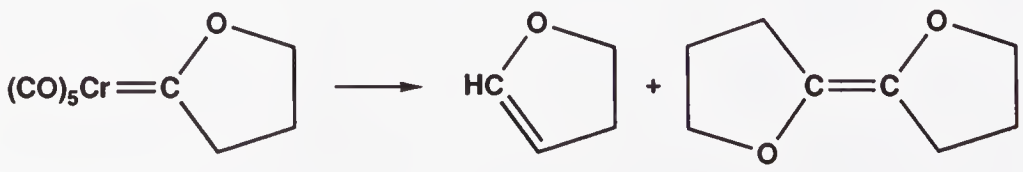
$$Cp(CO)_2FeCH_2OMe + H^+ \longrightarrow \text{`}Cp(CO)_2Fe{=}CH_2^+\text{'} \longrightarrow \text{other products} \quad (11.8)$$

$$Cl(CO)(MeCN)L_2RuCF_3 + Me_3SiCl \longrightarrow Cl_2(CO)L_2Ru{=}CF_2 + Me_3SiF \quad (11.9)^{9}$$

Alkylidenes can sometimes be made from organic carbene precursors such as diazomethane[10a] or R_2CCl_2.[10b]

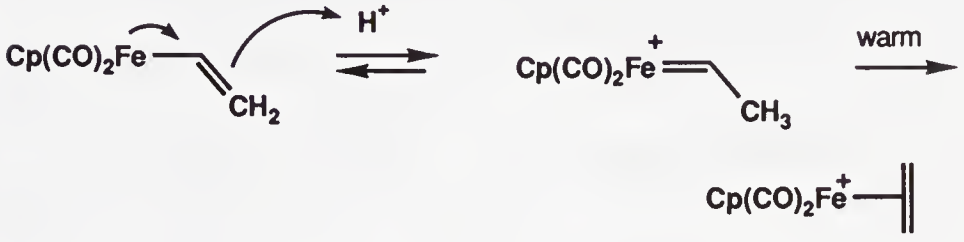
Spectroscopy ^{13}C NMR is a very valuable technique for detecting carbene complexes because the carbene carbon is very deshielded and resonates at ~200–400 ppm to low field of TMS. It is tempting to ascribe this deshielding to the ∂^+ character of the carbene carbon, but as we shall see, Schrock carbenes, which are ∂^- in character at carbon, show similar shifts. In fact, the shift is probably a result of the existence of low energy electronic excited states for the complex, which leads to a large "paramagnetic" contribution to the shift. A proton substituent at the carbene carbon resonates from +10 to +20δ.

Reactions Thermal decomposition of carbene complexes usually leads to one or both of two types of alkenes:[11a] one type is formed by rearrangement, and the other by dimerization of the carbene. Equation 11.10[11b] shows both types of product. The reaction does not go via the free organic carbene, because cyclobutanone, which is known to be formed in the rearrangement of the free carbene, was not detected in the products.



(11.10)

Fischer carbenes without a heteroatom substituent are very reactive.[12a] The protonation of vinyl complexes is one route to these species (e.g., Eq. 11.11):[12b]



(11.11)

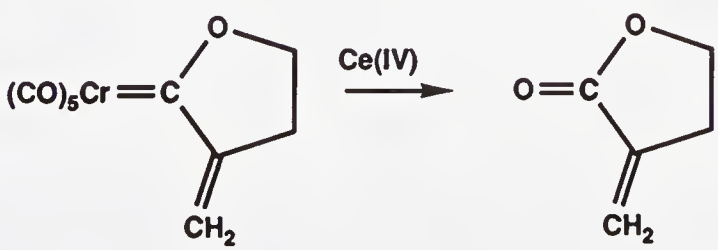
The addition of base reverses the reaction by a nucleophilic abstraction. The ethylidene complex readily gives a 1,2 shift of the β-proton to give the thermodynamically more stable alkene complex. Even carbenes that lack β hydrogens are unstable: $[Cp(CO)_2Fe{=}CH{-}CMe_3]^+$ and $[Cp(CO)_2Fe{=}CH{-}CMe_2Ph]^+$ both rearrange by a 1,2 shift of a methyl or a phenyl group, respectively, to the electron-deficient carbene carbon (Eq. 11.12).[13] This reaction, analogous to the Wagner–Meerwein rearrangement in carbonium ions, is fast because of the electron-deficient character of the carbene carbon in this complex.

(11.12)

(R = Me or Ph)

$[Cp(Ph_2PCH_2CH_2PPh_2)Fe{=}CH{-}CMe_3]^+$ does not rearrange, however, probably because the increased back donation by the more electron-rich phosphine-substituted iron decreases the electron deficiency at the carbene carbon.[14]

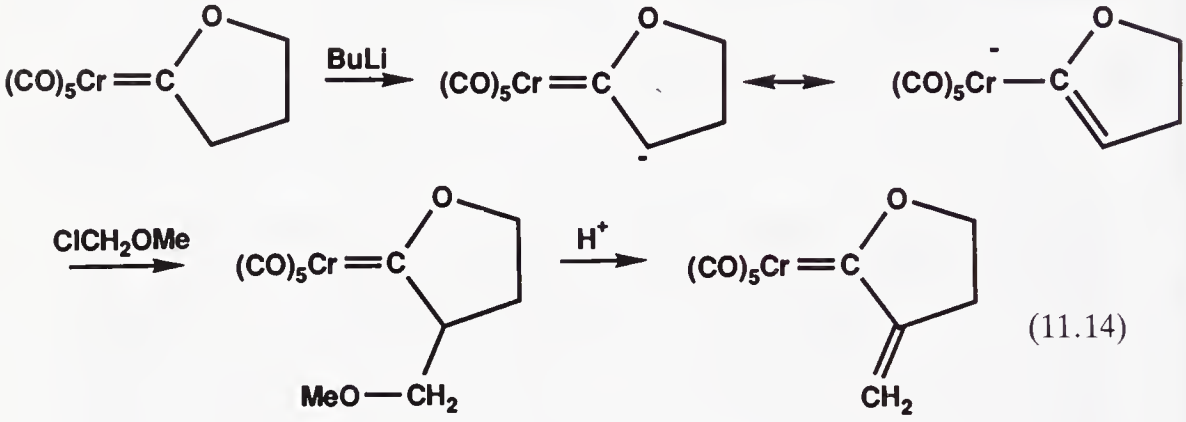
Oxidative cleavage of a carbene ligand can be achieved with reagents such as Ce(IV) compounds, pyridine N-oxide, or dmso, or even with air. The product is normally the ketone corresponding to the starting carbene. This reaction is useful not only for synthetic purposes but also for characterizing the original carbene (e.g., Eq. 11.13):[15]



(11.13)

11.10

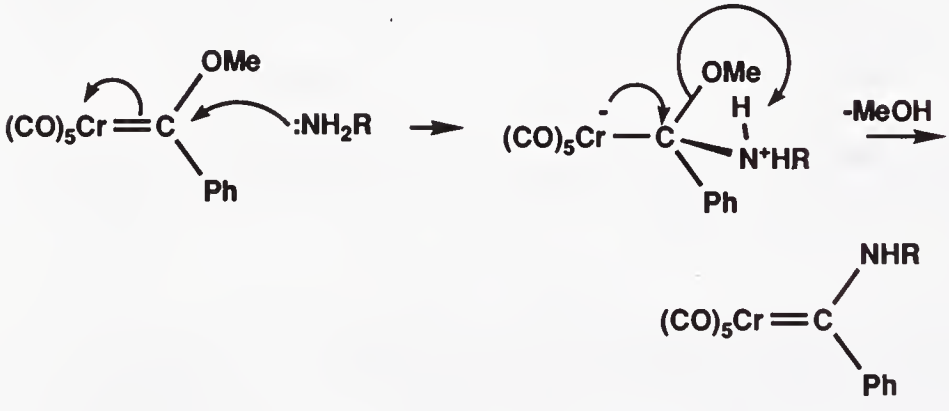
The synthesis of **11.10** illustrates another useful reaction of Fischer carbenes, the abstraction of a proton β to the metal by a base such as an organolithium reagent. The resulting negative charge can be delocalized onto the metal as shown in Eq. 11.14,[15] and is therefore stabilized. The anion can be alkylated by carbon electrophiles as shown.



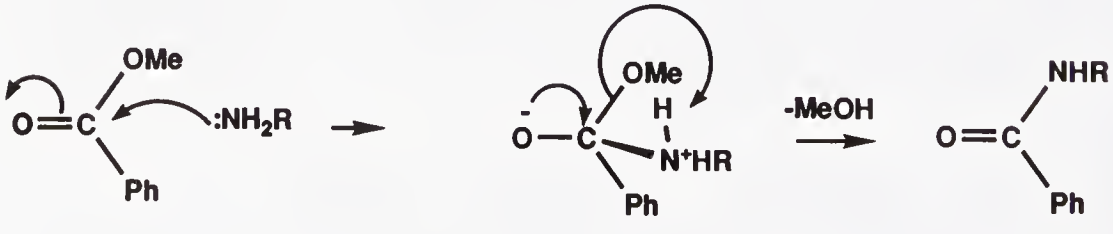
(11.14)

11.10

Fischer carbenes readily undergo nucleophilic attack at the carbene carbon, as shown in Eq. 11.15.[16] The attack of amines can give the zwitterionic intermediate shown, or by loss of methanol, the aminocarbene. If we mentally replace the $(CO)_5Cr$ group an oxygen atom, we can see the relation of this reaction to the aminolysis of esters to give amides (Eq. 11.16).



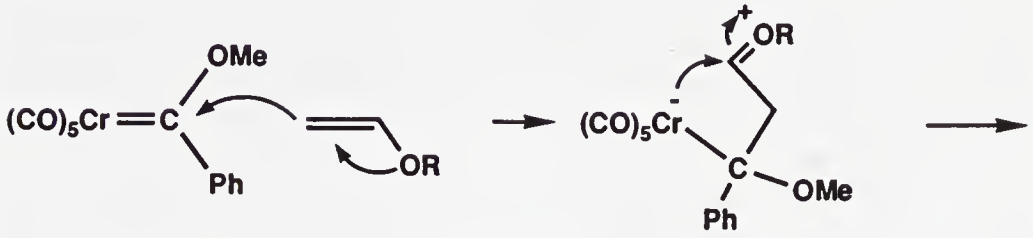
(11.15)

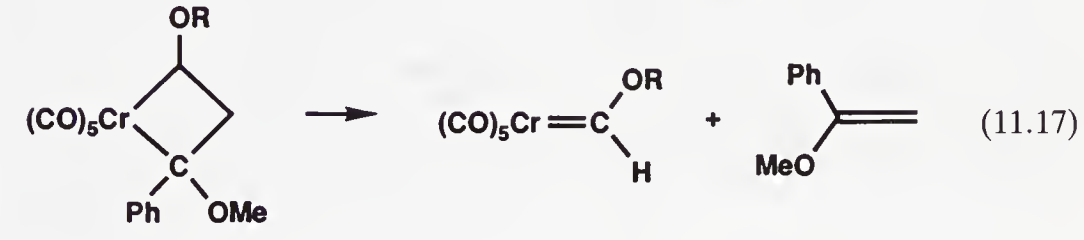


(11.16)

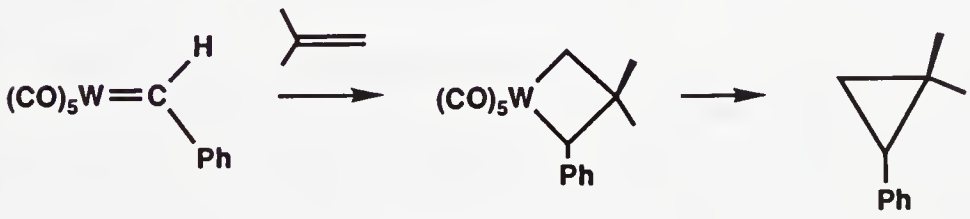
The addition of carbon nucleophiles or of alkenes can lead to the formation of metalacycles. These can break down to a carbene and an alkene (Eq. 11.17),[17] or reductive elimination may take place to give a cyclopropane (Eq. 11.18).[18] We will return to the formation of metalacycles from alkenes and

carbenes because this is the key reaction in the alkene metathesis reaction (Section 11.4).



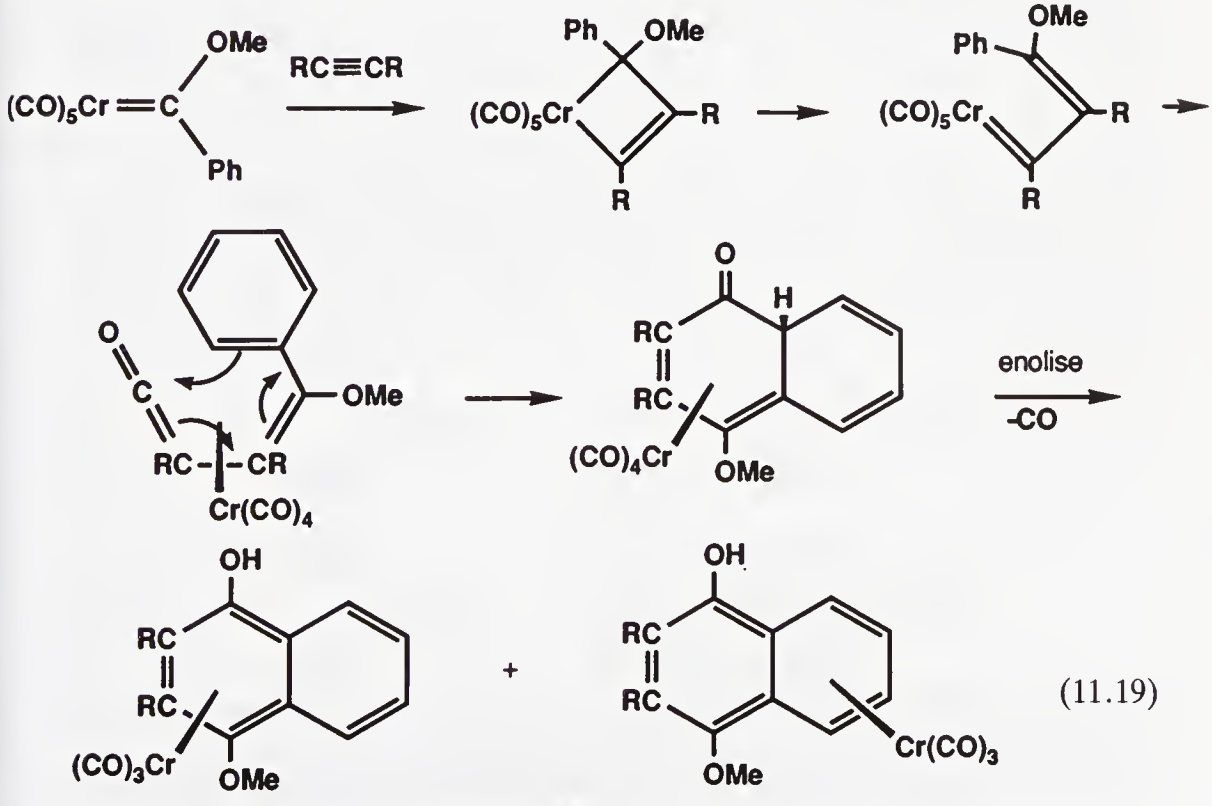


(11.17)



(11.18)

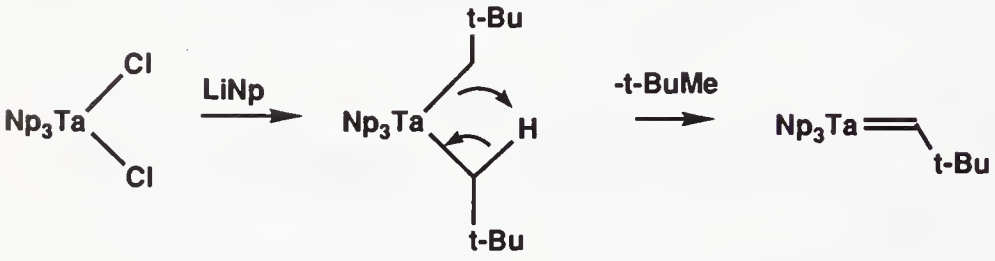
The reaction of carbenes with alkynes seems to give metalacyclobutenes, but these often rearrange. Equation 11.19 shows the Dötz reaction for the synthesis of naphthols.[19] Note that two naphthol haptomers are found.



(11.19)

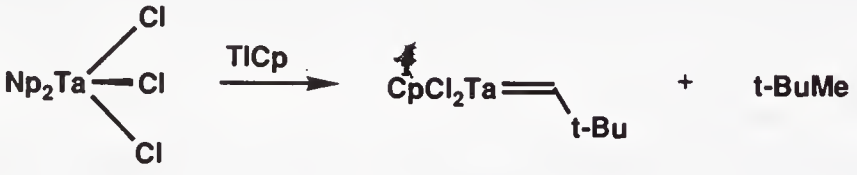
haptomers

Schrock Carbenes High-valent metal alkyls, especially of the early metals, can undergo proton abstraction at the α carbon to give nucleophilic Schrock[20] carbenes. The first high-oxidation-state carbene was formed in an attempt to make $TaNp_5$ (Np = CH_2CMe_3, or neopentyl), by the reaction of $TaNp_3Cl_2$ with LiNp.* In fact, the product is $Np_3Ta{=}CH(t\text{-Bu})$ (Eq. 11.20). The reaction probably goes via $TaNp_5$, which then loses neopentane by an α-proton abstraction from one (possibly agostic) Np ligand by another.[2,21]

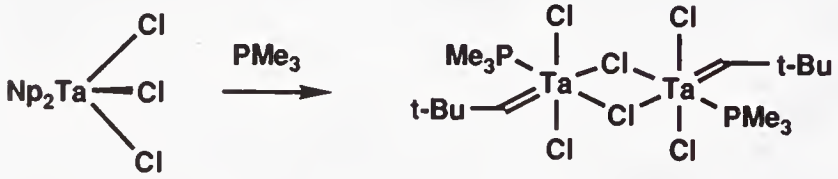


(11.20)

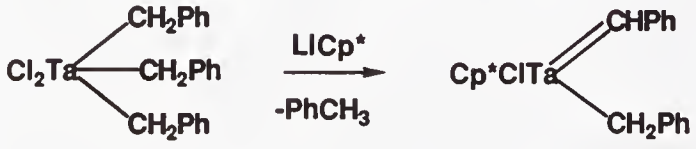
One requirement for this α elimination is that the molecule be crowded. Substitution of a halide in Np_2TaCl_3 with a Cp group (Eq. 11.21)[22] is enough to do this, for example, as is addition of a PMe_3 (Eq. 11.22).[2] The corresponding benzyl complexes require one of the more bulky pentamethylcyclopentadienyls, Cp* (Eq. 11.23),[23] or two plain Cp groups (Eq. 11.24).[22]



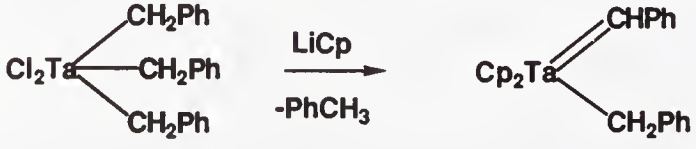
(11.21)



(11.22)



(11.23)



(11.24)

*Interestingly, Wittig was trying to make Ph_3PMe_2 when he discovered $Ph_3P{=}CH_2$.

By adding two PMe_3 ligands, we see that the α proton of a benzylidene can undergo abstraction to give a benzylidyne (Eq. 11.25).

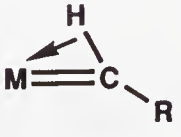
$$Cp^*Ta(=CHPh)(CH_2Ph)Cl \xrightarrow{2PMe_3} Cp^*Ta(\equiv CPh)(PMe_3)_2Cl + PhCH_3 \quad (11.25)$$

The methyl group is so sterically undemanding that it does not α-eliminate under the same conditions (Eq. 11.26). The synthesis of a methylene complex requires a deprotonation of a methyl complex by a strong base. By putting a net positive charge on the complex, we can activate the methyl for this reaction. Equation 11.27 shows how this can be done by an electrophilic abstraction of Me^-. Note that if this had been a low valent metal, electrophilic abstraction of H^- by Ph_3C^+ to give an electrophilic (Fischer) methylene complex might have taken place.

$$TaMe_3Cl_2 \xrightarrow{LiCp} CpTaMe_3Cl \xrightarrow{LiCp} Cp_2TaMe_3 \quad (11.26)^{20}$$

$$Cp_2TaMe_3 \xrightarrow{Ph_3C^+} Cp_2TaMe_2^+ \xrightarrow{base} Cp_2Ta(=CH_2)Me \quad (11.27)^{24}$$

Structure and Spectra You may have noticed that few of the early metal complexes we have been looking at seem to be 18e. $TaMe_3Cl_2$ is ostensibly 10e, for example. This is not unusual for high-oxidation-state complexes, especially in the early metals, where the *d* orbitals are not so stabilized as in lower oxidation states or for later metals (Chapter 15). The halide has lone pairs that might be partially donated to the empty d_π orbitals, and the alkyls have C—H bonds that might become agostic, so the metal may be able to obtain some extra electron density from these. It is a feature of Schrock carbene complexes that have <18e that they commonly have agostic C—H bonds. When this happens, the proton on the carbene carbon bends back toward the metal, the M=C bond becomes shorter, and the C—H bond becomes longer (**11.11**). Note the contrast with late metals where these d_π orbitals are usually full and the complex is often 18e, so we do not see agostic C—H bonds.



11.11

Agostic binding leads to a high-field shift for this proton and a lowering of the C,H coupling constant in the ^1H NMR, together with a lowering of ν(C—H) in the IR. In 18e carbene complexes, such protons are not agostic

and usually appear at 12δ with a J(C,H) of 105–130 Hz; in the complexes with <18e, they can come as high as −2δ with a J(C,H) of 75–100 Hz. At the same time a ν(C—H) band appears in the IR at a position indicating that it has been weakened by the interaction, for example, at 2510 cm^{-1} in $CpTa\{CH(t\text{-}Bu)\}Cl_2$. Crystal structures[25] show that the M=C—R angle can open up to as much as 175°, while the M=C—H angles fall to as little as 78°. The M=C bond length is always short (at least 0.2 Å shorter than an M—C single bond) in all cases studied, but is even shorter in the complexes with <18e. Interestingly, the oxo alkylidene $Cl_2(PEt_3)_2W(=O)(=CHCMe_3)$ has a much less distorted alkylidene group. This is probably because the lone pairs on the oxo group are more basic and so more available for the metal than the C—H bonding pair.[26]

The structure of $Cp_2Ta(CH_2)Me$ (by neutron diffraction) is interesting because the orientation of the methylene group is not the one predicted on steric grounds, with the CH_2 lying in the mirror plane of the molecule, but nearly at right angles (88°) to this plane, with the proton substituents pointing in the direction of the Cp groups. Whenever we see a countersteric conformation like this, an electronic factor is usually at work. Here, the filled p_z orbital of the CH_2 group is interacting with one of the empty orbitals on the metal. Since these orbitals are in the mirror plane of the molecule (see Section 5.4), this fixes the orientation of the CH_2 (Fig. 11.2). The larger CHR alkylidenes deviate only slightly from the orientation shown by CH_2, and so the two Cp groups become inequivalent. The ^1H NMR spectrum of the complexes shows this inequivalence but the two Cp groups become equivalent on warming. If we assume that the fluxional process is rotation about the M=CHR bond, then in the transition state, the alkylidene probably lies in the mirror plane and has no π interaction with the metal. The $\Delta G^{\ddagger}$ deduced from the data, 25 kcal/mol, therefore gives an estimate of the strength of the Ta=C π bond.

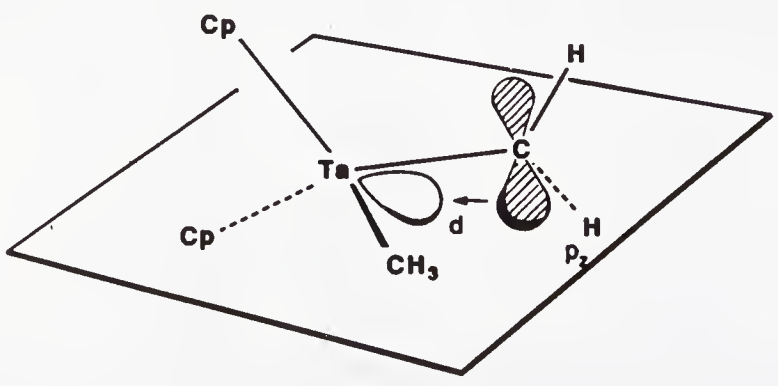
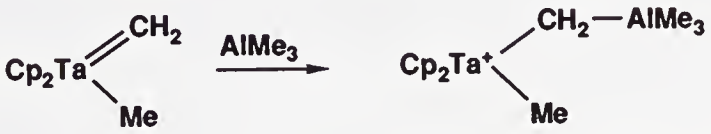


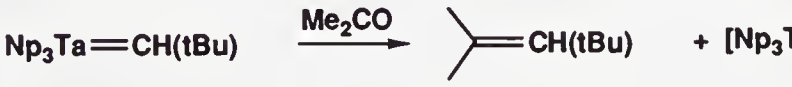
FIGURE 11.2 The orientation of the methylene group in $Cp_2Ta(CH_2)Me$ is contrary to what would be expected on steric grounds and is controlled by the overlap of the C(p_z) with a metal d orbital that lies in the plane shown.

Reactions The reactions of Schrock carbenes illustrate their nucleophilic character. For example, they form adducts with the Lewis acid $AlMe_3$:



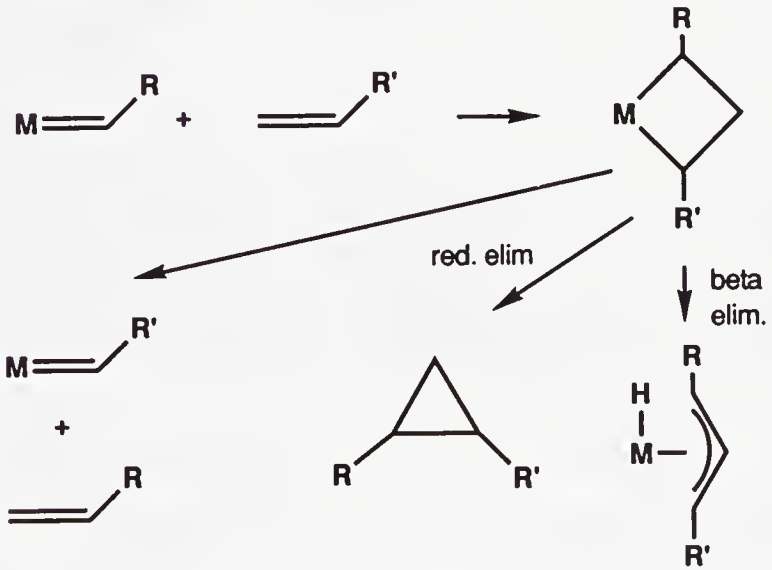
(11.28)

They also react with ketones in the same way as a Wittig reagent (eq. 11.29).[27]

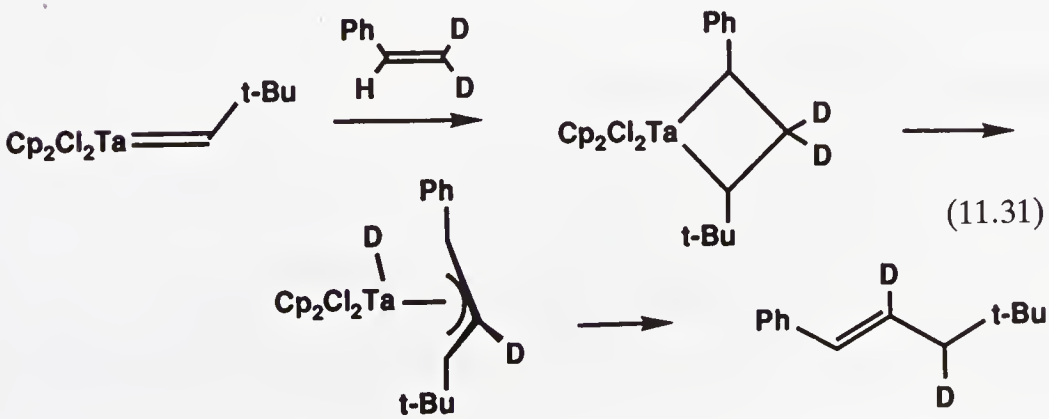


(11.29)

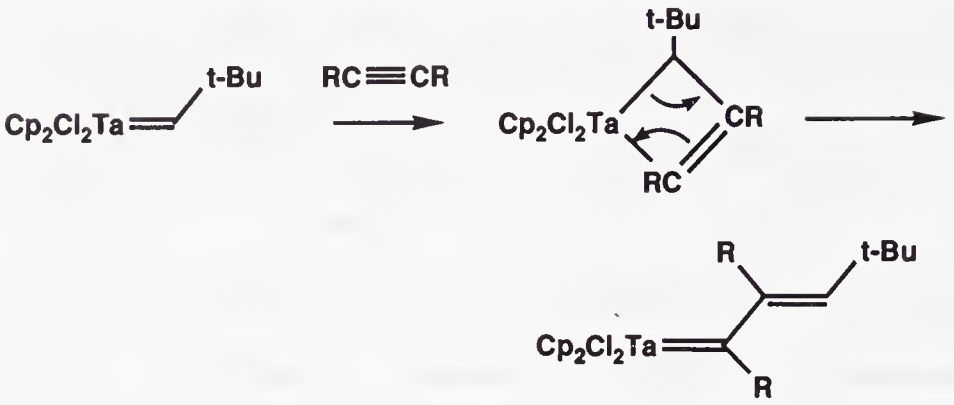
Alkenes react with carbenes to give metalacycles. The alkene may coordinate to the metal first, if only transiently. The carbene carbon then attacks the coordinated alkene to give the product. The metalacycle can decompose in several ways (Eq. 11.30), either by reversal of the formation reaction to give alkene and a carbene, by reductive elimination to give a cyclopropane, or by β elimination to give an alkene. The latter route is usually observed in the Ta complexes (Eq. 11.31). Alkynes give a metalacyclobutene, which can rearrange as shown in Eq. 11.32.[20]



(11.30)

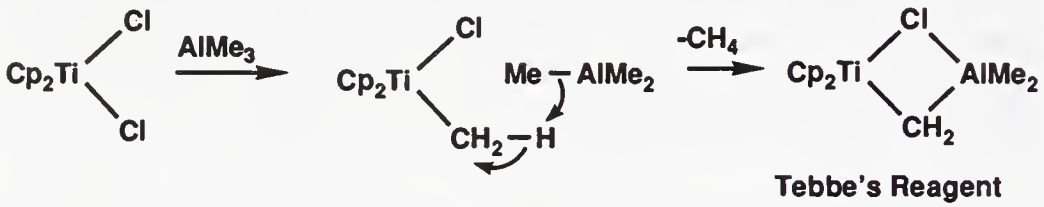


(11.31)



(11.32)

As might be expected, the more electropositive Ti forms even more nucleophilic carbene complexes. One of the most interesting species of this class is Tebbe's reagent, formed from Cp_2TiCl_2 and $AlMe_3$ (Eq. 11.33):[28]

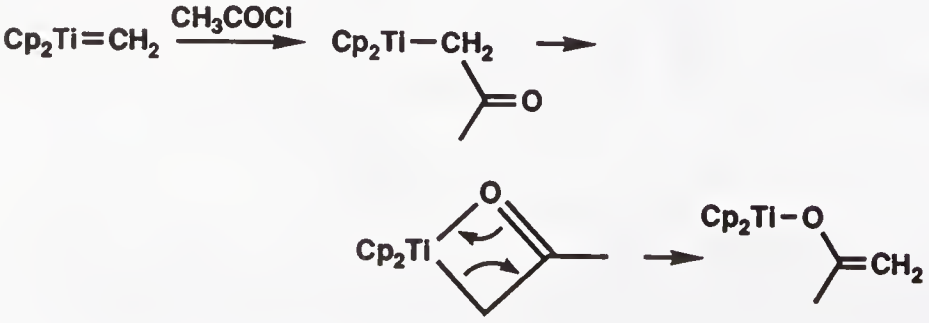


(11.33)

This is an example of a bridging carbene, but in its reactions it almost always loses Me_2AlCl first to give the mononuclear 16e $Cp_2Ti{=}CH_2$; a base is sometimes added to help remove the aluminum fragment by complexation. This reagent even gives a Wittig-type product with esters, substrates that are not methylenated with $Ph_3P{=}CH_2$. In addition, Tebbe's reagent does not racemize enolizable ketones as do the phosphorus ylids.[29a]

$$\text{`}Cp_2Ti{=}CH_2\text{'} + RCOOR' \longrightarrow R(OR')C{=}CH_2 \qquad (11.34)$$

Acyl halides, on the other hand, do not methylenate, but give an enolate (Eq. 11.35):[29b]



(11.35)

Tebbe's complex reacts with alkenes to give stable metalacycles, which are more convenient precursors for the "$Cp_2Ti{=}CH_2$" carbene than is Tebbe's reagent itself. The metalacycles undergo a number of useful reactions shown in Fig. 11.3.[29a] Protonation gives the alkanes. Bromination gives the 1,3-dibromides. Oxidation with I_2 leads to net reductive elimination to give the cyclopropane; this probably goes via an intermediate iodopropyl iodide.

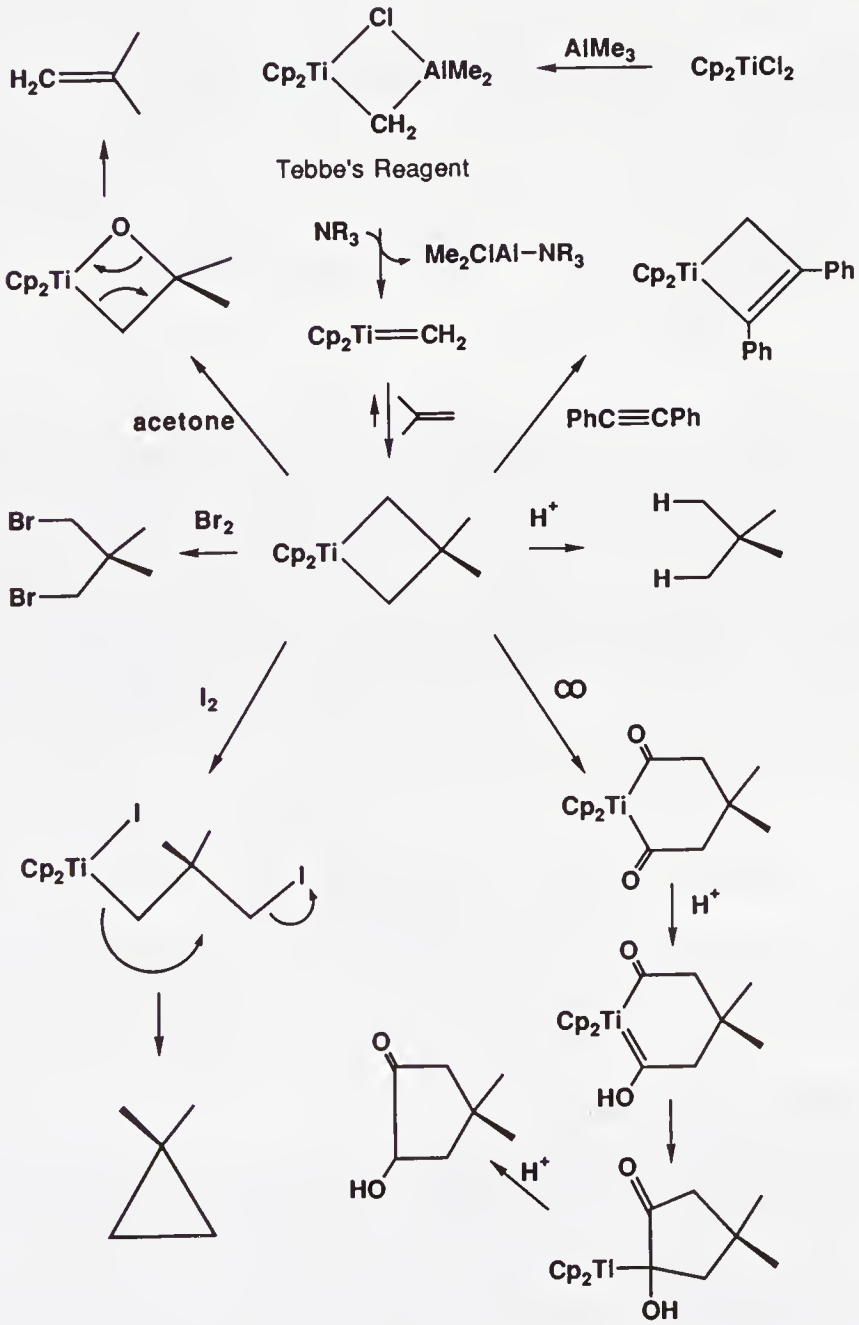
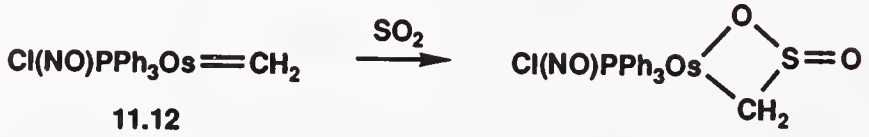
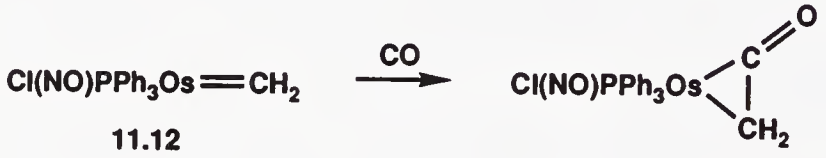


FIGURE 11.3 Some reactions of "$Cp_2Ti{=}CH_2$," formed from Tebbe's reagent.

Intermediate Cases In the Os complex **11.12**, Roper[29c] has a carbene with character intermediate between the Fischer and Schrock extremes because it reacts both with electrophiles [e.g., SO_2 (Eq. 11.36)[29c] or H^+] and with nucleophiles [e.g., CO (Eq. 11.37)[29c] or CNR]. This is reasonable based on our bonding picture. The osmium has π-donor (Cl) as well as π-acceptor (NO) ligands, the metal is in an intermediate oxidation state [Os(II) if we count the carbene as L, Os(IV) if X_2], and the carbene carbon has non-π-donor substituents (H).

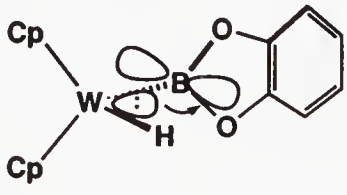


11.12 (11.36)



11.12 (11.37)

Boryl Complexes The BR_2 group is isoelectronic with CR_2 and a few boryl complexes have now been isolated, including $Cp_2WH(B\{cat\})$, $CpFe(CO)_2(B\{cat\})$[29d] (cat = catecholate {**9.30**}), and $RhHCl(B\{cat\})(PPh_3)_2$, which is one of the products formed from the oxidative addition of H—B(cat) with Wilkinson's catalyst.[29e] As in a carbene, a M=B multiple bond seems to be present; for example in $Cp_2WH(B\{cat\})$, the B(cat) group is aligned in the least sterically favorable conformation, shown below, so the empty *p* orbital on boron can π-bond with the filled metal *d* orbital shown. The π bond is not as strong as in a carbene, however, because the NMR spectrum shows that the B(cat) group is rapidly rotating.[29d]



11.2 METAL CARBYNES[30]

Synthesis Fischer first prepared carbyne complexes (1973) by electrophilic abstraction of methoxide ion from a methoxy methyl carbene.

$$L(CO)_4M{=}C(OMe)Me + BX_3 \longrightarrow$$
$$[L(CO)_4M{\equiv}CMe]^+BX_4^- + BX_2(OMe) \longrightarrow X(CO)_4M{\equiv}CMe \quad (11.38)^{13}$$

If L is CO, then the halide ion (Cl, Br, or I) displaces the CO trans to the carbyne in the intermediate cationic complex; this shows the high trans effect of the carbyne. On the other hand, if L is PMe_3, then the cationic species is the final product. Oxidation states for Fischer carbynes are normally assigned by considering CR as an LX ligand, CR^-; that is, $X(CO)_4M{\equiv}CMe$ is M(II).

By carefully controlled oxidation, Mayr[31a] has been able to remove the carbonyl ligands in a Fischer carbyne to give a Schrock carbyne, thus making a direct link between the two types. This also allows synthesis of Schrock carbenes and carbynes with substituents other than the ones that can be obtained by the standard methods. In Eq. 11.39, we can think of the Br_2 oxidizing the metal by two units. This destabilizes the metal d_π orbitals relative to the carbon p orbitals, and so switches the polarity of the metal–carbon multiple bond. Note how the coligands change on going from the soft carbonyls in the W(II) starting material to the hard dme ligand in the W(VI) product. Schrock carbynes are nearly always d^0 (counting the carbyne as an X_3 ligand) as here.

$$Br(CO)_4W{\equiv}CMe \xrightarrow{Br_2,\ dme} Br_3(dme)W{\equiv}CMe \qquad (11.39)^{31a}$$

(dme = $MeOCH_2CH_2OMe$).

Otherwise, Schrock carbynes can be made by deprotonation of an α-CH (Eq. 11.40); by an α elimination, in which this CH bond in effect oxidatively adds to the metal (Eq. 11.41); or in rare cases by a remarkable metathesis reaction[32] (Eq. 11.42). This reaction fails for coligands other than *t*-butoxide, showing the sensitivity of the different reaction pathways to the electronic and steric environment of the metal. MeCN is cleaved in the same way to a carbyne and a nitride $(t\text{BuO})_3W{\equiv}N$.

$$CpCl_2Ta{=}CHR \xrightarrow{\text{(i) } PMe_3,\ \text{(ii) } Ph_3P{=}CH_2} CpCl(PMe_3)Ta{\equiv}CR \qquad (11.40)$$

$$Cp^*Br_2Ta{=}CHt\text{Bu} \xrightarrow{\text{(i) dmpe, (ii) Na/Hg}} Cp^*(dmpe)HTa{\equiv}Ct\text{Bu} \qquad (11.41)$$

$$(t\text{BuO})_3W{\equiv}W(Ot\text{Bu})_3 + t\text{BuC}{\equiv}Ct\text{Bu} \longrightarrow 2(t\text{BuO})_3W{\equiv}Ct\text{Bu} \qquad (11.42)$$

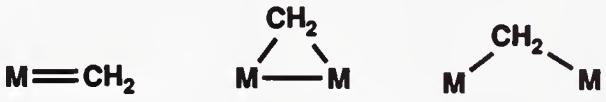
Structure and Spectra The carbyne ligand is linear, having *sp* hybridization, and the M≡C bond is very short (first row, 1.65–1.75 Å; second and third rows, 1.75–1.90 Å). The ^{13}C NMR shows a characteristic low-field resonance for the carbyne carbon at +250 to +400 ppm.

Reactions A carbyne can couple[31b] with another carbyne to give an alkyne or alkyne complex.[33] For instance, $Br(CO)_4Cr{\equiv}CPh$ reacts with Ce(IV) to give free $PhC{\equiv}CPh$. Carbynes also have extensive photochemistry.[34] In the Fischer series, the carbyne carbon is electrophilic and subject to nucleophilic attack, for example, by PMe_3, pyridine, RLi, or isonitrile (= Nu) to give a carbene of the type $L_nM{=}CR(Nu)$.[30] Alternatively, the nucleophile may attack the metal in $L_n(CO)M{\equiv}CR$ and produce a ketenyl complex

$L_n(Nu)M(\eta^2\text{-}OC{=}CR)$ or $L_n(Nu)_2M(\eta^1\text{-}OC{=}CR)$. On the other hand, Schrock carbynes are nucleophilic and subject to attack by electrophiles, for instance, $(t\text{-}BuO)_3W{\equiv}C(t\text{-}Bu)$ reacts with HCl to give $(t\text{-}BuO)_2Cl_2W{=}CH(t\text{-}Bu)$.

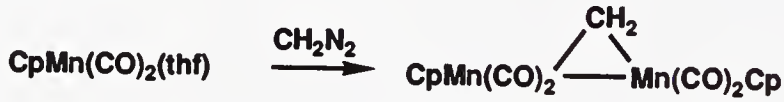
11.3 BRIDGING CARBENES AND CARBYNES

Like CO, carbenes can act not only as terminal (**11.13**) but also as bridging ligands.[35] When they bridge, there is usually a metal–metal bond present as well (**11.14–11.15**). In bridging, carbenes lose some of their unsaturation, and therefore the very high reactivity of their mononuclear analogs. Fischer methylenes are very reactive and barely isolable, while bridging methylenes are well known and relatively stable.



11.13 **11.14** **11.15**

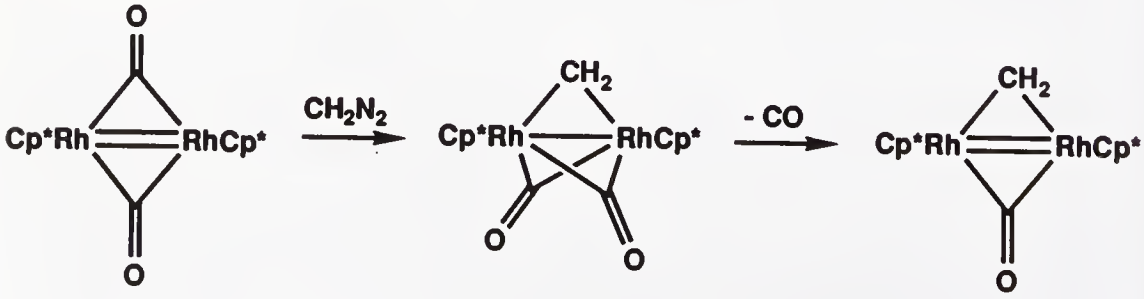
One of the most valuable synthetic routes to bridging carbenes involves the use of diazomethane (Eq. 11.43) and related compounds (Eq. 11.44)[36], which are precursors for free carbenes in organic chemistry.



(11.43)

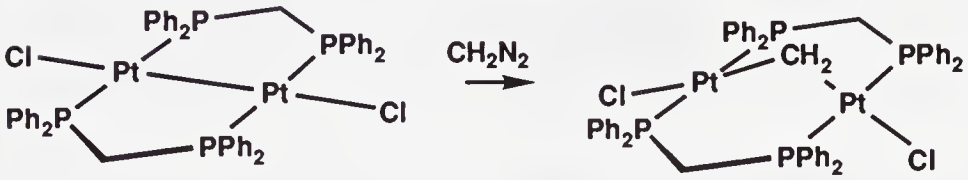
(11.44)

Diazomethane will add not only to monomeric metal complexes but also to compounds containing metal–metal double bonds, a reaction somewhat analogous to the addition of a free carbene to a C=C double bond to give a cyclopropene. This analogy suggested itself to three groups at the same time, and, remarkably, they tried exactly the same reaction, Eq. 11.45:[37]



(11.45)

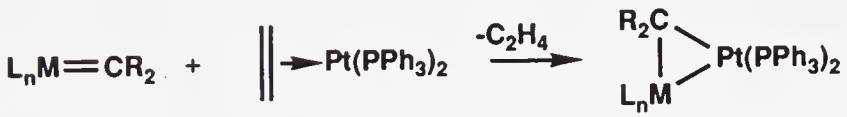
Note how loss of CO regenerates the Rh=Rh double bond in what is really a substitution of CO by CH_2. Insertion of CH_2 into a metal–metal single bond is seen in the synthesis of the platinum "A-frame" (so-called because the structure resembles the letter A) complex **11.16** in Eq. 11.46,[38] a rare example of a bridging methylene complex without an M—M bond.



(11.46)

11.16

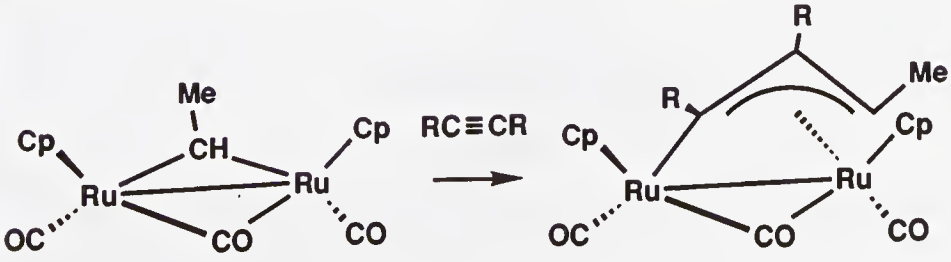
The second general method of bridging carbene complexes involves the analogy between C=C and M=C double bonds. Since many metal complexes will react with C=C double bonds to give alkene complexes, Stone investigated the reactions of the same metal complexes with compounds containing an M=C bond (Eq. 11.47). This is a very powerful method of making a variety of homo- and heterometallic complexes, and can be extended to the M≡C triple bond as well.



(11.47)

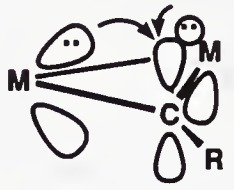
Structure and Spectra The ^{13}C NMR resonance positions of the carbene carbon for terminal and bridging carbenes reflects the greater unsaturation of the terminal type. Terminal groups resonate at a range from 250 to 500δ, while bridging groups appear from 100 to 210δ if an M—M bond is present, and between 0 and 10δ if not; for comparison, simple metal alkyls resonate at −40 to 0δ. These values probably reflect the change in hybridization required for the carbon atom to form bonds at the angles required by the geometry of the complex. If no metal–metal bond is present (**11.15**), then these angles will be close to 109° apart and no special rehybridization will be required. If an M—M bond is present, the two M—C bonds are usually 75–85° apart. In a terminal carbene, the two bonds are, of course, formed with the same metal atom.

Reactions Bridging carbenes are highly reactive toward alkynes, which give insertion as shown in Eq. 11.48:[39]



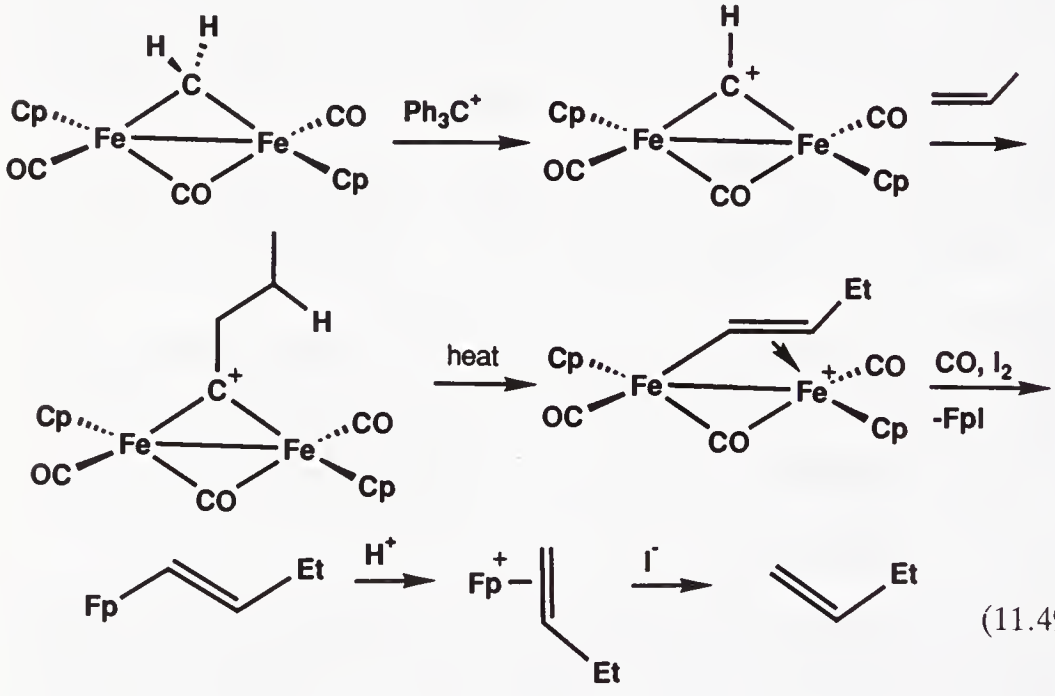
(11.48)

Hydride abstraction from a bridging carbene can give a μ_2-bridging carbyne, which is unsaturated, is very reactive, and shows pronounced carbonium ion character. The bonding scheme resembles the one we saw for Fischer carbenes, except that this is a bis-metal-stabilized carbonium ion, **11.17**.



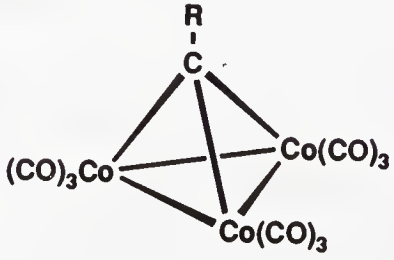
11.17

The reaction with alkenes has been called *hydrocarbation,*[40] by analogy with hydroboration; here, a C^+—H bond reacts in the same way as the isoelectronic B—H group, as shown in Eq. 11.42, which also shows how the product can be released from the metal in the form of an alkene.[40b]



(11.49)

Carbynes can also bridge three metals, as in the long-known and very stable tricobalt complex **11.18**; these are much less reactive than the unsaturated μ_2-carbynes discussed above.



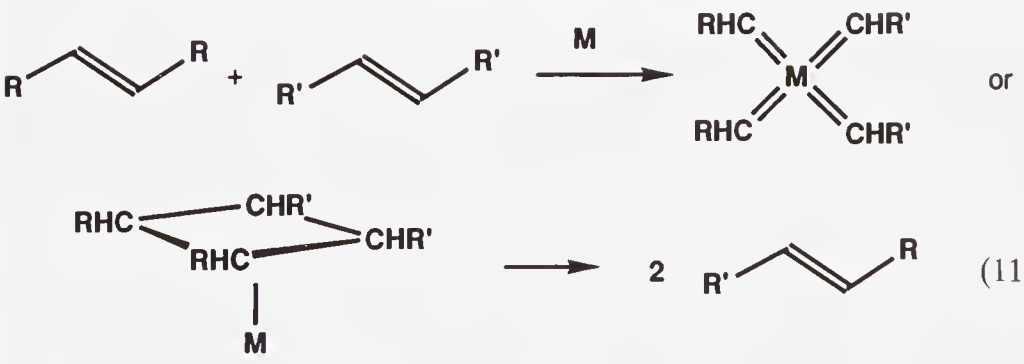
11.18

11.4 ALKENE METATHESIS

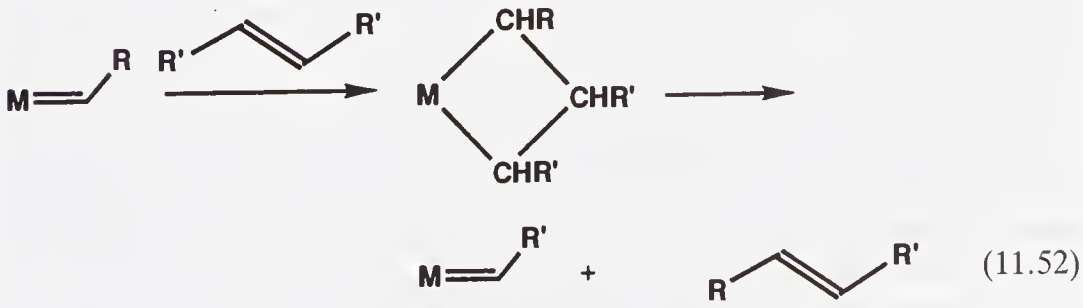
The alkene metathesis reaction[41] exchanges alkylidene groups between different alkenes, and is catalyzed by a variety of high-oxidation-state, early transition metal species (Eq. 11.50). The reaction is of interest because it is the strongest bond in the alkene, the C=C bond, that is broken during the reaction. It is also commercially important in the Shell higher-olefins process (SHOP) (Section 11.5) and in the polymerization of cycloalkenes.

$$RCH{=}CHR + R'CH{=}CHR' \rightleftharpoons RCH{=}CHR' \qquad (11.50)$$

Mechanism The mechanism of the reaction remained mysterious for many years. Several early papers, the first by Chauvin,[42] suggested the correct solution, but this was not generally accepted until much later. The question was whether the two alkenes bound to the metal and underwent rearrangement (called the pairwise mechanism), or whether the alkenes reacted one at a time (the nonpairwise mechanism). Examples of the two possibilities are shown in Eqs. 11.51 and 11.52. Equation 11.52, the *Chauvin mechanism*, is now the accepted pathway, and was a particularly imaginative suggestion at a time when both the required metalacyclobutane formation and cleavage reactions and non-heteroatom-substituted carbenes were all unknown.



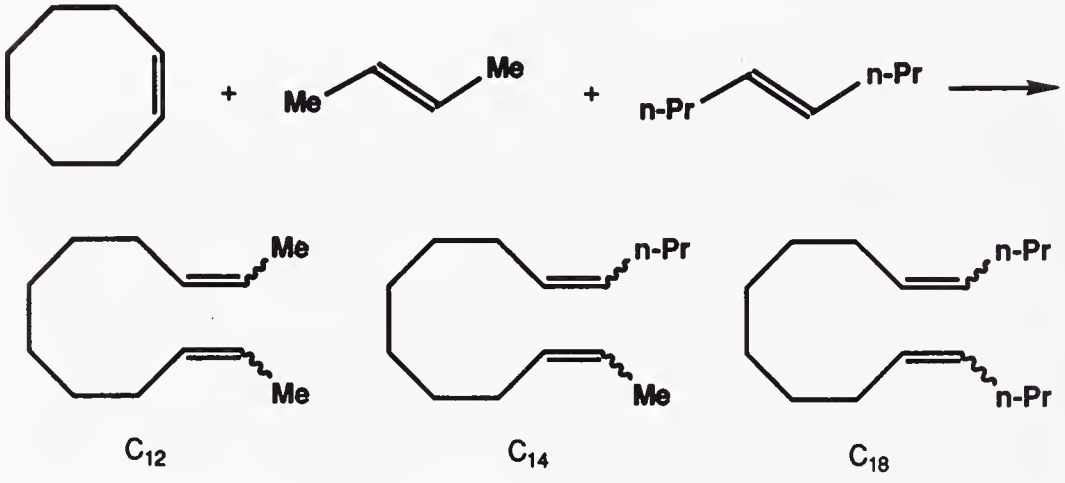
(11.51)



(11.52)

One critical experiment to decide between these two routes was the "double cross," shown in Eq. 11.53, and which is a more elaborate form of the cross-

over experiment. The idea is that if the reaction is pairwise, then at the beginning of the reaction we will see products from only two of the alkenes (e.g., the C_{12} and C_{16} products in Eq. 11.53), not the double-cross product containing fragments of all three alkenes (C_{14} in Eq. 11.53), which would be expected on the nonpairwise mechanism. The pairwise mechanism requires that no C_{14} form initially; later on in the reaction, double-cross products are bound to form, whatever the mechanism, by metathesis of C_{12} with C_{16}.

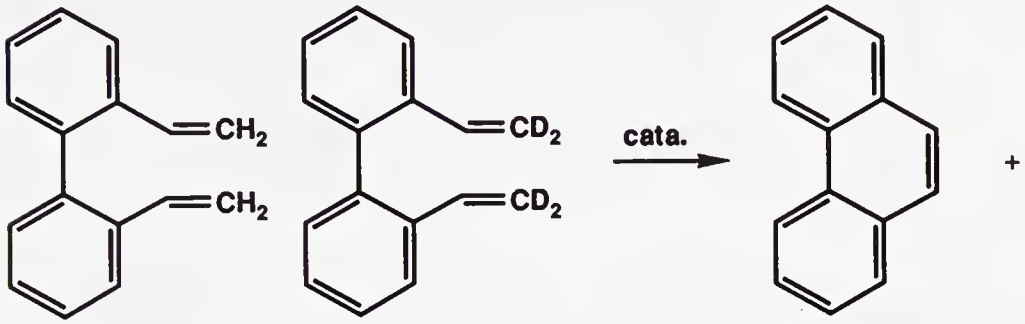


(11.53)

The amounts of C_{12}, C_{14}, and C_{16} were measured as a function of time and the $[C_{14}]/[C_{12}]$ and $[C_{14}]/[C_{16}]$ ratios extrapolated back to time zero. These ratios should be zero for the pairwise and nonzero for the nonpairwise routes. The results showed that a nonpairwise mechanism operates: $[C_{14}]/[C_{12}]$ extrapolated to 0.4 and $[C_{14}]/[C_{16}]$ to 11.1 for one of the best-known metathesis catalysts, $MoCl_2(NO)_2(PPh_3)_2$ and $Me_3Al_2Cl_3$.[43] Staunch adherents of the pairwise mechanism suggested the "sticky olefin" hypothesis. This held that the alkene, once metathesized by a pairwise mechanism, was retained by the metal at the active site, rather than being immediately released into solution. While it remains at the site, the single cross product might metathesize several times and so only the double-cross product would be released into solution and detected. This salvages the pairwise mechanism, and requires a more sophisticated experiment to test the new hypothesis.

We need to study a system in which the metathesis products do not themselves metathesize, so that we can be sure that we are seeing the *initial* products. Perhaps the best example is shown in Eq. 11.54,[44] in which labeled **11.19** is converted into ethylene and phenanthrene, neither of which metathesize further with the particular Mo catalyst chosen. The initial isotope distributions in the products will then truly reflect a single catalytic cycle. The results of this reverse double cross showed a 1:2:1 mixture of the d^0, d^2, and

d^4 isotopomers of the resulting ethylene, which successfully defends the non-pairwise mechanism against the sticky olefin idea.



11.19 **11.19-d_4** **phenanthrene**

$$H_2C{=}CH_2 \;+\; D_2C{=}CH_2 \;+\; D_2C{=}CD_2 \qquad (11.54)$$

$$1 \;:\; 2 \;:\; 1$$

As we might expect on the idea that metal carbenes are the active catalysts, the isolable $(CO)_5W(=CPh_2)$ initiates some metathesis reactions, for example, of strained alkenes and of cyclooctene.[45]

Applications The commercial synthesis of the house fly pheromone **11.20** illustrates the technique of driving the metathesis reaction by removing the more volatile alkene product, in this case, ethylene; undesired non-cross-products can easily be separated by distillation. Unfortunately, the presence of the alkylaluminum cocatalyst severely limits the range of functional groups tolerated by this system.

$$Me(CH_2)_7CH{=}CH_2 + Me(CH_2)_{12}CH{=}CH_2 \longrightarrow$$

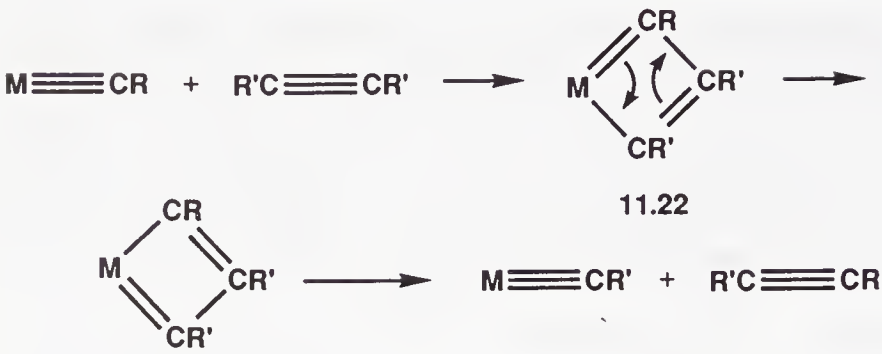
$$Me(CH_2)_7CH{=}CH(CH_2)_{12}Me + C_2H_4 + \text{other products} \qquad (11.55)^{46}$$

11.20

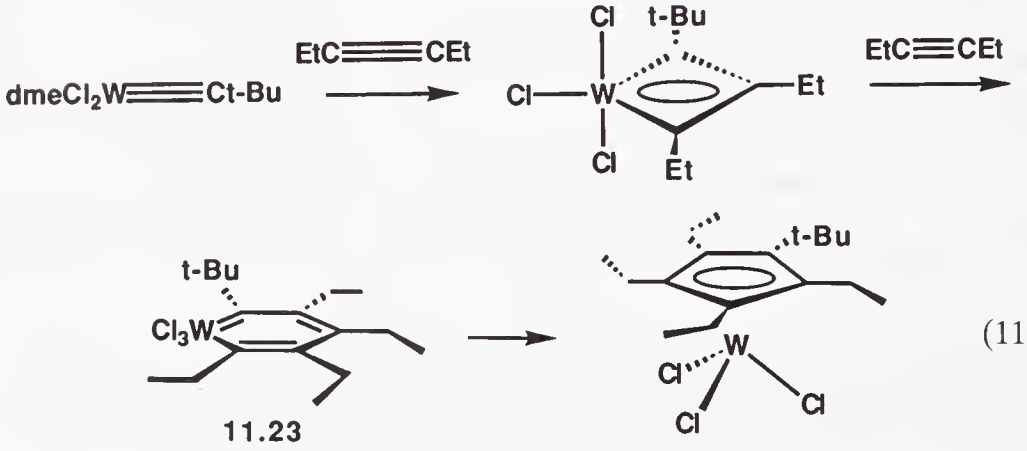
Alkynes can be metathesized by the complex[47] (*t*-BuO)$_3$W≡C(*t*-Bu) (**11.21**), apparently via the tungstenacyclobutadiene species **11.22** in Eq. 11.56. In the absence of alkoxide ligands, stable analogs of **11.22** can be isolated (Eq. 11.57):[20]

(t-BuO)$_3$W≡C(t-Bu)

11.21



(11.56)



(11.57)

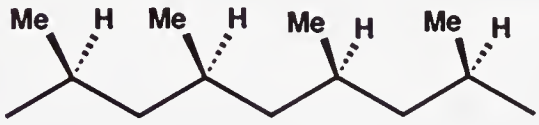
These react with excess alkyne to give a cyclopentadienyl complex, via a metalabenzene **11.23**. This is how the alkyne metathesis catalyst deactivates.

It is still unclear how the initiation step in alkene metathesis occurs and how the initial carbene forms. Commercial applications of metathesis include the *triolefin process,* in which propylene is converted to ethylene and butene, the *neohexene process,* in which the dimer of isobutylene, $Me_3CCH{=}CMe_2$, is metathesized with ethylene to give $Me_3CCH{=}CH_2$, an intermediate in the manufacture of synthetic musk, and a 1,5-hexadiene synthesis from 1,5-cyclooctadiene and ethylene.[48] Two other applications, SHOP and ROMP (Shell higher olefins process and ring-opening metathesis polymerization), are discussed in the next section.

11.5 ALKENE POLYMERIZATION AND OLIGOMERIZATION

Alkene polymerization[49] is one of the most important catalytic reactions in commercial use. The Ziegler–Natta catalysts, for which Ziegler and Natta won the Nobel Prize in 1963, account for some 15 million tonnes of polyethylene and polypropylene annually. These catalysts are rather similar to the metathesis catalysts in that mixtures of alkylaluminum reagents and high-valent early metal complexes are used. The best known is $TiCl_3/Et_2AlCl$, which is active at 25°C and 1 atm; this contrasts with the severe conditions required for thermal polymerization (200°C, 1000 atm). Not only are the conditions milder, but the product shows much less branching than in the

thermal method. Propylene also gives highly crystalline stereoregular material, in which long sequences have the same stereochemistry at adjacent carbons in a head-to-tail polymer; this is called an isotactic polymer (**11.24**). The commercial catalysts are heterogeneous in the sense that the active centers are on crystallites of $TiCl_3$, but homogeneous analogs are known.



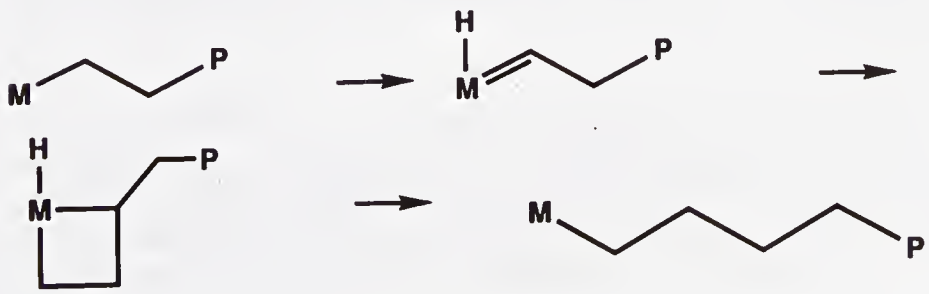
11.24

Mechanism Cossee was the first to propose a mechanism in which the polymer chain (P in Eq. 11.58) grows by successive insertion of ethylene.[50]

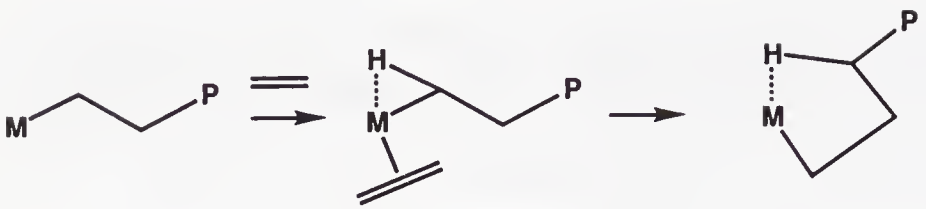
$$M{-}CH_2{-}(P) + CH_2{=}CH_2 \longrightarrow M{-}CH_2{-}CH_2{-}CH_2{-}(P) \quad (11.58)$$

There is an obvious problem with this route: Why does the polymer chain not chain-terminate by β elimination? The answer seems to be that the high-valent d^1 metal has insufficient ability to back-donate in order to break the C—H bond; recall that **3.7** failed to β-eliminate for the same reason. A second difficulty is that ethylene insertion into an alkyl group is rather rare (see Section 3.3).

To counter these problems, Green and Rooney[51] came up with an interesting alternative mechanism (illustrated in Eq. 11.59). The polymer chain first α-eliminates to give a carbene hydride, and this inserts ethylene by a metathesis-like mechanism to give a metalacycle that finally opens up by reductive elimination with the hydride. This mechanism is also problematic: Why should the polymer chain α-eliminate when it does not β-eliminate, and why does it eliminate to give the straight-chain product (ethyl side-chains are not found in the polymer)? In its original form it cannot apply to d^0 or d^1 catalysts because the alkylidene hydride would then exceed the permitted oxidation state for the metal [e.g., a Zr(VI) species would be required with the common catalyst system "$Cp_2Zr(CH_2CH_2P)^+$"], and so the carbene hydride was replaced by an agostic alkyl in the *modified Green–Rooney mechanism* (Eq. 11.60). The formation of an agostic alkyl might accelerate insertion by rotating the alkyl in the direction of the alkene.

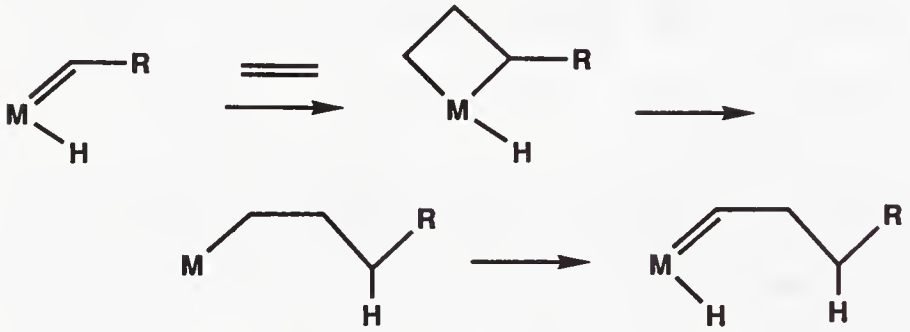


(11.59)



agostic intermed. (11.60)

Schrock[52] has found an ethylene oligomerization catalyst, Ta(=CH*t*-Bu)-$HI_2(PMe_3)_3$, which does appear to go via metalcycles (Eq. 11.61). After 20–50 ethylene units have been inserted, the chain β-eliminates to give a 1-alkene. Since the alkyl form of the catalyst is d^2, the unmodified Green–Rooney mechanism is allowed.



(11.61)[53]

It is difficult to test these Ziegler–Natta polymerization mechanisms, because it is not easy to analyze the results of a labeling experiment when the product is a polymer rather than a small molecule. The challenge was taken up by Grubbs,[53a] Brintzinger,[53b] and Bercaw,[53c] who developed an elegant mechanistic experiment to determine whether agostic species were involved. In Fig. 11.4, we look at one version[53b] of the experiment in which the polymerization of *trans-n*BuCH=CHD is halted after one insertion by hydrogenolysis with H_2. Cp_2Zr—H first inserts to give **11.25**. This can then insert in one of two ways to give **11.26**. The approach shown, with the alkyl RCH_2 and alkene R groups pointing away from one another, is not only reasonable, but known to be favored from other work. Either **11.26a** or **11.26b** can be formed. On the *Cossee* mechanism a 50:50 ratio is expected, but on the modified *Green–Rooney* mechanism, the ratio will depend on whether C—H or C—D prefers to be agostic. As we saw in Fig. 10.9, C—H prefers to be agostic, so we expect the erythro product to predominate (Fig. 11.4). Experimentally, erythro is favored by 1.3:1 (by ^{2}H NMR), and so the *Green–Rooney* mechanism is followed in this case.

In her studies on the *f*-block metals, Patricia Watson[54] found a remarkable system in which successive alkene insertions into a Lu—R bond can be observed step by step (Eq. 11.62). Not only do the alkenes insert, but the reverse reaction, β elimination of an alkyl group, as well as the usual β elimination of a hydrogen, are also observed. For the *d*-block this β elimination of an alkyl group would normally not be possible; it is probably the larger M—R

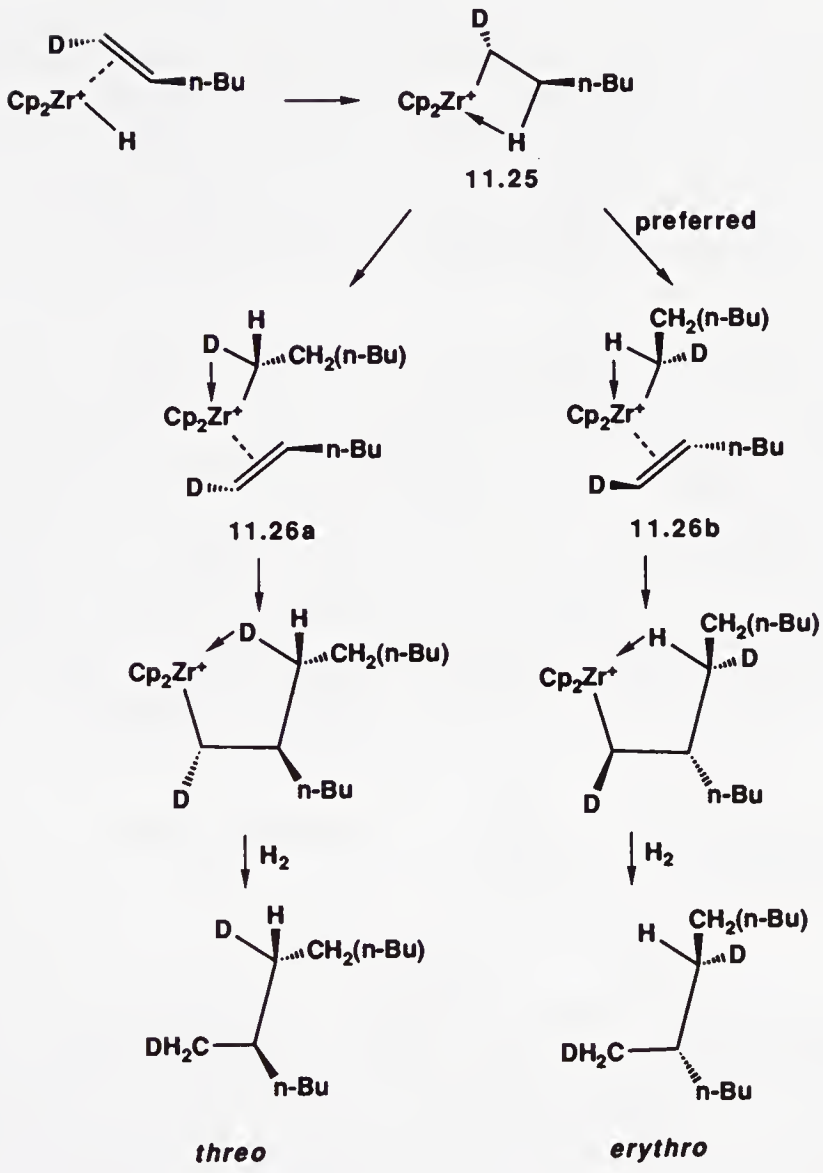
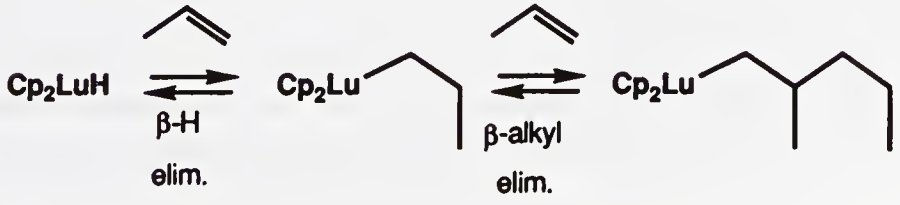


FIGURE 11.4 The Grubbs experiment. Since the α-CH bonds of the metal alkyl are not involved in the Cossee mechanism (Eq. 11.58), we expect a 50:50 mixture of isotopomers, as observed in some situations. On the modified Green–Rooney mechanism shown here, we would expect a preferential binding of C—H over C—D in the agostic intermediate, which leads to a non-50:50 ratio as observed for certain systems.

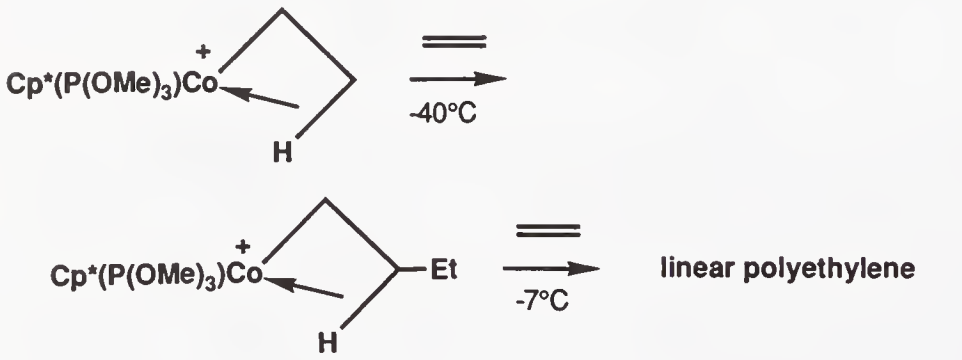
bond dissociation energies in the *f*-block that make the thermodynamics of the overall process favorable.



(11.62)

Most late metals only dimerize or oligomerize alkenes (oligomers are trimers, tetramers, and other short-chain molecules), rather than polymerize them. This is because β elimination very soon stops the chain from growing. One of the best-known systems is $NiCl_2/EtAlCl_2$, in which a nickel hydride is believed to be the active catalyst. If we consider ethylene, the first insertion gives an ethyl complex, this can either β-eliminate or insert another ethylene, the same is true for the *n*-butyl product of the second insertion. The product distribution therefore depends on the ratio of the rates of insertion and β elimination.[55]

Among the late transition metals, β elimination is usually too fast relative to insertion for long chains to be formed. Brookhart[56a] has studied some unusual Co complexes that do polymerize alkenes. It appears that if the metal is sufficiently weakly π-basic, even cobalt will refrain from β elimination. An added point of interest in the system (Eq. 11.63) is that the intermediate alkyls are agostic. This is a sign of the weak π basicity of the site; the alkyls cannot go further along the pathway for β elimination than the agostic stage. Brookhart proposes that agostic alkyls may generally give more rapid insertion than do normal alkyls; since the agostic alkyl has to open up to let in the alkene, it may be the weak π basicity of the site that encourages insertion.



(11.63)

Protonation of $Cp^*Rh(C_2H_4)_2$ gives a related catalyst that dimerizes methyl acrylate with tail-to-tail regiochemistry to give hexenedioates that can be hydrogenated to the nylon precursor, adipic acid ($HOOC(CH_2)_4COOH$).[56b]

Applications The Shell higher-olefins process (SHOP) is a industrial process based on homogeneous nickel catalysts of the type shown in Fig. 11.5, and discovered by Keim.[57] These oligomerize ethylene to give 1-alkenes of various chain lengths (e.g., C_6–C_{20}). Insertion is therefore considerably faster than β elimination. The C_{10}–C_{14} fraction is a desirable feedstock; for example, hydroformylation gives C_{11}–C_{15} alcohols that are useful in detergent manufacture. The non-C_{10}–C_{14} fraction consists of 1-alkenes with longer (e.g., C_{16}), and shorter (e.g., C_8) chain lengths. Figure 11.5 shows how isomerization and metathesis can be combined to manipulate the chain lengths so as to produce more C_{10}–C_{14} material from the longer and shorter chains. The fact

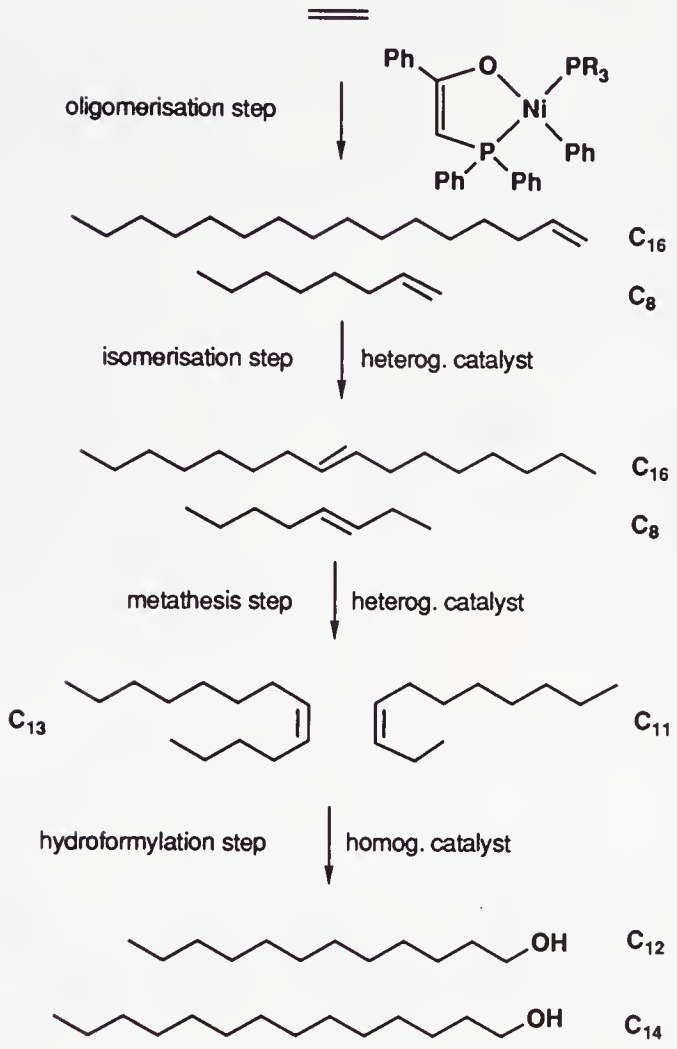


FIGURE 11.5 A schematic description of the Shell higher olefins process (SHOP). Keim's nickel catalyst gives 1-alkenes of various chain lengths. The subsequent steps allow the chain lengths to be manipulated to maximize the yield of C_{10}–C_{14} products. Finally, SHOP alkenes are often hydroformylated, in which case the internal alkenes largely give the linear product, as discussed in Chapter 9.

that internal C_{10}–C_{14} alkenes are formed does not matter, because hydroformylation gives linear alcohols even from internal alkenes, as discussed in Section 9.3. Homogeneous catalysts were strong contenders for the isomerization and metathesis steps of SHOP, but in practice heterogenized catalysts were adopted. There are now several plants operating.

Nickel complexes are also used for the oligomerization of butadiene. Here it is believed that Ni(0) mediates the oxidative coupling of two butadienes to give the bis-π-allyl complex **11.27** (Fig. 11.6). According to the exact conditions, the dimers, cyclooctadiene **11.28**, vinylcyclohexane **11.29**, and even divinylcyclobutane **11.30** can be formed by reductive elimination from **11.27**.[56]

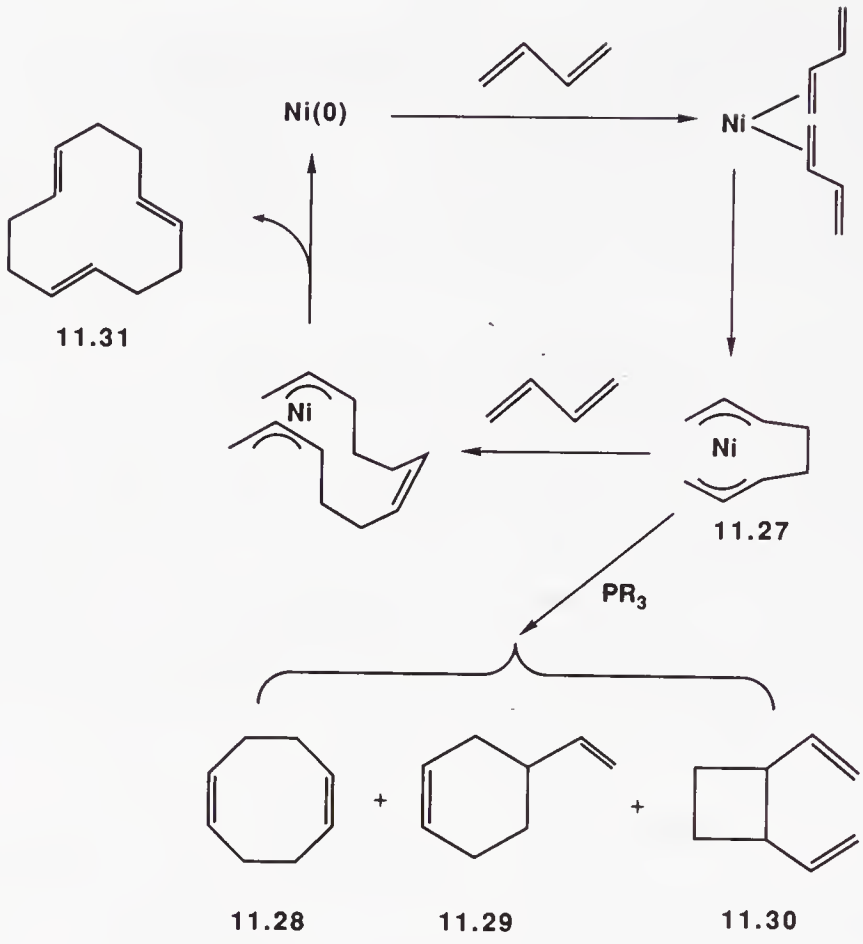


FIGURE 11.6 The Wilke oligomerization of butadiene. "Naked" nickel catalysts give **11.31,** while the presence of ligands like PPh_3 causes the reaction to produce the dimers **11.28–11.30**.

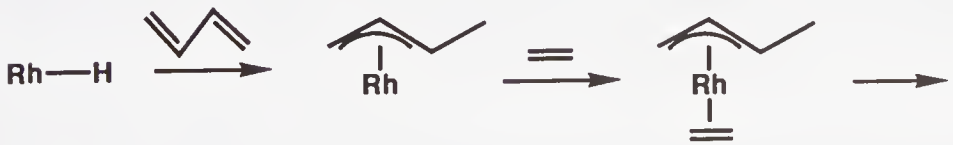
Alternatively, a third molecule of butadiene can add to give 1,5,9-cyclododecatetraene **11.31**. Only naked Ni(0) can give the trimerization, addition of PR_3 diverts the reaction to give dimers by occupying the site to which the third butadiene would otherwise bind.

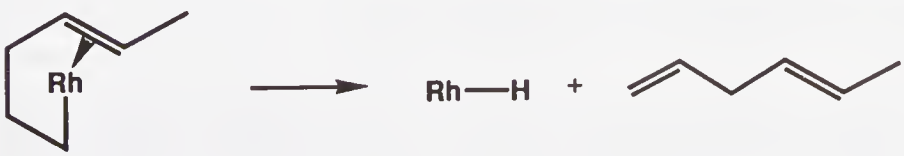
Another commercially important reaction is du Pont's synthesis of 1,4-hexadiene. This is converted to synthetic rubber by copolymerization with ethylene and propylene, which leaves the polymer with unsaturation. This is present in natural rubber, a 2-methylbutadiene polymer **11.32**, and is necessary for vulcanization.

11.32

The 1,4-hexadiene is made by codimerization of ethylene and butadiene, with a $RhCl_3$/EtOH catalyst (Eq. 11.64).[58] The catalyst is about 80% selective for the *trans*-1,4-hexadiene, a remarkable figure considering all the different dimers that could have been formed. The catalyst is believed to be a rhodium hydride formed by reduction of the $RhCl_3$ with the ethanol solvent (Section 3.4). This must react with the butadiene to give mostly the *anti*-methylallyl (crotyl) intermediate, which selectively inserts an ethylene at the unsubstituted end. The cis/trans ratio of the product probably depends on the ratio of the two isomers of the crotyl intermediate. Adding ligands such as HMPA to the system greatly increases the selectivity for the trans diene. By increasing the steric hindrance on the metal, the ligand probably favors the anti isomer of the crotyl ligand over the more hindered syn isomer. The rhodium hydride is also an isomerisation catalyst and so the 1,4-hexadiene is also converted to the undesired conjugated 1,3 isomers. The usual way around a problem like this is to run the reaction only to low conversion, so that the side product is kept to a minimum. The substrates, which are more volatile than the products, are easily recycled.

(11.64)

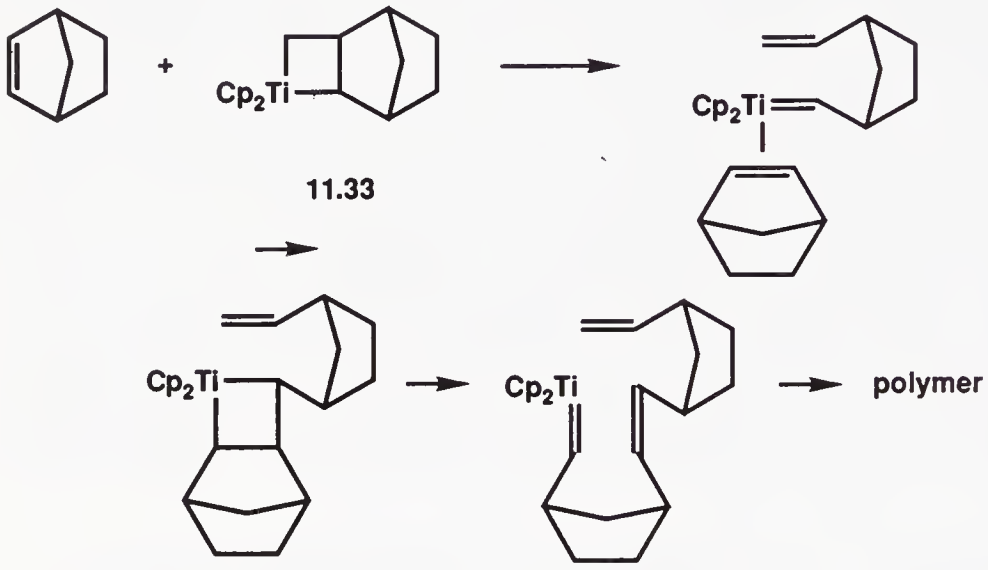




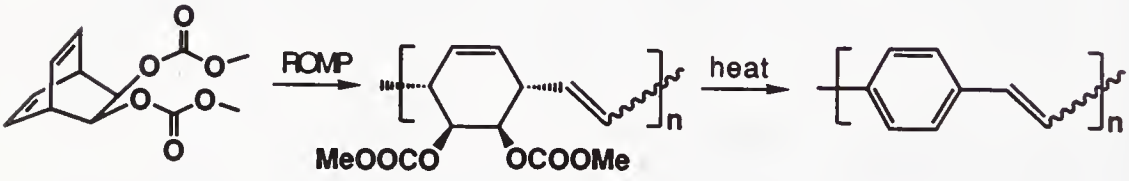
(11.65)

ROMP Metathesis catalysts also have important applications in alkene polymerization via *ring-opening metathesis polymerization* (ROMP). This leads to the formation of an unsaturated polymer, which means that it can be vulcanized, or cross-linked, for greater strength. Commerical norbornadiene polymerization (molecular weight $> 2 \times 10^6$) dates from 1976 (CdF Chimie, France). Both Schrock and Grubbs[59] have shown that carbene complexes or their precursor metalacycles such as **11.33** in Eq. 11.66, are active in ROMP. Very good control of chainlength is achieved, and a block copolymer (···AAABBB···) can be made by adding a second cycloalkene when the first has been consumed. Catalysts that keep their activity even after the substrate has been consumed are called *living systems*. Poly(1,4-phenylenevinylene), (p-C_6H_4—CH=CH—)$_n$, has high conductivity when doped, and has useful optical and photochemical properties but is too insoluble to be processable.

Grubbs[59b] has made a diester derivative as shown in Eq. 11.67, which gives a processable polymer. Pyrolytic loss of MeOH and CO_2 gives polyphenylenevinylidene.



(11.66)



(11.67)

11.6 MULTIPLE BONDS TO HETEROATOMS

Related to carbenes and carbynes are species with multiple bonds to heteroatoms, of which the most important are terminal oxo M≡O, nitrido M≡N and imido M≡NR. The high electronegativity of O and N give these ligands "Schrock" character; that is, they can be regarded as O^{2-}, NR^{2-}, and N^{3-}, respectively.[60a] Stable compounds of these types tend to be found along a diagonal of the Periodic Table that runs from V to Os, with Mo being the element with the most examples; the great majority of examples have electron configurations from d^0 to d^2. Oxo groups have a high tendency to form M—O—M bridges; for some metals, such as Zr, terminal oxo complexes are rare.[29b]

For M≡O in an octahedral complex, there are strong interactions between two of the M d_π orbitals and the O lone pairs (Fig. 11.7). When the two d orbitals are empty (d^0, d^1, or d^2), the interaction is bonding, and the M≡O group has triple-bond character **11.34** with the LX_2 O atom as a 4e donor.

11.34

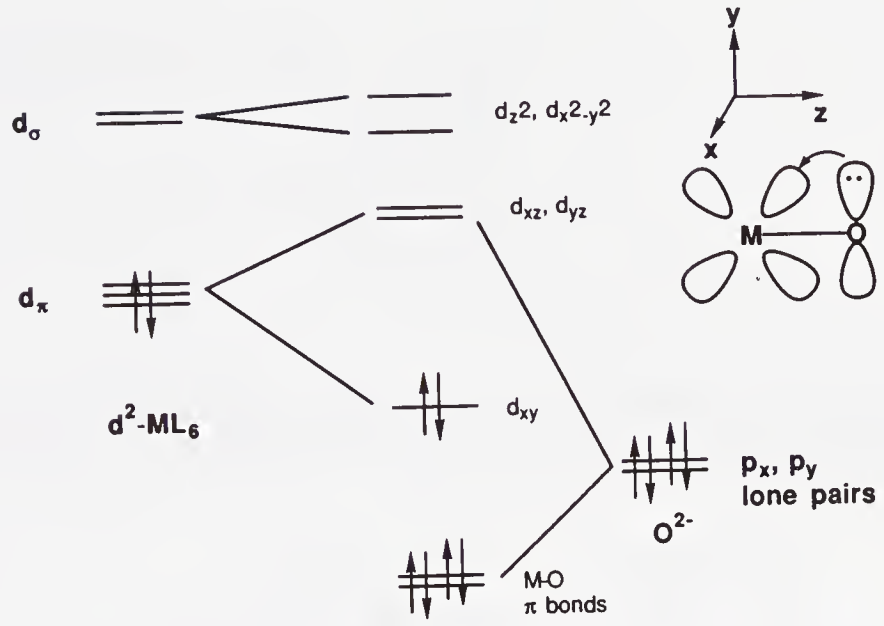
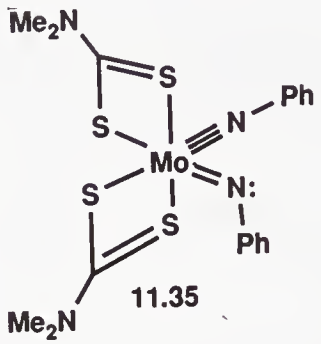


FIGURE 11.7 π-Bonding in metal oxo complexes. After the σ bonds have been considered, a d^2 ML_6^{2+} species has a two-above-three orbital pattern characteristic of an octahedron. As long as they remain empty, two of the three d_π orbitals (xz and yz) can accept electrons from the O^{2-} lone pairs; one of these interactions is shown at the top right. This is a special case of the situation shown in Fig. 1.8. With one σ bond and two π bonds, the net M≡O bond order is three.

With more electrons on the metal, the bond order drops and electron–electron repulsions between M(d_π) electrons and heteroatom lone pairs destabilize the system and stable octahedral oxo complexes with d^4 or higher configurations are unknown. Mayer's[60c] d^4 oxo species, Re(=O)X(RC≡CR)$_2$, adopts a tetrahedral structure and the d^6 (η^6-C_6H_4(*i*-Pr)Me)Os≡NAr and (η^5-C_5Me_5)Ir≡NAr of Bergman[61a] are linear, thus avoiding the destabilization that would arise in an octahedral ligand field. Otherwise, octahedral late metal species normally have bridging oxo structures. A rare terminal oxo in [py(porph$^{\cdot+}$)Fe^{IV}=O] (porph = bulky porphyrin ligand) makes this species extremely reactive, even with alkane C—H bonds, and it is only observable at low temperatures.[62] This means that species such as d^8 $(Me_3P)_3Pt$=O are not plausible ones to suggest in a mechanistic scheme; L_3Pt^+—O^- or $L_3Pt^{\cdot}$—O· are not forbidden but would be extremely reactive and have not been observed or proposed. Similar ideas hold for M≡NR and M≡N. M≡NR species have a linear geometry at nitrogen, as expected for a M≡N triple bond. A rare bent M=NR double-bonded structure is found in **11.35**, where the M=NR bond length of 1.789 Å can be compared with the adjacent M≡NR at 1.754 Å. The reason for the unusual structure is that since =NR is an X_2 and ≡NR is an LX_2 ligand, if both imides were linear the Mo would have 20 electrons.



11.35

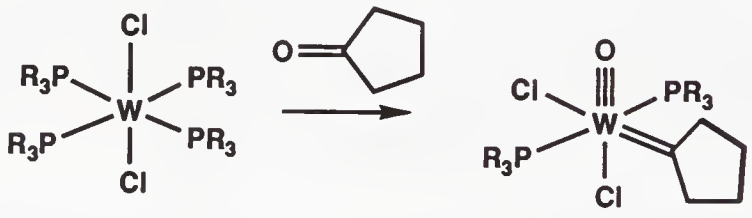
Synthesis The complexes are often formed by oxidation, hydrolysis,[63] or aminolysis (Eqs. 11.68–11.72). Equation 11.71 shows an unusual and very interesting route that forms multiple bonds to O and to C at the same time.[64]

$$[Os^{III}(NH_3)_6]^{3+} \xrightarrow{Ce^{4+}} [N{\equiv}Os^{VI}(NH_3)_5]^{3+} \tag{11.68}$$

$$WCl_6 + t\text{BuNH}_2 \longrightarrow [(t\text{BuNH})_4W(\equiv N t\text{Bu})_2] \tag{11.69}$$

$$Np_3W{\equiv}Ct\text{Bu} + H_2O \longrightarrow Np_2W(\equiv O)(=CHt\text{Bu}) + \text{NpH} \tag{11.70}$$

(Np = Me_3CCH_2)



(11.71)

(L = PMe_2Ph)

$$WF_6 + \text{MeOMe} \longrightarrow WOF_4(OMe_2) + 2\text{MeF} \tag{11.72}$$

The most oxophilic elements are even able to extract O from organic compounds, which prevents use of oxygenated solvents in many of these systems (Eq. 11.72). The nitride ligand has a lone pair that can sometimes be alkylated in a synthesis of an imido complex (Eq. 11.73):[65]

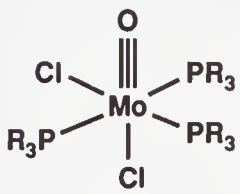
$$[R_4Os{\equiv}N]^- + Me_3O^+ \longrightarrow R_4Os{\equiv}N\text{Me} \tag{11.73}$$

(R = Me_3SiCH_2)

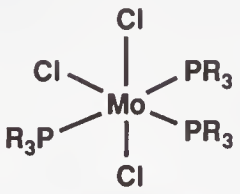
Spectra and Structure The M≡O band at 900–1100 cm^{-1} in the IR spectrum is characteristic of the terminal oxo group; M≡NR appears at 1000–1200 cm^{-1} and M≡N at 1020–1100 cm^{-1}. The assignment can be confirmed by ^{18}O or ^{15}N substitution. An exception is $Cp_2M{=}O$ (M = Mo, W) with ν(M—O) frequencies below 880 cm^{-1}; electron counting shows that these must be M=O, not M≡O species, however. The long M=O bond length

of 1.721 Å in $(MeC_5H_4)_2Mo{=}O$ is consistent with this idea. Low frequencies are also seen in bis-oxo species where the two oxo groups probably compete for electron donation into the empty $M(d_\pi)$ orbital(s). Useful NMR spectra can be obtained with ^{17}O- and ^{15}N-substituted species (both $I = \frac{1}{2}$) and these can be used to assign a bridging or terminal mode for the ligands present.

The presence of two *distortional isomers* was suggested for a number of metal oxo species, such as $MoOCl_2(PR_3)_3$ (**11.36**). The blue and green isomers of this series was found to have different M=O bond lengths. Parkin[66] has found that $MoCl_3(PR_3)_3$ (**11.37**) can cocrystallize with **11.36** in such a way as to cause an apparent lengthening of the crystallographically determined M—O distance, and so distortional isomerism may not be real. This is an illustration of how easy it is to miss alternative interpretations of the data.

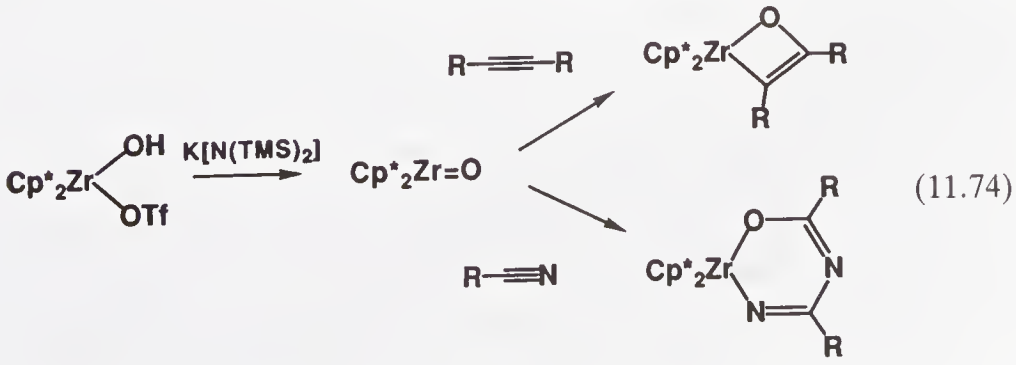


11.36



11.37

Reactions Two general reactivity principles seem to apply. As the electronegativity of M increases on moving to the right in the Periodic Table, the orbital energies move from situation (c) in Fig. 11.1 to a situation where the $M(d_\pi)$ and O or N(p) orbitals have comparable energy. The basic character of the O or N therefore falls. High-valent oxo, imido, or nitrido species are often stable enough to be isolated, but low-valent ones tend to be much more reactive. For example, $(CO)_5Mo{=}NPh$ has been implicated by McElwee-White as a transient intermediate in a variety of reactions.[67] Bergman's[61a] $(\eta^6\text{-}C_5Me_5)Ir{\equiv}NAr$ is isolable but very reactive (Fig. 11.8). $Cp^*_2Zr{=}O$ can be made by deprotonating $Cp^*_2Zr(OH)(O_3SCF_3)$ with the strong base $K[N(TMS)_2]$ and reacts with acetylenes and nitriles to give metallacycles (Eq. 11.74).[61b] OsO_4 and other late metal oxo complexes give cis hydroxylation of alkenes, possibly via organometallic intermediates (Eq. 11.75).[68]



(11.74)

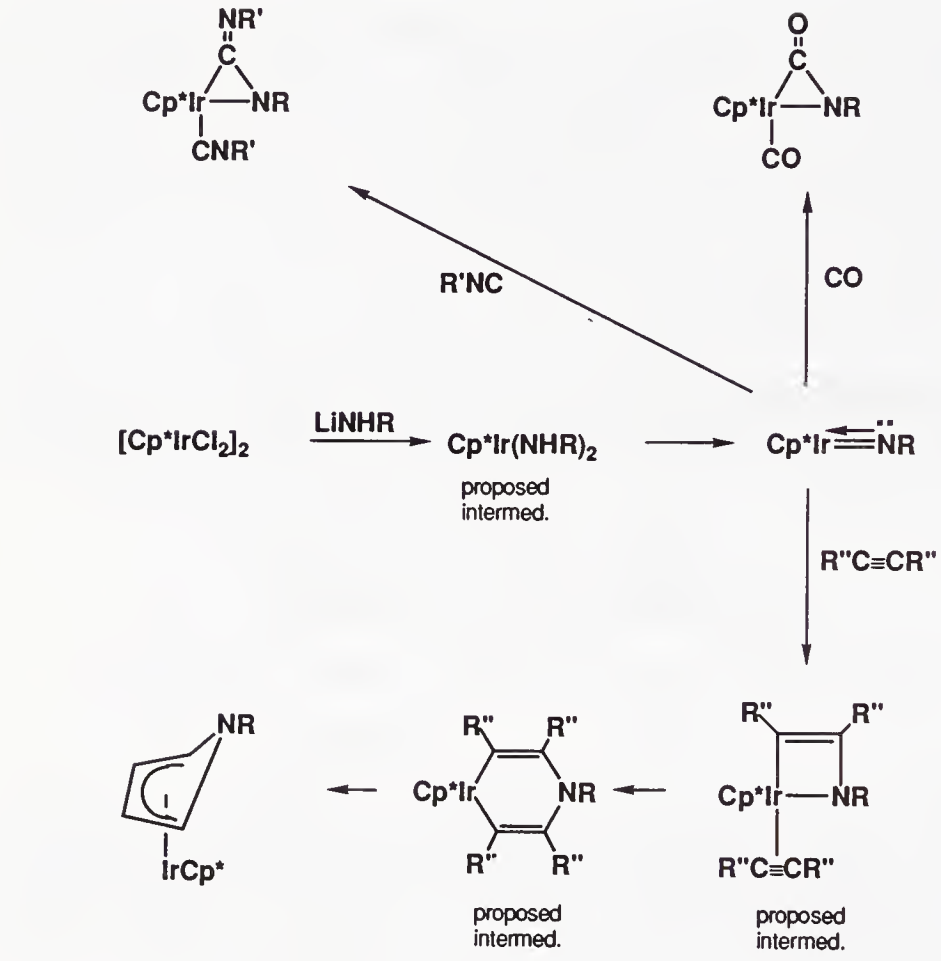
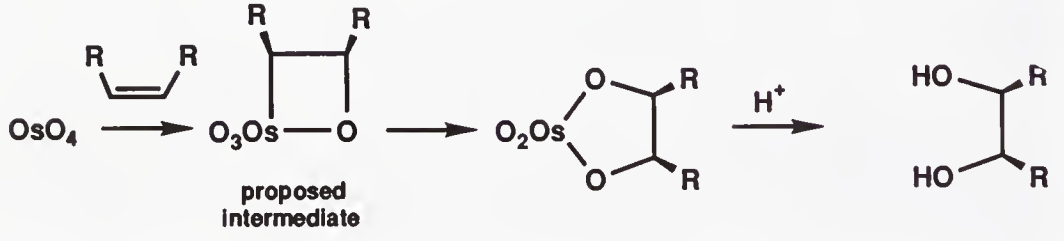


FIGURE 11.8 Some reactions of one of Bergman's[61] late metal imido complexes.



(11.75)

REFERENCES

1. E. O. Fischer and A. Maasbol, *Angew. Chem., Int. Ed.*, **3,** 580, 1964.
2. R. R. Schrock, *J. Am. Chem. Soc.*, **96,** 6796, 1974.
3. (a) P. J. Brothers and W. R. Roper, *Chem. Rev.*, **88,** 1293, 1988; (b) N. J. Cooper, *Pure Appl. Chem.*, **56,** 25, 1984.
4. K. H. Doetz et al., *Transition Metal Carbene Complexes,* Verlag Chemie, Weinheim, 1983.

5. E. O. Fischer and A. Maasbol, *Chem. Ber.*, **100,** 2445, 1967.
6. J. S. Miller and A. L. Balch, *Inorg. Chem.*, **11,** 2069, 1972.
7. L. Chugaev, *J. Russ. Chem. Soc.*, **47,** 776, 1915; J. H. Enemark, A. L. Balch, et al., *Inorg. Chem.*, **12,** 451, 1973.
8. (a) M. Bullock et al., *J. Am. Chem. Soc.*, **109,** 8087, 1987; (b) M. H. Chisholm and H. C. Clark, *Inorg. Chem.*, **10,** 1711, 1971; M. H. Chisholm et al., ibid., **16,** 677, 1977.
9. M. A. Gallop and W. R. Roper, *Adv. Organometal. Chem.*, **25,** 121, 1986.
10. (a) W. Herrmann et al., *J. Organometal. Chem.*, **97,** 245, 1975; (b) K. Öfele, *Angew. Chem., Int. Ed.*, **7,** 950, 1968.
11. (a) E. O. Fischer, U. Schubert, and H. Fischer, *Pure Appl. Chem.*, **50,** 857, 1978; (b) C. P. Casey and R. L. Anderson, *Chem. Commun.*, 895, 1975.
12. T. Bodner and A. R. Cutler, *J. Organometal. Chem.*, **213,** C31, 1981.
13. R. S. Bly and R. K. Bly, *Chem. Commun.*, 1046, 1986.
14. A. Davidson and J. P. Selegue, *J. Am. Chem. Soc.*, **102,** 2455, 1980.
15. C. P. Casey and R. L. Anderson, *J. Am. Chem. Soc.*, **96,** 1230, 1974; K. H. Doetz et al., *J. Organometal. Chem.*, **182,** 489, 1979.
16. H. Werner, E. O. Fischer, et al., *J. Organometal. Chem.*, **28,** 367, 1971.
17. E. O. Fischer et al., *Chem. Ber.*, **105,** 3966, 1972.
18. C. P. Casey et al., *J. Am. Chem. Soc.*, **101,** 7282, 1979.
19. K. H. Dötz et al., *Angew. Chem., Int. Ed.*, **23,** 97, 1984.
20. R. R. Schrock, *Acct. Chem. Res.*, **12,** 98, 1979; *Science,* **219,** 13, 1983.
21. R. R. Schrock et al., *J. Am. Chem. Soc.*, **100,** 359, 1978.
22. R. R. Schrock, L. W. Messerle, C. D. Wood, and L. J. Guggenberger, *J. Am. Chem. Soc.*, **100,** 3793, 1978.
23. R. R. Schrock, W. J. Youngs, M. R. Churchill, et al., *J. Am. Chem. Soc.*, **100,** 5962, 1978.
24. R. R. Schrock, *J. Am. Chem. Soc.*, **97,** 6577, 1975; R. R. Schrock and P. R. Sharp., *J. Am. Chem. Soc.*, **100,** 2389, 1978.
25. J. M. Williams, R. R. Schrock, et al., *J. Am. Chem. Soc.*, **103,** 169, 1981.
26. J. H. Wengrovius and R. R. Schrock, *Organometallics,* **1,** 148, 1982.
27. R. R. Schrock, *J. Am. Chem. Soc.*, **98,** 5399, 1976.
28. F. N. Tebbe, G. W. Parshall, and G. S. Reddy, *J. Am. Chem. Soc.*, **100,** 3611, 1978.
29. (a) R. H. Grubbs et al., *Pure Appl. Chem.*, **55,** 1733, 1983; (b) J. R. Stille and R. H. Grubbs, *J. Am. Chem. Soc.*, **105,** 1664, 1983; (c) W. R. Roper et al. *Adv. Organomet. Chem.*, **25,** 121, 1986; (d) J. Hartwig, *J. Am. Chem. Soc.*, **115,** 4908, 1993; (e) K. Burgess, R. T. Baker, et al., *J. Am. Chem. Soc.*, **114,** 9350, 1992.
30. H. Fischer et al., *Carbyne Complexes,* VCH, Weinheim, 1988.
31. (a) A. Mayr and G. A. McDermott., *J. Am. Chem. Soc.*, **108,** 548, 1986; (b) A. Mayr et al., *J. Am. Chem. Soc.*, **109,** 580, 1987.
32. (a) J. S. Murdzek and R. R. Schrock, Chap. 5 in ref. 30; R. R. Schrock et al., *J. Am. Chem. Soc.*, **104,** 4291, 1982.
33. G. Huttner et al., *Angew. Chem., Int. Ed.*, **88,** 649, 1976.

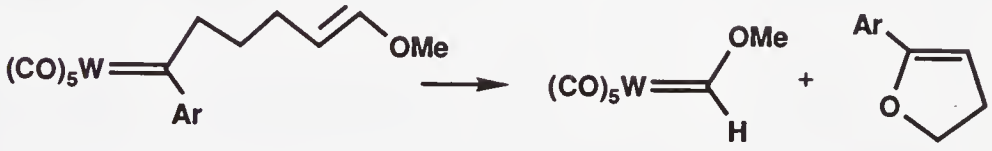
34. L. McElwee-White et al., *J. Am. Chem. Soc.*, **113,** 2947, 1991.
35. W. A. Herrmann, *Adv. Organometal. Chem.*, **20,** 159, 1982.
36. K. K. Mayer and W. A. Herrman, *J. Organometal. Chem.*, **182,** 361, 1979.
37. (a) J. R. Shapley et al., *J. Organometal. Chem.*, **201,** C31, 1980; (b) N. M. Boag, M. Green, F. G. A. Stone, et al., *Chem. Commun.*, 1171, 1980; (c) W. A. Herrmann et al., *Angew. Chem., Int. Ed.*, **20,** 183, 1980.
38. R. J. Puddephatt, K. R. Seddon, et al., *Inorg. Chem.*, **18,** 2808, 1979.
39. S. A. R. Knox, *Chem. Commun.*, 2803, 1980.
40. (a) C. P. Casey and P. J. Fagan, *J. Am. Chem. Soc.*, **104,** 4950, 1982; (b) C. P. Casey et al., *Organometallics*, **5,** 196, 199, 1986.
41. T. J. Katz, *Adv. Organometal. Chem.*, **16,** 283, 1977; N. Calderon, J. P. Lawrence, and E. A. Ofstead, ibid., **17,** 449, 1979.
42. J. L. Hérisson and Y. Chauvin, *Makromol. Chem.*, **141,** 161, 1970; see also M. F. Lappert et al., *Chem. Commun.*, 927, 1972.
43. T. J. Katz and J. McGinnis, *J. Am. Chem. Soc.*, **99,** 1903, 1977.
44. T. J. Katz and R. Rothchild, *J. Am. Chem. Soc.*, **98,** 2519, 1976.
45. T. J. Katz et al., *Tetrahedron Lett.*, 4247, 1976.
46. R. Rossi, *Chimica e Industria*, **57,** 242, 1975.
47. R. R. Schrock et al., *J. Am. Chem. Soc.*, **103,** 3932, 1981.
48. R. L. Banks et al., *J. Mol. Catal.*, **15,** 21, 1982.
49. J. C. W. Chien, *Coordination Polymerisation*, Academic Press, New York, 1975.
50. E. J. Arlman and P. Cossee, *J. Catal.*, **3,** 99, 1964.
51. M. L. H. Green, J. J. Rooney, et al., *Chem. Commun.*, 604, 1978.
52. H. W. Turner and R. R. Schrock, *J. Am. Chem. Soc.*, **104,** 2331, 1982.
53. (a) R. H. Grubbs et al., *J. Am. Chem. Soc.*, **107,** 3377, 1985; (b) H. Kraulendat and H. H. Britzinger, *Ang. Chem., Int. Ed.*, **29,** 1412, 1990; (c) W. E. Piers and J. E. Bercaw, *J. Am. Chem. Soc.*, **112,** 9406, 1990.
54. P. Watson and D. C. Roe, *J. Am. Chem. Soc.*, **104,** 6471, 1982.
55. B. Bogdanovic, *Adv. Organometal. Chem.*, **17,** 105, 1979; P. W. Jolly and G. Wilke, *The Organic Chemistry of Nickel*, Academic Press, New York, 1975.
56. (a) G. F. Schmidt and M. Brookhart, *J. Am. Chem. Soc.*, **107,** 1443, 1985; (b) M. Brookhart and E. Hauptman, *J. Am. Chem. Soc.*, **114,** 4437, 1992.
57. W. Keim et al., *Organometallics*, **2,** 594, 1983; K. Hirose and W. Keim, *J. Mol. Catal.*, **73,** 271, 1992.
58. A. C. L. Su, *Adv. Organometal. Chem.*, **17,** 269, 1979.
59. (a) R. R. Schrock, *Acct. Chem. Res.*, **24,** 158, 1990; R. H. Grubbs and W. Tumas, *Science*, **243,** 907, 1989; (b) R. H. Grubbs et al., *J. Am. Chem. Soc.*, **114,** 9708, 1992.
60. (a) J. M. Mayer, *Comments Inorg. Chem.*, **8,** 125, 1988; W. A. Nugent and J. M. Mayer, *Metal Ligand Multiple Bonds*, Wiley, New York, 1988; (b) G. Parkin et al. *J. Am. Chem. Soc.*, **115,** 4917, 1993; (c) J. M. Mayer, D. L. Thorn, and T. H. Tulip, *J. Am. Chem. Soc.*, **107,** 7454, 1985.
61. (a) R. G. Bergman et al., *J. Am. Chem. Soc.*, **113,** 2041, 5100, 1991; (b) *Organometallics*, **11,** 761, 1992.

62. R. Ortiz de Montellano, *Cytochrome P-450: Structure, Mechanism and Biochemistry,* Plenum Press, New York, 1986.
63. R. R. Schrock, *J. Am. Chem. Soc.*, **105,** 7176, 1983.
64. J. M. Mayer, *J. Am. Chem. Soc.*, **109,** 2826, 1987.
65. P. A. B. Shapley et al., *Organometallics,* **5,** 1269, 1986; *J. Organometal. Chem.*, **335,** 269, 1987.
66. G. Parkin et al., *J. Am. Chem. Soc.*, **113,** 8414, 1991.
67. L. McElwee-White et al., *J. Am. Chem. Soc.*, **113,** 4871, 1991.
68. K. B. Sharpless et al., *J. Am. Chem. Soc.*, **102,** 4263, 1980.

PROBLEMS

1. How could you use Tebbe's reagent to convert cyclohexanone to 1,1-dimethylcyclohexane?

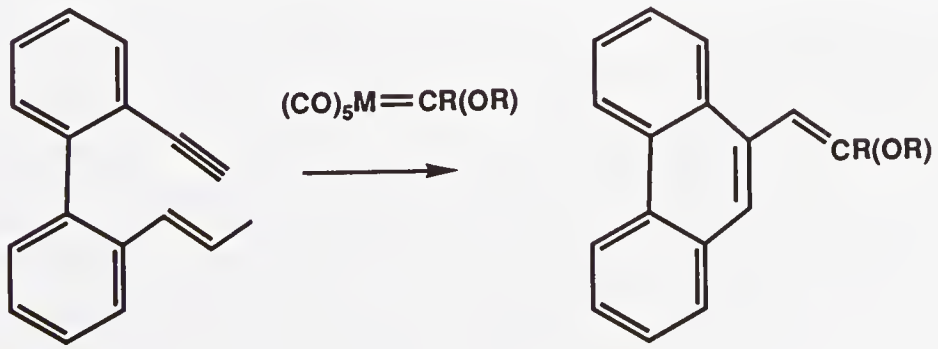
2. Provide a plausible mechanism for



3. Can you suggest an alternative mechanism for alkene polymerization that uses oxidative coupling as the C—C bond forming step.

4. (a) We can view $Ph_3P{=}CH_2$ as a carbene complex of a Main Group element. Does it show Fischer- or Schrock-like behavior? Using arguments of the type shown in Fig. 11.1, explain why it behaves as it does. (b) Metal oxo complexes, such as $Re(=O)Cl_3(PPh_3)_2$, might also be regarded as carbene-like if we make the isoelectronic substitution of O for CH_2. Do the same arguments of Fig. 11.1 give any insight into whether an M=O group will have greater or lesser nucleophilic character than the corresponding $M{=}CH_2$ species?

5. Propose a mechanism for



6. Internal alkenes are thermodynamically more stable than 1-alkenes. Why does the SHOP oligomerization give 1-alkenes?

7. In principle, cyclopentene might metathesize to 1,6-cyclodecadiene (cdd). In fact, a polymer is observed. What is the structure of the polymer, and how does its formation, rather than that of cdd, relate to the question of pairwise versus nonpairwise mechanisms?

8. A commercial metathesis catalyst consists of $Mo(CO)_6$ absorbed on an alumina support. It is found that it is necessary to pass CCl_4 vapor over the hot catalyst to activate it for metathesis. What is the role of the CCl_4?

9. In some $TiCl_3$-based polymerization catalysts, a small amount of $NiCl_2$ is added to control (i.e., slightly shorten) the chain length. What is the role of the Ni, and what feature of Ni, as opposed to Ti chemistry, do we rely on for the effect? What is the structure of the end group when the polymer dissociates from the Ni-doped catalyst? What might be the effect of the additives $FeCl_3$, $HgCl_2$, and VCl_5?

10. Would you expect changes in the formal orbital occupation to affect the orientation of a CH_2 group? Given the orientation shown in Fig. 11.2, draw the appropriate diagram for the isoelectronic $[Cp_2W(=CH_2)Me]^+$, which has an electrophilic methylene. What about the hypothetical $[Cp_2W(=CH_2)Me]^-$? What would be the CH_2 orientation, and would you expect the complex to be stable?

CHAPTER 12

THE ACTIVATION OF SMALL MOLECULES

One important general problem in organometallic chemistry is the binding and activation of the small molecules of Nature. We have seen in Chapter 9 how alkenes can be converted into any of a number of useful products in this way by catalytic reactions involving transition metals. We now turn our attention to some of the newer areas of interest involving less reactive molecules such as CO, CO_2, and alkanes. The goal has been to convert these relatively common carbon compounds into useful organic chemicals. If better methods for doing this were available, we might be able to make more efficient use of the global supply of hydrocarbons and coal. To take just one example, natural gas (methane) is wasted by being flared off in certain oil fields, for lack of an economic method of transport. A method of turning this methane into easily transportable liquids, such as methanol or higher alkanes, would be very valuable.

12.1 CO ACTIVATION

Carbon monoxide is efficiently incorporated into aldehydes and alcohols by the hydroformylation reaction presented in Section 9.3, but methods are now being sought to incorporate CO into other organic compounds and to reduce the oligomerize it to produce long-chain alkanes or alcohols. Most organic chemicals are currently made commercially from ethylene, a product of oil refining. It is possible that in the next several decades we may have to shift toward other carbon sources for these chemicals as depletion of our oil reserves continues. Coal can be converted into CO/H_2 mixtures with air and steam (Eq. 12.1), and it is possible to convert such mixtures, variously called

"water–gas" or "synthesis gas" to methanol (Eq. 12.1) and to alkane fuels with various heterogeneous catalysts. In particular, the Fischer–Tropsch reaction (Eq. 12.2) converts synthesis gas to a mixture of long-chain alkanes and alcohols. Much effort has gone into the idea that homogeneous analogs of the Fischer–Tropsch catalyst might selectively produce useful materials, now made from ethylene, such as ethylene glycol.

$$C + H_2O \xrightarrow{\text{heat}} \underbrace{H_2 + CO}_{\text{synthesis gas}} \xrightarrow{\text{het. catal.}} CH_3OH \tag{12.1}$$

$$H_2 + CO \xrightarrow{\text{het. catal.}} CH_3(CH_2)_nCH_3 + CH_3(CH_2)_nOH + H_2O \tag{12.2}$$

Water–Gas Shift It is often useful to change the $CO:H_2$ ratio in synthesis gas and this can be accomplished by the water–gas shift reaction (Eq. 12.3),[1] which can be catalyzed heterogeneously (Fe_3O_4 or Cu/ZnO) or by a variety of homogeneous catalysts, such as $Fe(CO)_5$[2a] or $Pt(i\text{-}Pr_3P)_3$.[2b] The reagents and products in Eq. 12.3 have comparable free energies; the reaction can therefore be run in either direction and this can be regarded as both CO and CO_2 activation.

$$H_2O + CO \rightleftharpoons H_2 + CO_2 \tag{12.3}$$

In the mechanism proposed for the homogeneous iron catalyst (Fig. 12.1), CO binds to the metal and so becomes activated for nucleophilic attack by OH^- ion at the CO carbon. Decarboxylation of the resulting metalacarboxylic acid probably does not take place by β elimination, because this would require prior loss of CO to generate a vacant site; instead, deprotonation may precede loss of CO_2, followed by reprotonation at the metal to give $HFe(CO)_4^-$. Protonation of this anionic hydride liberates H_2 and regenerates the catalyst. The platinum catalyst (Fig. 12.2) is perhaps more interesting in that it activates both the water and the CO, so no added base is needed. This happens because the platinum complex is sufficiently basic to deprotonate the water, leading to a cationic hydride complex. The cationic charge activates the CO for

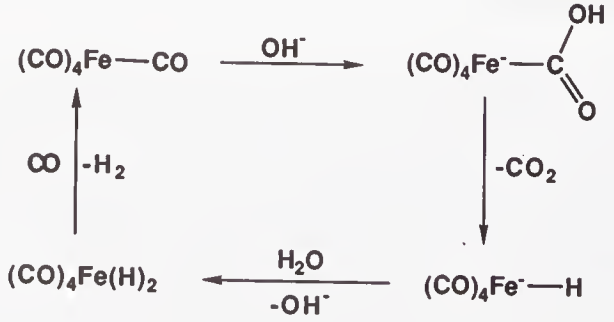


FIGURE 12.1 The cycle proposed for the $Fe(CO)_5$-catalyzed water–gas shift reaction.

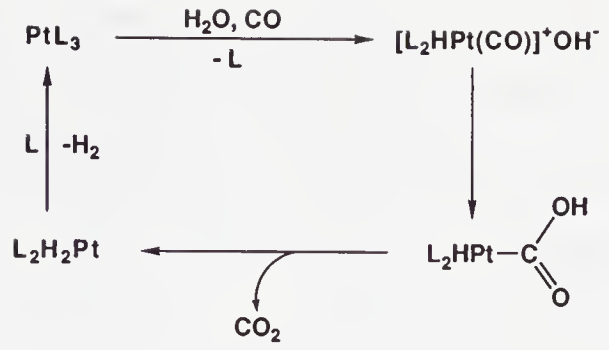


FIGURE 12.2 The cycle proposed for the PtL_3-catalyzed water–gas shift reaction {L = $P(i\text{-}Pr)_3$}.

nucleophilic attack by hydroxide ion to give the metala-carboxylic acid (M—COOH). Such a compound is seen as a stable intermediate when water reacts with $TpIr(CO)_2$ (Eq. 12.4, Tp = tris(pyrazolyl)borate). The final product, $TpIr(H)_2(CO)$, does not lose H_2, so this system is not a catalyst.[2c] We look at a biological analog of the water–gas shift in Section 16.4.

$$TpIr(CO)_2 \xrightarrow{H_2O} TpIr(H)(COOH)(CO) \xrightarrow{\text{heat, } -CO_2} TpIr(H)_2(CO) \tag{12.4}$$

Reppe Reaction[2a] This uses the water–gas shift to generate H_2/CO for subsequent hydroformylation of the substrate alkene to give an aldehyde, followed by hydrogenation to give an alcohol, as shown in Eq. 12.5. With the $Fe(CO)_5$/base catalyst mentioned above, the product is the linear alcohol.

$$RCH{=}CH_2 + 3CO + 2H_2O \xrightarrow{KOH,\ Fe(CO)_5,\ 15\ atm,\ 100^\circ} RCH_2CH_2CH_2OH + 2CO_2 \tag{12.5}$$

The alkene is believed[3] to insert into an Fe—H bond of the active catalyst, $H_2Fe(CO)_4$, formed as in Fig. 12.1, followed by migratory insertion to give $(RCH_2CH_2CO)FeH(CO)_3$, which in turn reductively eliminates the aldehyde RCH_2CH_2CHO. This aldehyde is then hydrogenated to the alcohol with $HFe(CO)_4^-$ as catalyst. By itself, $Fe(CO)_5$ is not a hydroformylation catalyst because H_2 cannot displace CO to form $H_2Fe(CO)_4$, hence the need for the base.

Monsanto Acetic Acid Process[4a] Over a million tons of acetic acid a year are produced by carbonylation of methanol, which happens in >99% selectivity with a rhodium catalyst. The rhodium can be introduced as $RhCl_3$ or as $RhCl(CO)(PPh_3)_2$, but the active catalyst is $[Rh^{I}I_2(CO)_2]^-$. The net effect is the cleavage of the methanol C—O bond and insertion of a CO. To be

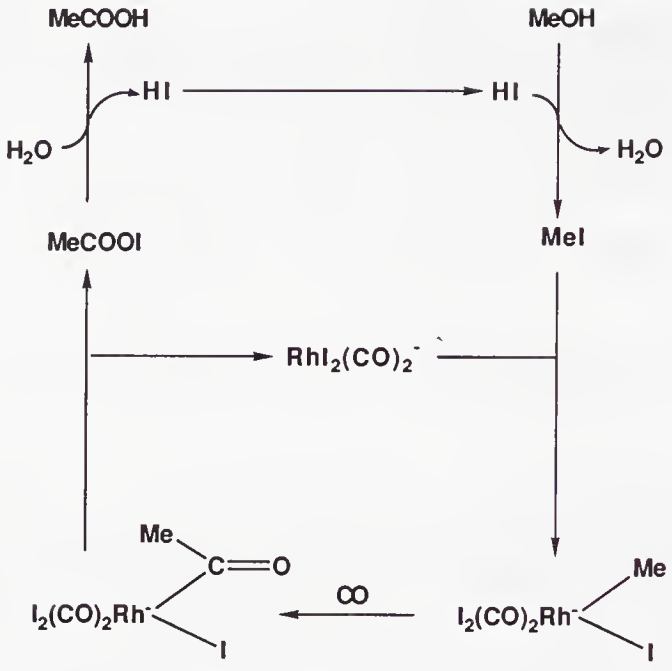


FIGURE 12.3 The catalytic cycle proposed for the Monsanto acetic acid process.

carbonylated, the methanol has to bind to the catalyst and this requires adding a certain amount of HI to the system,

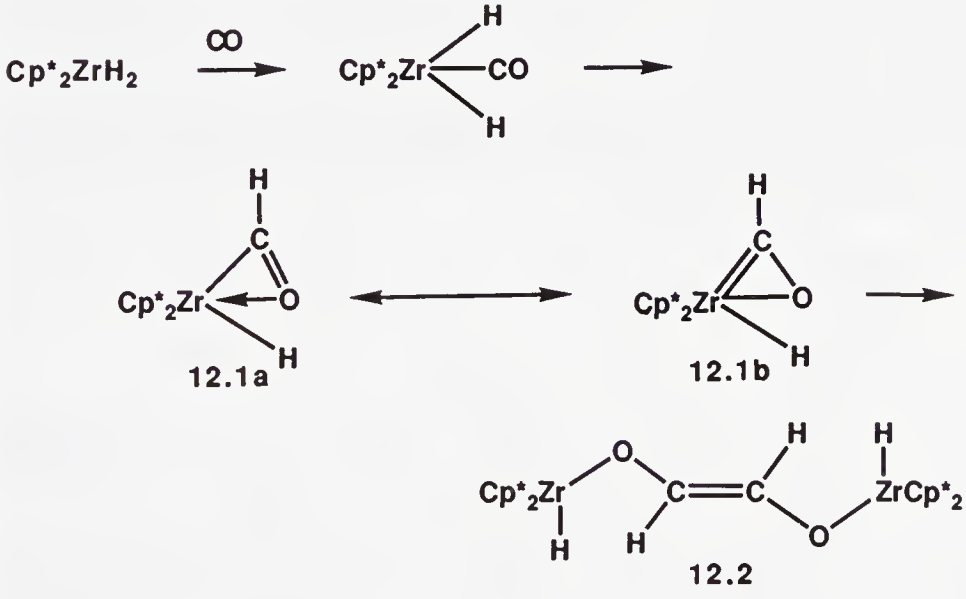
$$\text{MeOH} + \text{CO} \xrightarrow{180°,\ 30\ \text{atm},\ \text{MeI},\ 10^{-3}\ M\ \text{catal.}} \text{MeCOOH} \qquad (12.6)$$

$$\text{MeOH} + \text{HI} \rightleftharpoons \text{MeI} + \text{H}_2\text{O} \qquad (12.7)$$

which produces an equilibrium concentration of MeI, which can in turn oxidatively add to the metal in the turnover limiting step. Once we have the rhodium methyl, migratory insertion can take place with CO to give an acetylrhodium iodide. Reductive elimination of the acyl iodide completes the cycle (Fig. 12.3). The free acyl iodide is hydrolyzed by the methanol to give methyl acetate, and can be ultimately converted to acetic acid with water. The resulting acetic acid can be entirely derived from synthesis gas if the methanol comes from the reaction shown in Eq. 12.1. In a very closely related reaction, CH_3COOMe can be carbonylated to acetic anhydride $(CH_3CO)_2O$.[4b] The Monsanto Process for making acetic acid is replacing the older route that goes from ethylene by the Wacker process to acetaldehyde, which is then oxidized to acetic acid in a second step. This example shows how important it is that chemical companies carry out research into possible alternative ways to make a compound, even though the current route is working well; otherwise their competitors may discover a better one. A biological analog of this reaction is discussed in Section 16.4, and an application in organic synthesis, the Heck reaction, is discussed in Section 14.6.

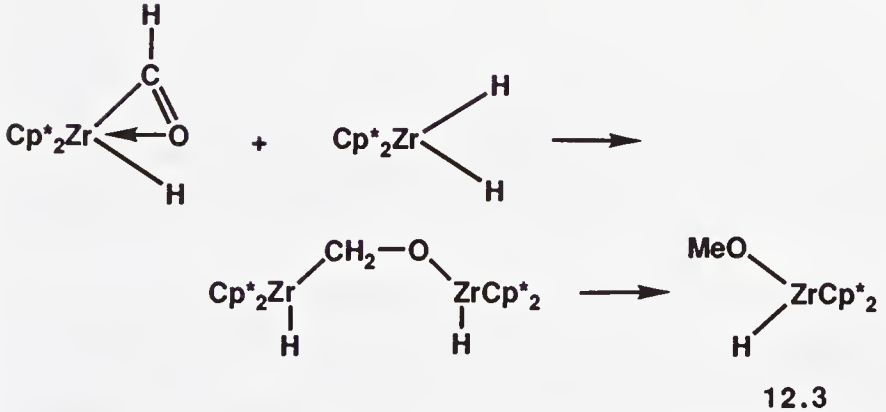
CO Reduction via Formyl Intermediates In planning an attack on the problem of CO reduction, one might think that the migratory insertion of CO into an M—H bond to give a formyl complex M—CHO (by analogy to

the well-known insertion into an M—alkyl bond) might play an important part. In fact this reaction is rare, probably for thermodynamic reasons; the M—H is usually stronger than the M—CHO bond of the product.[5] Additional driving force for the reaction can be obtained if the metal involved is sufficiently oxophilic to bind the formyl in the η^2 form. This can happen for the early *d*-[6] and the *f*-block[7] metals, as shown by Eq. 12.8.[6] The intermediate carbonyl dihydride is very unstable, as befits a d^0 complex in which there can be little, if any, back bonding. The insertion is believed to give an η^2 formyl, **12.1**, which has a resonance contributor **12.1b**, in which it acts as a carbene. This intermediate may do one of two things: couple to a coordinated enediolate (**12.2**), or react with excess zirconium hydride to give a methoxy hydride (**12.3** in Eq. 12.9). We can rationalize the formation of **12.2** on the basis of the coupling of the carbene form of the η^2-formyl. Species **12.3** probably arises by addition of a Zr—H bond across the formyl, perhaps even across an η^1-formyl in equilibrium with the η^2 form.



(12.8)

12.2



(12.9)

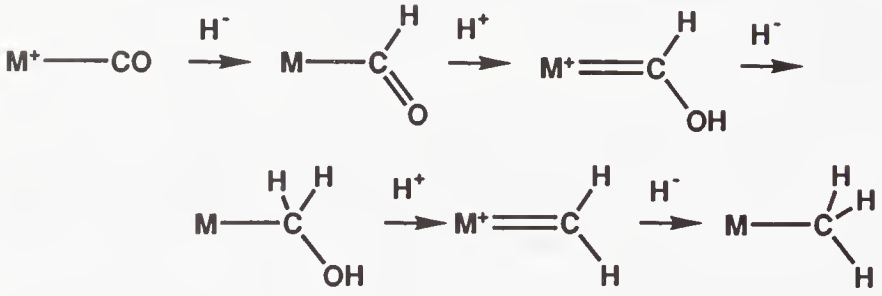
12.3

The marked hydridic character of the zirconium hydrides shown in their reaction with the formyl in Eq. 12.9, is also apparent in an analogous reaction with a coordinated carbonyl in Eq. 12.10.[8]

(12.10)

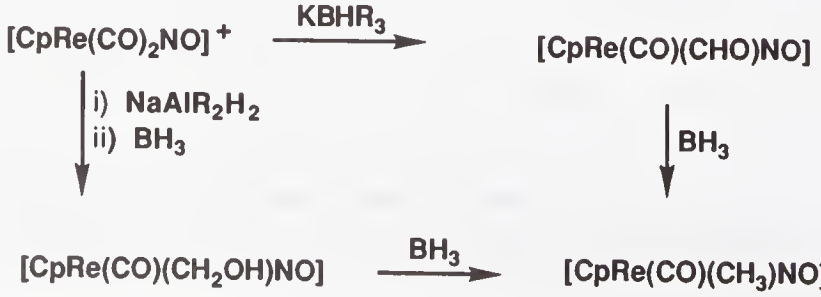
The late metals can also show interesting CO reduction chemistry; Eq. 12.11 is one of the earliest examples. At the time the transformation was not understood, but more recent work has provided a plausible pathway through formyl complexes, shown in Eq. 12.12. The CO in the cationic starting material is strongly activated to nucleophilic attack, and so H^- gives an η^1-formyl directly. This might well be more stable as a carbonyl hydride, but a 2e site on the metal would be required for such a rearrangement. All the ligands are tightly bound, and so the formyl is kinetically stable. Where protons are available from the solvent, the formyl can protonate at oxygen to give a hydroxymethylene complex. By protonating the formyl, we have made a Fischer carbene, which is sensitive to nucleophilic attack at the carbene carbon. This can happen either with an external source of hydride or by H^- transfer from any formyl complex that remains in the reaction mixture. A formyl complex can be a good H^- donor by reversal of the first step of Eq. 12.12. In order to reduce the hydroxymethyl group even further, we can repeat the H^+ addition–H^- addition cycle. Protonation at the OH of the hydroxymethyl group leads to loss of water and to the formation of a presumed methylene intermediate, which in turn rapidly adds H^- to give the final methyl complex.[9]

$$[CpMo(CO)_3(PPh_3)]^+ \xrightarrow{NaBH_4} CpMo(CO)_2(PPh_3)(CH_3) \qquad (12.11)$$



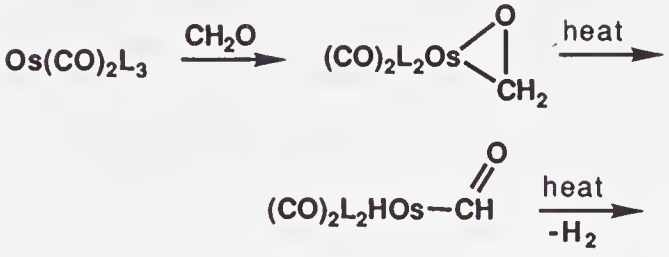
(12.12)

One of the best-known systems in which many of these transformations have been studied step by step is based on rhenium. Once again, we start with a cationic metal, and as shown in Eq. 12.13, several of the key intermediates can be isolated and studied.[10] In this system, BH_3 probably acts both as an H^- donor and as a Lewis acid to play the role assigned to the proton in Eq. 12.12.



(12.13)

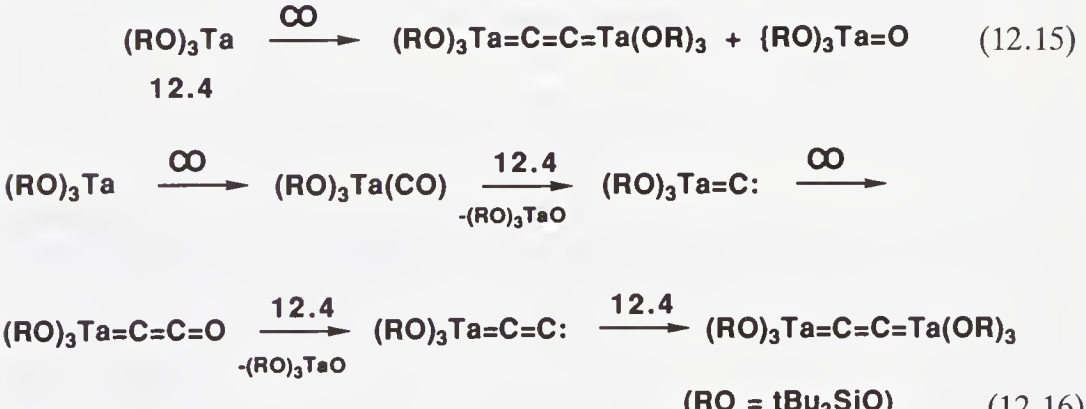
A tautomer of the hydroxycarbene intermediate is an η^2-formaldehyde complex, a species first observed by Roper:[11a]



(12.14)

($L = PPh_3$)

Wolczanski[11b] has found that the unusual trigonal planar Ta(III) complex $[(silox)_3Ta]$ (**12.4**), in which the bulky silox (t-Bu_3SiO^-) inhibits alkoxide bridging, cleaves CO as shown in Eq. 12.15. The proposed mechanism is shown in Eq. 12.16. Note the nontraditional O-donor ligand set (rather than Cp or PR_3). In the heterogeneous Fischer–Tropsch reaction it is believed that CO is cleaved to surface-bound oxide and carbide, possibly via a sequence resembling Eq. 12.16, which then hydrogenate to water and surface-bound CH_2, which oligomerizes to give the products, either linear alkanes $CH_3(CH_2)_nCH_3$ formed by hydrogenation of the surface bound alkyl groups or alcohols $CH_3(CH_2)_nCH_2OH$ formed by CO insertion to give an acyl followed by hydrogenation to the alcohol. CO cleavage in a homogeneous system is very rare, however.



(12.15)

(12.16)

Pruett[11c] at Union Carbide found that the cluster $[Rh_{12}(CO)_{34}]^{2-}$ is a catalyst precursor for the reduction of CO/H_2 to $HOCH_2CH_2OH$, a rare example of a system that produces a single oxygenate (oxygen-containing organic compound) as a major product from a CO reduction reaction.

Metalaradicals A very recent approach to CO activation by Wayland[11d] is the use of odd-electron metal complexes, such as the 17e species [Rh(TMP)] (where TMP = tetramesitylporphyrin). This reacts with CO to give [(TMP)Rh(μ-CO)Rh(TMP)] and [(TMP)Rh(μ-CO-CO)Rh(TMP)], presumably via an intermediate [(TMP)Rh(CO)] that behaves like an acyl radical (R—C•=O) and either dimerizes or combines with the starting metalaradical [Rh(TMP)].

12.2 CO_2 ACTIVATION

Carbon dioxide, as a constituent of the atmosphere, is an abundant carbon source. It has been implicated as a factor in a predicted global warming over the next few decades, by the so-called 'greenhouse effect'. CO_2 is transparent to the incoming solar radiation, but not to the infrared frequencies at which the Earth reradiates heat into Space during the night. One of the chief problems in CO_2 chemistry is that it is so thermodynamically stable that only a very few potential products can be made from CO_2 by exothermic processes. One could reduce it to CO with hydrogen by the water–gas shift, and then use CO chemistry to make various carbon compounds, except that H_2 is very expensive. Indeed, the current methods of making H_2 involve the consumption of either coal or natural gas, which are valuable carbon sources:

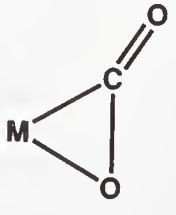
$$CH_4 + H_2O \longrightarrow H_2 + CO \qquad (12.17)$$

$$C + H_2O \longrightarrow H_2 + CO \qquad (12.18)$$

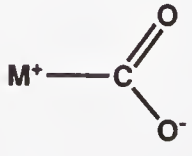
$$H_2 + CO_2 \xrightarrow{\text{water–gas shift}} CO + H_2O \qquad (12.19)$$

The most important CO_2 activation process is photosynthesis, in which solar photons drive a reaction that would otherwise be uphill thermodynamically: the reduction of CO_2 to carbohydrates coupled to water oxidation to O_2. Many metalloenzymes are involved in these processes, the one that "fixes" CO_2 is ribulose diphosphate carboxylase, in which an enolate anion of the sugar nucleophilically attacks the CO_2 carbon. Cu(II), Mn(II), and Mg^{2+} are all present in the active enzyme, and one of these probably plays a role in polarizing the CO_2, perhaps via an η^1-***O***CO complex.

CO_2 Complexes Apart from the η^1-***O***CO bonding mode mentioned above, which is characteristic for higher-valent metals, carbon dioxide can act as a ligand to low-valent metals in two other ways, either as an η^2-***OC***O (**12.5a**) or as an η^1-O***C***O ligand (**12.5b**). In **12.5a**, the bonding resembles that in an alkene complex, with the CO_2 acting as a 2e ligand. The case of **12.5b** is more interesting in that the CO_2 is acting as a zero electron ligand. As such, CO_2 can bind in an η^1-O***C***O fashion even to an 18e complex. The sequence of events can be thought of as follows. A sufficiently nucleophilic metal attacks the CO_2 carbon to give an η^1-***C***O_2 complex. If the complex has a vacant site, the anionic oxygen of the η^1-***C***O_2 complex can also coordinate to give an η^2 complex, in which case the O lone pair acts as a 2e donor to the metal.

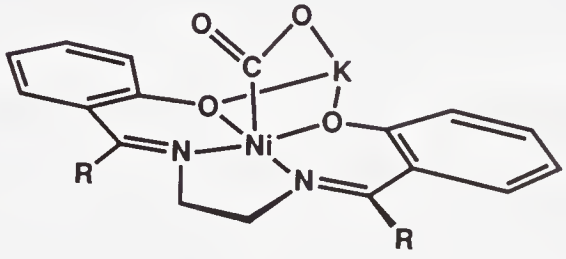


12.5a

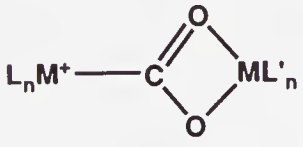


12.5b

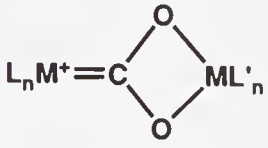
Examples of the two types are $[Ni(\eta^2\text{-}CO_2)(PCy_3)_2]$[12] and $[(dmpe)_2ClIr(\eta^1\text{-}\boldsymbol{C}O_2)]$.[13] In a variant of the $\eta^1\text{-}\boldsymbol{C}O_2$ complex, the anionic oxygen atom is stabilized by a Lewis acid of some sort, as is observed in Floriani's complex, **12.6**,[14a] where a K^+ ion plays this role. In other cases, a transition metal can replace the K^+ to give bridging CO_2 complexes. Examples close to each of the two extreme formulations, **12.7a** and **12.7b**, have been reported; for example, $Cp(CO)(PPh_3)Fe(=CO_2)Re(CO)_3(PPh_3)$ is of type **12.7b**,[14b] as suggested by the carbene-like ^{13}C NMR shift of the CO_2 carbon (246 ppm).



12.6

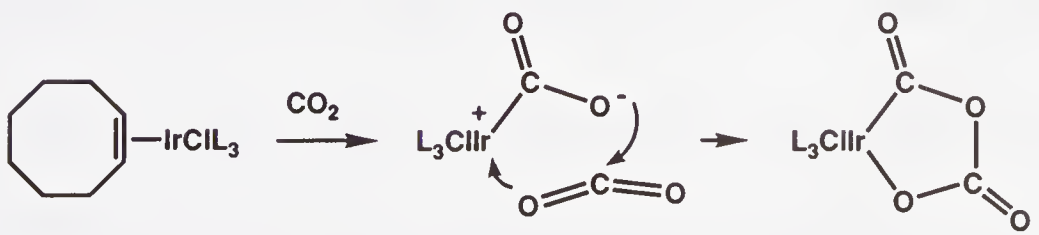


12.7a



12.7b

An unusual CO_2 complex is shown in Eq. 12.20; instead of forming an $\eta^2\text{-}CO_2$ complex, as might have been expected, the developing negative charge at oxygen in the initial $\eta^1\text{-}CO_2$ complex attacks a second molecule of CO_2. This allows the formation of the cyclic C_2O_4 complex shown in Eq. 12.21.[15] $[CpFe(CO)_2]^-$ reacts with CO_2 to give an $\eta^1\text{-}CO_2$ complex that reacts with HBF_4 at $-80°$ to give the carbonyl complex $[CpFe(CO)_2]^+$, presumably via Eq. 12.21:[16]



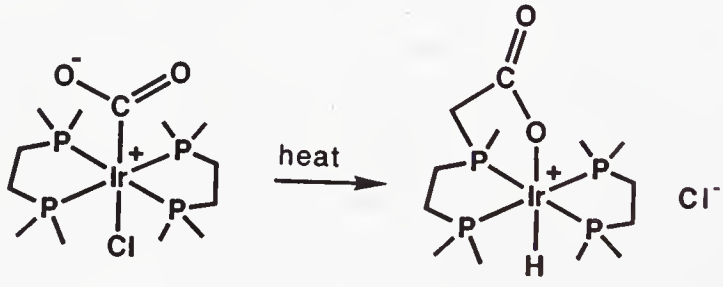
(12.20)

$$[CpFe(CO)_2]^- \xrightarrow{CO_2} [CpFe(CO)_2(\eta^1\text{-}\boldsymbol{C}O_2)]^- \xrightarrow{H^+}$$
$$[CpFe(CO)_2(\eta^1\text{-}\boldsymbol{C}O_2H)] \xrightarrow{H^+,\ -H_2O} [CpFe(CO)_3]^+ \quad (12.21)$$

So far, CO_2 complexes have not shown the rich chemistry of, say, the CO group, probably because the CO_2 is a much poorer ligand and so is easily lost. We would like to be able to incorporate CO_2 into an organic fragment already bound to the metal by an insertion reaction. This is what happens in the reaction of CO_2 with Main Group organometallic reagents, such as LiMe or MeMgBr, to give the acetates, such as LiO_2CMe. These reagents have both a nucleophilic Me^- to attack the CO_2 carbon, and a strongly Lewis acid Li^+ or $MgBr^+$ component to stabilize the developing charge on oxygen. Unfortunately, analogous reactions for the less electropositive transition metals are rare, although some cases are known.

$$[(OC)_5WMe]^- + CO_2 \longrightarrow [(OC)_5W(OCOMe)]^- \qquad (12.22)^{17}$$

A particularly interesting example is shown in the thermolysis of $[(dmpe)_2ClIr(\eta^1\text{-}CO_2)]$, in which the CO_2 apparently inserts into an Ir—C bond formed in a cyclometallation reaction (Eq. 12.23).[14] The reaction may in fact be somewhat more complicated, because in the related reaction of Eq. 12.24, the oxidative addition product shown is inert to CO_2. Only when the reaction with MeCN is carried out under CO_2, does the insertion product form. This may be due to the initial deprotonation of CH_3CN by some base, perhaps a trace of PMe_3, to give the carbanion $^-CH_2CN$, which attacks the CO_2; the resulting carboxylate ion then binds to the metal.[18]



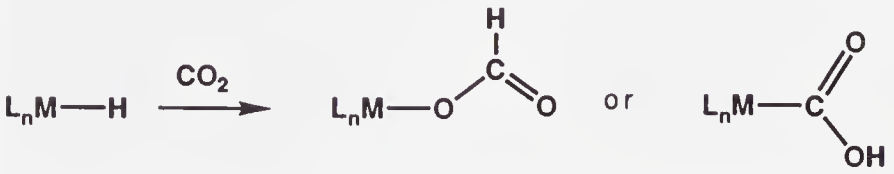
(12.23)

$$IrL_4^+ + CH_3CN \longrightarrow IrL_4H(CH_2CN)^+ \xrightarrow{CO_2} \text{no reaction} \qquad (12.24)$$

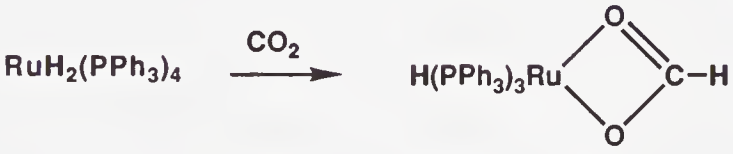
$$CH_3CN \xrightarrow[-LH^+]{L} {}^-CH_2CN \xrightarrow{CO_2} {}^-O_2CCH_2CN \xrightarrow{IrL_4^+,\ H^+} IrL_4H(O_2CCH_2CN)^+ \qquad (12.25)$$

Insertion Reactions CO_2 insertion into M—H bonds also takes place, but of the two possible regiochemistries (Eq. 12.26), only the formate, either η^1-, or η^2-bound, has been observed in a stable product (Eq. 12.27–

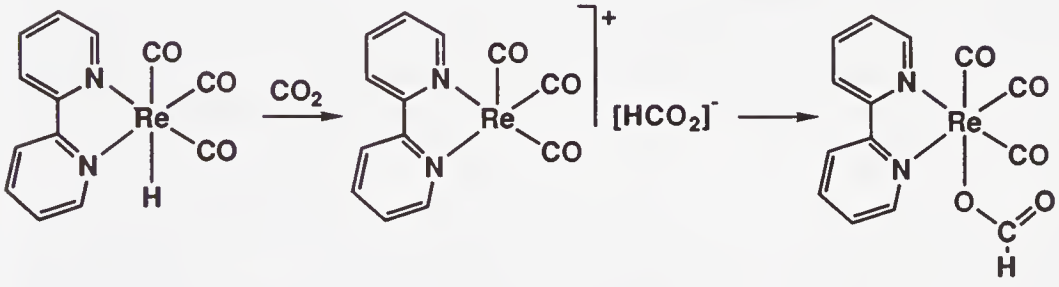
12.28).[19] Kinetic studies on Eq. 12.28[20a] suggest that the reaction goes by nucleophilic attack of the hydride on CO_2 to give the transient ion pair shown; this then collapses to give the final product. $[Rh(dpe)_2H]$ forms the stable salt $[Rh(dpe)_2][HCO_2]$.[20c]



(12.26)



(12.27)



(12.28)

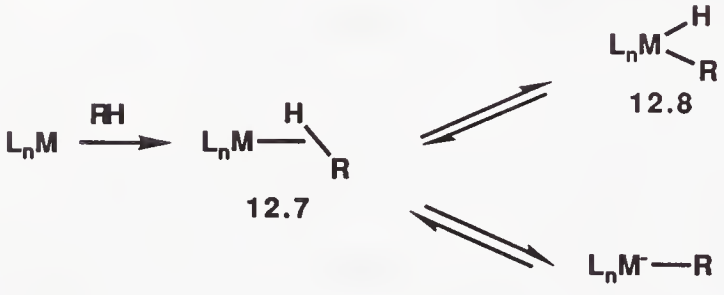
Chemistry of this type is probably involved in the catalytic reduction of CO_2 with H_2 to give HCOOH. Although this is "uphill" thermodynamically ($\Delta G^\circ = +8$ kcal/mol) the reaction becomes favorable under gas pressure and in the presence of base to deprotonate the formic acid formed. The best catalyst to date is $[Rh(cod)Cl]_2/Ph_2P(CH_2)_4PPh_2$, which gives 45 turnovers per hour at room temp. at 40 atm pressure.[20c]

12.3 ALKANE ACTIVATION

Alkanes are notably unreactive compounds and are among the most challenging substrates for activation.[21] After the discovery of the cyclometallation reaction (the oxidative addition of a C—H bond of a ligand to a metal complex; e.g., step i in Fig. 12.4) in the early 1960s, several attempts were made to add alkanes to low-valent metals. All of these met with failure, and interest in the subject waned until Shilov[22,23] reported his observations on the ability

of $PtCl_4^{2-}$ to catalyze H/D exchange between CH_3COOD and various alkanes (1969). In later work the Pt system was extended to oxidation of alkanes. Other observations in the field were (1979) stoichiometric[23,24] and (1980) catalytic[25,26] alkane dehydrogenation to alkenes (1982), the elusive direct alkane oxidative addition to a metal,[27–29] and (1987) "Mercat" chemistry.[30]

C—H Oxidative Addition The key step is the C—H bond cleavage, for which there are as yet only a small number of pathways possible. These probably all go through an alkane complex, **12.7**, followed by oxidative addition (**12.8** in Eq. 12.29a), proton loss (**12.9** in Eq. 12.29b) or C—H homolysis.



(12.29a)

(12.29b)

In oxidative addition, it is now believed that **12.8** is often thermodynamically unstable with respect to **12.7** because we break a strong C—H bond (e.g., 95 kcal/mol for C_6H_{12}) and make an M—H bond and an M—C bond. Although the M—H bond is usually worth about 60 kcal/mol, an M—C bond is worth only 30–45 kcal/mol. In addition, the formation of one particle (**12.8**) from two (L_nM and RH) is entropically unfavorable. H_2 addition has a higher driving force by 5–20 kcal/mol because although the H—H is slightly stronger (103 kcal/mol), two strong M—H bonds are formed, and this is enough to make H_2 addition a common reaction. We can circumvent this problem in one of two ways. Even if **12.7** → **12.8** is "uphill," **12.8** might still form in a small equilibrium concentration. If we can now trap it in a thermodynamically favorable subsequent step or series of steps, then we can still succeed in seeing useful products. In the first attempt of this sort, cyclopentane was chosen as the substrate in the hope that it would give an alkyl that could rapidly β-eliminate to cyclopentene, a compound that was already known to dehydrogenate further to a very stable cyclopentadienyl complex in the system under study.[24] The *t*-$BuCH{=}CH_2$ abstracts H_2 from the Ir(III) starting material and prepares it for oxidative addition of RH.

$$[IrH_2(Me_2CO)_2(PPh_3)_2]^+ + \text{cyclopentane} \xrightarrow{t\text{-BuCH=CH}_2} [CpIrH(PPh_3)_2]^+ \quad (12.30)$$

In some cases, the alkene, once formed, can dissociate and is not further dehydrogenated.[25,26] This makes the alkane → alkene conversion potentially catalytic, but the reaction is thermodynamically uphill below 300°C, so we need to drive the reaction. If *t*-BuCH=CH_2 is present, it can do so by acting as *hydrogen acceptor* (Eq. 12.31).

Figure 12.4 shows a catalytic cycle involving a system of this type. In steps *a–c*, the *t*-BuCH=CH_2 strips H_2 from the catalyst precursor to give the proposed 14e intermediate $Ir(\eta^1\text{-}CF_3COO)(PPh_3)_2$. In steps *d–f*, the alkane substrate is in turn dehydrogenated. Equation 12.31 is enthalpically (i.e., ΔH) favorable because *t*-BuCH=CH_2 has an unusually high heat of hydrogenation and is entropically neutral because Eq. 12.31 involves no increase in the number of molecules on going from left to right. In Eq. 12.31 the catalyst is $ReH_7(PPh_3)_2$, $IrH_5(PEt_3)_2$, $RhCl(PMe_3)_3$, or $IrH_2(\eta^2\text{-}CF_3COO)(PPh_3)_2$.[25,26]

$$\text{alkane} + t\text{-BuCH=CH}_2 \xrightarrow{\text{catalyst}} \text{alkene} + t\text{-BuCH}_2\text{CH}_3 \qquad (12.31)$$

Alternatively, the reaction can be driven by photon absorbtion (Eq. 12.32).[26] The iridium system of Fig. 12.4 also shows this cycle. In steps *g–h*, a photon dissociates H_2 and generates the same intermediate as before. In steps *d–f*, iridium acts as hydrogen acceptor by forming the stable hydride. The absorbtion of the next photon liberates H_2, and in so doing the photon energy helps drive the reaction.

$$\text{alkane} \xrightarrow{\text{catalyst, } h\nu} \text{alkene} + H_2 \qquad (12.32)$$

These systems are selective for 1° C—H bonds, for example, methylcyclohexane, $CH_3C_6H_{11}$, gives $CH_2{=}C_6H_{10}$ as kinetic (most rapidly formed) product. Subsequent slow isomerization to the thermodynamic (most stable) product, 1-methylcyclohexene, then takes place. Benzene can also oxidatively add to give the stable phenyl hydride, **12.10**. In the absence of substrate the system cyclometallates to give **12.11** (Figure 12.4). Nonprecious metals have generally proved to be inactive. For example, $WH_6(PMePh_2)_3$ fails to give Eq. 12.31 because it disproportionates to the inactive species $WH_4(PMePh_2)_4$ on heating. A useful general strategy is to use a chelating phosphine such as $Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2$ (triphos) to prevent disproportionation. Once this is done, WH_6(triphos) turns out to be a very active catalyst for Eq. 12.31.[26b]

The alkyl hydride may also be trapped by CO to give an acyl hydride, which can in turn gives aldehyde on reductive elimination.[25b] $RhCl(CO)(PMe_3)_2$ is one of the most effective catalysts. *n*-Pentane gives very high (>95%) selectivity for the formation of the linear aldehyde, $CH_3(CH_2)_4CHO$. The alkyl hydride intermediate formed by alkane oxidative addition to the $RhCl(PMe_3)_2$ intermediate formed after the photochemical ejection of CO is believed to bind CO, undergo migratory insertion to give the acyl hydride, and reductively eliminate the product aldehyde. The high

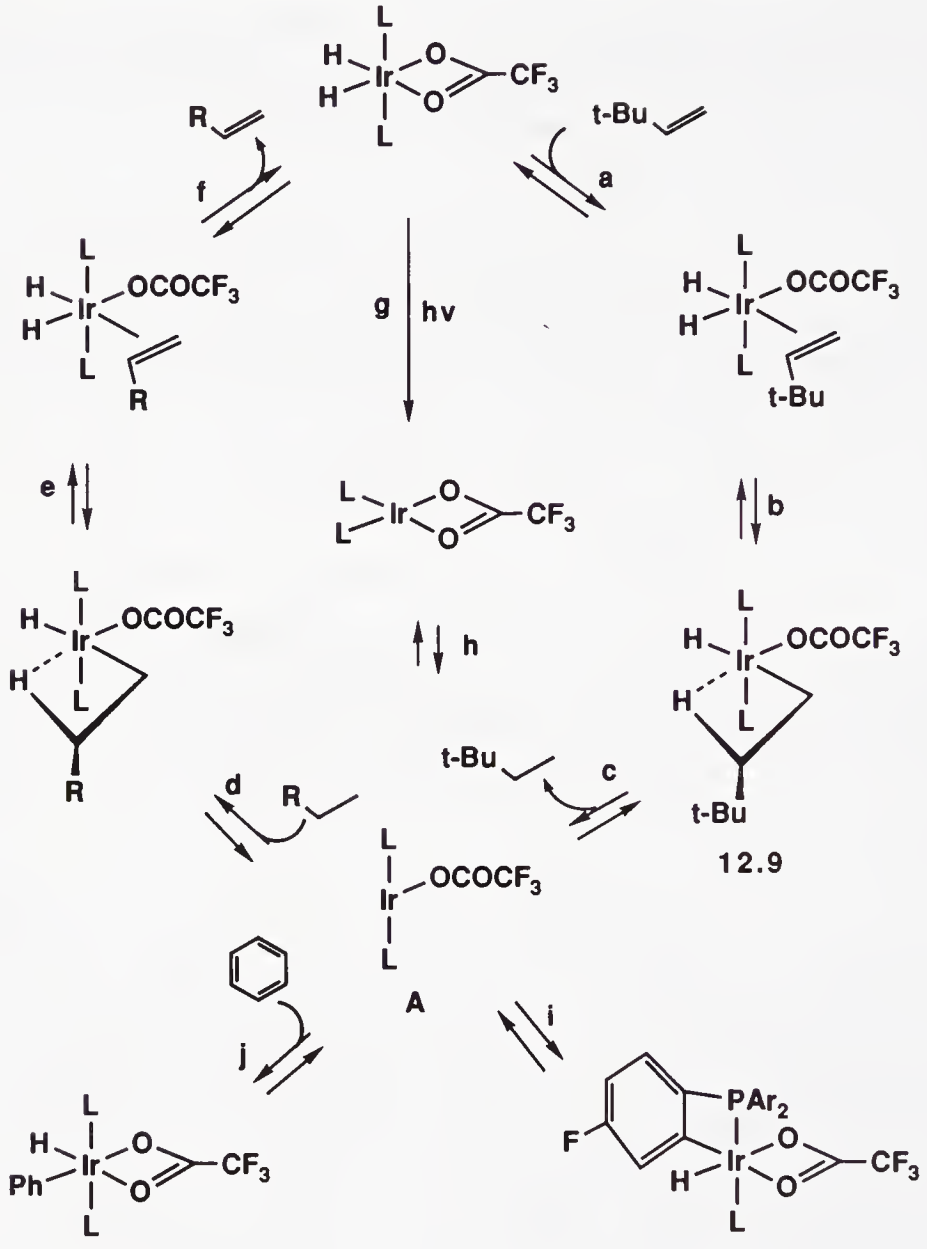


FIGURE 12.4 The catalytic cycle proposed for the dehydrogenation of the alkane RCH_2CH_3 to give the alkene $RCH{=}CH_2$ by an iridium complex, $[IrH_2(RCO_2)L_2]$. In the thermal process, which follows the route *a–b–c–d–e–f*, the hydrogen acceptor *t*-$BuCH{=}CH_2$ is required to provide thermodynamic driving force for the reaction so that products can be observed. In the photochemical process, which follows the route *g–h–d–e–f*, the hydrogen acceptor *t*-$BuCH{=}CH_2$ is no longer required because the thermodynamic driving force for the reaction comes from the photon energy. For the photochemical process, L = $P(C_6H_{11})_3$ and for the thermal process, L = PPh_3. The proposed intermediate **A** can reversibly oxidatively add to C—H bonds as shown in steps *i* and *j* to give the isolable species **12.10–12.11**. Species **12.9** was observed by NMR.

selectivity is probably due in part to preferential C—H bond breaking at the unhindered terminal site and by faster carbonylation of the *n*-pentyl rhodium species—recall that this also happened in alkene hydroformylation (Section 9.3).

Direct observation of the alkane oxidative addition product, an important goal of early work, requires that no subsequent reaction take place. This has proved possible in a number of systems,[27-29] such as $Cp^*Ir(PMe_3)H_2$ and $CpIr(CO)_2$, in which a highly reactive 16e fragment is generated by photoextrusion of H_2 or CO (Eq. 12.29a). The high reactivity may come from the fact that CpIrL cannot achieve the usual square planar geometry favored by Ir(I). After oxidative addition an 18e complex is formed, which is stable. In contrast, the catalytic systems are believed to involve 14e species, which give reactive 16e alkyl hydrides. These systems show preferential attack at unhindered C—H bonds; for example, in $Cp^*Ir(PMe_3)H_2$, attack at a 1° C—H of an *n*-alkane is favored by about 3:1 over attack at a 2° position. A surprise to come out of this work was the low barrier to alkane C—H oxidative addition; for example, the $CpIr(CO)_2$ system reacts with CH_4 even at −260°C.[28b] This suggests that the reason why examples of Eq. 12.29a are so rare is unlikely to be kinetic, and so **12.7** → **12.8** is probably thermodynamically uphill for most systems. The oxidative addition can often be reversed on heating. If $Cp^*Ir(PMe_3)(C_6H_{11})H$ is heated under methane at 150°, reductive elimination is followed by oxidative addition of methane to give the more stable methyl hydride. Examining the position of equilibrium in such reactions enables a comparison of M—C bond strengths; for example, $Cp^*(PMe_3)HIr$—*n*-pentyl is 5.5 kcal/mol stronger than $Cp^*(PMe_3)HIr$—cyclohexyl.[27c] Liquid Xe at −70°C and 10 atm pressure or Kr at −90°C prove to be useful inert solvents for this system that permit studies on solid substrates, such as cubane or naphthalene.[27b] Fast kinetic studies on $Cp^*Rh(CO)_2$ in Kr have also given strong evidence for noble gas and alkane complexes (of type **12.7**), $Cp^*Rh(CO)L'$ (L′ = Kr or C_6H_{12}), being intermediates in the chemistry. The barrier for cyclohexane C—H oxidative addition proved to be a surprisingly low 4.8 kcal/mol.[27b,d]

Direct oxidative addition of arene C—H bonds is easier even though they are much stronger (~110 kcal/mol) than alkane C—H bonds. For example, photoextrusion of H_2 from $CpWH_2$ gives $Cp_2W(R)H$ only with C_6H_6 but not with CH_4.[31a] The reason is in part thermodynamic[21b]; M—aryl bonds are much stronger than M—alkyl ones, perhaps because of the stronger bonding possible with sp^2 carbon and favorable π bonding, possible only in the aryl case. The reaction may also be favored kinetically by arene precoordination in an η^2 mode via the ring π system.[29b]

***Shilov Chemistry*[22,23]** Alkane C—H bonds can be split heterolytically with Pt(II) to give a Pt alkyl and a proton. The most likely pathway is deprotonation of a Pt(II) alkane complex (Eq. 12.29b). This is related to the facile deprotonation of dihydrogen complexes that we saw in Section 3.4. In both cases

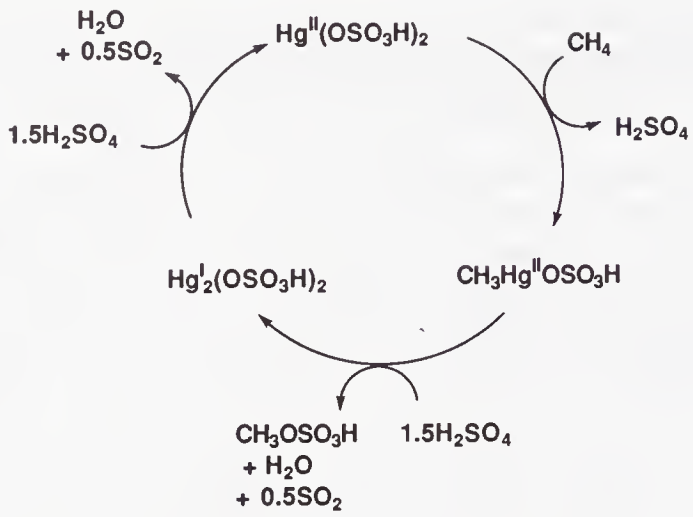


FIGURE 12.5 A possible catalytic cycle for the Catalytica methane oxidation. C—H bond breaking may occur by deprotonation of a methane complex.

predominant X—H bond to metal σ donation is not matched by M to X—H π back donation, and so the X—H proton becomes very ∂^+ in character. Reversal of Eq. 12.29b with D^+ leads to the observed deuteration of the alkane. Oxidation of the alkyl with Pt(IV) can lead to RCl or ROH. This may go by nucleophilic abstraction of a methyl group from Me—Pt(IV) by OH^- or Cl^-. A recent application of this chemistry is the selective oxidation of ethanol, CH_3CH_2OH, to ethylene glycol, $HOCH_2CH_2OH$. Instead of the usual oxidation products CH_3CHO and CH_3COOH, note how the very unusual direct attack at the CH bond of ethanol *remote* from the OH functionality leads to the glycol.[23b]

Figure 12.5 shows the proposed mechanism in a reaction from Catalytica Corp.,[23c] in which methane is oxidized to methyl bisulfate, CH_3OSO_3H, by conc. H_2SO_4 at 180°C with $Hg^{II}(OSO_3H)_2$ as catalyst. The selectivity (85%) for methyl bisulfate and the conversion of methane (50%) are both very high.* The details of the mechanism are still unclear, but deprotonation of a proposed methane complex, $[(CH_4)Hg(OSO_3H)]^+$ to give $[CH_3Hg(OSO_3H)]$ seems likely, and the methylmercury intermediate can be detected in the reaction mixture by NMR spectroscopy. Nucleophilic abstraction of Me^+ from this intermediate could then take place by attack of SO_4^{2-}, followed by oxidation of the reduced Hg species to Hg(II) by the H_2SO_4.

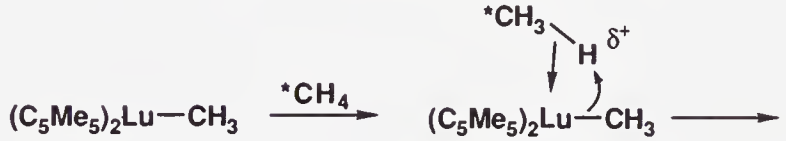
σ-Bond Metathesis Electrophilic early metals, including *f*-block metals, are especially effective in this type of C—H activation. In Eq. 12.33,[32] heating the starting alkyl is thought to form a transient imide intermediate via α

*The conversion is the mole percent of a given starting material that is converted into products and the selectivity is the mole percent of the material converted that ends up as a specified product. The conversion times the selectivity is the yield.

elimination. Formation of an alkane complex is followed by deprotonation of the bound C—H by the basic imide nitrogen.[32b] In Eqs. 12.34 and 12.35,[33,34] adjacent alkyl groups already present on the metal act as base. Methane is very reactive in these systems.

$$(\{t\text{-Bu}\}_3\text{SiNH})_3\text{Zr}(\text{CD}_3) \xrightarrow{\text{heat}} (\{t\text{-Bu}\}_3\text{SiNH})_2\text{Zr}{=}\text{NSi}(t\text{-Bu})_3 \xrightarrow{\text{X—H}} (\{t\text{-Bu}\}_3\text{SiNH})_3\text{Zr—X} \quad (12.33)$$

(X = H, CH_3, Ph)



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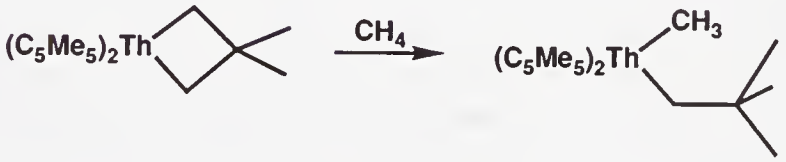


(12.35)

C—H Homolysis Certain metalloenzymes can also break alkane C—H bonds but via homolytic C—H bond breaking to give carbon radicals, and model systems have been developed that act in the same way.[35a] Abstraction of an H atom from the alkane is effected by a highly reactive oxo group coordinated to a high-valent iron center in the enzyme (Eq. 12.36). A d^4 oxo group like this is expected to be highly reactive for the reasons discussed in Section 11.6. The oxo group is then regenerated from molecular oxygen. This is believed to happen by reduction of an η^1-O_2 complex so that one O of the O_2 is reduced to H_2O, and the other O stays on the metal as the Fe=O group. No organometallic intermediates have been proposed in this process, however. The normal selectivity of the reaction toward different C—H bonds is 3° > 2° > 1° as a result of the higher stability of the more substituted radical (which is equivalent to saying that the 3° C—H bond is weaker). The *Gif systems*,[35b] which use iron dipyridyl complexes and an oxidant such as H_2O_2 in pyridine, also hydroxylate alkanes, but with a very unusual selectivity pattern (2° > 3° > 1° C—H). A new mechanism is probably at work, but its nature is unclear.

$$L_nFe{=}O + R{-}H \longrightarrow L_nFe{-}OH + R\bullet \longrightarrow L_nFe + ROH \quad (12.36)$$

The major characteristic of the catalysts described above is that they deactivate—a complex able to attack C—H bonds is also able to attack itself or the solvent. In the Mercat process,[30] the catalyst, a Hg atom, is completely stable to the reaction conditions. There is no solvent because this is a rare example of organometallic chemistry in the gas phase. The system easily

produces multigram amounts of a wide variety of products. The organic substrate is refluxed with a drop of mercury under UV irradiation at 254 nm, a wavelength that converts mercury into an excited triplet state (Hg*).[36] Hg* causes the weakest C—H bond of the substrate RH to be homolyzed, and the resulting R• radicals can dimerize[30a] (Eq. 12.37) to R_2 or be functionalized, for example, with SO_2 to give RSO_3H (Eq. 12.38) or with O_2 to give ROOH.[30c,d] Because the reaction works only in the vapor, not in liquid alkane, the dimer or functionalized product condenses and is protected from further reaction by *vapor-pressure selectivity*.[30a] Other substrates than alkanes can be dimerized, such as alcohols, ethers, and amines. The selectivity for attack of various C—H bonds in alkanes is 3° > 2° > 1°, and in other substrates attack occurs α to the heteroatom. Slightly modified conditions[30b] (Eq. 12.39) are needed for carboxylic acids, esters, alkenes, nitriles, amides, and certain amines. This is because Hg* easily forms an inactive *exciplexes* (excited state complexes) with these substrates. For C—H homolysis to occur, the Hg* probably has to bind to the C—H bond of the substrate in a way resembling **12.7**; Hg* probably binds unproductively to functionalized substrates via lone pairs or as a π-complex with the double bonds. In the presence of H_2, this problem is avoided because Hg^*/H_2 collisions produce H atoms that do not form exciplexes but abstract H atoms from the substrate. Alkenes are special in that H adds to $RCH{=}CH_2$ to give $RCH{\bullet}CH_3$, which then dimerizes. Although the compounds formed are apparently rather simple, they are often very difficult to obtain in other ways; an example is the useful ligand $H_2NCMe_2CMe_2NH_2$ formed by Eq. 12.39 (X = NH_2, OH, COOH).

$$RH \xrightarrow{Hg,\ h\nu} R_2 + H_2 \qquad (12.37)$$

(RH = Cy—H, H—CH_2OH; Cy = cyclohexyl)

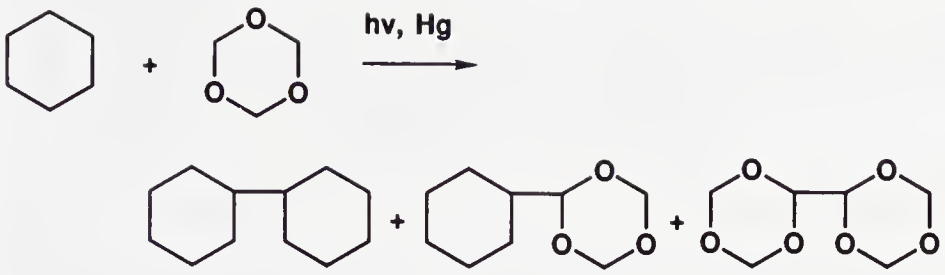
$$CyH \xrightarrow{Hg,\ h\nu,\ SO_2} CySO_2H \xrightarrow{[O]} CySO_3H \qquad (12.38)$$

$$Me_2CHX \xrightarrow{Hg,\ h\nu,\ H_2} XCMe_2CMe_2X + H_2 \qquad (12.39)$$

Even methane can be converted to $CH_2{=}NH$ by Hg* in the presence of NH_3; here the Hg* homolyzes the NH_3, and the resulting $\bullet NH_2$ abstracts an H from CH_4, a step that is favorable because the H—NH_2 bond strength (107 kcal/mol) exceeds the H—CH_3 bond strength (105 kcal/mol). In the final step, $MeNH_2$ is dehydrogenated to $CH_2{=}NH$.[30d]

$$CH_4 + NH_3 \xrightarrow{Hg^*} CH_2{=}NH \qquad (12.40)$$

If any two classes of substrate are mixed, cross dimerization can be seen—the products can often be readily separated by their polarity differences.



(12.41)

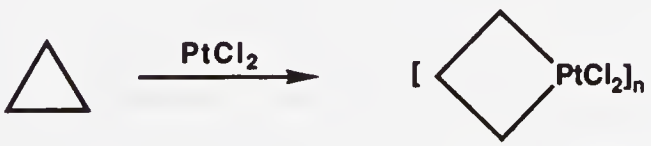
The cross product formed from the formaldehyde trimer can easily be hydrolyzed to $C_6H_{11}CHO$, and so is the equivalent of a CO insertion into a C—H bond. The quantum yields are very good (0.25–0.8). Some of these reactions are even under study for possible commercial application. The light is required to drive the reactions thermodynamically, and they have not yet been made catalytic in photons.

Metal Atom Chemistry Oxidative addition reactions of bare metal atoms with alkanes have been observed[37] on irradiation in an alkane matrix at low temperatures for a number of transition metal atoms and in metal vapor synthesis,[38] in which metal atoms and alkanes are cocondensed at low temperatures. A number of naked metal ions in the gas phase undergo reactions with alkanes in a mass spectrometer chamber;[39] the structures of the products are somewhat conjectural because they are deduced from their mass alone.

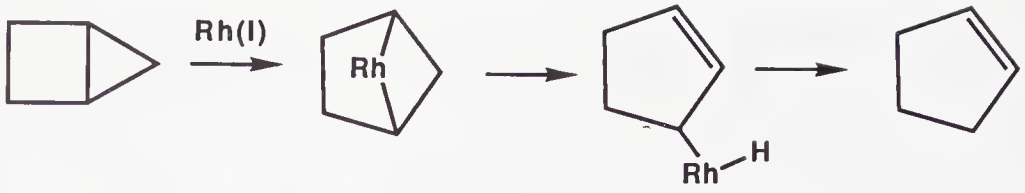
$$Fe + CH_4 \longrightarrow CH_3FeH \qquad (12.42)^{37}$$

$$Fe^+ + C_6H_{12} \longrightarrow [C_6H_{10}Fe]^+ + H_2 \qquad (12.43)^{38}$$

C—C Oxidative Addition Breaking the C—C bonds of alkanes is worse both thermodynamically and kinetically than breaking the C—H bond, because we make two relatively weak M—C bonds (together worth ~70 kcal/mol), for the loss of a C—C bond (~85 kcal/mol) and a C—C bond is less sterically accessible than a C—H bond. Direct alkane C—C bond breaking has been observed only in very strained alkanes in which the relief of strain provides a substantial extra driving force. The first example dates from 1955, when Tipper[40] observed the reaction between cyclopropane and $PtCl_2$ (Eq. 12.44); the correct metalacyclobutane structure of the product was suggested by Chatt[41] in 1961. The catalytic rearrangement of certain strained hydrocarbons is believed to go by initial C—C bond breaking (Eq. 12.45).[42]

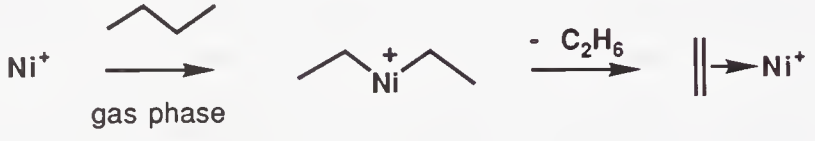


(12.44)

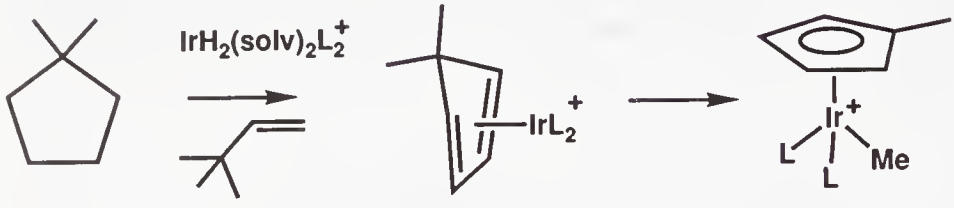


(12.45)

The product in Eq. 12.46 seems to be a C—C bond-breaking product of 1,1-dimethylcyclopentane, but isolation of the intermediate shows that the reaction goes via prior C—H bond breaking.[43] The system is set up so that the unfavorable C—C cleavage is accompanied by the formation of a thermodynamically very stable Cp—M bond. On the other hand, work in the gas phase with naked metal ions has shown that direct C—C bond breaking can occur easily (Eq. 12.47). In this case, the corresponding M—C bond strengths are much higher than in the case of a metal complex and the reagent, Ni^+, is extremely unhindered.[44]



(12.46)



(12.47)

In spite of these advances in alkane chemistry, the development of a series of robust and selective catalysts for different alkane conversion reactions remains a continuing challenge in organometallic chemistry today. Another related and very challenging problem is C—F activation in perfluorocarbons.

REFERENCES

1. P. C. Ford, *Acct. Chem. Res.*, **14,** 31, 1981; *Adv. Organometal. Chem.*, **28,** 139, 1988.
2. (a) J. W. Reppe, *Annalen*, **582,** 121, 1953; (b) T. Yoshida, Y. Ueda, and S. Otsuka, *J. Am. Chem. Soc.*, **100,** 3941, 1978.
3. R. Pettit et al., *J. Am. Chem. Soc.*, **99,** 8323, 1977.
4. (a) D. Forster, *Adv. Organometal. Chem.*, **17,** 255, 1979; (b) J. R. Zoeller et al., *Adv. Chem. Ser.*, **230,** 377, 1992; (c) M. L. Fernandez et al., *J. Organometal. Chem.*, **438,** 337, 1992.

5. B. B. Wayland et al., *J. Am.Chem. Soc.,* **106,** 3659, 1986.
6. J. E. Bercaw et al., *J. Am. Chem. Soc.,* **96,** 5087, 1974; **98,** 6733, 1976.
7. T. J. Marks et al., *J. Am. Chem. Soc.,* **100,** 3939, 7112, 1978.
8. P. T. Wolczanski, R. S. Threlkel, and J. E. Bercaw, *J. Am. Chem. Soc.,* **101,** 218, 1979.
9. P. M. Treichel and R. L. Shubkin, *Inorg. Chem.,* **6,** 1328, 1967.
10. C. P. Casey, *Pure Appl. Chem.,* **52,** 625, 1980; J. A. Gladysz et al., *J. Am. Chem. Soc.,* **101,** 1589, 1979.
11. (a) W. R. Roper et al., *J. Am. Chem. Soc.,* **101,** 503, 1979; (b) P. T. Wolczanski et al., *J. Am. Chem. Soc.,* **111,** 9056, 1989; (c) R. Pruett, U.S. Patent 3,857,957, 1976; (d) B. B. Wayland et al., *Adv. Chem. Ser.,* **230,** 249, 1992.
12. M. Aresta, C. F. Nobile, V. G. Albano, E. Forni, and M. Manassero, *Chem. Commun.,* 636, 1975.
13. T. Herskovitz, *J. Am. Chem. Soc.,* **99,** 2391, 1977.
14. (a) G. Fachinetti, C. Floriani, and P. F. Zanazzi, *J. Am. Chem. Soc.,* **100,** 7405, 1978; (b) D. H. Gibson et al., *J. Am. Chem. Soc.,* **114,** 9716, 1992.
15. T. Herskovitz and L. Guggenberger, *J. Am. Chem. Soc.,* **98,** 1615, 1976.
16. A. R. Cutler et al., *Chem. Rev.,* **88,** 1363, 1988.
17. D. Darensbourg et al., *Organometallics,* **10,** 3407, 1991.
18. A. D. English and T. Herskovitz, *J. Am. Chem. Soc.,* **99,** 1648, 1977.
19. S. Koyima and A. Yamamoto, *J. Organometal. Chem.,* **46,** C58, 1972.
20. (a) B. P. Sullivan and T. J. Meyer, *Organometallics,* **5,** 1500, 1986; (b) W. Leitner et al., *Angew. Chem. Int. Ed.,* **32,** 739, 1993; (c) E. Graf and W. Leitner, *Chem. Commun.,* 623, 1992.
21. (a) R. H. Crabtree, *Chem. Rev.,* **85,** 245, 1985; (b) J. Halpern, *Inorg. Chem. Acta,* **100,** 41, 1985.
22. N. F. Goldschleger, M. B. Tyabin, A. E. Shilov, and A. A. Shteinman, *Zh. Fiz. Khim.,* **43,** 2174, 1969.
23. (a) A. E. Shilov, *The Activation of Saturated Hydrocarbons by Transition Metal Complexes,* D. Riedel, Dordrecht, 1984; (b) J. A. Labinger, A. M. Herring, and J. E. Bercaw, *Adv. Chem. Ser.,* **230,** 221, 1992; and *J. Am. Chem. Soc.,* **115,** 3004, 1993; (c) R. Periana, *Science,* **259,** 340, 1993.
24. R. H. Crabtree, J. M. Mihelcic, and J. M. Quirk, *J. Am. Chem. Soc.,* **101,** 7738, 1979; ibid., **104,** 107, 1982.
25. (a) D. Baudry, M. Ephritikine, and H. Felkin, *Chem. Commun.,* 1243, 1980; 788, 1983; (b) M. Tanaka and T. Sakakura, *Adv. Chem. Ser.,* **230,** 181, 1992; Y. Saito et al., *Chem. Commun.,* 757, 1990; *Bull. Chem. Soc. Jpn.,* **64,** 938, 1991.
26. (a) M. W. Burk and R. H. Crabtree, *J. Am. Chem. Soc.,* **109,** 8025, 1987; (b) T. Aoki and R. H. Crabtree, *Organometallics* **12,** 294, 1993; (c) A. Goldman, *Coord. Chem. Rev.,* **97,** 179, 1990; *J. Am. Chem. Soc.,* **114,** 9492, 1992.
27. (a) A. H. Janowicz and R. G. Bergman, *J. Am. Chem. Soc.,* **104,** 352, 1982; (b) R. G. Bergman, *Adv. Chem. Ser.,* **230,** 211, 1992; (c) R. G. Bergman et al., *J. Am. Chem. Soc.,* **106,** 1121, 7272, 1984; (d) E. P. Wasserman, C. B. Moore, and R. G. Bergman, *Science,* **255,** 315, 1992.
28. (a) J. K. Hoyano and W. A. G. Graham, *J. Am. Chem. Soc.,* **104,** 3723, 1982; (b) A. J. Rest, W. A. G. Graham, et al., *Chem. Commun.,* 624, 1984.

29. W. D. Jones and F. J. Feher, *J. Am. Chem. Soc.*, **104,** 4240, 1982; (b) **108,** 4814, 1986.
30. (a) S. Brown, R. H. Crabtree, et al., *J. Am. Chem. Soc.*, **111,** 2935, 2946, 1989; (b) **113,** 2233, 1991; (c) *J. Chem. Educ.*, **65,** 290, 1988; (d) R. H. Crabtree et al., *Adv. Chem. Ser.*, **230,** 197, 1992; (e) D. Michos, C. Sassano, and R. H. Crabtree, *Angew Chem Int. Ed.*, **32,** 1491, 1993.
31. (a) M. L. H. Green, *Pure Appl. Chem.*, **50,** 27, 1978; (b) M. Brookhart and M. L. H. Green, *J. Organometal. Chem.*, **250,** 395, 1982.
32. (a) P. T. Wolczanski et al., *J. Am. Chem. Soc.*, **110,** 8731, 1988; (b) T. R. Cundari, *J. Am. Chem. Soc.*, **114,** 10557, 1992.
33. P. L. Watson, *J. Am. Chem. Soc.*, **105,** 6491, 1983.
34. C. M. Fendrick and T. J. Marks, *J. Am. Chem. Soc.*, **106,** 2214, 1984.
35. (a) J. T. Groves, T. E. Nemo, and R. S. Myers, *J. Am. Chem. Soc.*, **101,** 3413, 1979; (b) D. H. R. Barton and D. Doller, *Acct. Chem. Res.*, **25,** 504, 1992.
36. R. J. Cvetanovic, *Prog. React. Kinetics,* **2,** 39, 1964.
37. W. E. Billups, J. L. Margrave, et al., *J. Am. Chem. Soc.*, **102,** 7393, 1980; G. A. Ozin et al., ibid., **104,** 7351, 1982; K. Eller and H. Schwartz, *Chem. Rev.*, **91,** 1121, 1991.
38. M. L. H. Green et al., *Chem. Commun.*, 240, 1467, 1984; 355, 356, 1985.
39. D. P. Ridge et al., *J. Am. Chem. Soc.*, **101,** 1332, 1979, **102,** 7129, 1980; J. L. Beauchamp et al., ibid., **102,** 1736, 1980; **103,** 6628, 1981.
40. C. F. H. Tipper, *J. Chem. Soc.*, 2043, 1955.
41. J. Chatt et al., *J. Chem. Soc.*, 738, 1961.
42. J. Halpern et al., *J. Chem. Soc.* (*D*), 1082, 1971; K. W. Wiberg et al., *Tetrahedron Lett.*, 2727, 1973.
43. R. H. Crabtree, R. P. Dion, D. V. McGrath, and E. M. Holt, *J. Am. Chem. Soc.*, **108,** 7222, 1986.
44. (a) J. L. Beauchamp et al., *J. Am. Chem. Soc.*, **104,** 6293, 1982; (b) P. E. M. Siegbahn and M. R. A. Blomberg, *J. Am. Chem. Soc.*, **114,** 10548, 1992.
45. K. G. Moloy and R. W. Wegman, *Adv. Chem. Ser.*, **230,** 323, 1992.

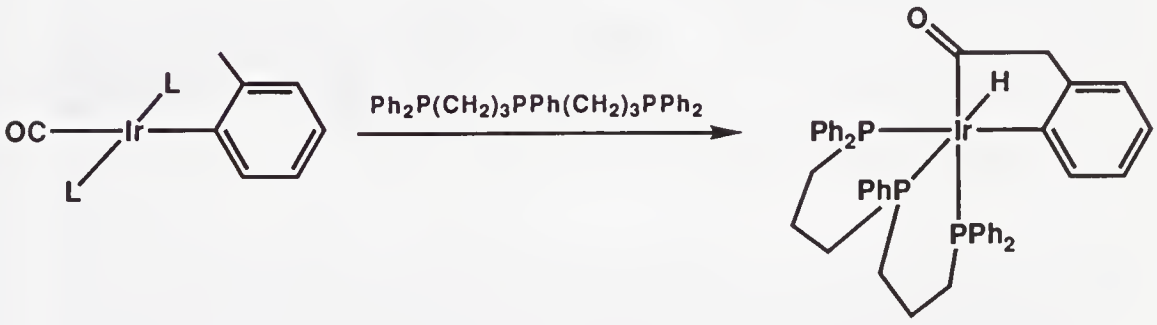
PROBLEMS

1. Given the mechanisms of the water–gas shift reaction starting from CO and H_2 shown in Fig. 12.2, what can you deduce about the mechanism of the reaction in the reverse sense, starting from CO_2 and H_2?
2. Why do you think Roper's formaldehyde complex, shown in Eq. 12.14, is bound in an η^2 form rather than via oxygen in an η^1 form, as is acetone in $[IrH_2(\eta^1\text{-}Me_2C\boldsymbol{O})_2(PPh_3)_2]^+$? Of the several possible reasons for the difference, be sure to state which you consider most likely.
3. The reaction shown below appears to be a cyclometallation, but is there anything unusual about it that might excite suspicion that it does not go by a conventional oxidative addition mechanism? Suggest an alternative. (R is a bulky carboranyl group.)

(12.48)

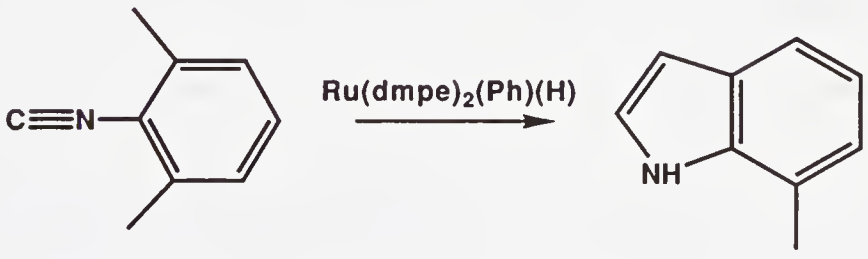
4. Suppose that you were about to study the following complexes to see if any of them bind CO_2. Describe what type(s) of product you would anticipate in each case: $Re(PR_3)_5^-$, (η^5-Indenyl)$Ir(PR_3)_2$, and $CpMo(CO)_3H$. Given that you had samples of all three, which would you try first as the most likely to bind CO_2 (R = Me)?

5. Suggest a plausible mechanism for



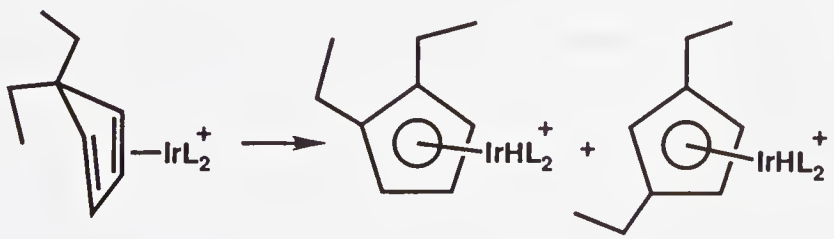
(12.49)

6. Suggest a plausible mechanism for



(12.50)

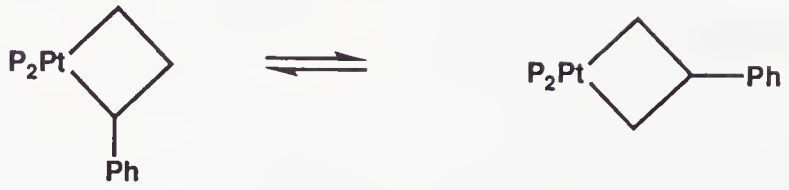
7. Suggest a plausible mechanism for



(12.51)

50:50 mixture

8. Suggest a plausible mechanism for Eq. 12.52 and some ways of testing your suggestion.

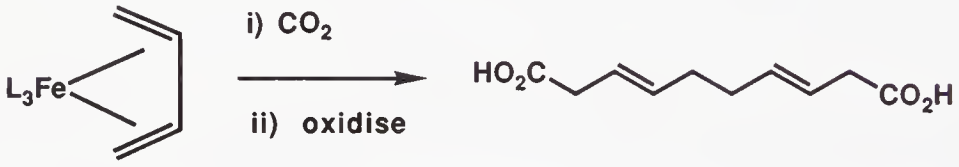


(12.52)

9. Suggest a plausible mechanism for Eq. 12.53 and some ways of testing your suggestion.

$$(\text{cod})\text{IrL(thf)}^{+} + \text{HCOONa} \longrightarrow (\text{cod})\text{IrLH} \qquad (12.53)$$

10. Account for the product formed in Eq. 12.54.



(12.54)

11. What is the energy of a 254-nm photon? Is a single 254-nm photon sufficiently energetic to drive reaction 12.40, for which $\Delta G = +20$ kcal/mol? [C = 3×10^8 m/s; h = 1.58×10^{-34} cal.s]

12. Hydrosilation (shown below) is mediated by a variety of catalysts, both homogeneous and heterogeneous. Write a plausible mechanism for a generalized homogeneous catalyst L_nM.

$$\text{RCH}{\equiv}\text{CH} + \text{R}_3\text{Si—H} \longrightarrow \text{RCH}{=}\text{CH—SiR}_3 + \text{RC(SiR}_3){=}\text{CH}_2. \qquad (12.55)$$

Account for the formation of the following by-products, and why there is always equal amounts of each formed: $\text{RC}{\equiv}\text{CSiR}_3$ and $\text{RCH}{=}\text{CH}_2$.

13. If methanol/HI is carbonylated in a system resembling the Monsanto acetic acid process, but with [(dpe)RhI(CO)] as catalyst and H_2 present, ethanol is formed from methanol. Provide two reasonable mechanisms and suggest an experimental test to distinguish between them (see ref. 45).

CHAPTER 13

CLUSTERS AND THE METAL—METAL BOND

Up to now, we have looked at mononuclear complexes. In this chapter we see what happens when several metal atoms are bound together in a *cluster.* Rather than form chains like carbon, they tend to agglomerate so as to form the maximum number of M—M bonds—the structures resemble the close-packed structures of the elemental metals themselves.[1] The reason is that clusters form from unsaturated L_nM fragments. The triangular cluster $Os_3(CO)_{12}$ can be regarded as the stable trimer of the unsaturated fragment $Os(CO)_4$. $Rh(CO)_3$ is even more electron-deficient and forms $Rh_4(CO)_{12}$, with a tetrahedron of metal atoms. The condensed structures of clusters allow the few available electrons to be maximally shared over the cluster as a whole. We then move on to study the new bonding and reactivity patterns possible for organic fragments bound to a cluster.

Organometallic clusters are almost always rich in carbonyl ligands, probably because $M(CO)_n$ fragments are sufficiently unhindered to approach to within M—M bonding distance of each other. It is surprising that stable *homoleptic** clusters of other small high-field ligands, such as hydride, silyl, methyl, or methylene, are not yet known.

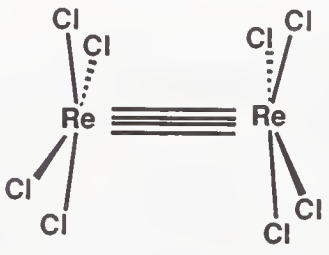
An early stimulus to cluster chemistry was the cluster–surface analogy[2] which proposed that cluster chemistry would resemble the surface chemistry of metals, because both surfaces and clusters consist of arrays of metal atoms. Supported metals such as Pd/C are very active catalysts. Clusters have so far not shown the high catalytic activity of either metal surfaces or mononuclear homogeneous catalysts, probably because clusters are "poisoned" by the pres-

*A homoleptic compound has only one type of ligand.

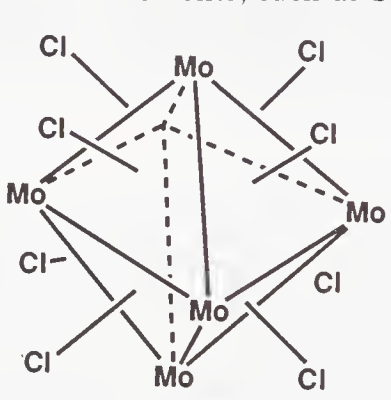
ence of a monolayer of CO. Organic compounds do bind to clusters differently than to single metals, however, and these new structures[3] provide important clues for surface chemistry, where direct structural data for surface-bound species are still very hard to obtain.

A second point of interest in cluster chemistry is the gradual evolution of cluster structure, magnetic behavior, and ionization potential with increasing cluster size. In principle, these properties should approach that of the bulk metal, but some may do so faster than others.

Apart from the low-valent carbonyl clusters, there are also a number of middle- and high-oxidation-state clusters, such as $(RO)_3Mo{\equiv}Mo(OR)_3$ and $Cl_4Re{\equiv}ReCl_4^{2-}$ (**13.1**), which contain metal–metal multiple bonds.[4,5] The halide cluster $Mo_6Cl_8^{4-}$ (**13.2**) contains an octahedron of molybdenum atoms with eight chloride ions bridging each of the faces. There are also a number of naked metal clusters[5] of the posttransition elements, such as Sn_9^{2-}.



13.1



13.2

The word "cluster" was once reserved for complexes containing at least three metals, bound by metal–metal bonds, but is now normally used for any aggregate, including di- and polynuclear complexes bound together only by bridging ligands. In this chapter, we emphasize M—M bonded species.

13.1 STRUCTURES

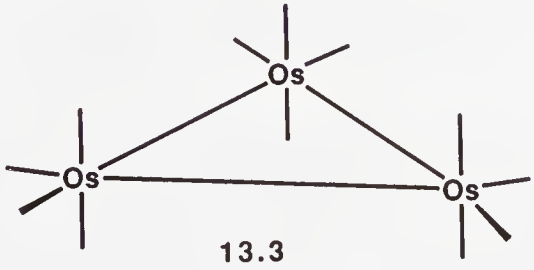
Cluster chemistry is the area of organometallic chemistry in which X-ray crystallography has played the largest role, and perhaps for this reason, structural questions have tended to be given most attention. Once a given structure has been determined, it is sometimes possible to use spectroscopic methods to deduce the structures of closely related species. In particular, IR studies are often useful in showing whether the CO ligands have been affected during a reaction, and ^1H NMR studies are often used to look at the organic ligands.

M—M single bond lengths are often comparable to those found in the metal, but the attractive interaction between the metals is often increased by the presence of bridging ligands such as CO. Not all M—M bonds are bridged; $[(CO)_5Mn—Mn(CO)_5]$ is an example of an unassisted M—M bond holding a cluster together, but this bond[6] is weak (28 ± 4 kcal/mol) and unusually

long at 2.93 Å versus 2.46 Å in $[(CO)_3Fe(\mu\text{-}CO)_3Fe(CO)_3]$. With a bond strength of only 17 kcal/mol, the unsupported M—M bond of $[CpCr(CO)_3]_2$ undergoes spontaneous breaking and reforming even at room temperature.

EAN Rule How can we rationalize the structures adopted by clusters? Only the simpler ones can be described in terms of the 18e rule. For example, each 16e $Os(CO)_4$ group in $Os_3(CO)_{12}$, **13.3**, can be considered as achieving 18e by forming two M—M bonds, one with each of the other metal atoms. Since each metal has the same electronegativity, the bond is considered as contributing nothing to the oxidation state. The complex is therefore an example of 18e, Os(0). It is usually more convenient in cluster chemistry to count the electrons for the cluster as a whole, rather than attempt to assign electrons, especially electrons from bridging ligands, to one metal rather than another. On this cluster electron counting convention, $Os_3(CO)_{12}$ is a $3 \times 8e$ (Os is in Group 8) $+ 12 \times 2e = 48e$ cluster. This is the appropriate number of electrons for a triangular cluster. We have $3 \times 9 = 27$ orbitals, which you might think ought to require 54e, but this assumes that we count each metal individually, and then sum the totals from each metal. By doing this, we would count the M—M bonding electrons twice over, because in counting Os^1, we count 1e "originating" (from a bookkeeping point of view) from Os^2. In counting Os^2, we would count these M—M bonding electrons again. Six M—M bonding electrons are involved so we expect $54 - 6 = 48e$ to be the right count for a system with three M—M bonds.

Since we always deal with electron counts that are >18, it is more convenient in cluster chemistry to use the alternative name of the 18e rule, the effective atomic number, or EAN rule. The closed-shell configuration resem-



13.3

bles that of the noble gases [Rn (radon) in the case of Os], and so the Os in the complex is said to have the same effective atomic number as Rn. is *coordinatively saturated*. This term is normally used for 18e mononuclear species.

The EAN electron count for a cluster of nuclearity x and having y metal–metal bonds is defined by

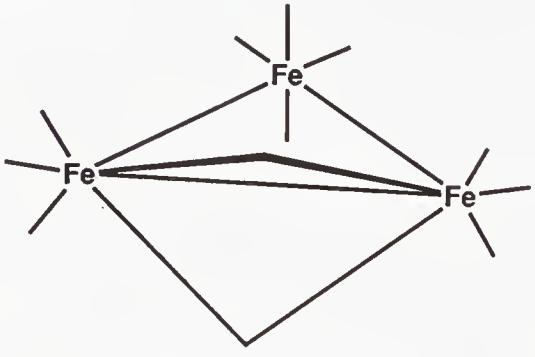
$$\text{EAN count} = 18x - 2y \tag{13.1}$$

To see whether any given cluster fits this pattern, we determine the real electron count as shown in Fig. 13.1. One advantage of this procedure is that the CO bonding mode is unimportant: whether a CO is terminal or bridging,

$Re_4H_4(CO)_{12}$	4 x Re	= 28	$Fe_6C(CO)_{16}^{2-}$	6 x Fe	= 48
	4 x H	= 4		1 x C	= 4
	12 x CO	= 24		16 x CO	= 32
		56		2 x e^-	= 2
					86
$Os_3H_2(CO)_{10}$	3 x Os	= 24	$Fe_3(\mu\text{-}CO)_2(CO)_{10}$	3 x Fe	= 24
	2 x H	= 2		2 x μ-CO	= 4
	10 x CO	= 20		10 x CO	= 20
		46			48

FIGURE 13.1 Electron counting in clusters. For the structure of $Fe_6C(CO)_{16}^{2-}$, see Fig. 13.7.

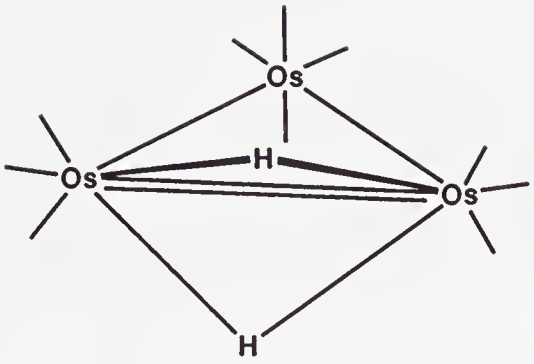
it still contributes 2e to the cluster as a whole. For this reason we cannot predict by counting electrons whether a given molecule will have any bridging COs or not. Of the isoelectronic Group 8 $M_3(CO)_{12}$ clusters, only the iron analog, **13.4**, has bridging COs; the others, like **13.3**, have only terminal carbonyls. Note that in the diagrams in this chapter a single unlabeled line drawn from the metal denotes a terminal carbonyl substituent and a bent line connecting two metals denotes a bridging CO; only non-CO ligands are shown explicitly.



13.4

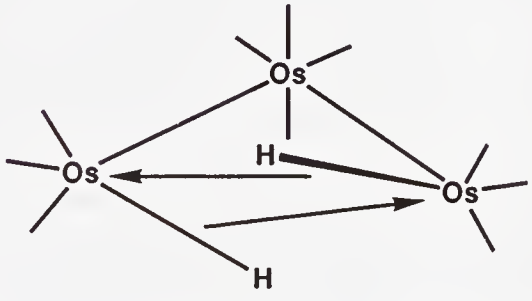
$Os_3H_2(CO)_{10}$ behaves as an unsaturated cluster in that it is much more reactive than $Os_3(CO)_{12}$. One way of looking at this is to say that, as a 46e cluster, it lacks 2e from the EAN count of 48e. It is often viewed as containing an Os=Os "double bond" because the EAN count for a system with four M—M bonds in a three-atom cluster is 46e. We would then regard an Os=Os double bond, like a C=C double bond, as being unsaturated. Structure **13.5** shows that there are two Os—H—Os bridges.

In our discussion of M—H—M bonding (Section 3.4), we saw that the presence of such a bridge implies M—M bonding. The representation shown in **13.5** is the conventional one, but it should not be taken to mean that there are separate M—M and M—H—M bonds. In fact, each M—H—M unit



13.5

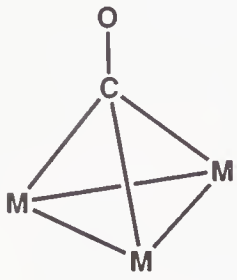
constitutes a 2e, three-center bond as shown in **13.6**. This means that the Os=Os "double bond" is really a reflection of the presence of the two hydride bridges. The bridge can open and generate a vacant site. This makes the dihydride far more reactive than $Os_3(CO)_{12}$ itself and therefore a very useful starting material in triosmium cluster chemistry.



13.6

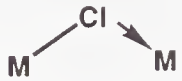
The tetranuclear Group 9 clusters $M_4(CO)_{12}$ have 60e. Reference to Eq. 13.1 shows that six M—M bonds must be present if the cluster is to conform with the EAN rule. As expected, a tetrahedral cluster framework with six M—M bonds is adopted. In summary, we can deduce whether the molecule has the EAN count if we know how many M—M bonds are present, or we assume that the molecule is an EAN one, and deduce the number of M—M bonds we expect to find.

Face (μ_3) bridging is a bonding mode unique to polynuclear complexes. If we have a face bridging CO (**13.7**), we count only the 2e of the carbon lone pair as contributing to the cluster. On the other hand, some ligands have additional lone pairs they can bring into play. A Cl ligand is 1e when terminal, **13.8**, but 3e when edge (μ_2) bridging, **13.9**, and has 5e to donate to the cluster if it is face bridging (**13.10**), as two of its lone pairs come into play (the corresponding numbers for the ionic model are 2e, 4e, and 6e, respectively, but this model is not commonly used in cluster chemistry).

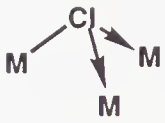


13.7

13.8

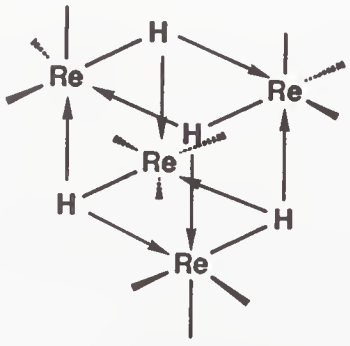


13.9

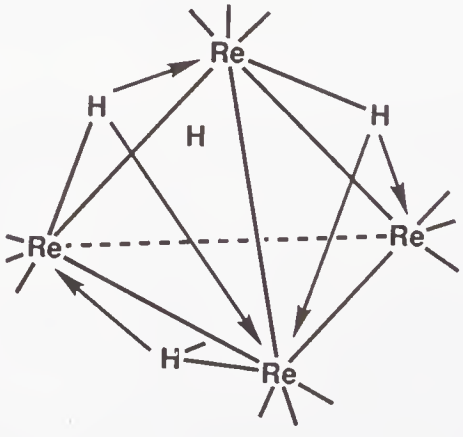


13.10

As shown in Fig. 13.1, $Re_4H_4(CO)_{12}$ (**13.11**) has 56e. This requires the presence of eight M—M bonds, rather than the six normally implied by a tetrahedral arrangement of four metals. The distortions which would be expected for a static structure of type **13.12** with two localized M=M double bonds are not found, and so the extra M—M bonds are conventionally considered to be delocalized over the metal framework, so as to make each M—M bond slightly shorter. An alternative picture comes from our discussion of the nature of the hydride bridge in Section 3.4. Each H in **13.11** is found to be face bridging (μ_3-H). We can regard the 2e of the M_1—H bond to be donated to both M_2 and M_3 as shown in **13.13**. This gives an EAN cubane-like structure (**13.11a**) for $Re_4H_4(CO)_{12}$. In this model, the delocalized M—M bonds are included in the μ_3-H bridging.[7] In this way, each μ_2-H reduces the EAN by 2e, and each μ_3-H reduces it by 4e. Note that on the conventional model the position of the hydrogen (whether terminal, μ_2-H, or μ_3-H) is irrelevant to the EAN count. The alternative picture successfully predicts the position of the hydrogen in a large number of clusters.*



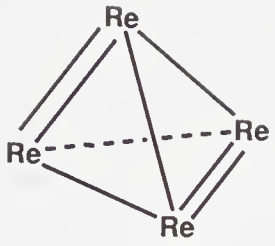
13.11a



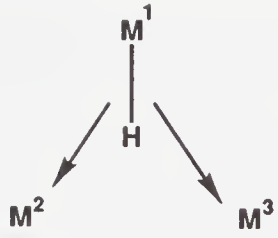
13.11b

In M_5L_n clusters, we can have a trigonal bipyramid (TBP) of metals with nine M—M bonds or a square pyramid (SP) with eight. By Eq. 13.1, the TBP is

*Students sometimes ask which model is "right"—models are only mental constructs that reflect some aspect of reality. One model may work for one compound, a second model for another. Model **13.12** is certainly more widely used.

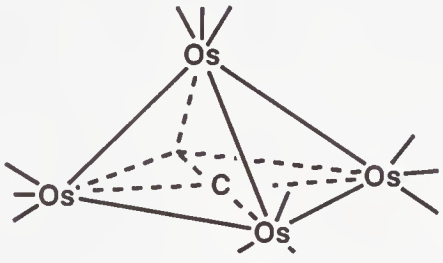


13.12



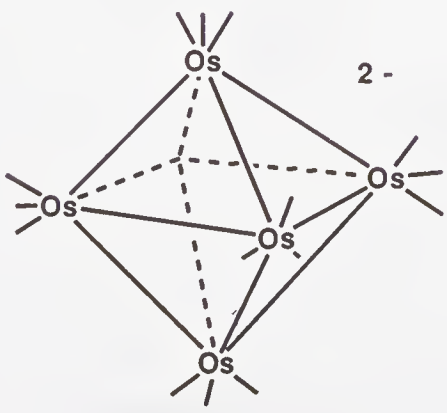
13.13

adopted for a 72e system like $Os_5(CO)_{16}$ and the SP for a 74e cluster like $M_5(CO)_{15}C$ (**13.14**). Note how all four valence electrons of the C are counted as contributing to the cluster.

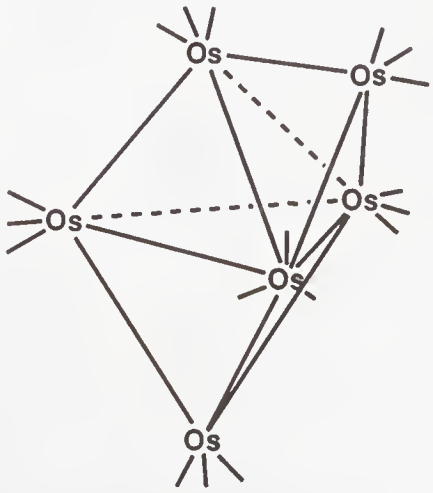


13.14

Wade's Rules When we get to six metal clusters and beyond, the EAN picture starts to fail. For example, the octahedral $Os_6(CO)_{18}^{2-}$, **13.15** is an 86e cluster. On the basis of Eq. 13.1, and assuming there are 12 M—M bonds, the EAN should be 84e. Yet the cluster shows no tendency to lose electrons or expel a ligand. $Os_6(CO)_{18}$, **13.16**, which is an authentic 84e cluster, does not adopt the octahedral framework at all but does have 12 M—M bonds.



13.15



13.16

The cluster counting model that is often applied to these non-EAN clusters is the polyhedral skeletal electron pair theory, sometimes known as *Wade's rules.*[8] On this picture, an analogy is drawn between the metal cluster and the corresponding boron hydride cluster. Elements like C and H, which have the same number of electrons and orbitals, can form closed-shell molecules, such as CH_4. Elements to the right of carbon, such as N, have more electrons than orbitals and so give molecules with lone pairs, like NH_3. Like transition metals, boron has fewer electrons than orbitals, and so it forms compounds in which the BH_x units cluster together to try and share out the few electrons that are available by using 2e, three-center bonds, such as B_2H_6. The higher borane hydride anions $B_nH_n^{2-}$ (n = 6–12) form polyhedral structures, some of which are shown in Fig. 13.2; these form the basis for the polyhedral structures adopted by all molecules covered by Wade's rule ideas. The shape of the cluster is decided purely by the number of cluster electrons (called skeletal electrons), not by any other factor.

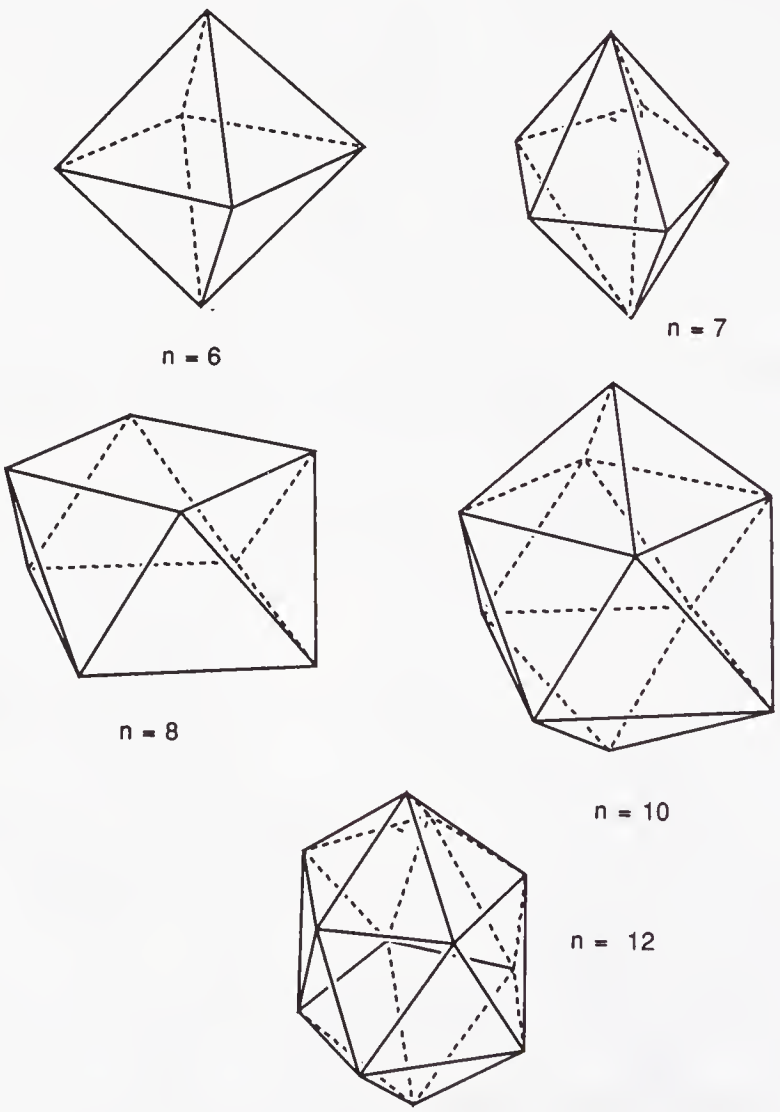


FIGURE 13.2 Some polyhedral structures adopted by boranes.

The number of skeletal electrons appropriate to the borane clusters, $B_nH_n^{2-}$, can be deduced as follows. First, we assume that each B—H bond is a normal 2e covalency, requiring 1e from H and 1e from B. As boron starts with 3e it has 2e left to contribute to the cluster, and this means that $B_nH_n^{2-}$ has $2n + 2$ cluster electrons, $2n$ electrons of which come from the n BH groups, and the remaining two electrons come from the 2- net charge. In order to see where these electrons go, we consider that each BH unit has an *sp* orbital pointing directly toward the center of the cluster, and a p_x and a p_y orbital, pointing along the surface (Fig. 13.3). The m.o. analysis of this arrangement suggests that the *sp* orbitals contribute to one low-lying orbital, when they are all taken with the same sign (in phase). Other combinations are high-lying and empty. The *p* orbitals, $2n$ in number, combine to give n filled bonding m.o.'s and n empty antibonding m.o.'s. This picture provides $n + 1$ orbitals, which offer an appropriate home for $2n + 2$ skeletal electrons.

Since the cluster shape depends only on the number of skeletal electrons, we should be able to remove a vertex group, say, BH, from the cluster without changing the cluster structure, as long as we leave behind the two skeletal

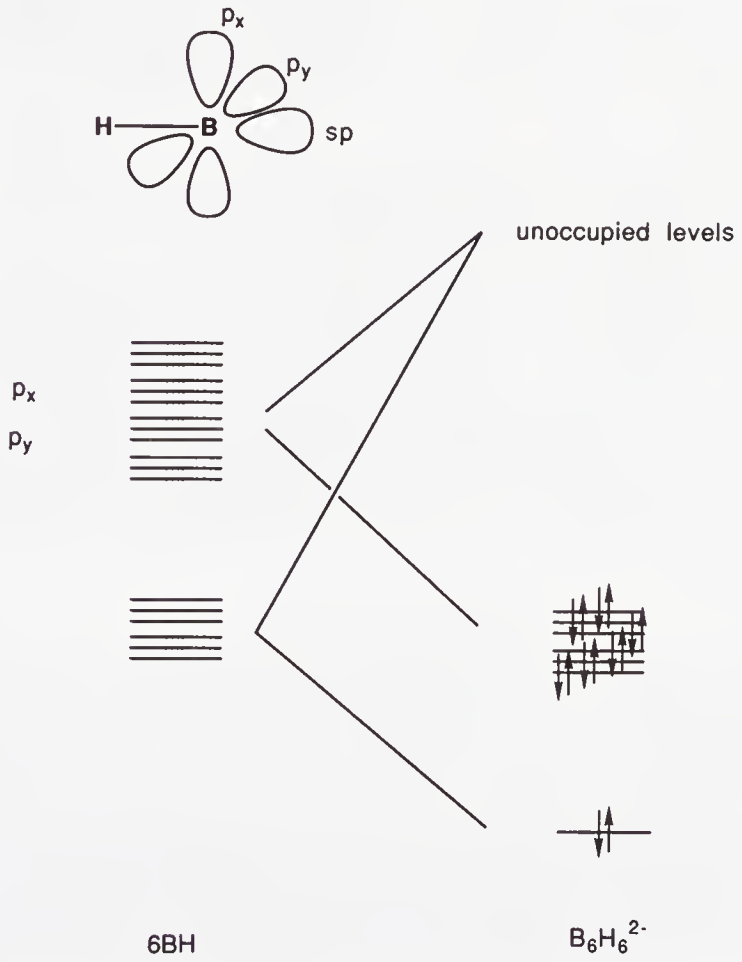
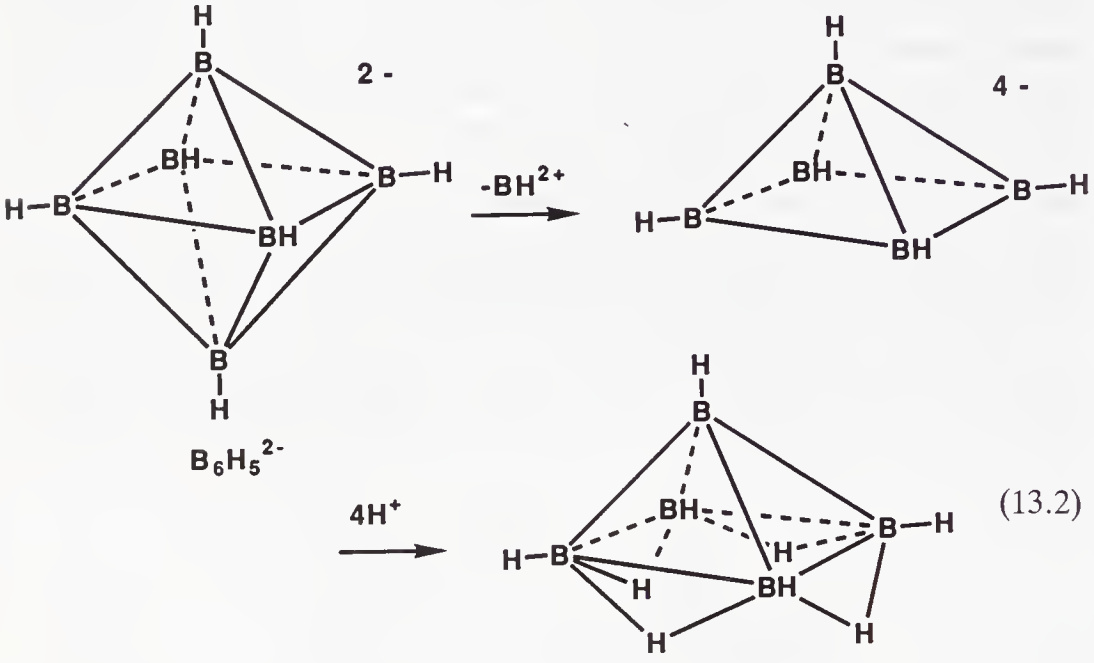


FIGURE 13.3 The Wade analysis of a close borane cluster.

electrons that the vertex BH group was contributing. This means we must remove a BH^{2+}, not a BH unit, in order to leave one vertex of the cluster empty. If we remove a BH^{2+} unit in the case of $B_6H_6^{2-}$, we get the hypothetical $B_5H_5^{4-}$ fragment.



(13.2)

This will have exactly the same polyhedral structure, because the electron count has not changed, but one vertex is now empty. To make the known neutral borane, B_5H_9, we add four protons, which, as zero-electron species, do not alter the electron count. Note that the protons bridge the faces of the polyhedron which include the missing vertex; they could be said to sense the electron density left behind in the cluster faces when we removed the BH^{2+} group. As a species with one empty vertex, B_5H_9 is given the descriptor *nido*. Molecules which have every vertex occupied are designated *closo*. In general, a species $B_xH_y^{z-}$ will have $\frac{1}{2}(x + y + z)$ skeletal electron pairs. The appropriate number of vertices, v, is

$$v = \tfrac{1}{2}(x + y + z) - 1 \tag{13.3}$$

The number of BH groups we have to find vertices for is x. If the number of vertices v called for by Wade's rules also happens to equal x, then each vertex can be occupied and we will have a closo structure. On the other hand, if x happens to be one less than this, one vertex will be empty and a nido structure will result. If x is two or three units less than v, then the structures are called *arachno* and *hypho* with two or three empty vertices, respectively. Normally adjacent (rather than nonadjacent) vertices are left empty.

Wade's rules can also apply to other main group elements: the 14 skeletal electron octahedral Sn_6^{2-} has been isolated as $[SnCr(CO)_5]_6^{2-}$ in which all the

exo-lone pairs on Sn are bound to the 16 valence electron fragment, $\{Cr(CO)_5\}$.[9a]

Surprisingly, the same model also describes many transition metal clusters, including many of the non-EAN ones. In order to see how we can do this we first have to find a way of replacing the BH groups by transition metal equivalents which donate the same number of skeletal electrons. Since transition metals have nine orbitals but only three are required for cluster bonding on the Wade picture, we first have to fill the six orbitals not required for cluster bonding and see how many electrons remain for the cluster bonding orbitals. If we take the $Os(CO)_3$ fragment, we have to assign the nine orbitals as follows: (1) three orbitals are filled with the three CO lone pairs; (2) three more orbitals are filled with six electrons out of the eight electrons appropriate for a Group 8 element like Os—these electrons back-bond to the COs; and (3) two metal electrons are now left for the remaining three orbitals, which are the ones that bond to the cluster (Fig. 13.4). This implies that $Os(CO)_3$ contributes the same number of skeletal electrons (two) as does a BH group. We can therefore replace all the BHs in $B_6H_6^{2-}$ with $Os(CO)_3$ groups without altering the structure. We end up with $Os_6(CO)_{18}^{2-}$, exactly the cluster we could not explain on the EAN model.

There also exist many clusters, called *metalaboranes*,[9b] in which some of the vertices of the polyhedron have a boron atom and others a transition metal [e.g., *closo*-$(CpCO)_2(BH)_4(\mu_3\text{-}H)_2$, **13.17**].

For the fragment MX_aL_b, the Wade analysis leads us to predict that the cluster electron contribution, F, of that fragment will be

$$F = N + a + 2b - 12 \tag{13.4}$$

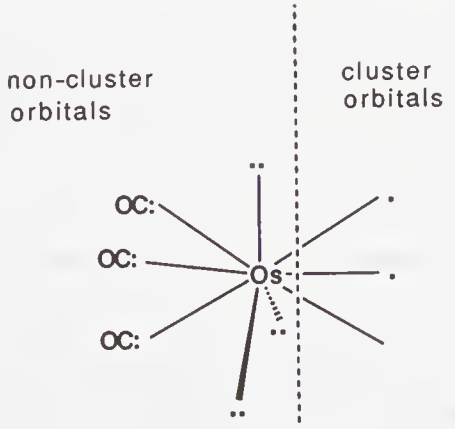
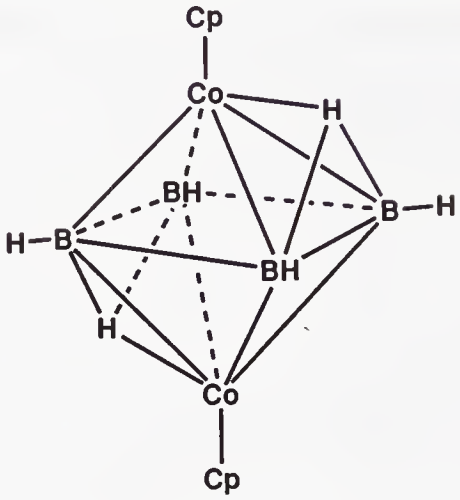


FIGURE 13.4 Applying Wade's rules to a transition metal fragment. The three CO groups of the $Os(CO)_3$ fragment supply 6e, and these electrons occupy three of the metal's nine orbitals. Six of the eight metal electrons occupy the d_π orbitals and back-bond to the CO groups. Two metal electrons are left to fill the three cluster bonding orbitals shown to the right of the dotted line.



13.17

(where N = Group number of metal). To find the total number, T, of cluster electrons, we then sum the contribution from all the fragments in the cluster, add the sum of the contributions from the bridging ligands (ΣB) to account for any electrons donated to the cluster by edge bridging, face bridging, or encapsulated atoms (see example below), and adjust for the total charge, z^-, on the cluster as a whole:

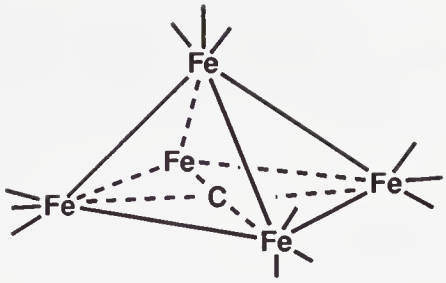
$$T = \Sigma F + \Sigma B + z \tag{13.5}$$

(where B = 1 for bridging H, 2 for bridging CO, 3 for η^2-Cl, etc.). The number of vertices, v, in the cluster will then be given by

$$v = \frac{T}{2} - 1 \tag{13.6}$$

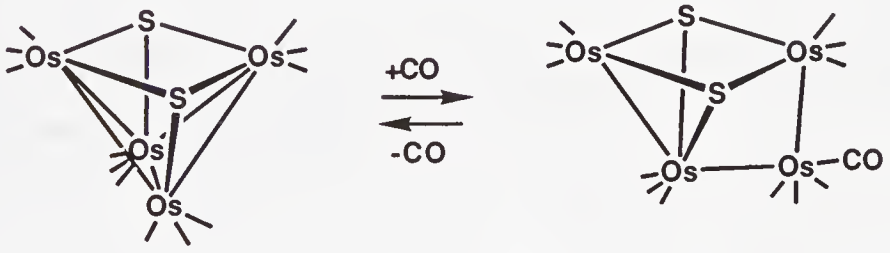
We have seen what happens in a borane cluster if there are not enough BH fragments to fill the vertices: we get a nido structure with an empty vertex. The same is true for transition metal clusters, for example, in $Fe_5(CO)_{15}C$, the carbon atom, which is not considered as a vertex atom, is encapsulated within the cluster and gives all its four valence electrons to the cluster. The $Fe(CO)_3$ fragment contributes two cluster electrons as it is isoelectronic with $Os(CO)_3$. The total count is therefore $(5 \times 2) + 4 = 14$, and the number of vertices is $\frac{14}{2} - 1 = 6$. This requires the structure shown as **13.18**, as is observed for this and the analogous Ru and Os species.

What happens when there are more atoms than vertices into which they can fit? For example, $Os_6(CO)_{18}$ is a $(6 \times 2) = 12$ cluster electron species. This means that the number of vertices required by Wade's rule is $\frac{12}{2} - 1 = 5$. The structure found for the molecule, **13.16**, shows that the extra metal atom bridges to a face of the five-vertex base polyhedron, and so is able to contribute its electrons to the cluster, even though it cannot occupy a vertex.



13.18

Only when we move up to clusters of nuclearity 6–12, do the EAN and Wade predictions become different. Often the Wade structure is the one observed, but sometimes we find that both a Wade's rule, and an EAN cluster are stable. Adams[10] has shown how in such situations there can be facile interconversion between the two forms by gain or loss of a ligand:



(13.7)

Wade cluster **EAN cluster**

Large Clusters Even Wade's rules break down for the larger clusters. This is not surprising, because the Wade description in terms of a polyhedral arrangement is somewhat artificial for close-packed metal clusters that can be decidedly nonpolyhedral in shape. Lauher[11] has looked at the m.o. patterns for a wide variety of different cluster geometries and has predicted the electron count to be expected for each. Some of these are shown in Table 13.1.

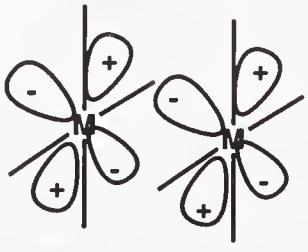
M—M Multiple Bonds Multiply bonded species, such as $Cl_4Re{\equiv}ReCl_4^{2-}$ (**13.1**), were first recognized by Cotton[4] and tend to be formed from the middle transition elements, the same elements that give strong M≡O multiple bonds (Section 11.6).[3,4] For $\{L_nM\}_2$ to form a bond of order n, the L_nM fragment has to have a d^n or higher configuration because it needs a minimum of n electrons, just as the CH fragment needs three available electrons to form HC≡CH. In **13.1**, two square planar d^4 $ReCl_4^-$ fragments face each other in the unusual eclipsed (Cl atoms face-to-face) geometry with a very short Re—Re distance. Taking the M—M direction as the z axis, the quadruple bond is formed from overlap of the d_{z^2} (the σ bond) the d_{xz} and d_{yz} (which form two π bonds) and of the d_{xy} on each Re, which forms the so-

TABLE 13.1 Some Cluster Electron Counts Predicted by the Lauher Scheme

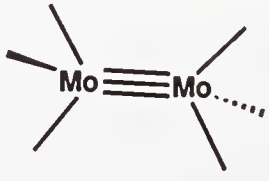
Shape	Electron Count	Example
Monomer	18	$Ni(CO)_4$
Dimer	34	$Fe_2(CO)_9$
Trimer	48	$Os_3(CO)_{12}$
Tetrahedron	60	$Ir_4(CO)_{16}$
Butterfly	62	$Re_4(CO)_{16}^{2-}$
Square plane	64	$Pt_4(OAc)_8$
Trigonal bipyramid	72	$Os_5(CO)_{16}$
Square pyramid	74	$RuC(CO)_{15}$
Bicapped tetrahedron[a]	84	$Os_6(CO)_{18}$
Octahedron	86	$Ru_6(CO)_{17}C$
Capped square pyramid	86	$Os_6(CO)_{18}H_2$

[a]A capped tetrahedron is a tetrahedron with an atom lying over one face; a bicapped tetrahedron is the same as a monocapped trig bipyramid.

called δ bond. It is this last δ bond that causes the eclipsed geometry because only in this geometry is overlap possible, as illustrated in **13.19**. The electronic structure of **13.1** is often represented as $\sigma^2\pi^4\delta^2$, which indicates how many electrons are present in each type of bond. $(RO)_3Mo{\equiv}Mo(OR)_3$ has an M—M triple bond of the $\sigma^2\pi^4$ type, in which good overlap is still possible in the staggered geometry, **13.20**.



13.19



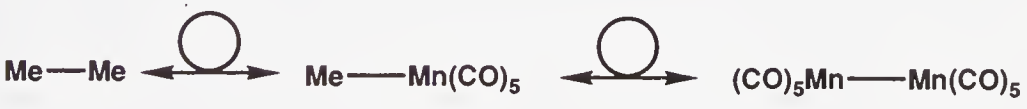
13.20

M—M multiple bonds are short; for example, typical values for Mo are 2.1 Å, Mo≡Mo; 2.2 Å, Mo≡Mo; 2.4 Å, Mo=Mo; 2.7 Å, Mo—Mo; and 2.78 Å, Mo metal. Bond strengths are known for few systems, but for Re≡Re in **13.1** it is 85 ± 5 kcal/mol, of which only ca. 6 kcal/mol is assigned to the δ bond. (This δ bond strength is comparable to a hydrogen bond.)

13.2 THE ISOLOBAL ANALOGY

Hoffmann's[12] isolobal analogy is a general unifying principle that goes far beyond the confines of cluster chemistry. Nevertheless it has found most

application in this area, and so we will look at it now. The idea is very simple; the backbone of most organic compounds is made up of the familiar groups CH_3, CH_2, and CH, which we can put together at will. What is the special property of a methyl radical that makes it univalent: clearly, the singly occupied sp^3 orbital. We will consider this fragment as having one orbital and one "hole"; a hole for this purpose simply means that the fragment has one electron less than the 8e closed-shell configuration CH_3^-. As far as the rest of the molecule is concerned, a methyl radical can be considered as providing a hole and an orbital. Hoffmann points out that any fragment with a half-filled orbital of a σ type may be able to form structures similar to those found for the methyl group. $Mn(CO)_5\bullet$ is an example of such a radical. We can imagine that it is formed by removing a CO from the 18e species $Mn(CO)_6^+$ to give $Mn(CO)_5^+$, a 16e species with an empty orbital (two holes) pointing toward the missing ligand. To make the 17e radical, we merely have to add 1e to this orbital. The resulting $Mn(CO)_5\bullet$ can replace one methyl group in ethane to give $MeMn(CO)_5$, or both of them to give $(CO)_5Mn—Mn(CO)_5$, for example. The two fragments are not isoelectronic, because $Mn(CO)_5\bullet$ has far more electrons than $CH_3\bullet$, but the significant orbital by which the two fragments form bonds to other groups, are the same both in symmetry and in occupancy. The isolobal analogy is expressed by a double-headed twirly arrow, as follows:



(13.8)

Suppose that we moved one element to the left. How could we treat $Cr(CO)_5$, a fragment that, like $Mn(CO)_5$ has one orbital, but that is empty (two holes)? Clearly, CH_3^+ is the appropriate organic fragment, because it too has an unfilled σ-type orbital. As we know, $Cr(CO)_5$ reacts with CO to give $Cr(CO)_6$. The linear acetyl cation CH_3CO^+, an important intermediate in Friedel–Crafts reactions, can now be seen as a CO complex of CH_3^+. This is not a conventional way of looking at this species and illustrates how the isolobal principle can give new insights in organic, as well as in inorganic chemistry.

The CH_2 fragment has two orbitals, and two electrons with which to make bonds; in other words, CH_2 has two orbitals and two holes. If the CH_2 fragment is to bond to two H atoms to give methane, we will hybridize these two orbitals in such a way as to have two sp^3 lobes. If two CH_2 fragments are to dimerize to give ethylene, then we will rehybridize the system to give an sp^2 and a p orbital, so that we can form a σ and a π bond. The question is to discover what metal fragments are isolobal with CH_2. It turns out that $Mo(CO)_5$ is one such fragment. This is not so obvious until one recognizes that the key point in the isolobal analogy is that the number of holes has the fixed value of (18 − the electron count of the ML_n fragment). The number

TABLE 13.2 Isolobal Relationships[a]

Inorganic Fragment	n_H	n_o	Organic Fragment		Example
$Mn(CO)_5$	1	1	CH_3	$Me—Mn(CO)_5$	Me—Me
$Mo(CO)_5$	2	1	CH_3^+	$Me_3P—Mo(CO)_3$	$Me_3P—Me^+$
	2	2[b]	CH_2	$OC=Mo(CO)_5$	$OC=CH_2$
	2	3[b]	CH^-	—	—
$Fe(CO)_4$	2	2	CH_2	$(C_2H_4)—Fe(CO)_4$	Cyclopropane
$Cp(CO)_2Mo$	3	2[b]	CH_2^+	—	—
	3	3[b]	CH	$Cp(CO)_2Mo\equiv CR$	Acetylene
CpRh(CO)	2	2	CH_2	$\{CpRh(CO)\}_2(\mu\text{-}CH_2)$	Cyclopropane
$PtCl_3^-$	2[c]	1[d]	CH_3^+	$Cl^-—PtCl_3^-$	$Cl^-—CH_3^+$
	2[c]	2[b,d]	CH_2	$(C_2H_4)—PtCl_3^-$	Cyclopropane

[a] n_H and n_o are the number of holes and of orbitals.
[b] After rehybridizing to include one or more d_π orbitals. Note that on the deprotonation analogy, CH_3, CH_2^-, and CH^{2-} are isolobal, as are CH_3^+, CH_2, and CH^- and DH_3^{2+}, CH_2^+, and CH.
[c] On the basis of a 16e closed shell.
[d] On a square planar basis.

of orbitals can vary according to the hybridization. For example, we can hybridize the single empty orbital of $Mo(CO)_5$ with one of the filled d_π orbitals to give a fragment that still has two holes but now has two orbitals. This picture in turn implies that CH_3^+ is isolobal with CH_2. Hoffmann has called this the *deprotonation analogy*. This extension of the analogy is more useful for organometallic rather than organic fragments, because in the organic case, we can only take a C—H bonding orbital for the rehybridization; this, which is more stable than the nonbonding d_π orbital of the organometallic fragment, is more reluctant to cooperate. We can see the $Mo(CO)_5$ fragment acting as isolobal with CR_2 in the Fischer carbenes $(CO)_5Mo=CR_2$. Just as $Mo(CO)_5$ forms a carbonyl complex, $Mo(CO)_6$, so does CH_2, in the form of $CH_2=C=O$, ketene.

Table 13.2 shows how the analogy works. We need to calculate n_H, the number of holes in our metal fragment (Eq. 13.9 shows this explicitly for the $MX_aL_b^{c+}$, where N is the Group number of the metal).

$$n_H = 18 - N - a - 2b + c \tag{13.9}$$

This shows us at once which organic fragments are isolobal with the organometallic fragment in question. The most direct analogy will be with the organic fragment that has the same number of orbitals. For the metal fragments, the number of orbitals n_o, is calculated on the basis of an octahedral model. If there are three ligands in the fragment, three orbitals of the octahedron are available; Eq. 13.10 shows the general expression

$$n_o = 6 - a - b \tag{13.10}$$

By the deprotonation analogy, metal fragments can make up to three more orbitals available by using their d_π set; reference to Table 13.2 will show how often we have to resort to using the d_π set. For example, $Mo(CO)_5$ in Table 13.2 is isolobal with CH_3^+ by Eqs. 13.9 and 13.10 ($n_H = 2$, $n_o = 1$). If we bring in an extra filled d_π orbital, we move to ($n_H = 2$, $n_o = 2$), which makes the fragment isolobal with CH_2. This means that the $Me_3P—Mo(CO)_5$ or $Me—Mn(CO)_5$ bonds are formed without a significant contribution from a d_π orbital, while the $OC=Mo(CO)_5$ double bond with its strong Mo-to-CO π back-bonding component requires a strong contribution from a d_π orbital. The deprotonation analogy gets its name from the fact that CH_2 can be formed by deprotonation of CH_3^+.

Because CH has three orbitals and three holes, the most direct analogy is therefore with the Group 9 $M(CO)_3$ fragments, such as $Co(CO)_3$. Figure 13.5 shows the conversion of the hydrocarbon tetrahedrane into a tetrahedral $M_4(CO)_{12}$ cluster by the isolobal replacement of $M(CO)_3$ groups by CH. $Co_4(CO)_{12}$ has a bridged structure, and only the Rh and Ir analogs are all-terminal; since the all-terminal structure can only be unstable with respect to the real structure by a few kilocalories per mole for Co, we must not hold it against the isolobal analogy, or any counting rule for not being able to predict the pattern of CO bridges. Structure **13.24**, best known for Co, is normally considered as μ_3-carbyne cluster. Structure **13.23** is usually considered as a

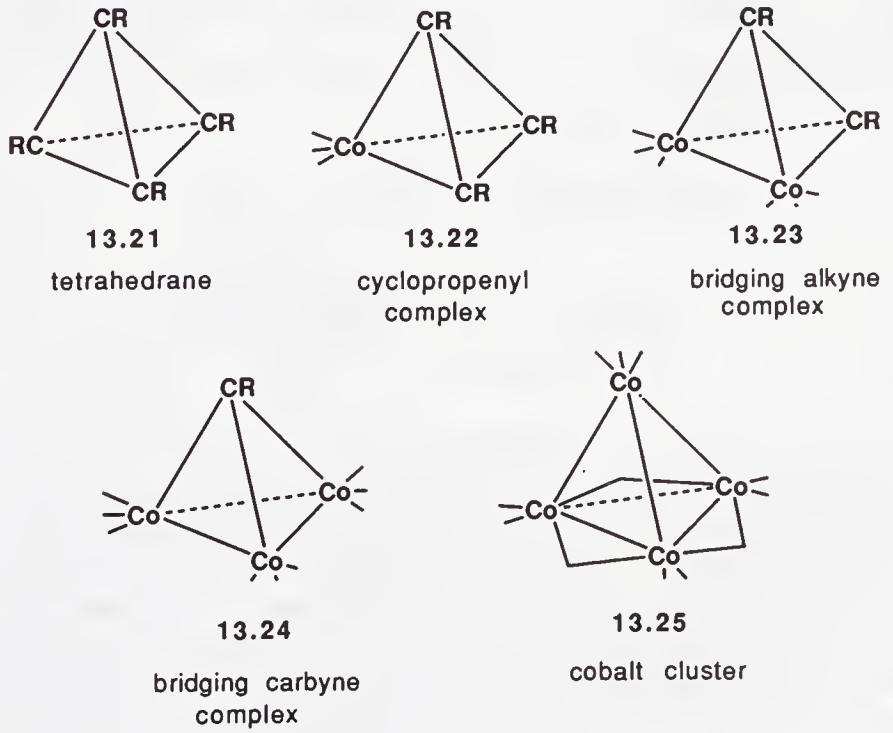
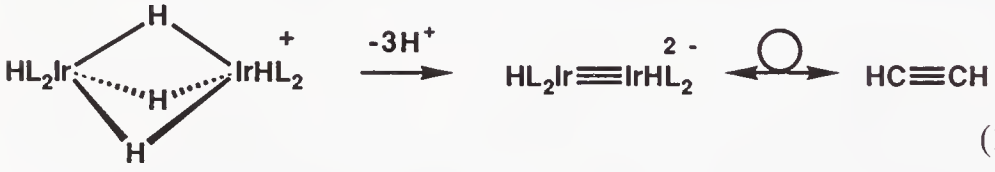


FIGURE 13.5 The stepwise isolobal replacement of CH by $Co(CO)_3$ in tetrahedrane. $Co_4(CO)_{12}$ has the CO bridged structure shown.

bridging alkyne complex of $Co_2(CO)_8$, and **13.22** as a cyclopropenyl complex of $Co(CO)_3$. The all-carbon compound, **13.21**, is unstable, and reverts to two molecules of acetylene. Only recently have stable tetrahedranes C_4R_4 been made by using very bulky R groups.

Those metals that prefer to be 16e, such as Pt(II), can also be treated on isolobal ideas, but the number of holes is determined on the basis of a closed shell of 16e not 18e. The argument is that the fifth *d* orbital, although empty, is too high in energy to be accessible, and so its two holes do not count. For example, the 14e $PtCl_3^-$ fragment is considered as having two holes, not four. The number of orbitals is also calculated on the basis of a square planar structure, so that $PtCl_3^-$ has one orbital, and is therefore isolobal with CH_3^+. Both species form a complex with NH_3, for example, $(NH_3)PtCl_3^-$ and $CH_3NH_3^+$. An extra nonbonding orbital on Pt can also be considered to contribute, giving two orbitals and two holes, which makes $PtCl_3^-$ isolobal with CH_2. Both fragments form complexes with ethylene—$(C_2H_4)PtCl_3^-$ and cyclopropane, respectively.

Any bridging hydrides can be removed as protons; for example, the dinuclear hydride in Eq. 13.11 is isolobal with acetylene because the 15e $IrHL_2^+$ fragment has three holes and three orbitals. CO ligands contribute in the same way whether they are bridging or terminal (e.g., Eq. 13.12), but the rhodium dimer (Eq. 13.13) has bridging CO groups.



(13.11)

(13.12)

(13.13)

As we shall see in the next section, we can even use the isolobal analogy to plan synthetic strategies, but we must guard against expecting too much from such a simple model. There are many cases in which molecules isolobal with stable organic compounds have not been made. This may be because the right route has not yet been found, or it may be that another structure is more favorable. C—C multiple bonds are stronger than M—M multiple bonds, and so a species like $(CO)_3Co{\equiv}Co(CO)_3$ is unlikely, although it is isolobal with acetylene. Similarly, we saw that acetylene is more stable than tetrahedrane. Finally, the isolobal analogy is a structural one; we cannot expect it to predict such things as reaction mechanisms, for example.

13.3 SYNTHESIS

Many metal cluster complexes were originally synthesized by unplanned routes, or as by-products in other reactions. Only recently have systematic procedures been developed for making metal–metal bonds and building up clusters.

Clusters are formed efficiently in a number of ways:

1. By pyrolysis of mononuclear carbonyl complexes[13] (it appears that CO is lost first, and the unsaturated fragment then attacks the original carbonyl):

$$Ru(CO)_5 \xrightarrow{50°C} Ru_3(CO)_{12} \qquad (13.14)$$

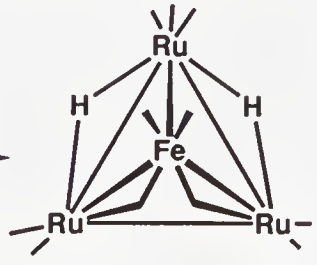
Photolysis can also be used to expel the CO.[14]

$$Fe(CO)_5 \xrightarrow{h\nu} Fe_2(CO)_9 \qquad (13.15)$$

2. By nucleophilic attack of a carbonyl anion:[15,16]

$$Mn(CO)_5^- + BrRe(CO)_5 \longrightarrow (CO)_5Mn—Re(CO)_5 \qquad (13.16)[15]$$

$$Ru_3(CO)_{12} \xrightarrow{Fe(CO)_4^{2-}} FeRu_3(CO)_{12}^{2-} \xrightarrow{2H^+} \qquad (13.17)$$



$H_2FeRu_3(CO)_{12}$

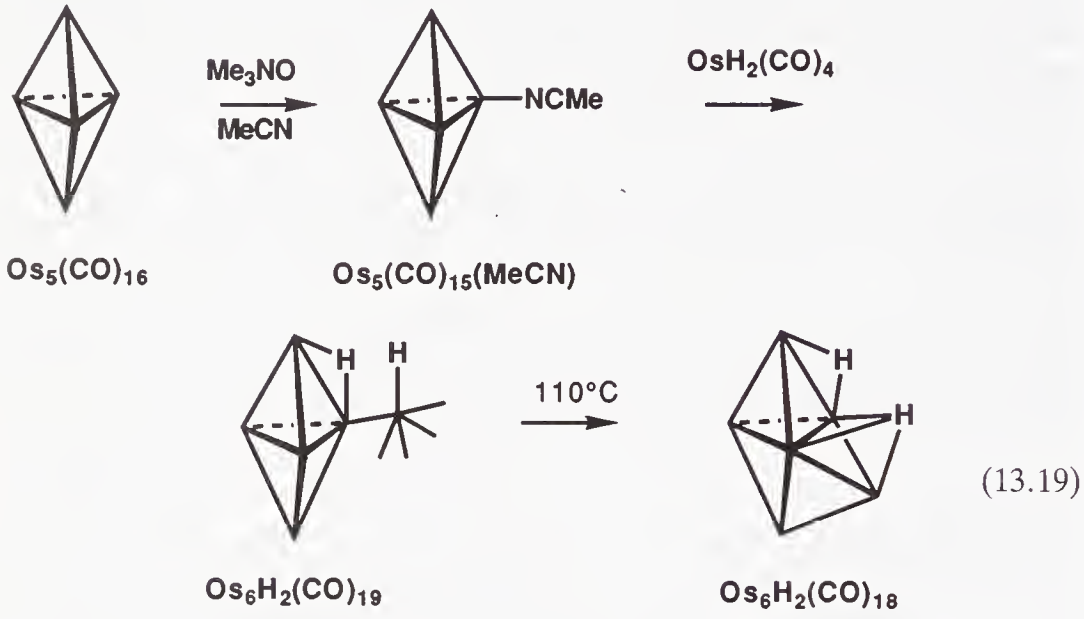
3. By binuclear reductive elimination:[17]

$$HMn(CO)_5 + MeAuL \longrightarrow (CO)_5Mn—AuL + MeH \qquad (13.18)$$

We saw some other examples of this reaction in Section 6.5.

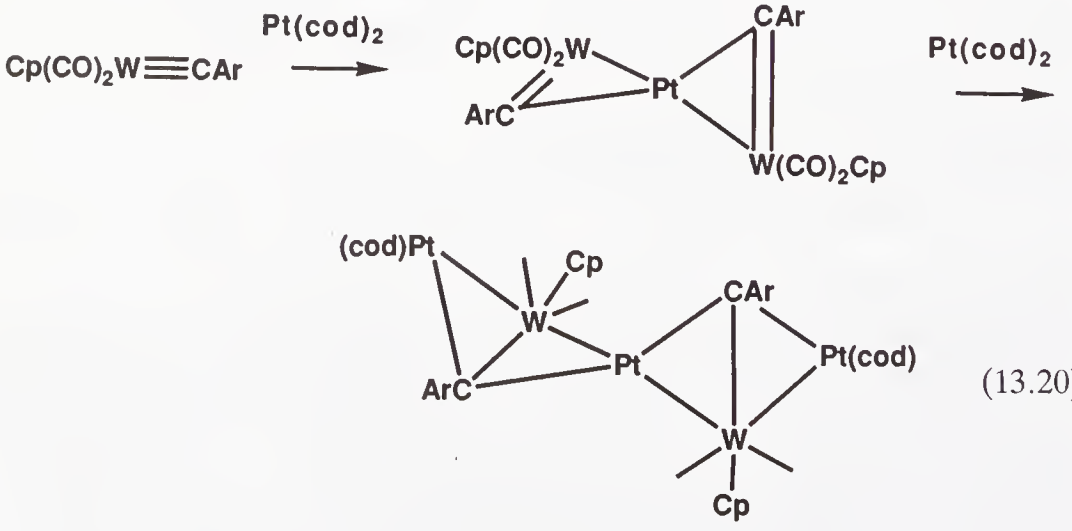
4. By addition of a coordinatively saturated cluster to an unsaturated one via a bridging group (Eq. 13.19). In this method, we rely on a bridging ligand, such as hydride, to link the coordinatively saturated species to an unsaturated cluster. In the example shown,[18] MeCN is introduced by the use of the Me_3NO reagent, which oxidizes a CO to CO_2 (Section 8.1). Ready dissociation of the MeCN provides the unsaturation, which allows an Os—H bond to bind to give a "spike" structure with one metal bound to the cluster by a single bond. The last thermal step shows the high tendency for clusters to agglomerate in such a way as to produce the maximum number of M—M bonds. In this and

some later high nuclearity systems, the CO groups have been omitted for clarity.



(13.19)

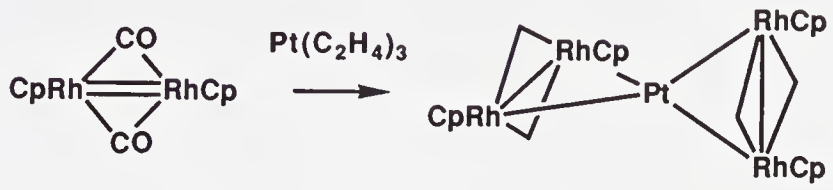
5. By addition of an M—C multiple bond to a metal (Eq. 13.20). This method was developed by Stone[19] on the basis of the isolobal analogy. Because the M=C double bond is isolobal with the C=C double bond, those metals that form alkene complexes might also be expected to form complexes with metal carbenes. This reaction is a very rich source of clusters.



(13.20)

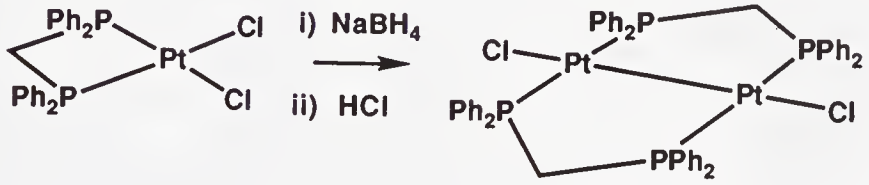
6. By addition of an M—M multiple bond to a metal (Eq. 13.21). Stone[20] has taken the isolobal analogy one step further by invoking an analogy be-

tween the M=M multiple bond and an alkene. Both of these methods are likely to be very powerful.



(13.21)

7. By the use of bridging ligands. The common diphosphine $Ph_2PCH_2PPh_2$ has a high tendency to bring two metals close together, rather than chelate to a single metal (Eq. 13.22).[21a] This is presumably the result of geometric factors associated with the different ring sizes in the two cases. A large number of related ligands, such as $CN(CH_2)_3NC$ can behave similarly.[21b]



(13.22)

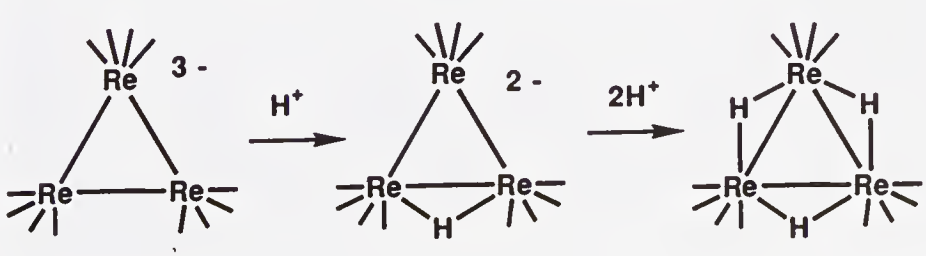
8. By using Main Group elements to bring about cluster formation or expansion:

$$CpMn(CO)_2(thf) + PbCl_2 \longrightarrow Cp(CO)_2Mn{=}Pb{=}Mn(CO)_2Cp \qquad (13.23)^{22}$$

13.4 REACTIONS

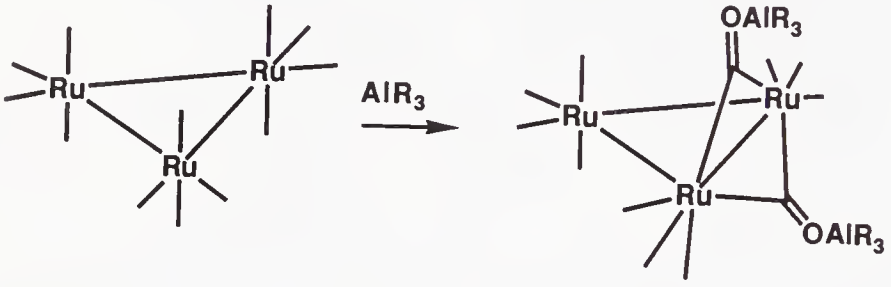
Clusters give a rich reactivity pattern with the usual organometallic ligands, often involving bridging of the ligand to several metals. Unfortunately, it is still a difficult area in which to try to rationalize or to predict.

With Electrophiles Perhaps the simplest reaction of a cluster is the addition of a zero-electron electrophilic reagent such as H^+, because this should take place without any change in the cluster geometry. Anionic clusters are especially easy to protonate and the resulting hydrides tend to be bridging (Eq. 13.24). Note that a μ without a subscript means that the ligand is bridging to two metals (i.e., $\mu = \mu_2$); bridging to three metals is shown as μ_3.

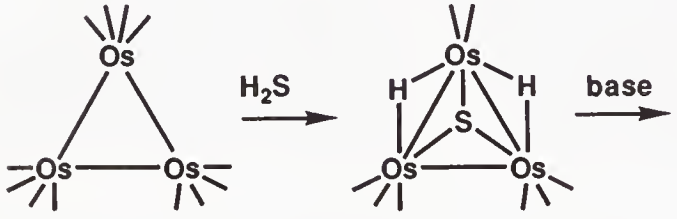


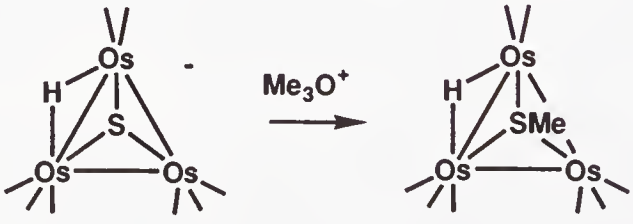
(13.24)

Electrophiles more bulky than the proton often add to the carbonyl oxygen, as we saw in Eq. 4.15. The same is true for clusters; for example, $Ru_3(CO)_{12}$ is converted from the normal CO-unbridged structure to a bridged $Ru_3(\mu\text{-}COAlR_3)_2(CO)_{10}$ structure with $AlBr_3$ (Eq. 13.25).[23] This structure resembles that of $Fe_3(CO)_{12}$, which is really $Fe_3(\mu\text{-}CO)_2(CO)_{10}$. On rare occasions, the proton may also add to a CO oxygen, as in the protonation product of $Fe_3(CO)_{11}^{2-}$, which is $(\mu\text{-}H)Fe_3(\mu\text{-}COH)(CO)_{10}$.[24] Carbon electrophiles may also add to a sufficiently nucleophilic vertex atom such as a sulfur, such as in $Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}S)^-$ (Eq. 13.26),[25] which shows that the sulfur has a lone pair not involved in cluster bonding, and therefore this S should be considered as contributing only four of its six valence electrons to the cluster.



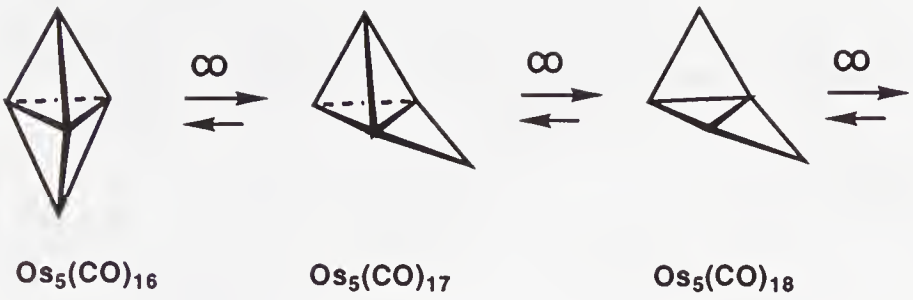
(13.25)





(13.26)

With Nucleophiles The addition of nucleophiles adds 2e to the cluster, and so it must either rearrange or lose a 2e ligand. Equation 13.27 shows an interesting example of the reversible conversion of the trigonal bipyramidal $Os_5(CO)_{16}$ to the "bow tie" cluster $Os_5(CO)_{19}$ with CO,[26] and Eq. 13.28 shows rearrangement of the dicapped tetrahedral $Os_6(CO)_{18}$ to the raft cluster $Os_6(CO)_{17}L_4$ with $P(OMe)_3$ (= L).[27] In each case the addition of CO or of L, which adds 2e to the cluster, causes breakage of an Os—Os bond, which "absorbs" the two electrons.

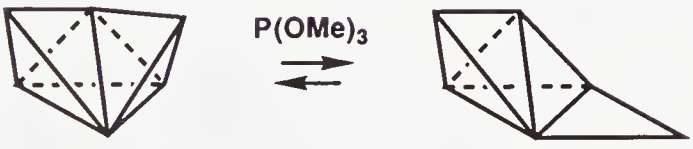


$Os_5(CO)_{16}$ $Os_5(CO)_{17}$ $Os_5(CO)_{18}$

'bow tie'

$Os_5(CO)_{19}$

(13.27)



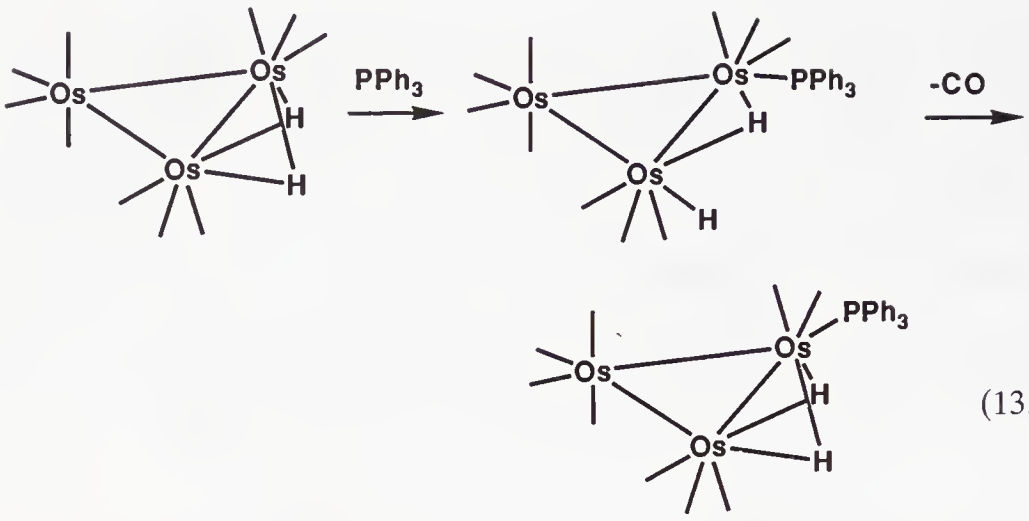
$Os_6(CO)_{18}$ $Os_6(CO)_{18}L$

'raft'

$Os_6(CO)_{18}L_2$ $Os_6(CO)_{18}L_3$

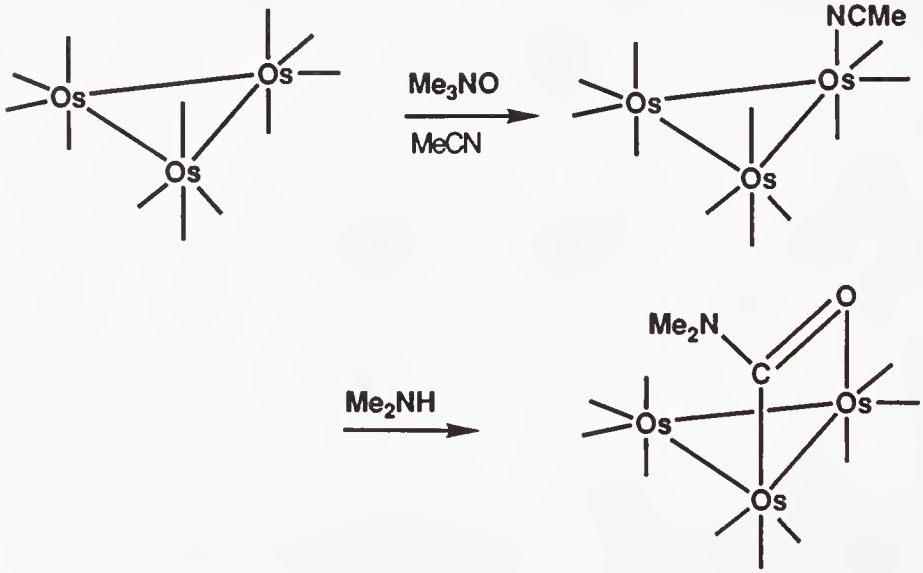
(13.28)

An "unsaturated" cluster, such as $(\mu_2\text{-H})_2Os_3(CO)_{10}$ does not have to lose a ligand on addition of a nucleophile, because one of the M—H—M bridges can open up and generate a vacant site. This is why the triosmium dihydride is such a popular starting material in cluster studies. For example, CO adds to give a product, $(\mu\text{-H})HOs_3(CO)_{11}$, in which one of the two M—H—M bridges has opened and the hydride has become terminal. This turns the Os=Os "double bond" into an Os—Os single bond and means that the cluster is still an EAN one. This reaction can lead to substitution if a CO is expelled, as shown in Eq. 13.29.[28] Cluster breakdown into smaller fragments is also a possible outcome of substitution. The less stable cluster $Ru_3(CO)_{12}$ gives not only $Ru_3(CO)_9L_3$ but also $Ru(CO)_3L_2$ and $Ru(CO)_4L$ as substitution products with PPh_3. For osmium, mononuclear products are observed only under forcing conditions.



(13.29)

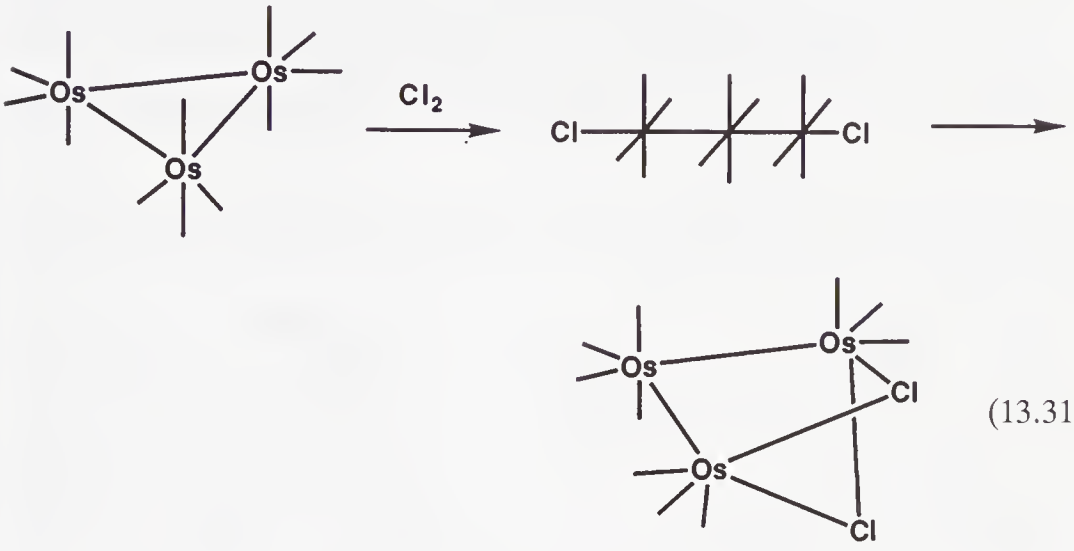
Nucleophiles may also attack the ligands. The use of Me_3NO to liberate CO from clusters has already been mentioned. Kaesz[29] has shown that when amines attack a CO in $Os_3(CO)_{12}$, the metala-amide that is formed can labilize other CO's in the molecule by bridging:



(13.30)

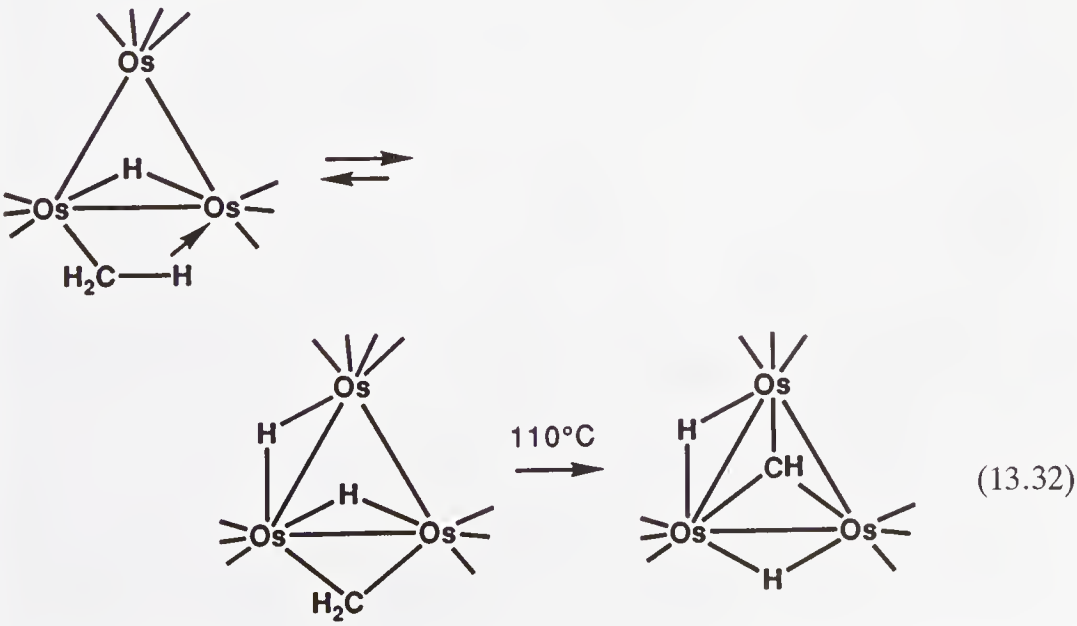
Oxidative Addition As this reaction adds 2e to the cluster, subsequent loss of CO is required if the structure is not to change. The addition of H_2 to $Os_3(CO)_{12}$ probably takes place by loss of CO. The initial product is believed to be $(\mu\text{-H})HOs_3(CO)_{11}$, which then loses another CO to go to the final product, $(\mu\text{-H})_2Os_3(CO)_{10}$. As in the case of oxidative addition to mononuclear metal centers, there are many different mechanisms at work in oxidative addition. For example, Cl_2 addition does not require prior CO dissociation. The Cl_2 directly oxidizes the cluster by taking two electrons from a metal–metal bond (Eq. 13.31). This leads to a linear cluster in which only two M—M bonds are left. Pyrolysis of this complex leads to a chloro-bridged cluster $(\mu_2\text{-Cl})_2Os_3(CO)_{10}$.[30] This is not unsaturated like $(\mu_2\text{-H})_2Os_3(CO)_{10}$, because Cl

is a 3e, not a 1e donor, and so the cluster has 50e. By the EAN rule, we only require two M—M bonds; this means that the Os atoms bridged by the chlorides are not also metal–metal-bonded.



(13.31)

One striking difference between clusters and mononuclear systems is the difference in selectivity for C—H oxidative addition in ligands. For example, a mononuclear species will activate the allylic C—H bond of a coordinated alkene to give an allyl hydride; a cluster, in contrast, breaks the vinyl C—H bond. An alkyl ligand in a mononuclear system gives β-elimination of hydride, an alkyl in a cluster usually gives α elimination (Eq. 13.32)[31]. In each case, the bond broken by the cluster is one atom closer to the point of attachment of the ligand to the metal than in the mononuclear case. This is probably because, in the cluster, the C—H bond is broken not by the metal to which the ligand is bound, but by the adjacent metal. This is shown in Fig. 13.6.



(13.32)

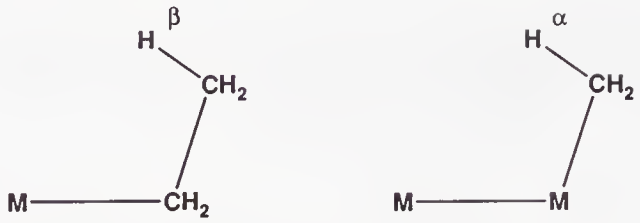
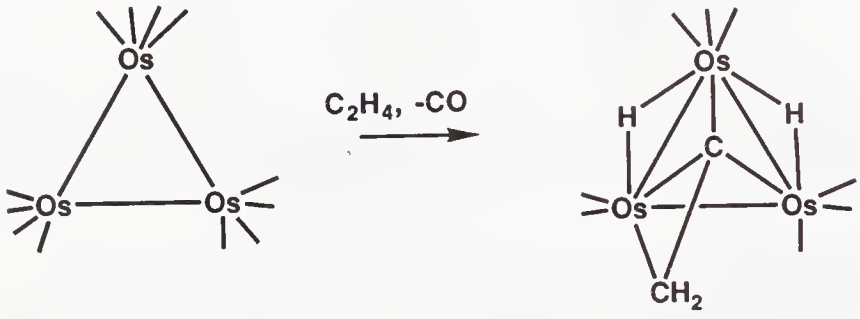


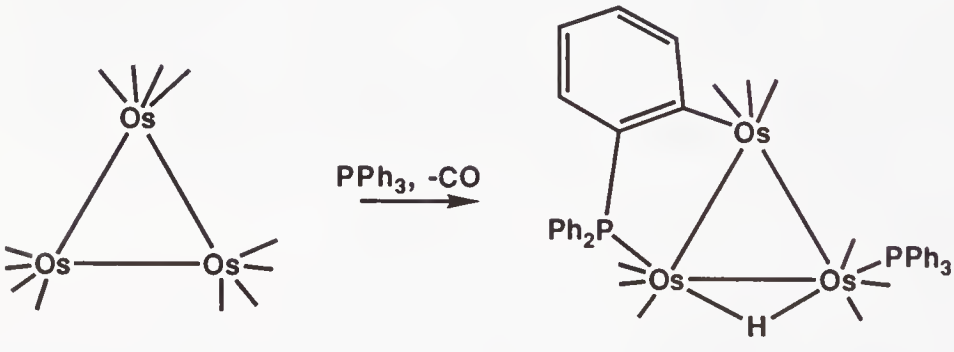
FIGURE 13.6 The geometric analogy between a β-CH in a mononuclear complex and an α-CH in a cluster.

Ethylene can undergo two successive C—H bond scissions at the same carbon (Eq. 13.33):[32]

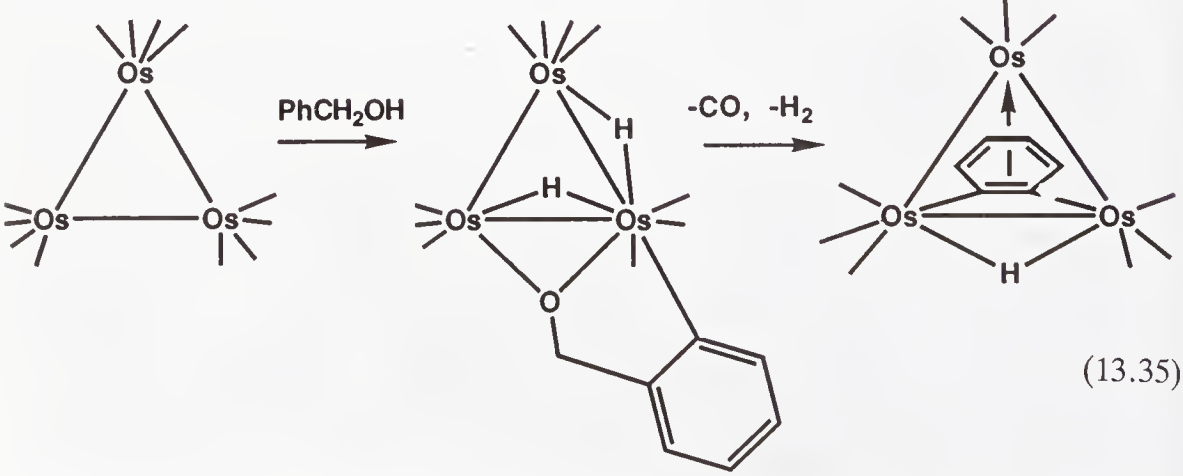


(13.33)

C—H bond breaking in γ and δ positions is also possible if dictated by the structure of the ligand (Eq. 13.34).[33] Further bond scissions can also occur (Eq. 13.35):[34]

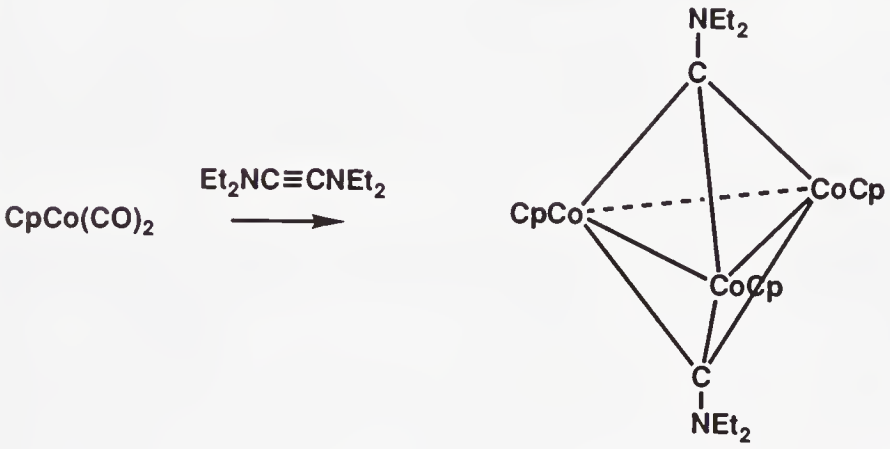


(13.34)



(13.35)

Another interesting bond cleavage reaction is the scission of the C—C triple bond in alkynes. We have already seen how metal–metal triple bonds can do this to give metal carbyne complexes (Section 11.2, Eq. 11.42). This reaction is not unusual in clusters, and can be encouraged by using an alkyne that forms a specially stabilized carbyne. $Et_2NC{\equiv}CNEt_2$ has even been used as a source of the Et_2NC fragment in a reaction that generates a cluster from a mononuclear cobalt complex (Eq. 13.36):[35]



(13.36)

Reactions Involving CO One of the objects of cluster carbonyl chemistry has been to find ways of reducing CO and incorporating it into organic compounds. As we saw when we looked at CO activation in Section 12.1, the heterogeneously catalyzed Fischer–Tropsch reaction is an interesting route from CO to long-chain alkanes and alcohols. This is believed to go by scission of the CO on metallic iron to give a surface-bound oxo group and a surface-bound carbide. Hydrogenation of these surface species then leads to H_2O and CH_2, which is believed to polymerize to give the long chains observed. Interestingly, carbide clusters, like $Fe_6(\mu_6\text{-}C)(CO)_{16}^{2-}$, can be made by reduction of metal carbonyls.[36] These carbide clusters were known for many years, but the reactivity of the carbide could not be studied because it was buried in the cluster. Later work (Fig. 13.7) has shown how the cluster can be opened up to give an Fe_4 "butterfly" by controlled oxidation. In spite of its name, the "carbide" reacts more like a carbonium ion. This carbon binds a CO, polarizing it so that the solvent methanol can attack to give the ester derivative **13.26**, hydrogenation of which gives methyl acetate.[36a] Related work (Fig. 13.7) has shown how a μ_3-CO can be dissected to a carbide with loss of water. Note the interesting tetrahedral to butterfly rearrangement on protonation. Structure **13.27** is unusual in that it is a carbyne ligand with an agostic C—H bond, the longest such bond yet discovered; further protonation leads to CH_4. Similar reductive transformations of other unsaturated groups, such as isonitriles and NO, are also known.[36b] Heterobimetallic systems such as $Cp_2(Me)Zr—Ru(CO)_2Cp$ have been prepared by Casey in the course of attempts to design clusters to reduce CO.[36c]

Catalytic activity is sometimes seen in metal clusters, but it is sometimes difficult to tell if this arises from cluster breakdown to mononuclear fragments

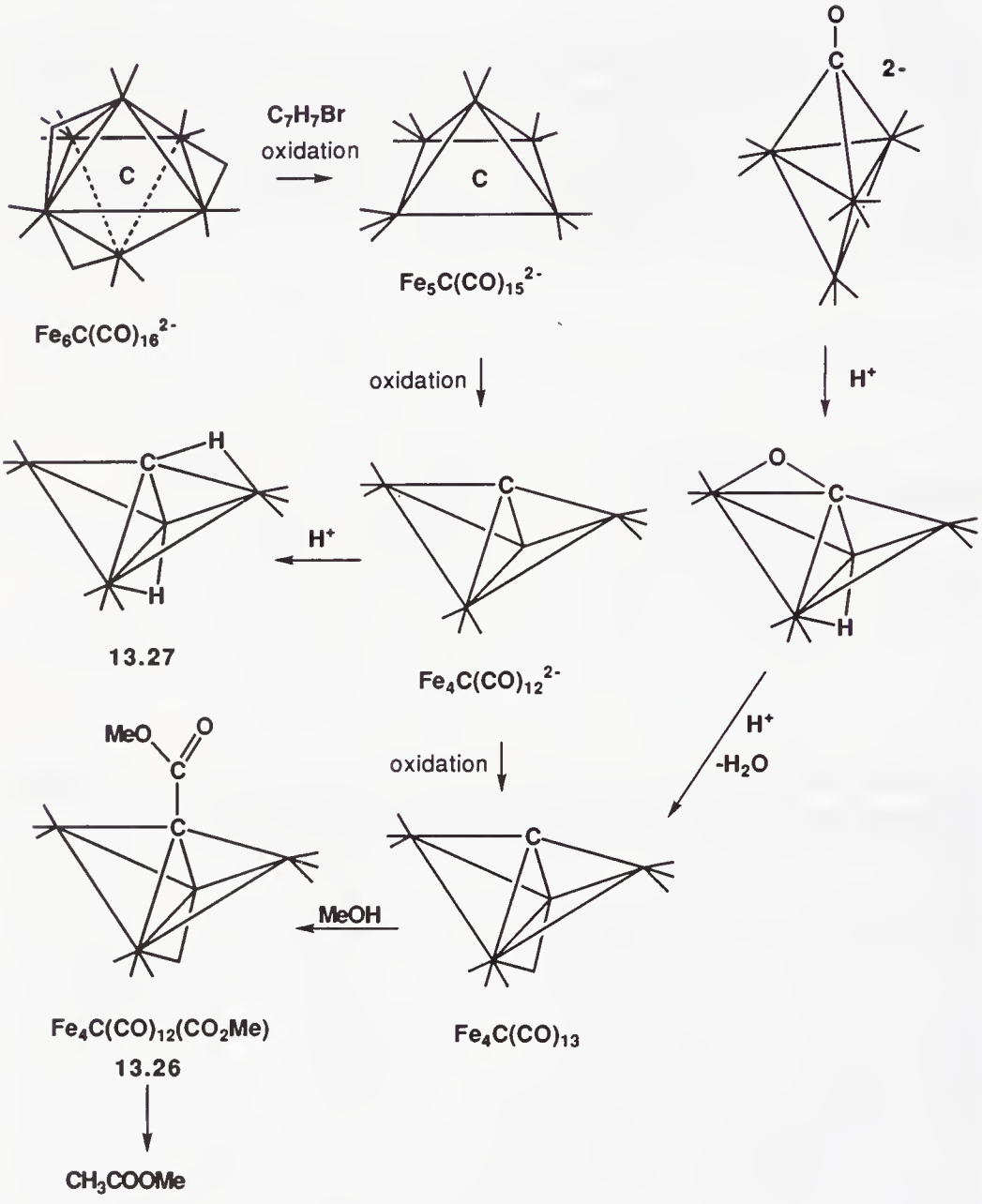
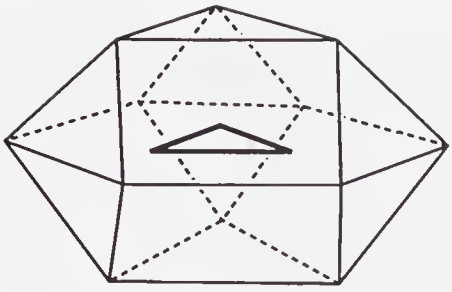


FIGURE 13.7 Some interesting chemistry of carbide clusters.

or whether the active catalyst is polynuclear. Some examples[37] are $[HRu_3(CO)_{11}]^-$ and $[Rh_2\{(Et_2PC_2H_4)_2PCH_2\}_2]$, which are both active for hydroformylation (Section 9.3) and in which the active catalysts are believed to be trinuclear and dinuclear, respectively.

Many metal–carbonyl clusters are fluxional, and the COs rapidly permute between the different available sites. This is believed to happen by terminal–bridge–terminal exchange of the CO groups. Indeed, only ligands that are capable of bridging are found to be fluxional; hydride is another ligand of this type. Johnson[38] has a different way of looking at these rearrangements. He



$M_3(CO)_{12}$

FIGURE 13.8 The Johnson picture of fluxionality. A close-packed cuboctahedron of carbonyl groups defines a cavity in which the triangle of metals fits. This triangle can rotate within a fixed set of CO groups.

considers that the COs in the cluster form a close-packed array of ligands within which there is a cavity into which the metal atoms fit. For example, in $M_3(CO)_{12}$ (M = Fe, Ru, and Os), we can consider the structure as consisting of an icosahedron of COs. The cavity is such that the larger Ru_3 and Os_3 fragments fit in best in such a way that all the COs are terminal. The Fe_3 triangle is smaller and "rattles" in the cavity. The $Fe_3(\mu\text{-}CO)_2(CO)_{10}$ structure adopted has the *same* icosahedral arrangement of COs, but the Fe_3 triangle is in a different orientation than was the Os_3 or Ru_3 (Fig. 13.8). Fluxionality is now seen as the rotation of the M_3 triangle within the COs, and so involves a concerted movement of all the COs in the cluster relative to the M_3 group.

M—M Multiple Bonds Chisholm[5] has studied the reaction of M—M multiple bonds as shown in Fig. 13.9. In forming **13.28**, it is not an M—M bond which is lost as would be the case for an Os carbonyl cluster. Instead two RO-to-metal π-bonding interactions are lost (the lone pairs on O are 2e donors), and this allows the 2e of the two incoming nucleophiles to be accommodated. The carbonyl complex **13.29** is interesting because the ν(CO) frequency is very low ($\sim$1600 cm^{-1}), and this is attributed to contributions from canonical forms of type **13.30**. The system is an alkyne cyclotrimerization catalyst, probably via the sequence **13.31** → **13.32**.

13.5 GIANT CLUSTERS

Metal colloids have been known for years—red stained glass is gold in colloidal form in glass, for example. Aqueous colloids are preparations that contain metal particles of 20–1000 Å diameter in which the metal does not precipitate because the surface of the particles is covered in a way that protects them from agglomeration; the hydrophilic polymer polyvinylalcohol (PVA) is an effective stabilizing agent. In a typical preparation, an aqueous solution of a metal salt is reduced in the presence of PVA. Small metal clusters have a precisely defined nuclearity (number of metals) and structure, but colloid

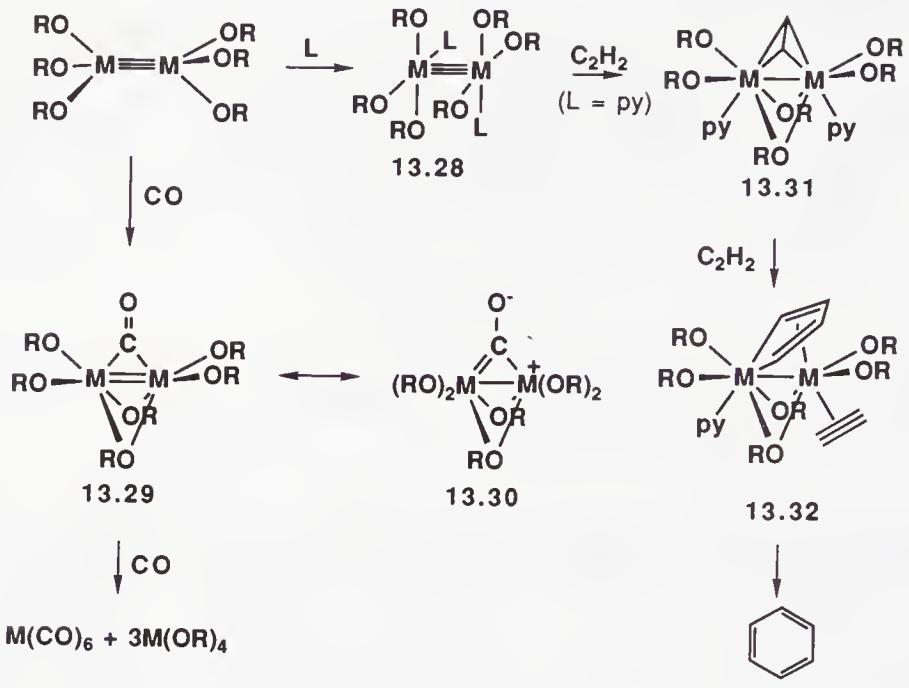


FIGURE 13.9 Some reactions of $M_2(OR)_6$. L = pyridine or PMe_3; M = Mo or W.

particles do not. There are now a number of examples of very large clusters of defined nuclearity as well as of small colloidal particles, in both cases protected by ligands.[39] For example, Moiseev[40] has used dipyridyl to protect a Pd colloid formed from H_2 and $Pd(OAc)_2$, and has synthesized a *giant cluster* that is believed to have an isocosahedral close-packed structure of *approximate* formulation "$[Pd_{561}(phen)_{60}](OAc)_{180}$." Electron microscopy (Fig. 13.10) shows that the 25-Å particle size distribution is very narrow and X-ray absorbtion spectroscopy shows the Pd—Pd distances are very close to those in metallic Pd but that the packing is probably icosahedral. The crystallites are catalytically active for O_2 or peroxide oxidation of ethylene, propylene, and toluene to vinyl acetate, allyl acetate, or benzyl acetate. Gold colloids are stabilized with $P(m\text{-}C_6H_4SO_3Na)_3$ to the extent of making them isolable as red solids.[41] When two different metals are reduced, alloy or "onion" structures can be formed. In the latter case a colloid of one metal is used as the seed particles for growing a second metal: Au encapsulated by Pt is an example. Lewis and Uriarte[42] have evidence that the active catalyst in Speier hydrosilation (Section 9.5) of $RCH{=}CH_2/R_3SiH$ to $RCH_2CH_2SiR_3$ with H_2PtCl_6/i-PrOH as catalyst is a Pt colloid. The surface may be capped with SiR_3 groups that act as protectant, the role taken by dipyridyl or PVA in the systems mentioned above. A 35-Å Pd colloid stabilized by a polymeric hydrosilane has substantially different selectivity than either Pd/C or homogeneous Pd catalysts in hydrogenation and hydrogenolysis reactions.[43]

Small clusters can be obtained as pure compounds. The largest clusters which can still be crystallized for X-ray studies and are found to be of a

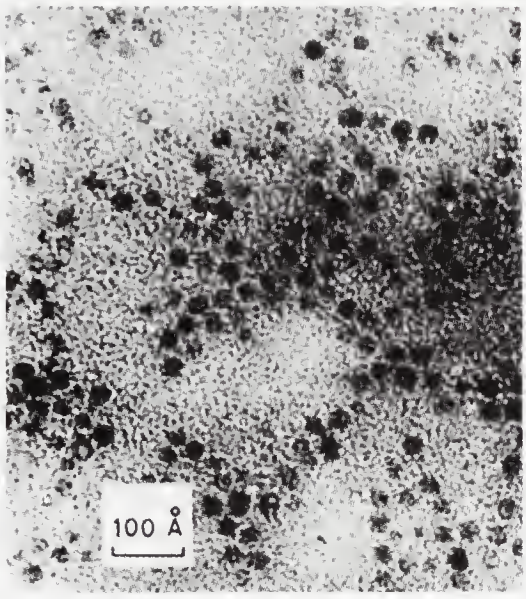


FIGURE 13.10 Electron micrograph of Moiseev's giant palladium clusters on a carbon support (reproduced from ref. 40a with permission of the Royal Society of Chemistry © 1985)

defined nuclearity are in the M_{30}–M_{40} range. Examples are the face-centered cubic close-packed $[Pt_{38}(CO)_{44}H_2]^{2-}$ and hexagonal antiprismatic $[Au_{39}(PPh_3)_{14}Cl_6]Cl_2$.[39] $Ni_{34}Se_{22}(PPh_3)_{10}$ is interesting in that the core is a particle of nickel selenium alloy, not of metallic nickel (Fig. 13.11).

Unusual physical properties are sometimes seen for these particles. For example, "$Pt_{309}(phen)_{36}O_{30}$" shows two ^{195}Pt NMR resonances that are as-

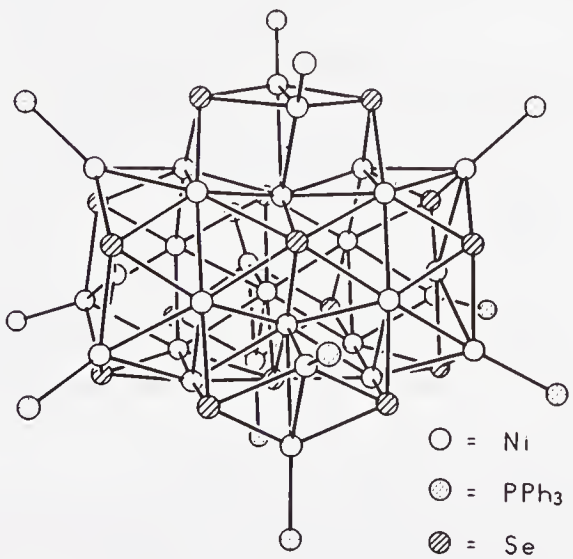


FIGURE 13.11 The molecular structure of $Ni_{34}Se_{22}(PPh_3)_{10}$. (Reproduced from ref. 39 with permission.)

signed to surface and bulk Pt. The latter show the so-called Knight shift, which is a shift in the resonance position as a result of metallic character.[44] $[Au_{55}(PPh_3)_{12}Cl_6]$ has been used in microelectronic devices.[45]

Several important questions remain unanswered in cluster chemistry. Can clusters be synthesized with other high-field ligands than CO, and will they have reactivity patterns different from those of the carbonyl clusters we have been looking at in this chapter? In particular, can a wider range of catalytically active clusters be prepared, by choosing more labile ligands than CO? Can cluster fragmentation be controlled, perhaps by using ligands that keep the cluster together in some way? A related question concerns mechanism: How do we know whether a given stoichiometric or catalytic reaction is a reaction of the intact multimetal cluster unit or of dissociated, even mononuclear intermediates that subsequently re-form a cluster once again?

REFERENCES

1. B. F. G. Johnson (ed.), *Transition Metal Clusters,* Wiley-Interscience, New York, 1980.
2. E. L. Muetterties, T. N. Rhoden, E. Band, C. F. Brucker, and W. R. Pretzer, *Chem. Rev.,* **79,** 91, 1979.
3. G. A. Somorjai, *Chemistry in Two Dimensions,* Cornell Univ. Press, Ithaca, N.Y., 1981.
4. F. A. Cotton and R. A. Walton, *Multiple Bonds between Metal Atoms,* Wiley, New York, 1982.
5. M. H. Chisholm and I. P. Rothwell, *Prog. Inorg. Chem.,* **29,** 1, 1982; M. H. Chisholm, D. M. Hoffman, and J. C. Huffman, *Chem. Soc. Rev.,* **14,** 69, 1985.
6. J. R. Pugh and T. J. Meyer, *J. Am. Chem. Soc.,* **114,** 3784, 1992.
7. M. L. H. Green, N. J. Cooper, et al., *J. Chem. Soc., Dalton,* 29, 1980.
8. K. Wade, *Adv. Inorg. Organometal. Chem.,* **18,** 1, 1976.
9. (a) G. Hultner, *Angew. Chem., Int. Ed.,* **32,** 297, 1993; (b) C. E. Housecroft and T. P. Fehlner, *Adv. Organometal. Chem.,* **21,** 57, 1982.
10. R. D. Adams and L. W. Yang, *J. Am. Chem. Soc.,* **105,** 235, 1983.
11. J. W. Lauher, *J. Am. Chem. Soc.,* **100,** 5305, 1978.
12. R. Hoffmann, *Angew. Chem., Int. Ed.,* **21,** 711, 1982.
13. F. Calderazzo, R. Ercoli, and G. Natta, Chap. 1 in *Organic Syntheses via Metal Carbonyls,* I. Wender and P. Pino (Eds.), Wiley-Interscience, New York, 1968.
14. B. F. G. Johnson and J. Lewis, *Adv. Inorg. Chem. Radiochem.,* **24,** 225, 1981.
15. J. E. Ellis, *J. Organomet. Chem.,* **86,** 1, 1975.
16. G. L. Geoffroy, *Acct. Chem. Res.,* **13,** 469, 1980.
17. F. G. A. Stone and C. M. Mitchell, *J. Chem. Soc., Dalton,* 102, 1972.
18. B. F. G. Johnson, J. Lewis, et al., *Chem. Commun.,* 507, 1986.
19. T. V. Ashworth, J. K. Howard, and F. G. A. Stone, *J. Chem. Soc., Dalton,* 1513, 1980; F. G. A. Stone, *Pure Appl. Chem.,* **58,** 529, 1986.

20. M. Green, F. G. A. Stone, et al., *J. Chem. Soc., Dalton,* 869, 1981.
21. (a) M. P. Brown, R. J. Puddephatt, M. Rashidi, and K. R. Seddon, *J. Chem. Soc., Dalton,* 951, 1977; (b) D. M. Hoffman and R. Hoffmann, *Inorg. Chem.,* **20,** 3543, 1983; K. R. Mann, N. S. Lewis, H. B. Gray, et al., *Inorg. Chem.,* **17,** 828, 1978; A. S. Balch, ibid., **98,** 8049, 1978.
22. W. A. Herrmann, *Angew. Chem., Int. Ed.,* **24,** 1062, 1985.
23. D. F. Shriver et al., *Inorg. Chem.,* **13,** 499, 1974.
24. D. F. Shriver et al., *J. Am. Chem. Soc.,* **100,** 5239, 1978.
25. B. F. G. Johnson, J. Lewis, P. R.Raithby, et al., *Chem. Commun.,* 551, 1978.
26. D. H. Farrar, B. G. F. Johnson, J. Lewis, P. R. Raithby, and M. J. Rosales, *J. Chem. Soc., Dalton,* 2051, 1982.
27. R. J. Goudsmit, B. F. G. Johnson, J. Lewis, P. R. Raithby, and K. H. Whitmire, *Chem. Commun.,* 640, 1982.
28. A. J. Deeming and S. Hasso, *J. Organometal. Chem.,* **114,** 313, 1976.
29. A. Mayr and H. D. Kaesz, *J. Organomet. Chem.,* **272,** 207, 1984.
30. A. J. Deeming, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. (A),* 897, 1970.
31. J. R. Shapley et al., *J. Am. Chem. Soc.,* **99,** 5225, 1977.
32. A. J. Deeming and M. Underhill, *J. Chem. Soc., Dalton,* 1415, 1974.
33. C. W. Bradford and R. S. Nyholm, *J. Chem. Soc., Dalton,* 529, 1973.
34. A. J. Deeming et al., *J. Chem. Soc., Dalton,* 1201, 1978.
35. R. B. King and C. A. Harmon, *Inorg. Chem.,* **15,** 879, 1976.
36. (a) J. S. Bradley, *Adv. Organometal. Chem.,* **22,** 1, 1983; (b) R. D. Adams and I. T. Horvath, *Prog. Inorg. Chem.,* 33, 127, 1985; (c) C. P. Casey, *J. Organometal. Chem.,* **400,** 205, 1990.
37. G. Süss-Fink, *Adv. Chem. Ser.,* **230,** 419, 1992; S. A. Laneman and G. G. Stanley, *Adv. Chem. Ser.,* 349, 1992.
38. B. F. G. Johnson, *Chem. Commun.,* 703, 1975; R. E. Benfield and B. F. G. Johnson, *J. Chem. Soc., Dalton,* 1554, 1978.
39. G. Schmid, *Chem. Rev.,* **92,** 1709, 1992.
40. (a) I. Moiseev et al., *Chem. Commun.,* 937, 1985; (b) I. Moiseev, K. I. Zamaraev, et al., *J. Mol. Catal.,* **53,** 315, 1989.
41. C. Larpent and H. Patin, *J. Mol. Catal.,* **44,** 191, 1988.
42. L. N. Lewis, N. Lewis, and R. J. Uriarte, *Adv. Chem. Ser.,* **230,** 541, 1992.
43. L. Fowley, D. Michos, and R. H. Crabtree, *Tetrahedron Lett.,* **34,** 3075, 1993.
44. M. A. Marcus et al., *Phys. Rev.,* **B42,** 3312, 1990.
45. A. Schmid et al., *Angew. Chem. Int. Ed.,* **32,** 250, 1993.

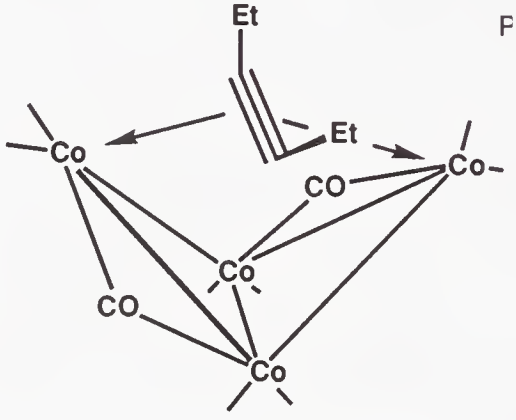
PROBLEMS

1. Given the existence of cyclopropenone, suggest two cluster complexes that are isolobal with this species, and how you might try to synthesize them.

2. Give the cluster electron counts (see Fig. 13.1) of the following: $Cp_3Co_3(\mu_3\text{-}CS)$ $(\mu_3\text{-}S)$; $Fe_3(CO)_9(\mu_3\text{-}S)_2$; $Fe_3(CO)_{10}(\mu_3\text{-}S)_2$. In deciding how to count the S atoms, take account of the fact that these seem to have one lone pair not engaged in cluster bonding, as shown by their chemical reactivity in methylation with Me_3O^+, for example.

3. For the species listed in question 2, how many M—M bonds would you expect for each? Draw the final structures you would predict for these species.

4. $Co_4(CO)_{10}(EtC{\equiv}CEt)$ has structure **A** shown below. What is the cluster electron count? Does it correctly predict the number of M—M bonds? How would you describe the structure on a Wade's rule approach?



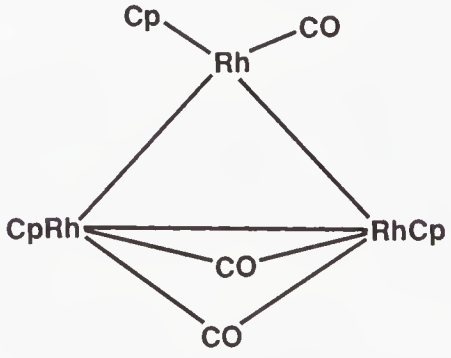
A

$Co_4(CO)_{10}(EtCCEt)$

5. What light do the isolobal ideas throw on structures **B** and **C** (below)?

$Cp_4Fe_4(\mu_3\text{-}CO)_4$

B



C

6. What structures would you predict for $Fe_4(CO)_{13}^{2-}$, $Ni_5(CO)_{12}^{2-}$, and $Cr_2(CO)_{10}(Ph_2PCH_2PPh_2)$?

7. Pt(0) forms an RC≡CR complex $Pt(C_2R_2)_n$. Predict the value of n based on an isolobal relationship with structure **D** (below). Why are the two W—C vectors orthogonal in **D**?

$$\{Cp(CO)_2WCR\}_2Pt$$

D

8. Predict the structure of **E** (below), making it as symmetric as possible. With what organoiron complex is **E** isolobal?

$$Fe(CO)_3\{B_4H_4\}$$

E

9. Why do boron and transition metal hydrides tend to form clusters, when carbon and sulfur hydrides tend to form open-chain hydrides $Me(CH_2)_nMe$, and $HS(S)_nSH$? Why is sulfur able to form clusters in the compounds mentioned in question 2?

10. $Os_3(CO)_{10}(\mu_2\text{-}CH_2)(\mu_2\text{-}CO)$ reacts with CO to give structure **F** (below), which reacts with H_2O to form acetic acid. Suggest a structure for **F**.

$$Os_3(CO)_{12}(CH_2CO)$$

F

CHAPTER 14

APPLICATIONS TO ORGANIC SYNTHESIS

One of the fastest growing areas of organic chemistry is the application of organometallic and coordination compounds to synthetic problems.[1a] Both transition and Main Group elements are involved, and so we take the opportunity to look at some Main Group chemistry here. We saw in Chapter 9 how organometallic chemistry has responded to the challenge of synthesizing organic compounds on an industrial scale. Such commodity chemicals as ethylene or acetic acid are not expensive and so practical syntheses must use catalytic, rather than stoichiometric, amounts of organometallic compounds. The organic compounds we look at now are synthesized on a smaller scale.[1b] These fine chemicals are usually additives, plasticizers, drugs, or other high-value items. Here, stoichiometric quantities of one of the cheaper metal reagents, and in some cases, even of the precious-metal reagents, can be used.

14.1 METAL ALKYLS AND HYDRIDES

Metal alkyls tend to be polarized M^+-R^-, especially for electropositive metals, and so the R group often acts as a nucleophile. By changing metal, we alter the polarization of the bond as we alter the electronegativity of M. LiR is very reactive, as Li is electropositive, but the R group cannot contain halo, keto, or carboxymethyl functionality or RLi will decompose by reacting with itself. For the electronegative Hg, in contrast, R can vary widely and still form a stable species RHgX, but the reactivity of RHgX is much lower than that of RLi. A different reactivity–stability compromise and therefore a different metal may be needed for different applications.

Alkyls QR_n of elements (Q) to the left of carbon are electron-poor in the sense that they have fewer electron pairs than orbitals and the octet is not achieved (LiMe, 2e; RMgX, 4e; $AlMe_3$, 6e), and so they show a strong tendency to associate with themselves (e.g., Al_2Me_6 or Li_4Me_4) or with electron donors (e.g., $Me_2O{:}\rightarrow AlMe_3$). Self-association allows easy exchange of R groups between metals; for example, although $Me_2Al(\mu\text{-}Me)_2AlMe_2$ has two types of methyl group, a single methyl resonance is seen in the proton NMR at room temperature. Elements to the right of carbon are electron-rich, having more electron pairs than orbitals, so they form alkyls $:QR_n$ having one or more lone pairs (PMe_3, 1 lone pair, SMe_2, 2 lone pairs) and act as lone pair donors (ligands). Elements of the carbon group form electron-precise alkyls QR_4 that lack both empty orbitals and lone pairs. This is the origin of the unreactivity of alkanes CR_4.

Lithium and Magnesium The metal alkyls with the longest history of organic applications are the Grignard reagents, RMgX, and alkyllithiums, RLi.[1,2] These act as sources of R^- and are highly reactive carbon nucleophiles toward R'_2CO and RCOOR′, for example. Alkyls of the more electropositive elements, such as Na [Pauling electronegativity (EN): 0.9], are less suitable because they are less stable. Li^+ and Mg^{2+} (EN: Li, 1.0 and Mg, 1.3), as small and therefore highly polarizing ions, also tend to coordinate the substrate, such as a ketone, and polarize it so as to favor nucleophilic attack by the R group. RLi and RMgX are usually very air- and moisture sensitive and are made and used under an inert gas.

Organolithium or organomagnesium reagents are prepared from the metal and an alkyl halide or from an alkylmetal reagent and a compound with a labile X—H proton such as cyclopentadiene and RC≡CH (Eqs. 14.1 and 14.2). Specially activated "Rieke" magnesium is useful for less reactive halides such as vinyl halides and alkyl fluorides.[2b] In Grignard synthesis from Mg and RX, electron transfer to give $RX\bullet^-$ is thought to be followed by loss of X^- and recombination of R• with the surface, which then releases RMg^+.[2c]

$$EtBr + Li \longrightarrow EtLi + LiBr \qquad (14.1)$$

$$EtMgBr + CpH \longrightarrow EtH + LiCp \qquad (14.2)$$

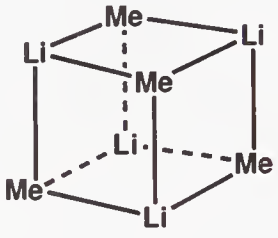
A very useful feature of the deprotonation route is that heteroatoms on the substrate can bind the organolithium reagent and direct the deprotonation to the ring C—H bond ortho to the heteroatom. For example, —OMe, $—CONMe_2$, $—NMe_2$, $—SO_2Me$, and even —F substituents on a benzene ring act in this way:

(14.3)

Organolithium reagents and aryl bromides and iodides tend to undergo metal–halogen exchange (Eq. 14.4):

(14.4)

Organolithium reagents are oligomers (i.e., dimers, trimers, and higher species) in nondonor solvents such as alkanes: LiMe is a tetramer with a cubane structure **14.1**, for example. $\{RLi\}_n$ forms solvates with THF. Addition of the chelating ligand $Me_2NCH_2CH_2NMe_2$ (TMEDA) leads to formation of a monomer, and this increases the reactivity. *n*-BuLi can deprotonate toluene



14.1

to form $PhCH_2Li$ only if TMEDA is present. The organomagnesium reagents are usually prepared from the alkyl or aryl halide and magnesium metal in ether or thf. The products are not usually isolated, but used directly in the ethereal solvent. Their constitution has been a subject of debate for many years, but the Schlenk equilibrium (Eq. 14.5) probably describes the situation well in most cases. The addition of dioxan complexes and precipitates the MgX_2 and leaves R_2Mg in solution.

$$2RMgX \rightleftharpoons R_2Mg + MgX_2 \tag{14.5}$$

The following are some of the numerous classical reactions of Grignard reagents:[1,2]

$$RMgX + R'R''C{=}O \longrightarrow RR'R''C{-}OMgX \xrightarrow{\text{hydrolysis}} RR'R''C{-}OH \tag{14.6}$$

(R′ and R″ = aryl, alkyl, or H)

$$RMgX \xrightarrow[\text{(ii) hydrolysis}]{\text{(i) ethylene oxide,}} RCH_2CH_2OH \tag{14.7}$$

$$2RMgX + R'COOEt \longrightarrow R_2R'C{-}OMgX \xrightarrow{\text{hydrolysis}} R_2R'COH \tag{14.8}$$

$$RMgX + CO_2 \longrightarrow RCO_2MgX \xrightarrow{\text{hydrolysis}} RCO_2H \tag{14.9}$$

An alternative pathway via a single-electron transfer mechanism has also been invoked in some cases (Eq. 14.10).[2d] Chiral auxiliaries such as binaphthols can make Grignard and related reactions asymmetric:[2c]

$$RMgX + R_2CO \longrightarrow R\bullet + R_2CO\bullet^- + MgX^+ \longrightarrow R_3COMgX \quad (14.10)$$

While organomagnesium reagents only very rarely add to C=C double bonds, EtLi can add to dienes. The resulting allyllithium can continue adding to further diene molecules in the *anionic polymerization* reaction.

Boron and Aluminum Organoboranes are of special importance because they are easily formed in borane addition to C=C bonds (*hydroboration*). The high electronegativity of B (2.0) means that the B—C bond is not very polar and BR_3 species are usually water-, although not air-stable but sufficiently reactive to be useful. In contrast to most other reagents, a B—H bond adds in an anti-Markownikov manner to an alkene to give the corresponding organoboron reagent (Eq. 14.11). This can be converted to a variety of useful organic compounds (e.g., alcohols, alkanes, and alkyl bromides; Eqs. 14.12–14.14) in a subsequent step. This hydroboration procedure has an important place in organic synthesis:[3]

$$RCH{=}CH_2 + [BH_3]_2 \longrightarrow (RCH{-}CH_2)_3B \quad (14.11)$$

$$(RCH{-}CH_2)_3B + H_2O_2 \longrightarrow RCH{-}CH_2OH \quad (14.12)$$

$$(RCH{-}CH_2)_3B \xrightarrow{\text{acid}} RCH{-}CH_3 \quad (14.13)$$

$$(RCH{-}CH_2)_3B \xrightarrow{Br_2,\ \text{base}} RCH{-}CH_2Br \quad (14.14)$$

Organoaluminum reagents are important in Ziegler–Natta catalysts (Section 11.5), but are not widely used in organic synthesis. They can be violently pyrophoric and water-sensitive and can add readily to alkenes. The *Aufbau* reaction (Eq. 14.15) is a commercial synthesis of C_{12}–C_{16} linear alcohols that are useful in detergents.

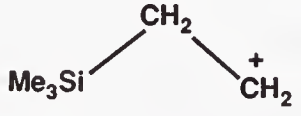
$$AlEt_3 + 3nC_2H_4 \longrightarrow Al\{(C_2H_4)_nEt\}_3 \xrightarrow{O_2}$$
$$Al\{OC_2H_4(C_2H_4)_{n-1}Et\}_3 \longrightarrow HOC_2H_4(C_2H_4)_{n-1}Et \quad (14.15)$$

Trimethylaluminum is a methyl-bridged dimer Al_2Me_6. In contrast to transition metals, the bridge contains Al—C—Al bonds only and is not agostic, presumably because the metal is incapable of back donation into the C—H σ^*. The small Al—C—Al angle at the bridging C suggests a direct Al—Al interaction similar to the M—M bonding present in M—H—M transition metal systems. NMR studies in solution show bridge–terminal alkyl exchange. In alkylaluminum hydrides, such as $[Me_2AlH]_3$, the hydrides prefer the bridge positions.

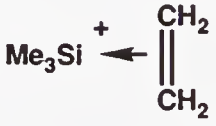
Up to now we have looked at metal alkyls from groups to the left of carbon (RLi, R_2Al, . . .). These are electron-deficient as monomers (RLi, 2e; R_3B, 6e) and are commonly found as dimers or polymers. As electron-precise (8e, all bonding) species, R_4Si are monomeric and do not coordinate extra ligands as avidly as the electron deficient alkyls.

Si, Ge, Sn, and Pb Organosilicon reagents[4] are of special importance in organic synthesis because they share some but not all of the properties of alkanes. The Si—C bond is strong and relatively nonpolar, and SiR_4, like CR_4, is electron precise so the reagents are stable and are not strong nucleophiles. Their usefulness is a result of a number of special properties: (1) the R_3Si—O (108 kcal/mol) and R_3Si—F (135 kcal/mol) bonds are unusually strong, (2) the "$SiMe_3^+$" group behaves like a proton that can be readily cleaved from carbon, and (3) Si stabilizes a carbonium ion in the β position. The first property is a result of the R_3Si group being an electron acceptor. This is clearly shown in the bond angles of silicon compounds such as Me_3Si—O—$SiMe_3$ (Si—O—Si = 148°). This is far larger than the sp^3 angle of Me—O—Me (109°) because there is partial O—Si double-bond character that in the extreme would lead to a linear molecule.

The acceptor orbital on the Me_3Si group is the Si—Me σ*, just as we saw for PR_3 in Fig. 4.3. The third property is an interesting one and its origin is still debated, but one possibility is that the "carbonium ion" (**14.2**) has some of the character of an alkene complex of a Si cation (**14.3**). Equation 14.18 shows how electrophilic cleavage of a $SiMe_3$ (= TMS) group can occur with retention of configuration and so be used in the stereospecific cleavage of a vinylsilane by DCl.

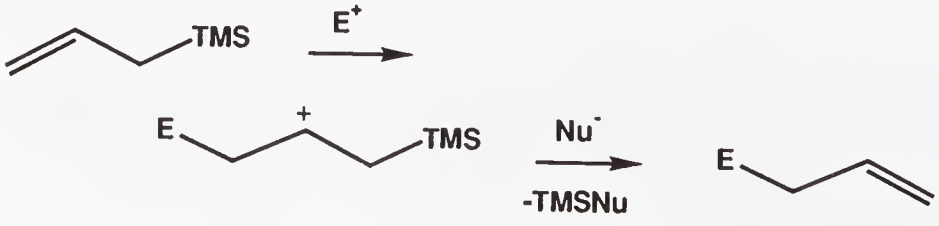


14.2



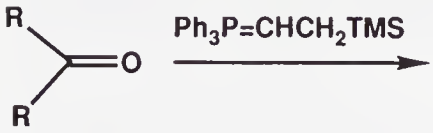
14.3

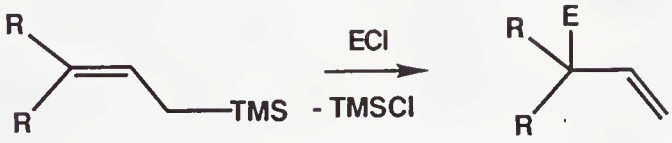
The stabilization of a β-carbonium ion is also involved in the reaction of an allylsilane with an electrophile (Eq. 14.16). An advantage of silicon over other metals in this context is that it does not undergo 1,3 shifts, and so the point of attachment of the electrophile can be reliably predicted (Eq. 14.17).[3,5] This β stabilization of the carbonium ion also has stereochemical implications; Eq. 14.18 shows how the stereochemistry of a vinylsilicon reagent can be retained on protonation. A TMS group on carbon has been described as a



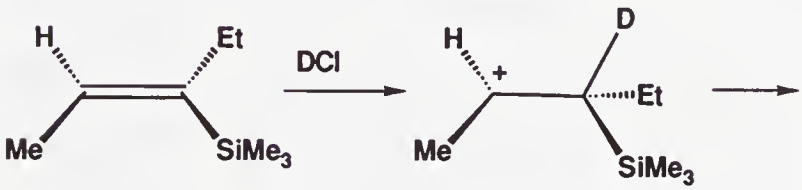
(14.16)

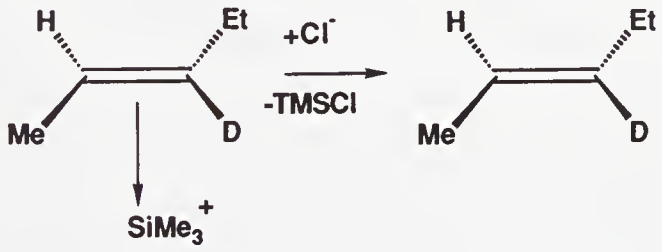
"superproton" in that it leaves easily, especially with fluoride ion as nucleophile (Eq. 14.19) consistent with the high Si—F bond strength.





(14.17)

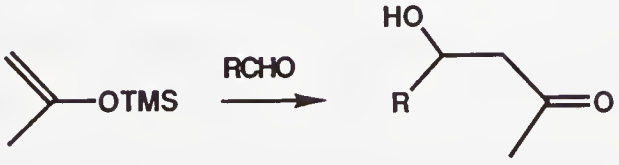




(14.18)

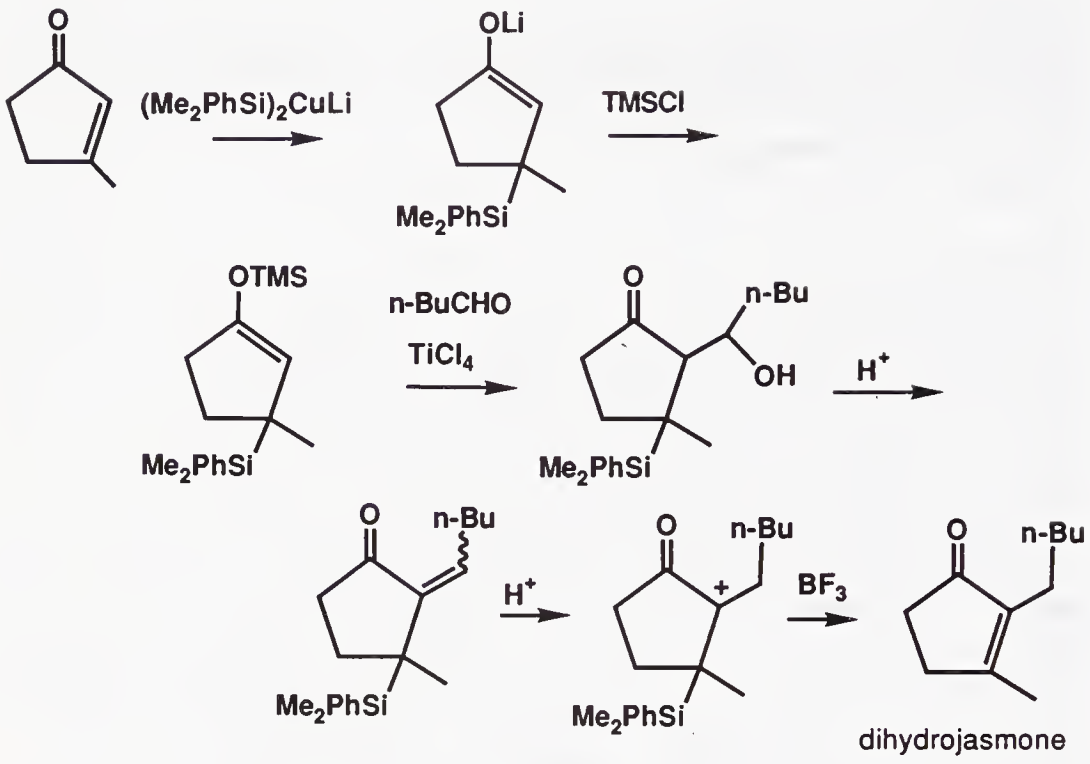
$$PhCHCl—C(SiPh)=CH_2 \xrightarrow{KF} PhCH=C=CH_2 + Ph_3SiF + KCl \quad (14.19)$$

The fact that Si—O bonds are strong is used in stabilizing enol forms of various carbonyl compounds. Generally, a base such as *i*-Pr_2NLi (LDA) is used to deprotonate the carbonyl compound, and Me_3SiCl then gives the silyl enol ether, which can react with a wide variety of carbon electrophiles, such as aldehydes, ketones, 3° alkyl halides, and α,β-unsaturated ketones, for example:



(14.20)

A synthesis of dihydrojasmone that uses some of these principles is shown in Eq. 14.21:[6]



(14.21)

Expansion of the octet is seen in Si, Ge, Sn, and Pb, especially for the larger elements with electronegative substituents, such as the 14e species[4b] Cp^*_2Si and the 18e $SnCl_6^{2-}$. The *double-bond rule*, by which elements of the second row and beyond do not tend to form p_π–p_π double bonds, has been increasingly shaken in recent years by the synthesis of compounds with Q=C and Q=Q double bonds (Q = Si, Ge, Sn). Normally, $R_2Si{=}SiR_2$ tends to polymerize to $(R_2Si)_n$, but if the R groups are large enough, this can be inhibited sterically: $R_2Si{=}SiR_2$ can be isolated with R = mestityl and similar groups.[4c] Cationic Si in R_3Si^+ is very unfavorable, so nucleophilic displacement of a group at Si never goes by an S_N1 route, but by attack at Si (S_N2). This can take place with or without inversion because the 5-coordinate intermediate is fluxional by the Berry process (Eq. 10.2).

The most important application of organostannanes is the initiation of radical reactions with *n*-Bu_3Sn-H, such as the replacement of halide (X) by H shown below:

$$R_3Sn{-}H \longrightarrow R_3Sn\bullet + H\bullet \text{ (initiation)} \qquad (14.22)$$

$$R_3Sn\bullet + RX \longrightarrow R_3SnX + R\bullet \text{ (chain propagation)} \qquad (14.23)$$

$$R\bullet + R_3Sn{-}H \longrightarrow R_3Sn\bullet + RH \text{ (chain propagation)} \qquad (14.24)$$

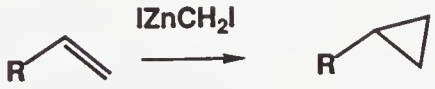
Lead alkyls such as $PbEt_4$ with their weak Pb—C bonds (~36 kcal/mol) were used in gasoline to promote combustion by thermolytic release of Et• radicals, but environmental concerns have led to its abandonment in many places.

Zinc Organozinc reagents are usually prepared from RLi or RMgX and $ZnCl_2$ or from RI and Zn. R_2Zn is monomeric, but bases readily associate, for example, $R_2Zn(TMEDA)$. In the Reformatsky reaction (Eq. 14.25) the Zn—C bond is sufficiently unreative to tolerate the ester group of the substrate, but sufficiently reactive to nucleophilically attack the ketone.

$$BrCH_2COOR \xrightarrow{\text{(i) Zn (ii) } Me_2CO\text{, (iii) } H^+} Me_2C(OH)CH_2COOR \quad (14.25)$$

In the Simmons–Smith reaction, the zinc forms a carbenoid reagent (Eq. 14.26), which acts as a carbene equivalent in the cyclopropanation of Eq. 14.27.

$$CH_2I_2 + Zn(Cu) \longrightarrow IZnCH_2I \quad (14.26)$$



(14.27)

Mercury Organomercury reagents[7a] are of interest because the Hg—C bond is relatively nonpolar, so that the compounds are much less reactive than the Group 1 and 2 alkyls, but more closely resemble organosilicon compounds. Most organomercurials are stable to water and even to acids. This means that a much wider variety of organic functionality can be incorporated into the R group than is the case for the organolithiums or magnesiums.

$$PhCHBrCO_2R \xrightarrow{Hg,\ h\nu} PhCH(HgBr)CO_2R \quad (14.28)$$

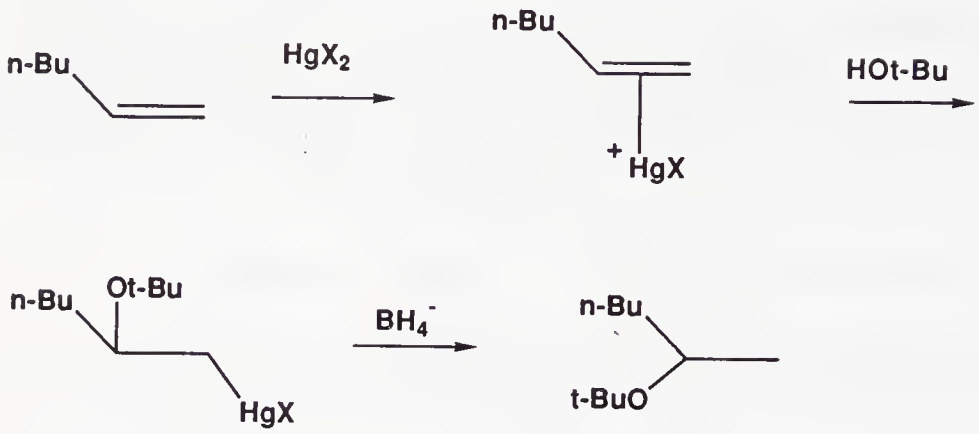
The direct mercuration of arenes by electrophilic attack with $Hg(OAc)_2$ or $HgCl_2$ is perhaps the most useful synthetic route.

$$C_6H_6 \xrightarrow{\text{(i) } Hg(OAc)_2\text{, (ii) NaCl}} PhHgCl \quad (14.29)$$

Another useful preparative procedure is transalkylation from the corresponding organoborane, which can be prepared from the alkene (see also below).

$$RCH{=}CH_2 \xrightarrow{B(OR)_2H} RCH_2CH_2B(OR)_2 \xrightarrow{HgCl_2} RCH_2CH_2HgCl \quad (14.30)$$

Oxymercuration of alkenes probably involves formation of a cationic alkene complex, which undergoes nucleophilic attack by solvent (Eq. 14.31) and gives the Markownikov product and so complements Eq. 14.30.



(14.31)

Organomercurials give the reactions shown in Fig. 14.1. Halogenation is useful not only to prepare organic halides but also to determine the position of attachment of the mercury atom in the original compound. Mercury-bound R groups are easily transferred to Pd, and if they resist β elimination, can be used in a variety of transformations shown in Fig. 4.1.

The relatively low reactivity of the RHgX reagent is shown by acylation with RCOCl; this gives a ketone that is stable to further attack by the organometallic species. The organomercury reagents with their very weak Hg—C bonds are a useful source of radicals. Once the first R• is released, the remaining R is very weakly bound (Eq. 14.31) and so both radicals are effectively released at the same time.

$$HgMe_2 \xrightarrow{\Delta H\ 51\ \text{kcal/mol}} Me\bullet + \bullet HgMe \xrightarrow{\Delta H\ 7\ \text{kcal/mol}} 2Me\bullet + Hg$$

(14.32)

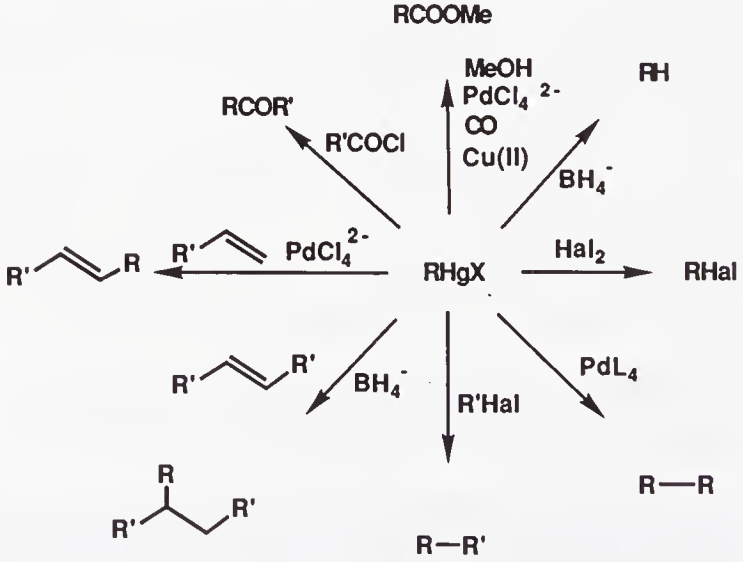


FIGURE 14.1 Some reactions of organomercury compounds.

Mercury also gives the synthetically useful transformation of R—H to R_2 in the Mercat reaction[7b] (Eqs. 12.37 and 12.39); the weakest C—H bond in the molecule is selectively cleaved. The product shown in Eq. 14.33 is a useful ligand, but very difficult to make by conventional routes.

$$Me_2CHNH_2 \xrightarrow{Hg,\ NH_3,\ h\nu} H_2N\text{-}CMe_2CMe_2\text{-}NH_2 \qquad (14.33)$$

Copper Although copper is a transition metal, it is sufficiently far to the right in the Periodic Table so that it begins to show Main Group characteristics, especially in the d^{10} Cu(I) state. Organocuprates $Li[CuR_2]$,[8] prepared by reaction of the organolithium compound with a Cu(I) salt such as CuI, do not β-eliminate and are sufficiently nucleophilic, thanks to the net anionic charge, to attack a usefully wide variety of organic electrophiles. The structures of these reagents is still a matter of discussion, but oligomeric forms are likely to be present. As shown in Eq. 14.34, the reagents suffer from the disadvantage that only one of the two R groups is transferred to the electrophile, E. The electrophile may be an alkyl iodide, or even a vinyl halide (Eq. 14.35), for which most nucleophiles are ineffective; perhaps the extra activating effect of the copper reagent comes from the coordination by the metal of the halide (Section 12.4) or of the C=C group of the vinyl halide.

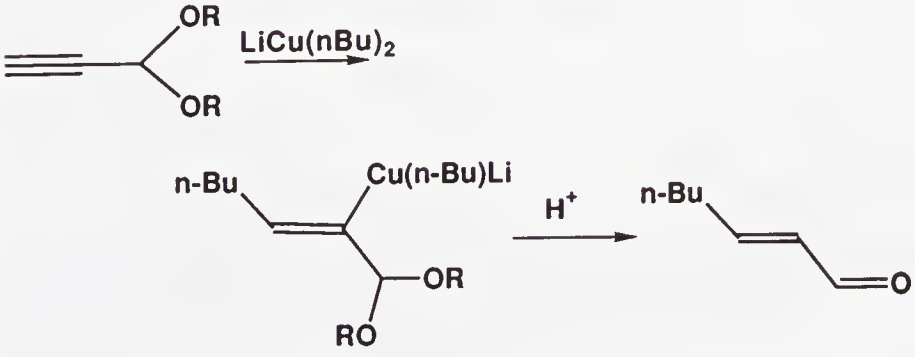
$$2LiR + CuI \xrightarrow{-LiI} Li[CuR_2] \xrightarrow{E} R—E + CuR + LiI \qquad (14.34)$$

$$\textit{trans}\text{-}PhCH{=}CHBr \xrightarrow{LiCuMe_2} \textit{trans}\text{-}PhCH{=}CHMe \qquad (14.35)$$

One of the most important applications of organocuprates is their addition to α,β-unsaturated carbonyl compounds, in which exclusive 1,4 addition is observed.

$$R'CH{=}CH—COOEt \xrightarrow{LiCuMe_2} R'CHMe—CH{=}C(OLi)OEt \xrightarrow{hydrolysis} R'CHMe—CH_2COOEt \qquad (14.36)[9]$$

With alkynes, insertion is observed to give a vinyl cuprate, which can then be quenched with an electrophile (Eq. 14.37).[10]



(14.37)

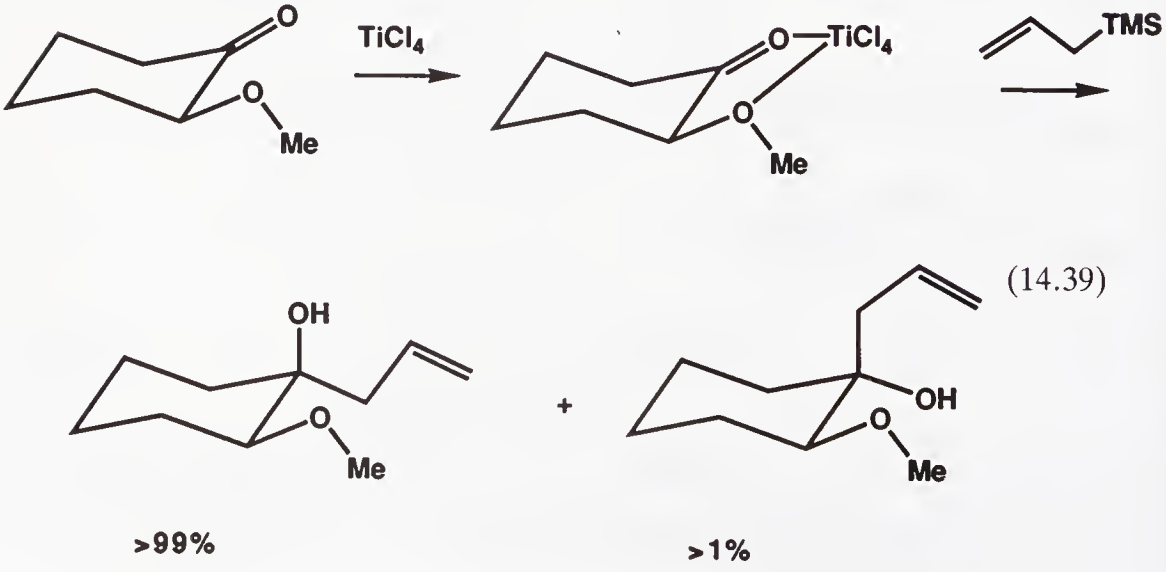
Ti and Zr Alkylmetal reagents are now available for a wide range of other metals, and some of these show useful selectivity. Grignard-like behavior implies the presence of a nucleophilic alkyl and therefore of an electropositive metal, so it is not surprising that the *f*-block and the very early transition metals have been most used. The later metal alkyls form less nucleophilic alkyls. Titanium reagents, such as $MeTiCl_3$, can be formed from Me_2Zn and $TiCl_4$. They are very selective in their nucleophilic additions to organic carbonyl compounds. While LiMe attacks a 50:50 mixture of an aldehyde and a ketone unselectively, $MeTiX_3$ can give >99% attack at the aldehyde. X = O*i*-Pr gives one of the highest selectivities in this reaction. The propoxide reagent is made by adding RMgX to $Ti(O\textit{i}\text{-}Pr)_4$, and one reason for its ready acceptance is that no special techniques other than those familiar from Grignard chemistry are required.

$$\text{RCHO} + \text{R}_2\text{CO} \xrightarrow{\text{X}_3\text{TiMe}} \text{RMeCHOH} + \text{R}_2\text{MeCOH} \qquad (14.38)$$

X = O*i*-Pr	>99%	<1%
X = NMe_2	2%	98%

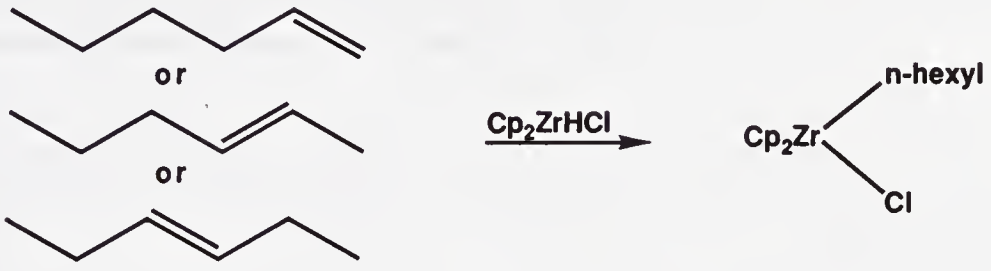
Changing X from O*i*-Pr to NMe_2 has the remarkable effect of reversing the selectivity. The reason appears to be that the NMe_2 groups are transferred to the aldehyde to protect it as $RCH(NMe_2)_2$. The alkyl then attacks the normally less reactive ketone to give the product.[11a,b]

A noteworthy feature of these reagents is that β elimination does not interfere under the conditions normally used (<0°C); we saw in Chapter 3 how d^0 metals, having no *d* electrons for back donation into the σ* orbital of the β-C—H bond, can be slow to β-eliminate. The titanium is a strong Lewis acid, especially where X is Cl. This means that the titanium can bind to a chelating substrate in such a way as to bias the direction of attack of the alkyl. This example (Eq. 14.39) also shows how the alkyl is introduced in the form the silicon reagent, and is subsequently transferred to the titanium.[11c]

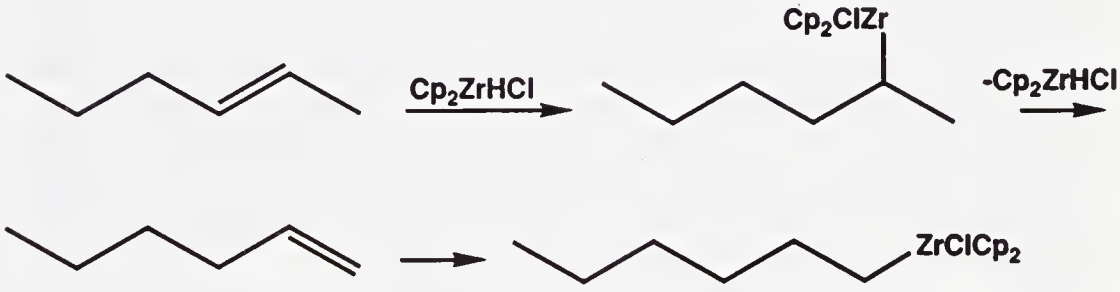


(14.39)

In hydrozirconation with Schwartz's[12] reagent, Cp_2ZrHCl, addition to alkenes leads to the anti-Markovnikov alkyl (Eq. 14.40). Remarkably, 1-, 2-, and 3-hexene all give the same *n*-hexyl product. The reason must be that the initially formed alkyls β-eliminate. This moves the C=C bond along the chain in an alkene isomerisation reaction (Section 9.1), until the least hindered and thermodynamically most stable *n*-hexyl complex is formed (Eq. 14.41):



(14.40)



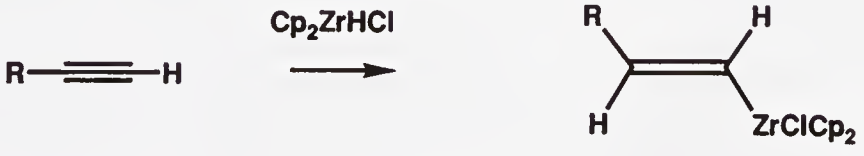
(14.41)

In hydroboration, in contrast, no isomerization is observed. Not only can the 16e alkylzirconium species be converted into the same products that an organoboron compound would give, but under CO an insertion takes place to give the acyl. This acyl can subsequently be converted into a variety of organic carbonyl compounds, such as the acyl halides by halogen oxidation, or the ester by bromine oxidation in an alcohol solvent.

$$Cp_2ZrRCl \xrightarrow{CO} Cp_2Zr(COR)Cl \xrightarrow{Hal_2 \text{ or } Br_2,\ MeOH} RCOHal \text{ or } RCOOMe$$

(14.42)

Addition to an alkyne takes place stereospecifically to the cis vinyl complex:



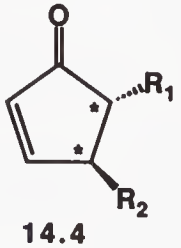
(14.43)

Most of the metals covered in this Section are also available in finely divided, highly active forms that are sometimes useful for synthetic applications.[2b]

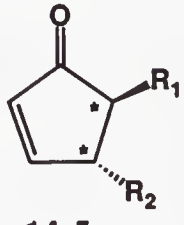
14.2 REDUCTION, OXIDATION, AND CONTROL OF STEREOCHEMISTRY

Organometallic compounds tend to be reducing in character and so tend to be applied in reduction. High-valent coordination compounds tend to be used in oxidation. Even in oxidation the intermediacy of species with M—C bonds has been proposed, which makes it difficult to maintain the somewhat artificial distinction between organometallic and coordination compounds in this area.

It is in the area of oxidation and reduction that directed and asymmetric reactions have been most successful. Organic synthesis is vitally concerned with the stereochemical outcome of a given reaction. A typical synthetic target (e.g., **14.4**; the cyclopentenone ring of prostaglandin A) will have more than one asymmetric (or stereogenic) center; these are starred in **14.4**. In a racemic synthesis, still the most common, the racemate of the target is formed, in this case **14.4** and **14.5** in a 50:50 mixture. The stereocenters have the right relative configuration but the compound is not a single enantiomer as in the natural product itself. In such a synthesis we will need reactions that selectively create new asymmetric centers with a defined stereochemistry with respect to preexisting centers. In recent years, increasing emphasis has been laid on asymmetric syntheses in which both the relative and absolute configurations of the target molecule are reproduced. If the target is a drug, then we prefer to synthesize the active enantiomer only. In this way, we avoid giving the patient the inactive enantiomer along with the active drug.



14.4

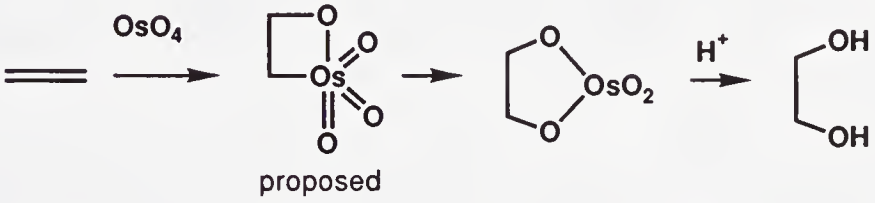


14.5

Directed and Asymmetric Oxidation The traditional method of asymmetric synthesis involves modifying the substrate with a resolved chiral auxiliary and finding a reagent that introduces an asymmetric center in a defined way relative to the auxiliary. The auxiliary is then removed, ideally leaving a single enantiomer of the product. This method requires a mole of auxiliary per mole of product formed. A more sophisticated approach is to mimic Nature's own solution: the use of an enantiomerically pure catalyst. In this case the handedness of the product is decided by the handedness of the catalyst, and only a small amount of resolved catalyst produces a large amount of asymmetric product.

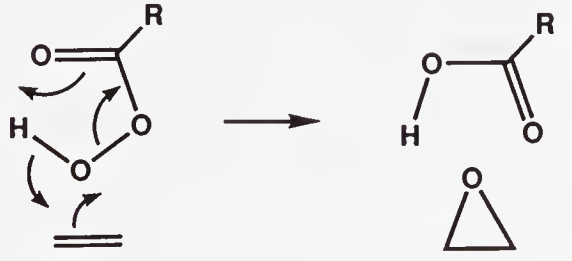
OsO_4 is the best reagent for the *cis*-dihydroxylation of alkenes. Sharpless[13a] has proposed that an organometallic species is an intermediate, as shown in Eq. 14.44. Of great practical importance, use of a chiral amine as L with an

unsymmetric alkene (RCH=CHR′) can lead to high asymmetric induction in the product diol. One enantiomer predominates as measured by the enantiomeric excess (e.e.) of the reaction. The percent e.e. is defined on p. 217. It is most convenient to carry out the reaction with catalytic quantities of osmium and excess *N*-methylmorpholine N oxide to reoxidize the Os back to Os(VIII).[13b] Free OsO_4 reacts with 0% e.e., so we need a system in which reaction via [L*OsO_4] is preferred. This is the case here because the chiral amine strongly promotes the oxidation rate.



(14.44)

The Sharpless[13c] epoxidation provides good examples of both directed and asymmetric catalytic reactions. It has long been known that alkenes can be epoxidized with peracids, which deliver an electrophilic oxygen atom, as shown in Eq. 14.45. Sharpless showed that alkyl hydroperoxides in the presence of high-valent metal catalysts, such as $VO(acac)_2$, can also epoxidise alkenes. Equation 14.46 shows a suggested mechanism for the Sharpless reaction; comparison with Eq. 14.45 shows the mechanistic analogy between the two processes: just as RCOOH is a good leaving group in the first case, departure of ROH and an M=O group delivers the electrophilic oxygen in the second. The oxophilicity of the early metals used as catalysts clearly plays a role in stabilizing the M=O group.

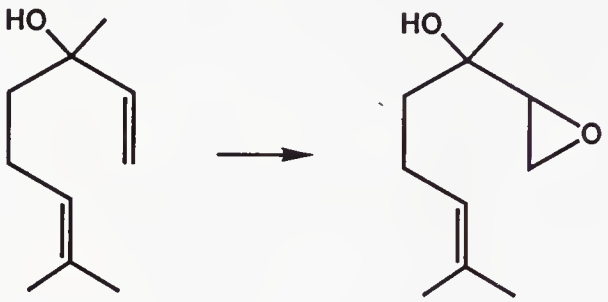


(14.45)

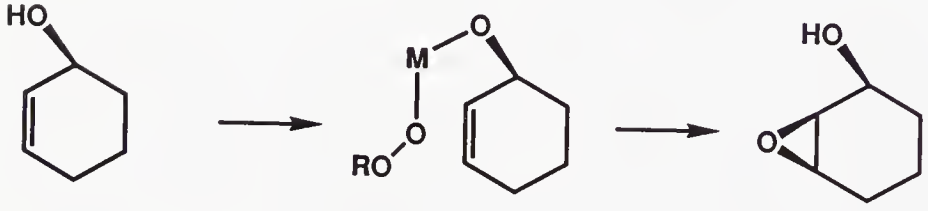
(14.46)

Normally, the most electron-rich, and therefore the most highly alkyl-substituted, alkene reacts first, but the vanadium catalyst shows strong di-

recting effects that allow the catalyst to overcome the usual selectivity order if an allylic or homoallylic —OH group is present (e.g., Eq. 14.47).[13d] In cyclic compounds the stereochemistry of the final epoxide is determined by the directing effect of the —OH group to which the catalyst binds (Eq. 14.48). Peracids tend to give the other isomer of the product, by a simple steric effect.

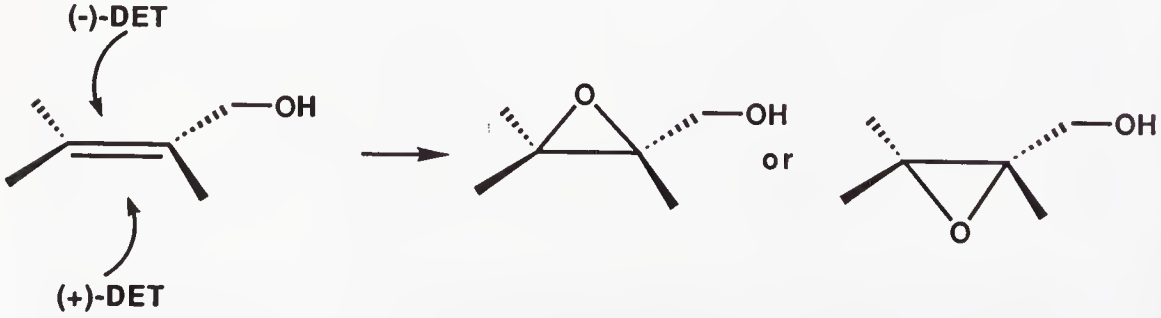


(14.47)



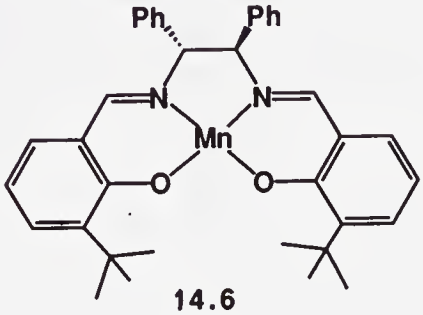
(14.48)

One of the most useful applications of the chemistry of transition metals in organic synthesis is the Sharpless asymmetric epoxidation.[13e] By using one or other enantiomer of diethyl tartrate (DET) as a ligand, Ti(IV) as the catalyst, and *t*-BuOOH as the oxidant, allylic alcohols can be epoxidized to give chiral epoxy alcohols of *predictable* stereochemistry. The product stereochemistry observed for each enantiomer of DET used as ligand is shown in Eq. 14.49. This means that the stereochemistry of the reaction is imposed by the reagent ("reagent control"), rather than the much more common situation in which it is a result of the substrate structure and conformation ("substrate control"). The attractive features of the system are the simplicity of the reagents used and the synthetic versatility of the epoxy alcohols obtained.



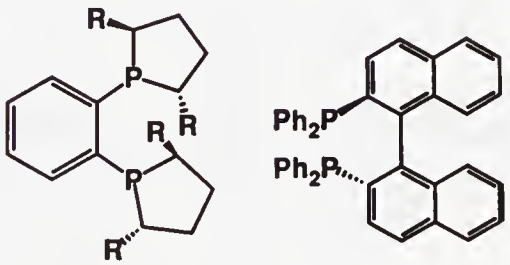
(14.49)

Jacobsen[15] has found a system using **14.6** that catalyzes asymmetric epoxidation of alkenes with ArIO as oxidant and does not require that the substrate contain a hydroxy group. For example, Z—PhCH=CHMe is converted to the epoxide with an 84% e.e.

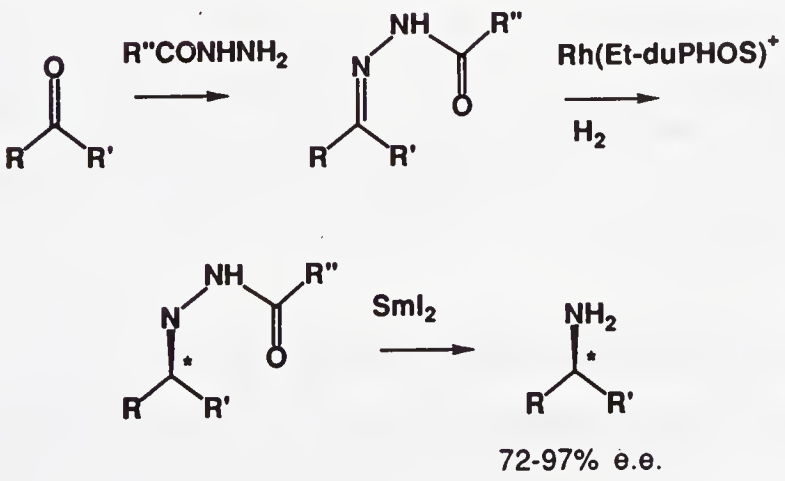


14.6

Directed and Asymmetric Reduction The principles of directed and asymmetric reactions were first developed for hydrogenation, as discussed in Section 9.2. Asymmetric hydrosilation of ketones can now be carried out catalytically with rhodium complexes of diop (**9.22**). The new chiral ligand Et-duPHOS, made by Burk[16] at du Pont, allows chiral amination of ketones via Eq. 14.50. Note how the use of the hydrazone generates an amide carbonyl to act as a ligand, as is known to favor high e.e. (see Section 9.2). Noyori's[17] powerful BINAP ligand has been applied to a large number of asymmetric reactions.



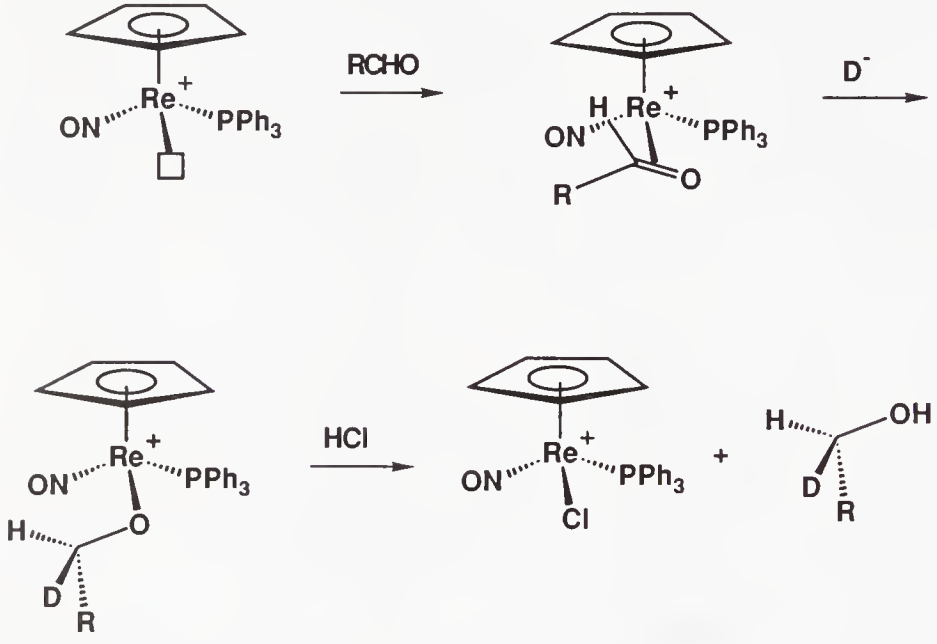
duPHOS **BINAP**



(14.50)

72-97% e.e.

Chiral metal complexes can also act as auxiliaries. In this case the reaction is stoichiometric, not catalytic. Gladysz[18a] has shown how aldehydes can be reduced to alcohols with high asymmetric induction by using the system shown in Eq. 14.51. Here the chirality is based on the metal, not on a ligand such as diop. The aldehyde substrate binds in the η^2 form with the C=O bond lined up with the Re—PPh_3 bond as shown to avoid competition of the C=O π^* with the strong π-acceptor NO for metal d_π electrons. The aldehyde prefers to have the small proton rather than the bulky R group pointing toward the Cp ring and the small =O group rather than the bulky RCH= toward the PPh_3 ligand and so is now set up to allow attack of a nucleophile such as D^- from only one of the two faces of the aldehyde, the one facing away from the metal; this gives a single enantiomer of the product. Davies[18b] has developed the chiral [CpRu(PROPHOS)X] auxiliary, in which the chirality is present on the diphosphine ligand.



(14.51)

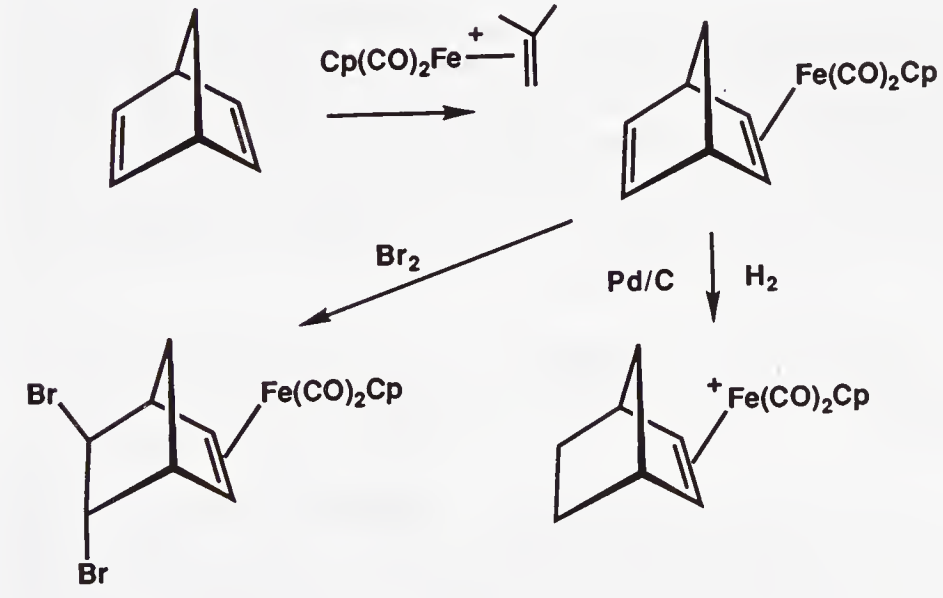
Even though borane addition to alkenes happens without a catalyst, the catalytic version is important because it has usefully different chemo-, regio- and stereoselectivities (Section 9.5).[18c] Enantiomeric excesses as high as 96% can be obtained with a Rh({R}-binap)$^+$ catalyst in the conversion of norbornene to *exo*-norborneol,[18d] and additions to allylic alcohols which give a 10:90 ratio of syn:anti product in the absence of a catalyst switch to a 96:4 ratio with Wilkinson's catalyst.[18e]

14.3 PROTECTION AND DEPROTECTION

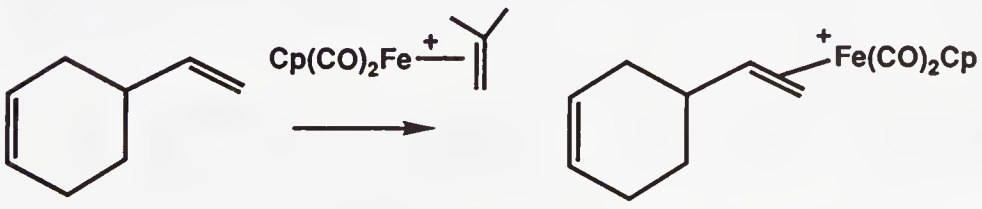
One role that a metal reagent plays is simply to act as a protecting group. Conventional protection works best for heteroatom functionalities, but alkene

alkyne, diene, and arene groups are perhaps best protected by organometallic reagents.

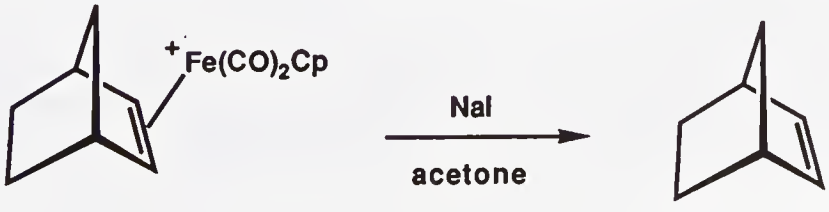
Cyclopentadienyliron Alkene Reagents The best-known reagent for alkenes is the $Cp(CO)_2Fe$ fragment, which is often designated simply as Fp (pronounced "fip"). Rosenblum[19] has shown how the isobutylene group in $Fp(CH_2{=}CMe_2)^+$ can be displaced by less bulky alkenes to give the Fp complex of the new alkene, which protects it from hydrogenation and from electrophilic attack. Protection of norbornadiene in Eq. 14.52 allows clean bromination without the usual carbonium ion rearrangements taking place.[20a] If there are several C=C double bonds in a molecule, the Fp group selectively complexes the least hindered or the most strained (Eq. 14.53).[20a] Such C=C groups are usually the most reactive, and so it is particularly useful to be able to protect them selectively. Deprotection takes place readily with iodide ion in acetone (Eq. 14.54):[19]



(14.52)

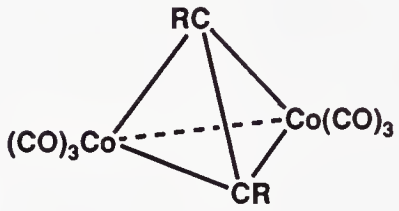


(14.53)



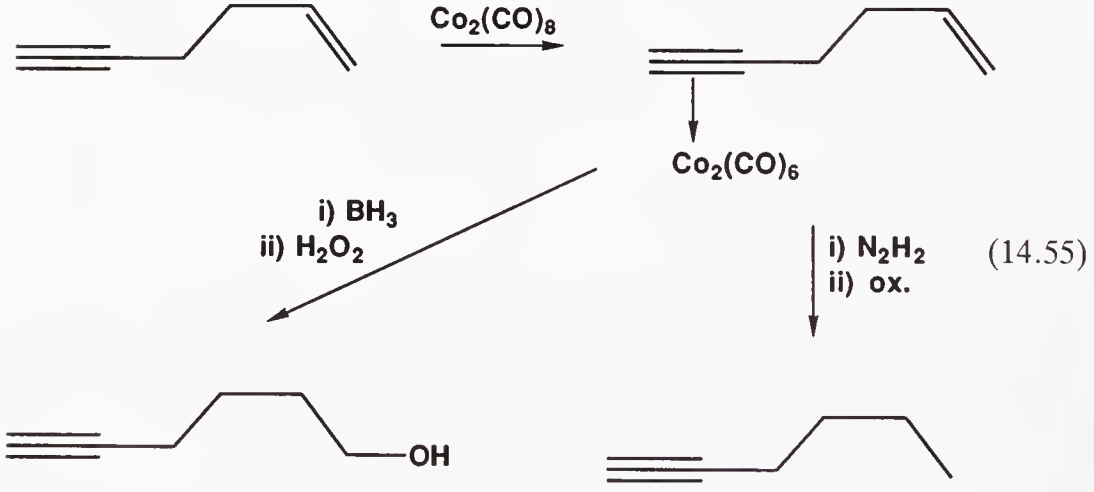
(14.54)

Alkyne Cobalt Carbonyl Alkynes are protected as the tetrahedrane-like clusters **14.7**.[21] In this case, deprotection is carried out oxidatively with a reagent such as $FeCl_3$, or Et_3NO; as we saw in Section 4.3, oxidation often



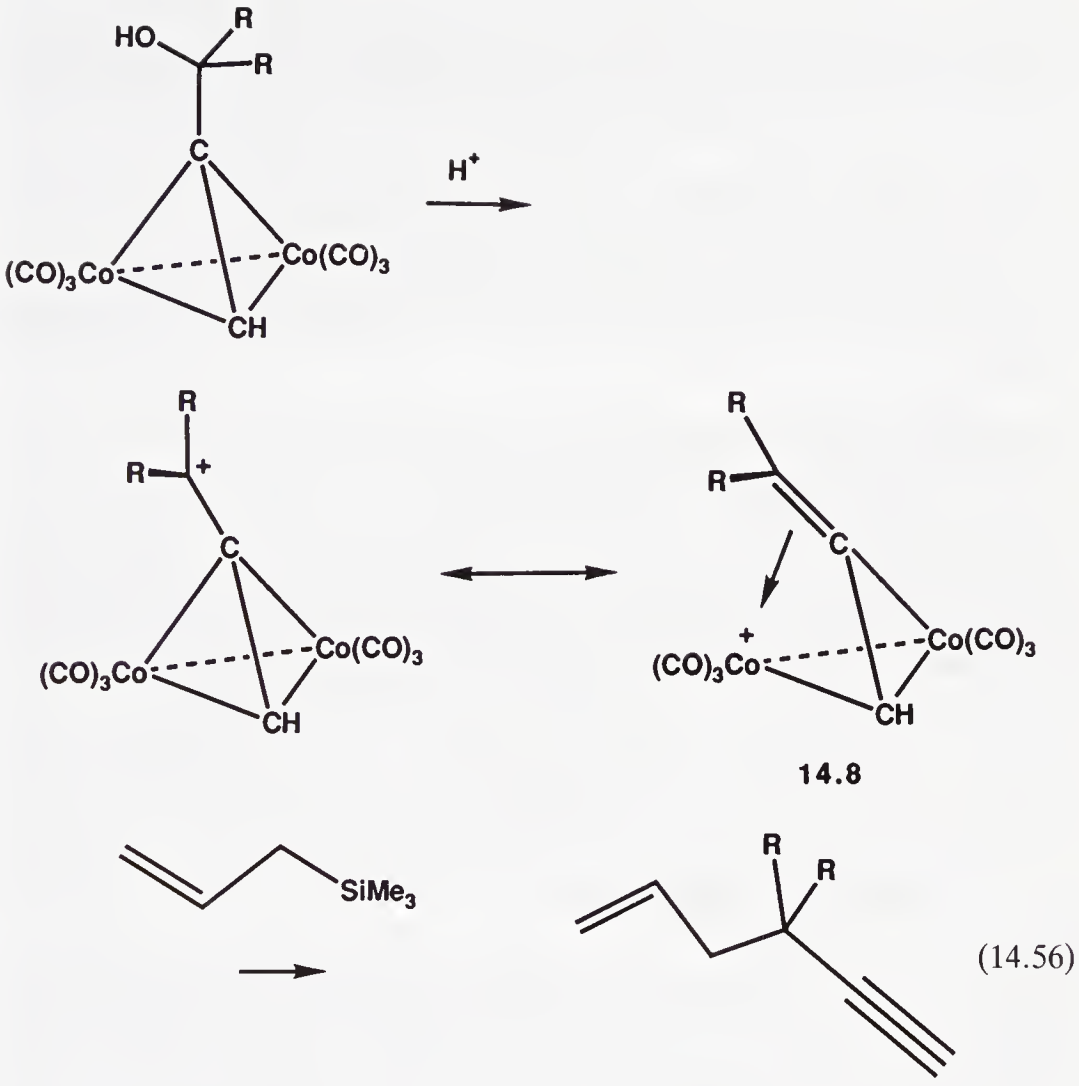
14.7

increases substitution rates at metal complexes and also reduces back donation to an unsaturated ligand, like an alkyne, which now dissociates more easily. The protecting group binds a C≡C selectively over a C=C group, and the complex is stable to the conditions required for the conversion of any free C=C group in the molecule to an alcohol by acid-catalyzed hydration or by hydroboration–oxidation, and to an alkyl group by diimine reduction (Eq. 14.55):[20b]



(14.55)

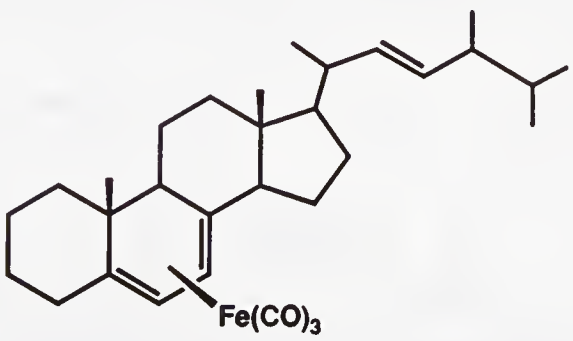
Nicholas[20c] has shown how carbonium ions alpha to the alkyne carbon are stabilized in the Co complex and can react with a variety of nucleophiles, such as the allylsilane in Eq. 14.56. The positive charge is probably stabilized by delocalization into the cluster by some such resonance form as **14.8**.



14.8

(14.56)

Diene Iron Carbonyl Dienes are most commonly protected with the $Fe(CO)_3$ group. Once again, an oxidative deprotection step with $FeCl_3$ is often used. One important application is the protection of a diene in the B ring of certain steroids (e.g., **14.9**). Under these circumstances, the side chain



14.9

C=C groups can be successfully converted into a number of useful derivatives by osmylation, hydroboration, or hydrogenation, without affecting the diene.[22]

Arene Chromium Carbonyl Arenes are generally protected with the $Cr(CO)_3$ group, but as this complexation leads to a number of other important changes in the chemical properties of the arene, in particular making it much more susceptible to nucleophilic attack, we will study this reagent in detail in Section 14.7.

Stabilizing Highly Reactive Species Complexation has also been used to trap highly reactive species that might otherwise decompose. An early example was cyclobutadiene, not isolable except in the complexed form, such as the $Fe(CO)_3$ complex. In the case of **14.10**, trapping as the $Pt(PPh_3)_2$ complex allowed this unusually strained and reactive alkene to be purified and stored. The alkene itself, which is stable for short periods under ambient conditions, is released by treatment of the complex with CS_2.[23]

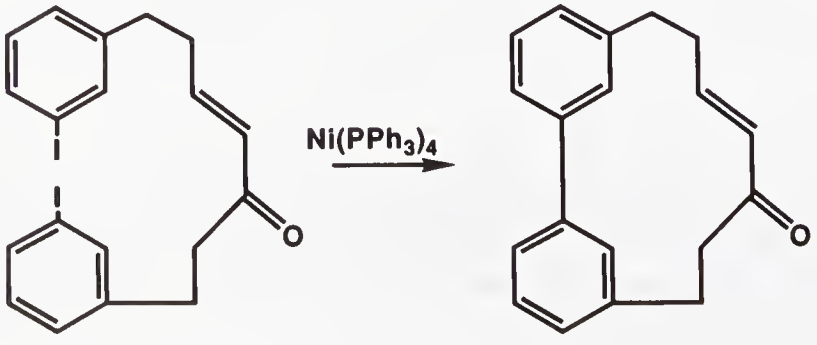
14.10

14.4 REDUCTIVE ELIMINATION

As early as 1901, Ullmann discovered the copper promoted coupling of aryl halides to biaryls, one of the first uses of transition metals in synthesis. The mechanism is still not entirely clear, but a binuclear reductive elimination of Ar—Ar from CuAr is possible.[24a]

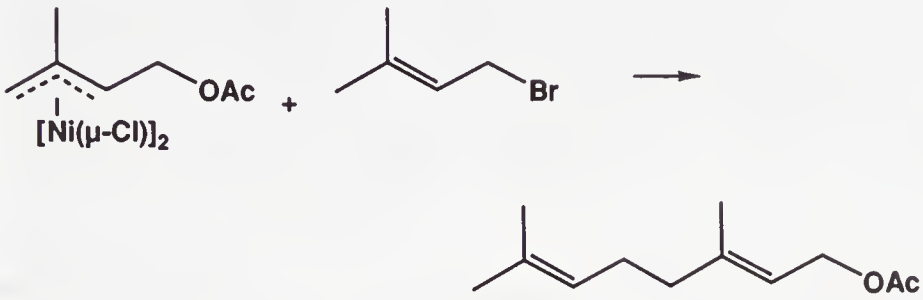
$$\text{Ar—Hal} \xrightarrow{\text{Cu powder}} \text{Ar—Ar} \qquad (14.57)$$

A more recent version of this type of reaction employs $Ni(PPh_3)_4$. Equation 14.58[24b] shows an application to the synthesis of alnusone:



(14.58)

Corey showed that allyl fragments could be coupled by treating the allyl halides with $Ni(CO)_4$. Unsymmetric coupling is possible if the π-allyl nickel halide from the first allyl halide addition is isolated and allowed to react with the second allyl halide. Equation 14.59[25] shows the synthesis of geranyl acetate by this procedure.



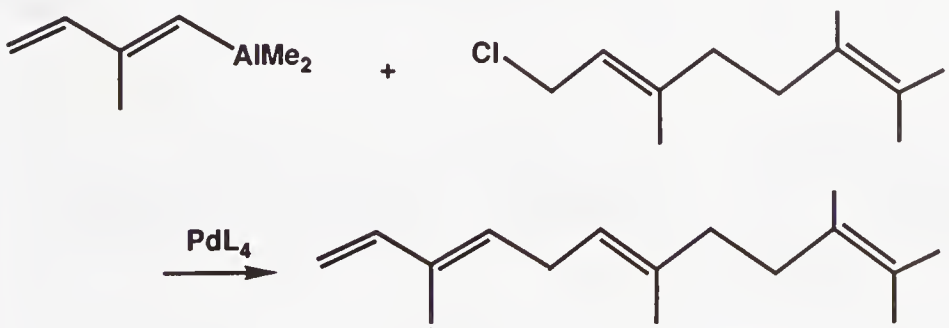
(14.59)

Cross-Coupling Reductive elimination is believed to be the C—C bond-forming step in the cross-coupling[26] of an organic magnesium, aluminium, or zirconium reagent (the latter can be formed from an alkene or alkyne by hydrozirconation as discussed in Section 14.2) with an organic halide (Eq. 14.60); $NiCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$ are among the most commonly used catalysts. A proposed mechanism, shown in Eq. 14.61, suggests that if either R or R′ have β hydrogens, β elimination might occur; this is often observed, although for some catalysts, β elimination is sufficiently slow compared to coupling that useful yields of cross-products can still be obtained.[27]

$$\text{RHal} + \text{R}'\text{M} \xrightarrow{\text{catal.}} \text{R—R}' + \text{MHal} \qquad (14.60)$$

$$\text{L}_n\text{M} \xrightarrow{\text{RHal}} \text{L}_n\text{M(R)Hal} \xrightarrow{\text{R}'\text{M}} \text{L}_n\text{M(R)R}' \longrightarrow \text{R—R}' + \text{L}_n\text{M} \qquad (14.61)$$

The stereo- and regiospecific synthesis of α-farnesene is shown in Eq. 14.62:[28]

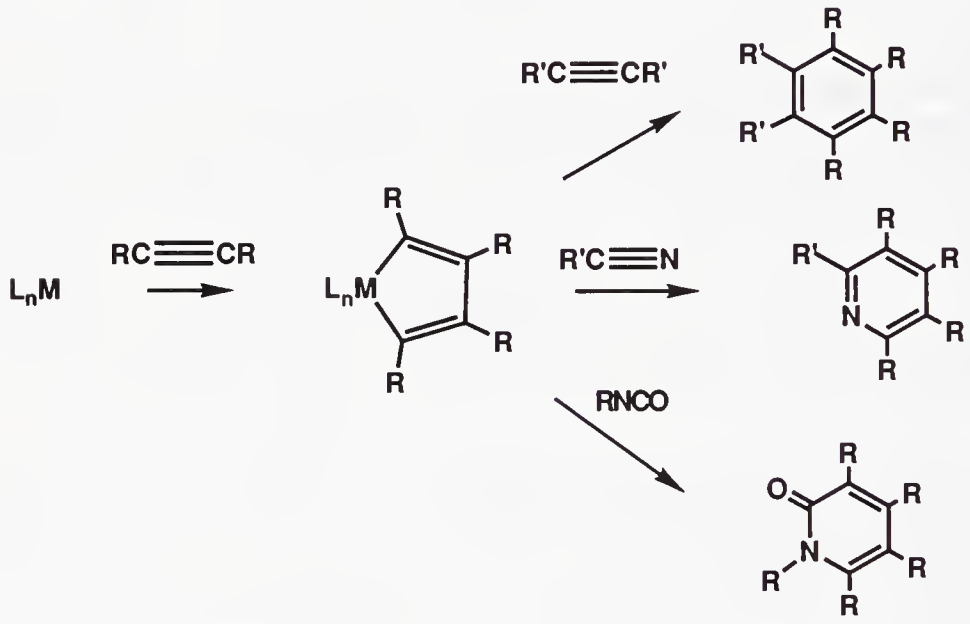


(14.62)

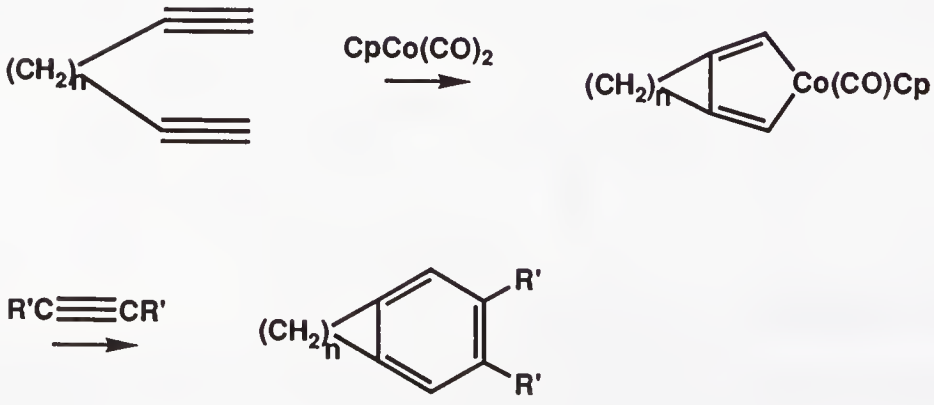
14.5 COUPLING REACTIONS

Cyclotrimerization of Alkynes We saw in Section 6.6 that the oxidative coupling of two acetylenes is a common process for a variety of low-valent

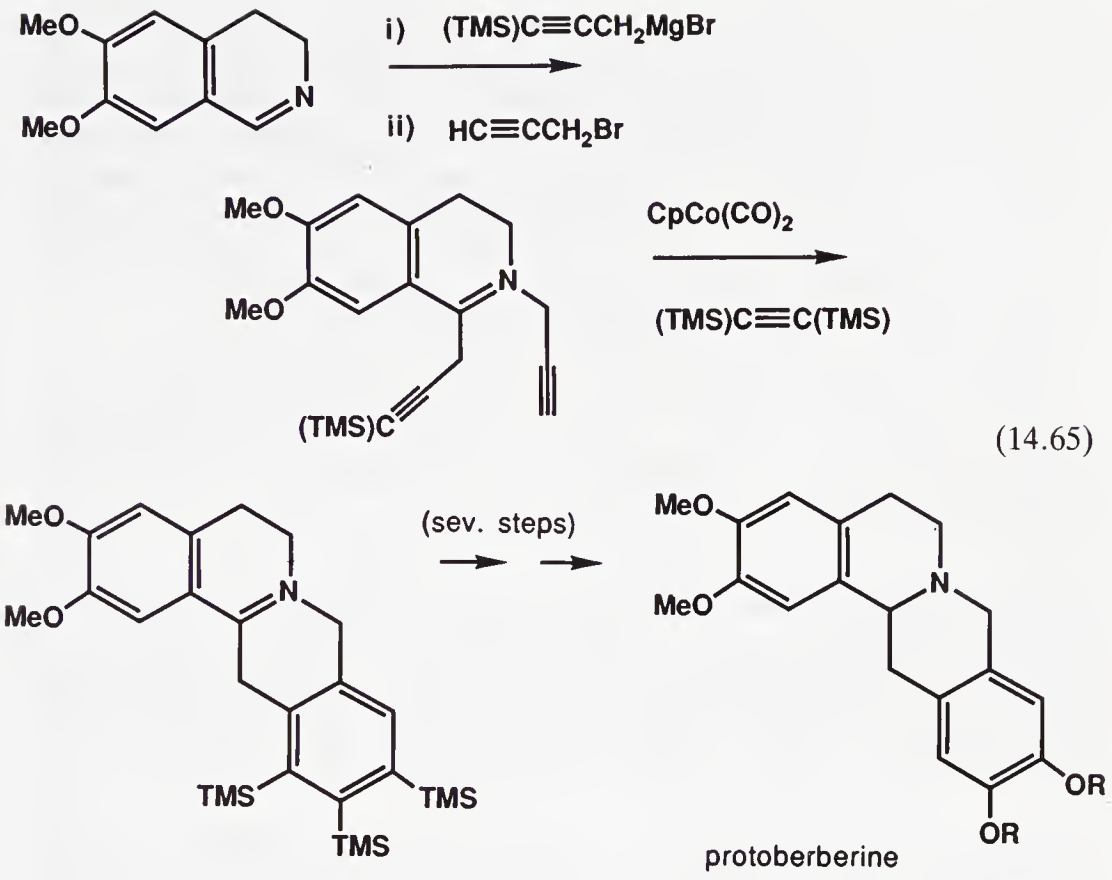
metal complexes. The metalacyclic product can go on to an arene with excess alkyne, leading to a catalytic cyclotrimerization of the alkyne (Eq. 14.63). Vollhardt[29] has adapted this reaction for the organic synthesis, by using the strategy shown in Eq. 14.64. The bis alkyne component is thought to form a metalacycle, which then reacts with the free mono alkyne. This alkyne is chosen so as to be too bulky to cyclotrimerize, but reactive enough to convert the metalacycle to the arene: $Me_2SiC{\equiv}CSiMe_3$ and related alkynes fulfill these conditions, and have the added advantage that the TMS groups can be easily removed or used to introduce further functionality. Equation 14.65 shows the system applied to the synthesis of the protoberberine alkaloids.[30]



(14.63)

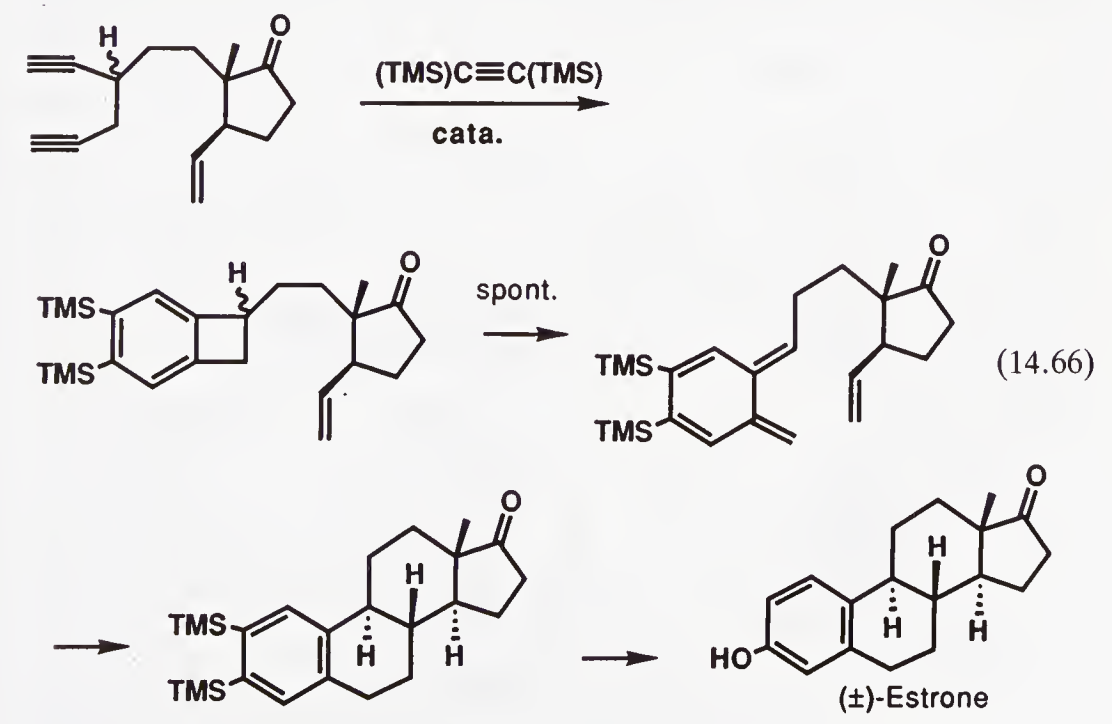


(14.64)



(14.65)

The skeletons of the steroids and the anthracyclines can also be constructed in a similar way. The strategy used for the steroids is exemplified in Eq. 14.66,

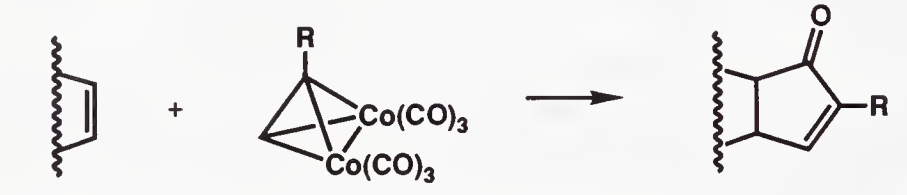


(14.66)

which shows the key step. The usual cobalt-catalyzed [2 + 2 + 2] reaction gives a reactive benzocyclobutane; this spontaneously opens to the *o*-quinodimethane, which undergoes an internal Diels–Alder reaction to give the steroid skeleton. The formation of the arene has enough thermodynamic driving force to make the very strained benzocyclobutane. Some of the exothermicity of this first step, stored in the strained C_4 ring, then drives the subsequent ring opening leading to the final product. The desired trans–anti–trans product of the Diels–Alder step is thought to result from a "chair" transition state. Two further steps lead to estrone.[31a]

The reaction can be extended to the case in which two alkynes and a nitrile are trimerized to give a pyridine or two alkynes and an isocyanate are trimerized to give an α-pyridone, also shown in Eq. 14.63, as exemplified in syntheses of vitamin B_6, a pyridine derivative,[31b] and the antitumor agent, camptothecin,[31c] an α-pyridone.

Pauson–Khand Reaction As shown in Eq. 14.67, this reaction leads to substituted cyclopentanones in which the bulkiest substituent of the alkyne usually ends up alpha to the carbonyl.[32a] In the following application by Schreiber[32] (Eq. 14.68), a complex tricyclic natural product is constructed. $[W(CO)_5(thf)]$ is a useful catalyst for the Pauson-Khand reaction.[32c]



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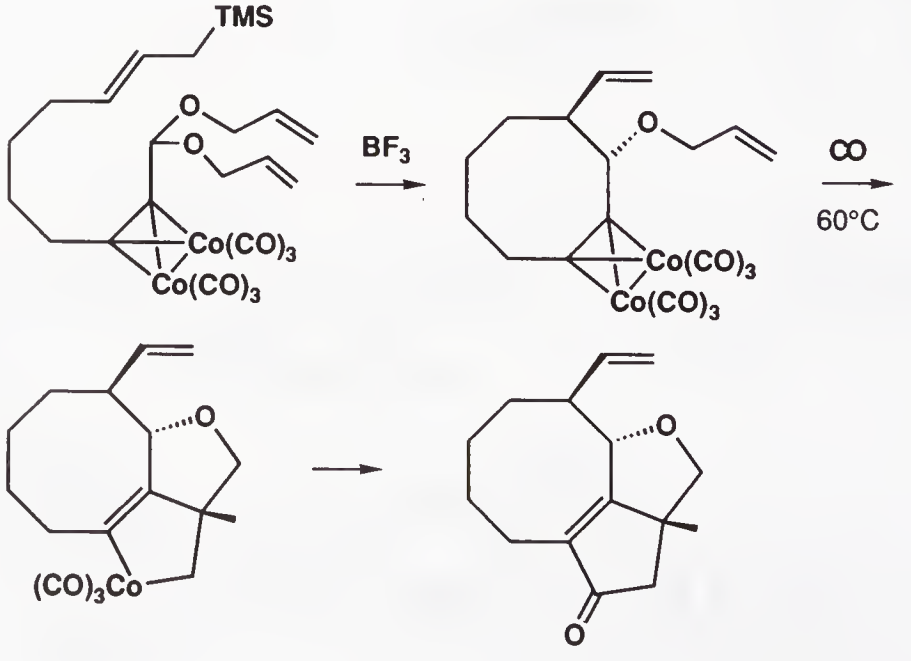
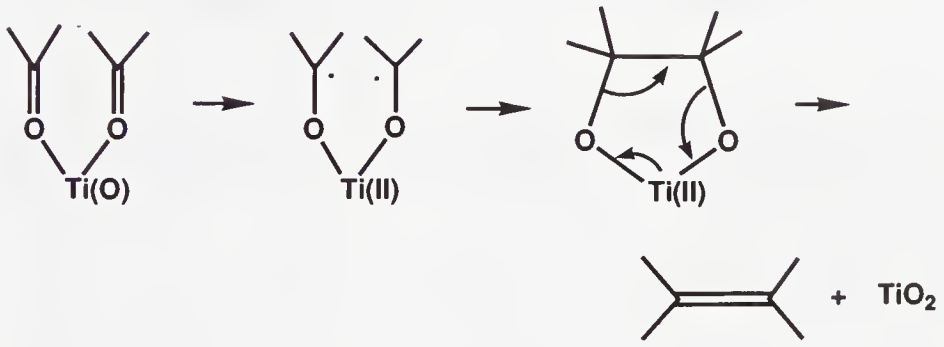


(14.68)

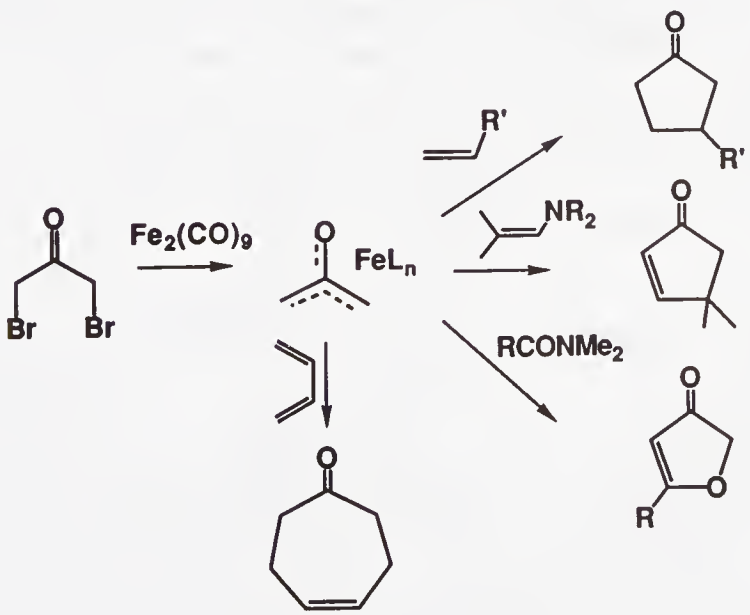
McMurry Reaction A coupling reaction of great interest is McMurry's[33] titanium-mediated synthesis of alkenes from two ketones (Eq. 14.69). This involves a reduced form of titanium, perhaps Ti(0), which may give the sequence of reactions shown in Eq. 14.70. These ideas are supported by the fact that 1,2-diols are also reduced to the alkene. Whatever the mechanism, the reaction shows the strongly oxophilic character of this early metal.

$$R_2C{=}O \xrightarrow{TiCl_3,\ LiAlH_4} R_2C{=}CR_2 + TiO_2 \qquad (14.69)$$

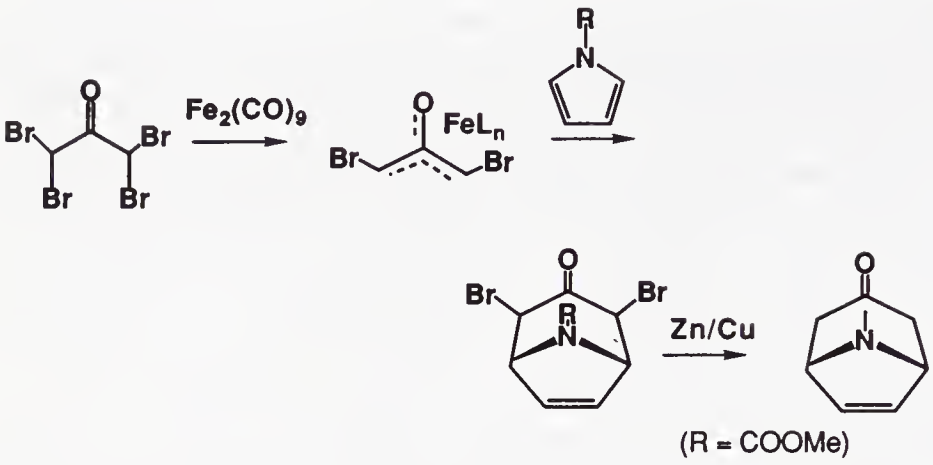


(14.70)

Other Reactions Oxallyls, formed from α,α′-dibromoketones and $Fe_2(CO)_9$, react with alkenes, enamines, enol ethers, amides, or dienes to give a variety of [3 + 2] and [3 + 4] cycloaddition products (Eq. 14.71). This provides a very short synthesis of the tropane skeleton from acetone and pyrrole (Eq. 14.72).[34a] As shown in Eq. 14.71, an oxallyl resembles trimethylenemethane (**5.22**) except that one $=CH_2$ of **5.22** is replaced by $=O$.



(14.71)

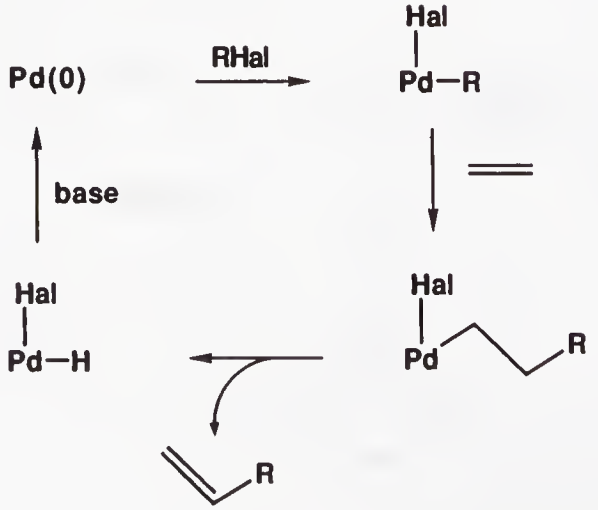


(14.72)

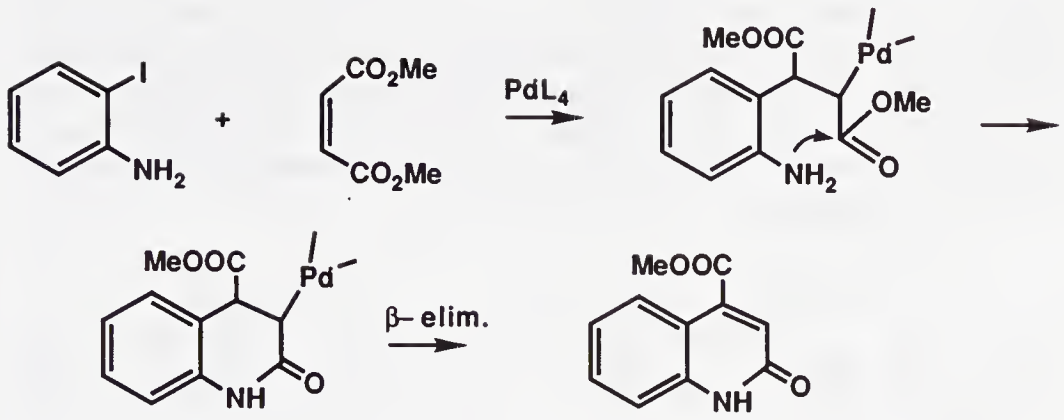
Diels–Alder reactions between α,β-unsaturated carbonyl compounds and dienes can be catalyzed by Lewis acids, such as $Cp_2M(OSO_2CF_3)_2$,[34b] or $[\{HC(2\text{-pyridyl})_3Mo(NO)_2\}]^{2+}$.[34c]

14.6 INSERTION REACTIONS

Heck Reaction From the point of view of the alkene or alkyne, an alkene insertion into an M—R bond is a *carbometallation* of the alkene or alkyne by the M—R group. The most important insertion reactions involve alkenes, alkynes, and CO. The first is exemplified in the Heck reaction,[35a] in which an alkene inserts into a Pd—R group. The resulting alkyl then β-eliminates to give the product (Eq. 14.73). The initial R group must be stable to β elimination, of course, and this limits the reaction to aryls, vinyls, and allyls. Equation 14.74[35b] shows a typical example, the synthesis of a 2-quinolone. The role of the base is to make the reaction catalytic by removing the hydrogen halide from the Pd(II) product and so regenerate the Pd(0) catalyst. This reaction has also been applied by Hegedus[35c] to the syntheses of *N*-acetyl claviciptic acid.

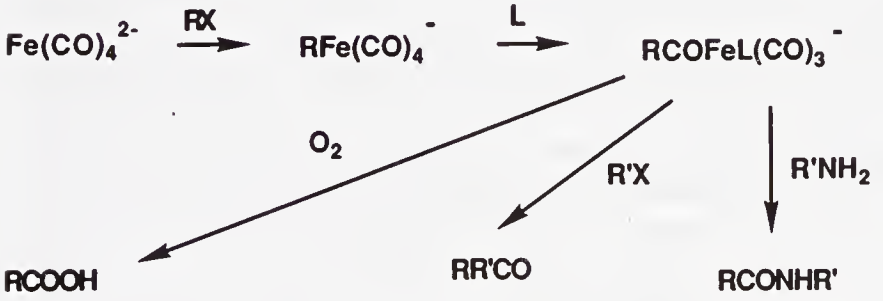


(14.73)



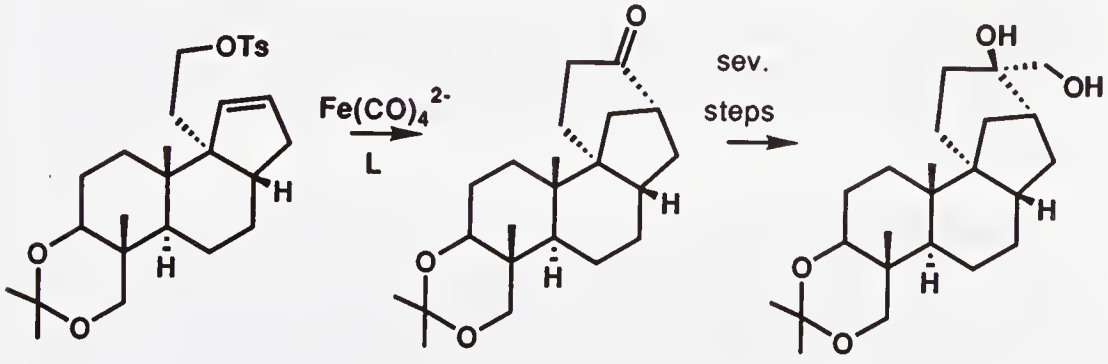
(14.74)

Collman's Reagent Carbonyl insertion can be useful and is often brought about with $Na_2Fe(CO)_4$, Collman's reagent. The dianion reacts with a variety of alkyl halides or tosylates to give $RFe(CO)_4^-$. Because this is an 18e complex with tightly bound ligands, neither β elimination nor racemization usually occurs, and so both chiral and long chain R groups can be used. One advantage of this reagent is that free CO is seldom required, because the insertion can often be induced with PPh_3. The resulting acyl iron anion can be converted into a number of useful species as shown in Eq. 14.75:[36a]



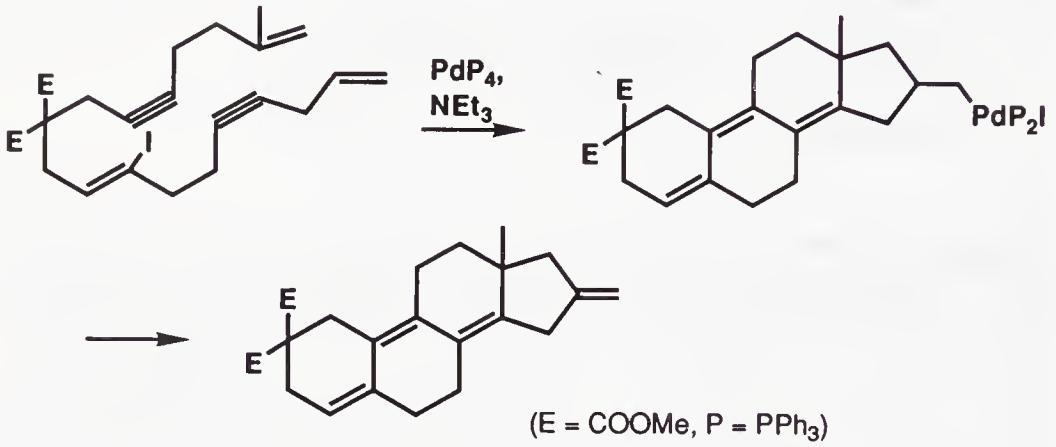
(14.75)

Nearby C=C bonds will insert into the product acyls, a reaction that has been used in a synthesis of aphidicolin (Eq. 14.76[36b]). We will see further examples of CO insertion reactions of metal alkyls in the next section.



aphidicolin (14.76)

Cascade Carbometallation This can be used to construct multiple rings as shown below.[37] The reaction starts with the oxidative addition of the vinyl iodide and the resulting alkyl undergoes insertion with two alkynes and two alkenes to give the tetracyclic Pd alkyl shown, which then β-eliminates to regenerate the Pd(0) catalyst. Many interesting variations of this reaction have been investigated.



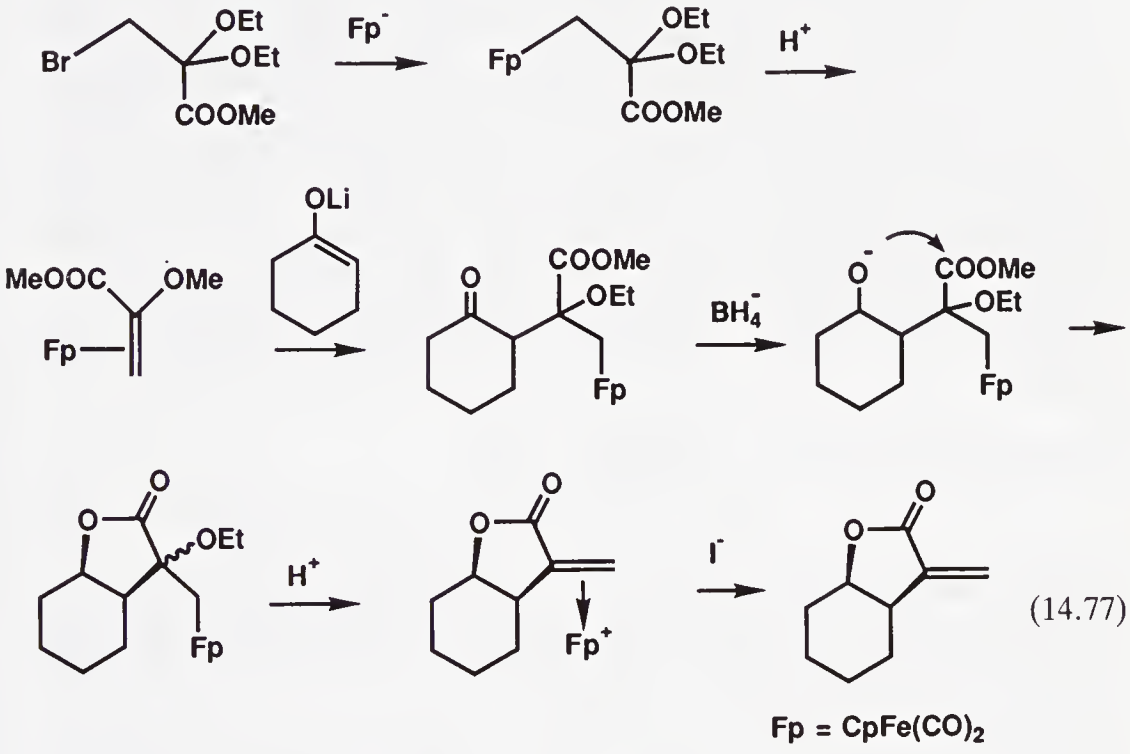
Decarbonylation The reverse of CO insertion is also a process that can be mediated by transition metal reagents in the case of aldehydes. For example, $RhCl(PPh_3)_3$ reacts with RCHO to give $RhCl(CO)(PPh_3)_2$ and RH. Oxidative addition of the aldehyde C—H bond to rhodium is followed by a retromigratory insertion to give $Rh(R)(H)Cl(CO)(PPh_3)_2$. This loses RH by reductive elimination, and the net reaction goes with retention of configuration at carbon. It is also intramolecular as shown by crossover studies on a mixture of RCHO and R′CDO. Unfortunately, the $RhCl(CO)(PPh_3)_2$ product is no longer sufficiently reactive to add to a new aldehyde C—H bond, and so the reaction is not catalytic.

14.7 NUCLEOPHILIC ATTACK ON A LIGAND

As we saw in Section 8.3, the binding of a polyene or polyenyl ligand to a metal can suppress the reactivity toward electrophiles usually seen for the free polyene, and encourages attack by nucleophiles instead. This reversal of the normal reactivity pattern (umpolung) has been very widely used in organic synthesis.

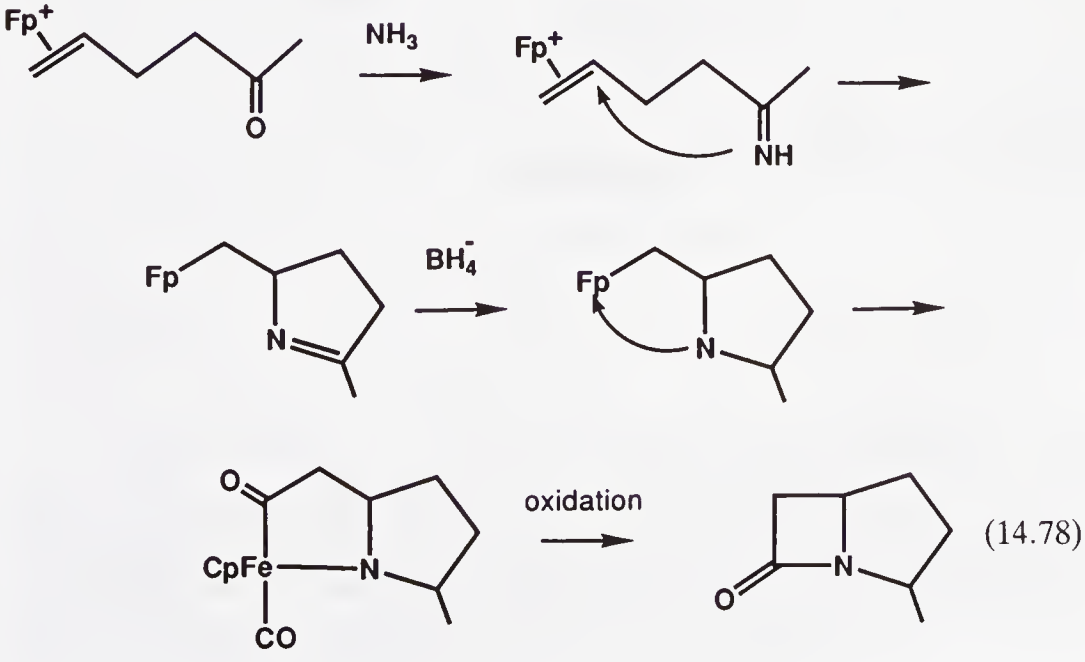
Cyclopentadienyl Iron Reagent In the case of simple alkenes, the best-studied system is Rosenblum's Fp reagent[19] (see also Section 14.3), $[CpFe(CO)_2(alkene)]^+$. Thanks to its positive ionic charge, it activates even simple alkenes for nucleophilic attack. The sequence shown in Eq. 14.77[38] illustrates how the alkene complex may be synthesized from a β-alkoxy alkyl

by protonation. The attack of an enolate anion gives a ketone, which subsequently cyclizes. A second protonation leads to an alkene complex, which is released with iodide ion. The sequence of Eq. 14.78[39] is also interesting, because the amine generated by the borohydride reduction induces carbonyl insertion by binding to the metal. On oxidation of the resulting adduct, the amine attacks the acyl carbon to form the carbapenem shown.



(14.77)

Fp = $CpFe(CO)_2$

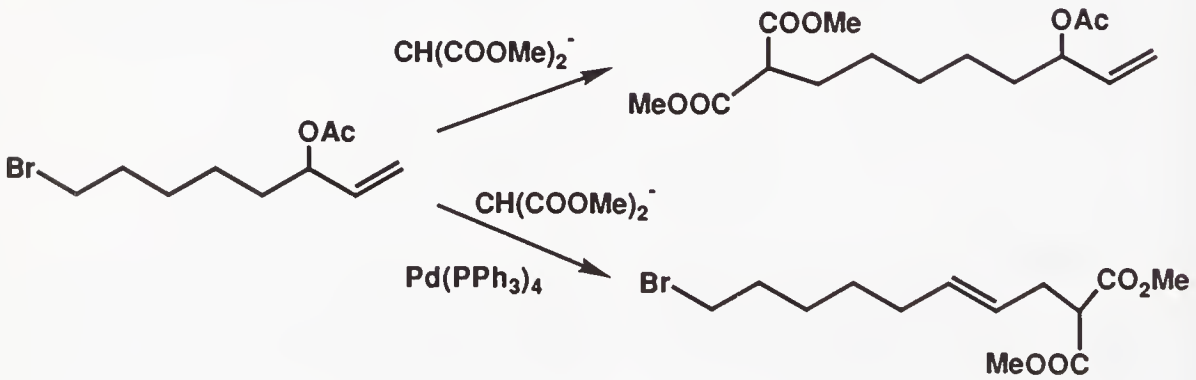


(14.78)

Palladium Allyls Of all the applications of nucleophilic attack, that on an allyl group coordinated to palladium is perhaps the one that has been most widely applied to organic synthesis.[40,41] The allyl group is usually formed either from $PdCl_2$ and an alkene by C—H activation or from Pd(0) and an allylic acetate by oxidative addition. Where the substrate is an alkene, a mixture of $[(\pi\text{-allyl})PdCl]_2$ complexes is sometimes formed, because there may be a choice of C=C groups or of C—H bonds to attack, but in general the more substituted alkene is more reactive and the regiochemistry of the C—H activation step can be moderately selective. The allylic acetate route is useful in that the Pd ends up attached to the allyl group of the substrate in a defined regio- and stereochemistry. Subsequent rearrangement can degrade the stereochemistry of the allyl, however, and so the nucleophilic attack step should be carried out without delay. In addition, the product of oxidative addition to $Pd(PPh_3)_4$ is the cationic $[(\text{allyl})PdL_2]^+OAc^-$, rather than the neutral halo complex formed from the halide. This cationic charge helps activate the allyl group for subsequent nucleophilic attack. In addition, the reactions are often catalytic with the acetates, an important consideration when precious metals are used.

$$CH_2{=}CHCH_2OAc \xrightarrow{Pd(0)} (\pi\text{-allyl})PdL_2^+ \xrightarrow{Li[Nu]} CH_2{=}CHCH_2Nu + Pd(0) + LiOAc \quad (14.79)$$

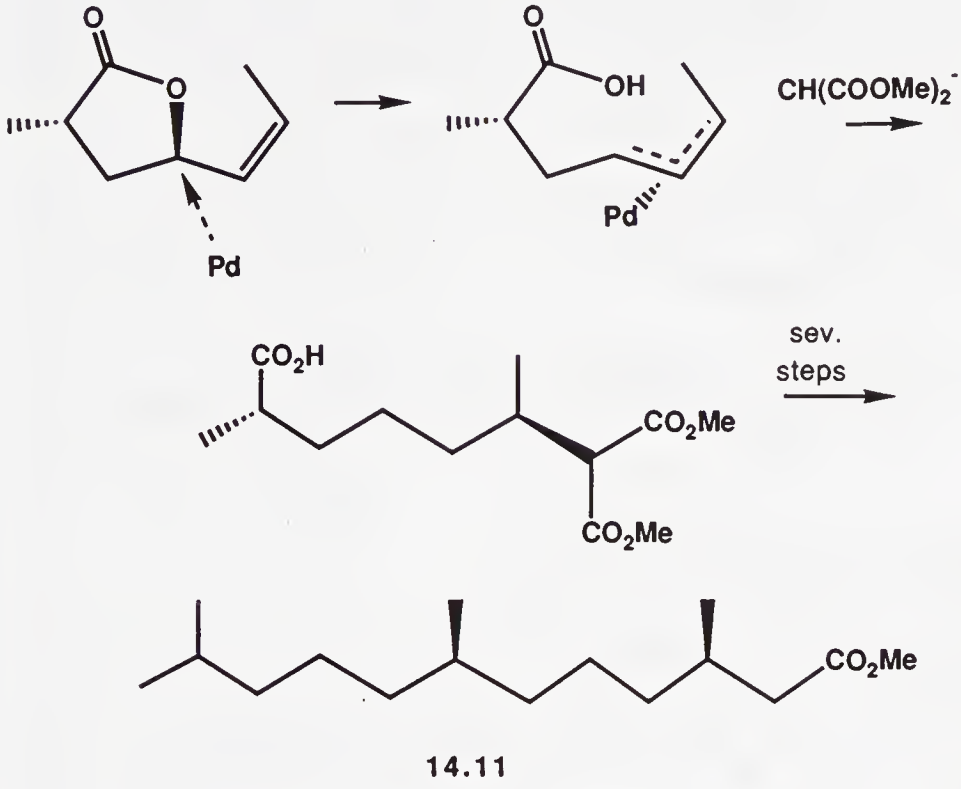
The palladium selectively attacks an allylic acetate with inversion, even in the presence of other reactive groups, such as a C—Hal bond; nucleophilic attack then occurs exclusively at the allyl group, showing the strongly activating effect of the metal (Eq. 14.80):[40a]



(14.80)

The nucleophile usually attacks the exo face of the allyl group (the one opposite the metal), and at the least hindered terminus of the allyl group (although this preference can be partially reversed by addition of ligands).[40b] The stereochemical consequences of this sequence have been used to define the relative stereochemistries of two chiral centers five carbons apart in an

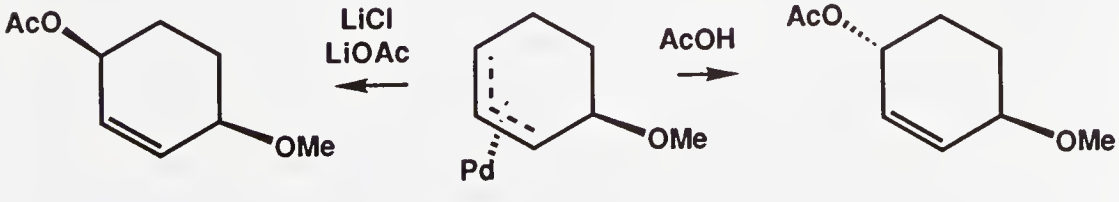
acyclic system, during the synthesis of the side chain (**14.11**) of vitamin E (Eq. 14.81).[42] Unfortunately, only stabilized carbanions, such as malonates, have proved effective carbon nucleophiles in most cases.



(14.81)

14.11

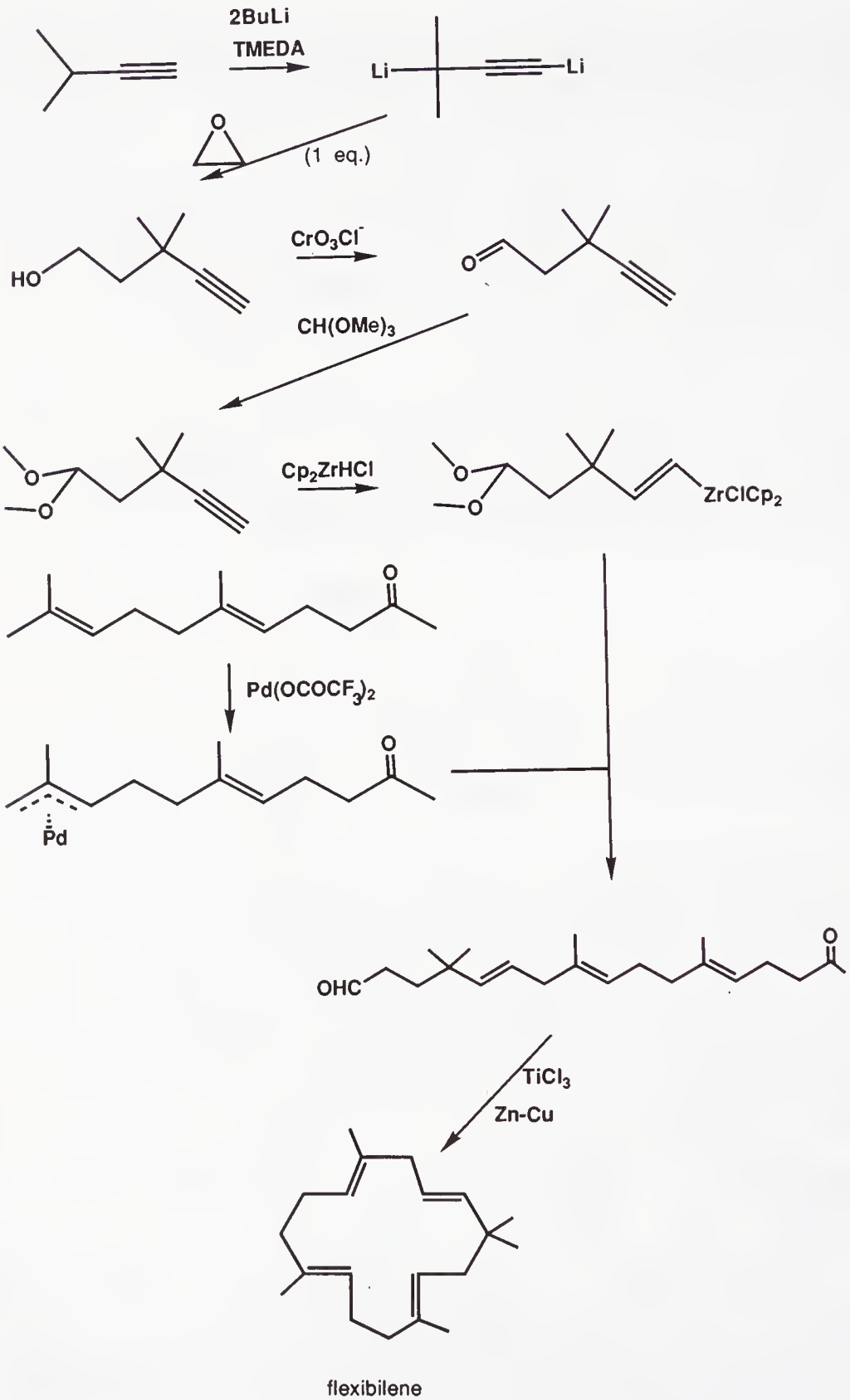
Rather than give direct attack at the exo face of the ligand, the nucleophile may bind to the metal first, in which case it can be transferred to the endo face of the allyl group; this changeover of stereochemistry can occur as a result of relatively small changes in the conditions (Eq. 14.82).[41] In the presence of excess LiCl, the acetate is prevented from coordinating to the metal and the cis product is formed; conversely, the presence of LiOAc encourages coordination of the OAc^- anion to the metal, and therefore, the production of the cis product.



>95% cis

>95% trans

(14.82)

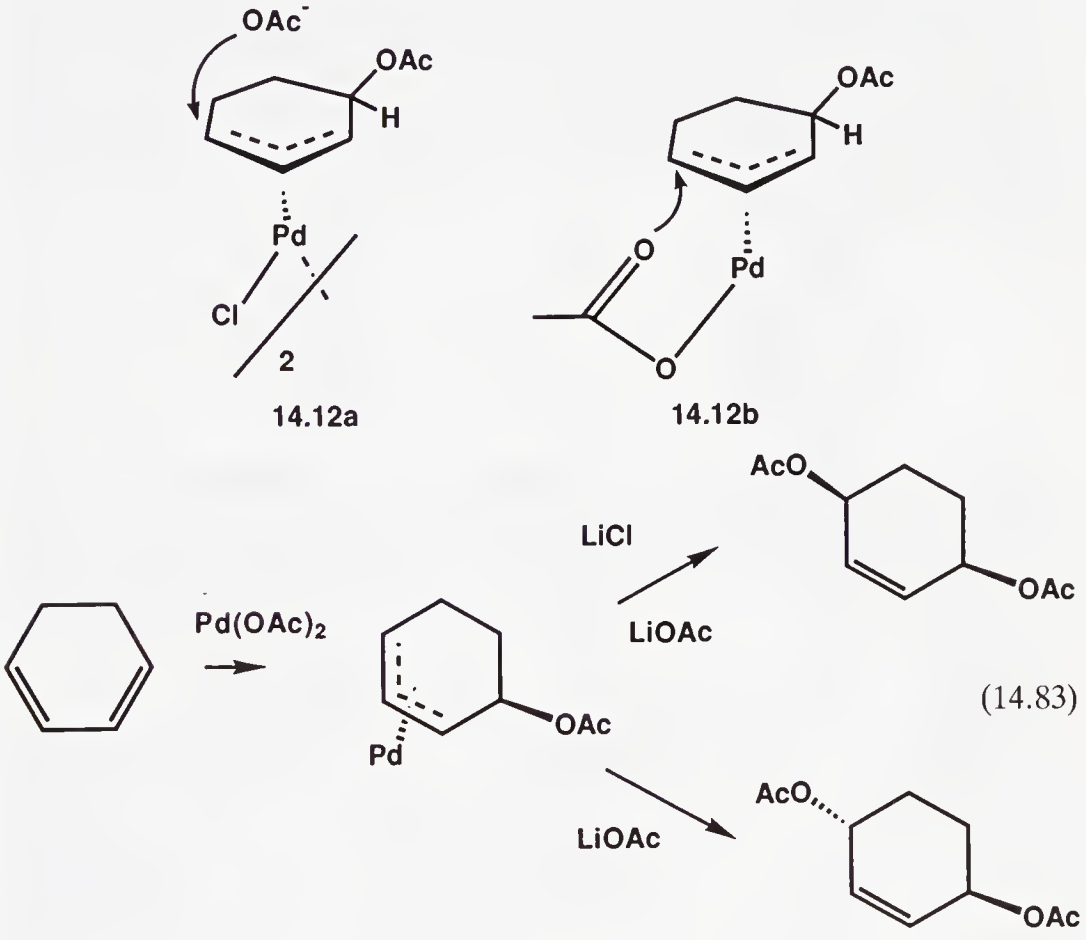


flexibilene

FIGURE 14.2 A synthesis of flexibilene.

Figure 14.2 shows a synthesis[43] of the diterpene, flexibilene, which uses metal-based reagents in almost every step; one of the key steps is nucleophilic attack of a vinylzirconium species on an allylpalladium complex.

By starting from the diene, a 1,4-bis acetoxylation can be carried out to give cis or trans product, according to the exact conditions. The intermediates **14.12a** and **14.12b** are invoked to explain these products. The benzoquinone serves to reoxidize Pd(0) and make the reaction catalytic (Eq. 14.83):

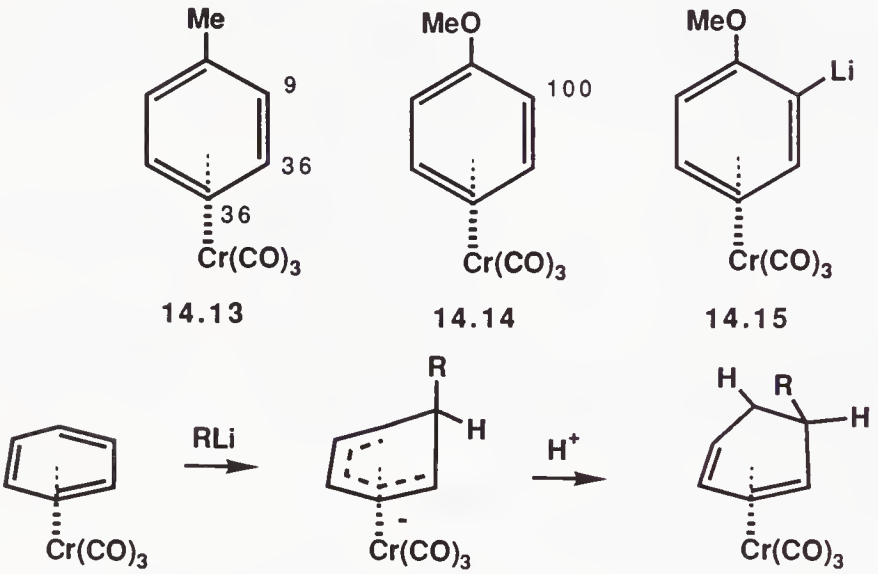


(14.83)

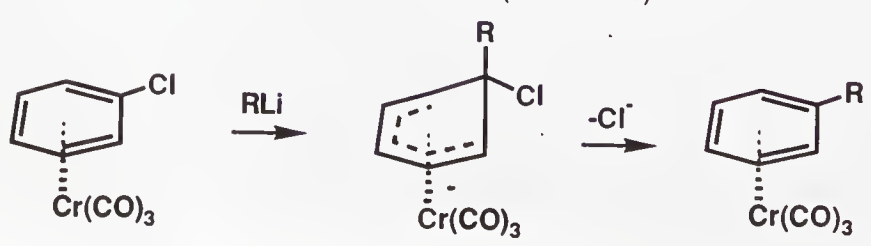
Diene and Arene Reactions Dienes bound to the $Fe(CO)_3$ fragment can be converted to η^5-cyclohexadienyl complexes with Ph_3C^+. Subsequent nucleophilic attack can lead to the formation of a substituted diene, a route that has been successfully applied by Pearson to the synthesis of limaspermine.[44a]

Nucleophilic addition to arene complexes has been developed by Jaouen[44b] and Semmelhack.[45] The binding of an arene to the $Cr(CO)_3$ fragment has a number of chemical consequences. The ring protons, and C—H bonds α to the ring become more acidic. BuLi will now deprotonate C—H bonds in the complex to give synthetically useful carbanions. Structure **14.13** is unselectively deprotonated as shown below (the numbers refer to the relative amount of deprotonation at each site). Thanks to the directing effect of the OMe group (see Section 14.1), **14.14** *is* selectively attacked ortho to the substituent.

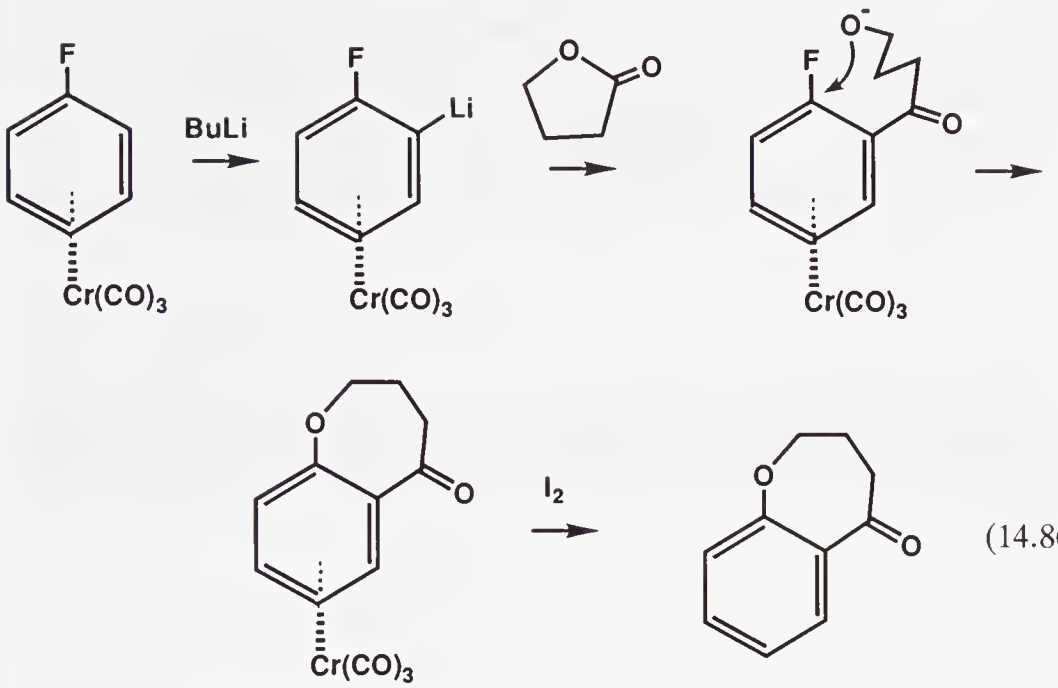
The resulting organolithium reagent **14.15** can be trapped with any of a variety of electrophiles: aldehydes, ketones, $MeOSO_2F$, TMSCl, etc. The $Cr(CO)_3$ group can then be displaced by pyridine[46] or light and air.[45] Binding to the metal also reduces the electron density on the ring and renders it liable to nucleophilic attack by a number of stabilized carbanions. Conversely, binding protects the ring against electrophilic attack. The products of nucleophilic attack can be liberated from the metal as the diene by protonation followed by oxidative decomplexation with I_2. The protonated intermediate, **14.16**, is presumably solvated; otherwise it would be 16e. Treatment of the adduct with I_2 directly gives the substituted arene (Eq. 14.84).[44,45] Haloarene complexes undergo nucleophilic displacement of the halide (Eq. 14.85). Equation 14.86[47] shows a synthesis in which a new ring is introduced using the principles discussed above.



(14.84)

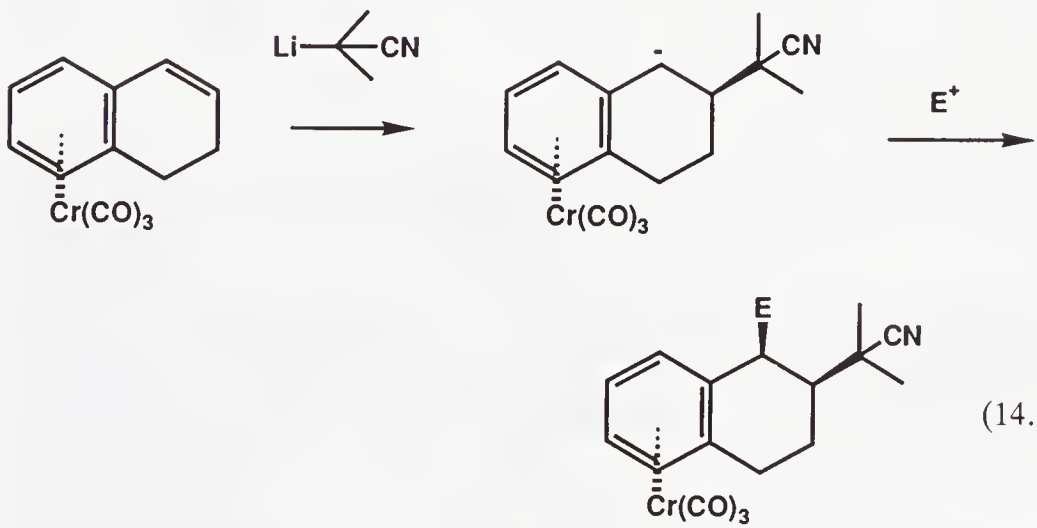


(14.85)



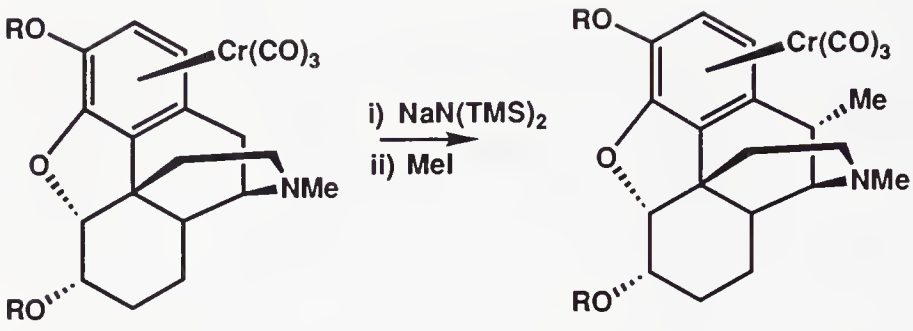
(14.86)

Attack takes place on the exo face of the ring, as a result of the steric effect of the metal fragment. This holds even in the case of a ring fused to the coordinated arene. Equation 14.87 shows how a nucleophile and an electrophile can be introduced on the same face of the dihydronaphthalene.



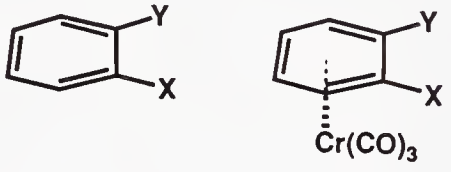
(14.87)

Binding often takes place to the least hindered face of the arene, but reactions take place on the face opposite the metal, and this therefore allows us to introduce substituents on the most hindered face of the original compound. Equation 14.88[48] shows the stereospecific introduction of a methyl group in compounds of the morphine type.

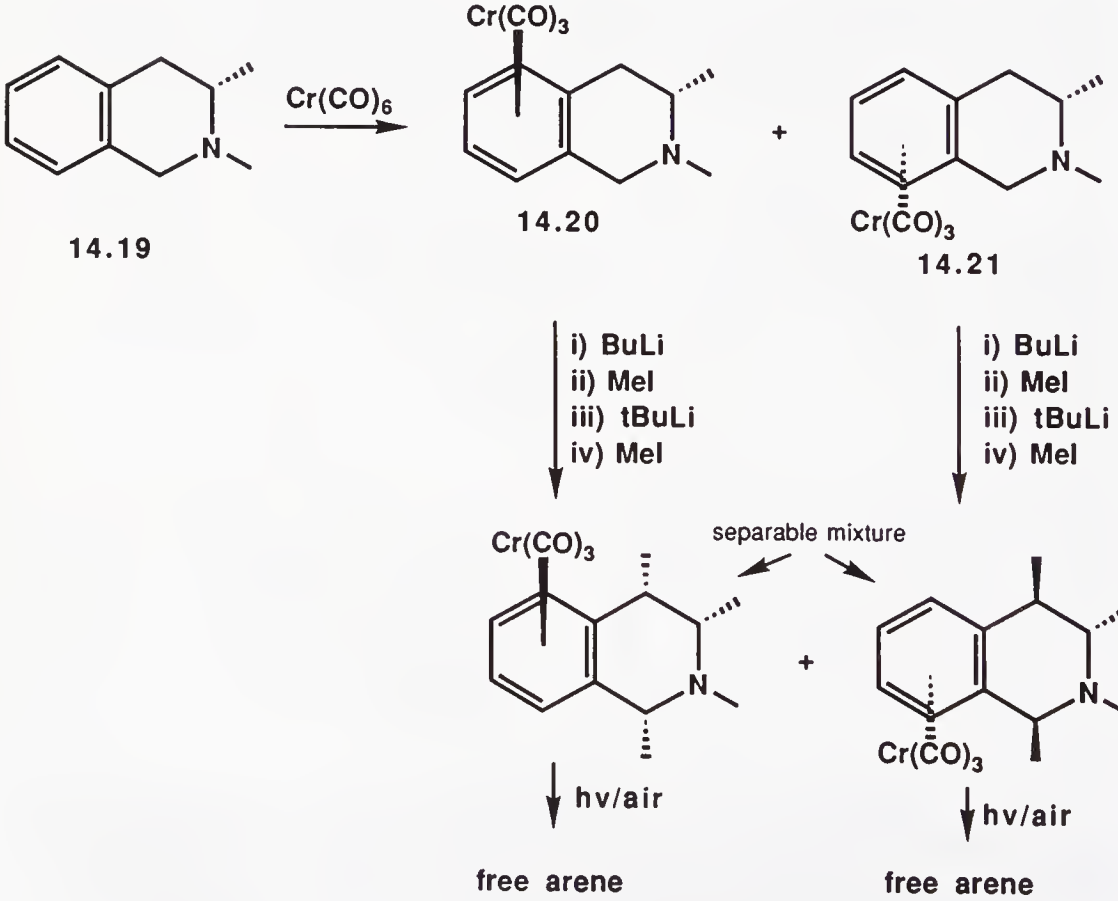


(14.88)

Finally, binding the metal differentiates the opposite faces of the arene ring; archiral arenes of type **14.17** give chiral complexes of type **14.18**, because the binding of the metal removes the only plane of symmetry present in the



14.17 **14.18**



14.19 **14.20** **14.21**

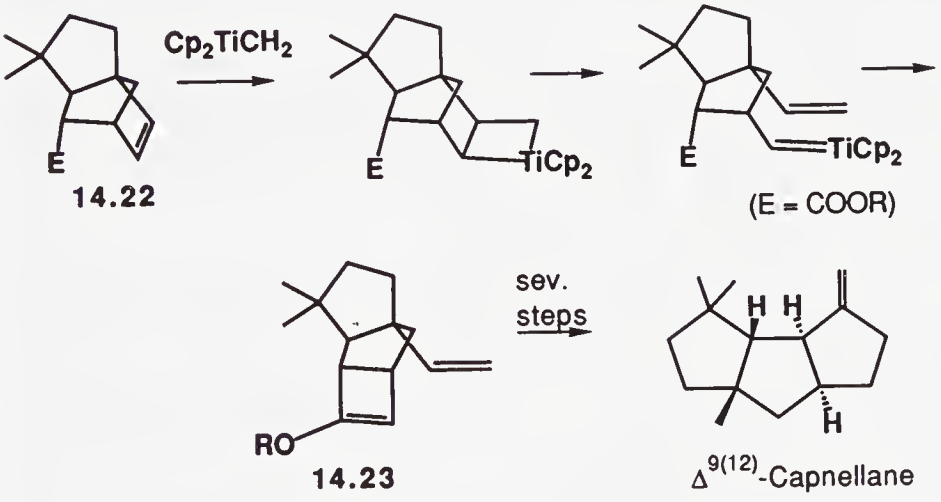
free arene free arene

(14.89)

free arene. If the substrate is chiral, then a mixture of diastereomers is often formed on coordination of the chromium. For example, (+)-(*S*)-amphetamine, **14.19**, gives a mixture of complexes **14.20** and **14.21**. The treatment shown introduces two methyl groups on the exo face. The mixture of isomers was separated at this stage, and the products found to be diastereomerically and optically pure (Eq. 14.89).[49]

14.8 CARBENE REACTIONS

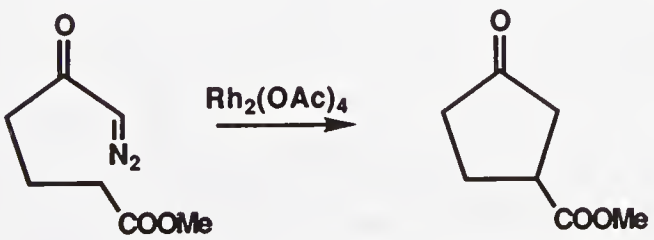
Tebbe's Reagent $Cp_2Ti{=}CH_2$ (Eq. 11.33) has been applied to the synthesis of $\Delta^{9(12)}$-capnellane by Stille and Grubbs (Eq. 14.90).[50] In the key steps, **14.22** is converted to **14.23** by a metathesis-like rearrangement followed by an ester group trapping the titanacarbene.



(14.90)

Many of the early metathesis catalysts were not very tolerant of organic functionality, but newer catalysts are more tolerant and should make metathesis a more commonly used reaction in organic synthesis.

Rhodium Acetate Catalyzed Carbene Reactions Another reaction involving a metal carbene is illustrated by Equation 14.91, where $Rh_2(OAc)_4$ is the catalyst. A diazoketone acts as a source of a carbene that inserts into an activated C—H bond.[51] The presumed intermediate rhodium carbene complex is too unstable to isolate.



(14.91)

We can confidently predict that the whole area of organometallic chemistry in organic synthesis will continue to grow strongly. It is likely that transition metal reagents will be involved in many of the new organic synthetic methods to be developed in the next few years.

REFERENCES

1. (a) D. Seebach, *Angew. Chem., Int. Ed.*, **29,** 1320, 1990; (b) P. J. Harrington, *Transition Metals in Total Synthesis,* Wiley, New York, 1990; *Comprehensive Organic Synthesis,* S. V. Ley (ed.), Pergamon Press, New York, 1991.
2. (a) R. G. Jones and H. Gilman, *Organic Reactions,* **6,** 339, 1951; (b) A. Fürstner, *Angew. Chem., Int. Ed.*, **32,** 164, 1993; (c) H. M. Walborsky, *Acct. Chem. Res.*, **23,** 286, 1990; (d) E. C. Ashby, *Pure Appl. Chem.*, **52,** 545, 1980; (e) R. Noyori and M. Kitamura, *Angew. Chem., Int. Ed.*, **30,** 49, 1991.
3. H. C. Brown, *Organic Synthesis via Boranes,* Wiley-Interscience, New York, 1975.
4. (a) E. W. Colvin, *Silicon in Organic Synthesis,* Butterworth, London, 1981; W. P. Weber, *Silicon Reagents for Organic Synthesis: Reactivity and Structure,* Springer Verlag, Berlin, 1982; I. Fleming, *Chem. Soc. Rev.*, **10,** 83, 1981; (b) P. Jutzi et al., *Chem. Ber.*, **122,** 1629, 1989; (c) R. West et al., *J. Am. Chem. Soc.*, **103,** 3049, 1981; S. Masamune et al., *J. Am. Chem. Soc.*, **104,** 1150, 1982.
5. I. Fleming and I. Paterson, *Synthesis,* 446, 1979.
6. I. Fleming et al., *Chem. Commun.*, 176, 1978.
7. (a) R. C. Larock, *Organomercury Compounds in Organic Synthesis,* Springer Verlag, New York, 1985; (b) R. R. Ferguson, P. Krajnik, and R. H. Crabtree, *Synlett,* 597, 1991.
8. G. H. Posner, *An Introduction to Synthesis Using Organocopper Reagents,* Wiley-Interscience, New York, 1980.
9. G. H. Posner, *Org. React.*, **19,** 1, 1972.
10. J. F. Normant and A. Alexakis, *Synthesis,* 841, 1981.
11. (a) M. T. Reetz et al., *Angew. Chem., Int. Ed.*, **19,** 1011, 1980; (b) M. T. Reetz and B. Wenderoth, *Tetrahedron Lett.*, **23,** 5259, 1982; (c) M. T. Reetz et al., *Angew. Chem., Int. Ed.*, **22,** 989, 1983.
12. D. W. Hart and J. Schwartz, *J. Am. Chem. Soc.*, **96,** 8115, 1974; J. Schwartz and J. A. Labinger, *Angew. Chem., Int. Ed.*, **15,** 333, 1976.
13. (a) K. B. Sharpless, A. Y. Teranishi, and J. E. Bäckvall, *J. Am. Chem. Soc.*, **99,** 3120, 1977; (b) K. B. Sharpless et al., *J. Am. Chem. Soc.*, **111,** 1123, 1989; (c) K. B. Sharpless, *Chem. in Brit.*, **22,** 38, 1986; (d) K. B. Sharpless and R. B. Michaelson, *J. Am. Chem. Soc.*, **95,** 6136, 1973; (e) R. M. Hanson and K. B. Sharpless, *J. Org. Chem.*, **51,** 1922, 1986.
14. R. B. Dehnel and G. H. Whitham, *J. Chem. Soc., Perkin I,* 953, 1979.
15. E. N. Jacobsen et al., *J. Am. Chem. Soc.*, **112,** 2801, 1990.
16. M. J. Burk, *J. Am. Chem. Soc.*, **113,** 8518, 1991; **114,** 6266, 1992.
17. R. Noyori et al., *J. Am. Chem. Soc.*, **106,** 5208, 1984.
18. (a) J. A. Gladysz et al., *J. Am. Chem. Soc.*, **108,** 7863, 1986; (b) S. G. Davies et al., *Adv. Organometal. Chem.*, **30,** 1, 1990; (c) K. Burgess et al., *Chem. Rev.*,

91, 1179, 1991; (d) T. Hayashi, Y. Matsumoto, and Y. Ito, *J. Am. Chem. Soc.*, **111,** 3426, 1989; (e) D. A. Evans, G. C. Fu, and A. H. Hoveyda, *J. Am. Chem. Soc.*, **110,** 6917, 1988.

19. M. Rosenblum et al., *J. Am. Chem. Soc.*, **95,** 3062, 1973; **99,** 8426, 1977; *J. Org. Chem.*, **45,** 1984, 1980.
20. (a) K. M. Nicholas, *J. Am. Chem. Soc.*, **97,** 3254, 1975; (b) K. M. Nicholas and R. Pettit, *Tetrahedron Lett.*, 3475, 1971; (c) K. M. Nicholas et al, *J. Am. Chem. Soc.*, **102,** 2508, 1980.
21. D. Seyferth and A. T. Wehman, *J. Am. Chem. Soc.*, **92,** 5520, 1970.
22. D. H. R. Barton et al., *J. Chem. Soc., Perkin I,* 821, 1976.
23. K. B. Wiberg et al., *J. Am. Chem. Soc.*, **96,** 6531, 1974.
24. (a) P. E. Fanta, *Synthesis,* 9, 1974; (b) M. F. Semmelhack and L. S. Ryono, *J. Am. Chem. Soc.*, **97,** 3873, 1975.
25. K. Sato, S. Inoue, S. Ota, and Y. Fujita, *J. Org. Chem.*, **37,** 462, 1972.
26. E. Negishi, *Acct. Chem. Res.*, **15,** 340, 1982; H. Felkin et al., *Tetrahedron,* **31,** 2735, 1975.
27. S. M. Neumann and J. K. Kochi, *J. Org. Chem.*, **40,** 599, 1975.
28. H. Matsushita and E. Negishi, *J. Am. Chem. Soc.*, **103,** 2882, 1981.
29. K. P. C. Vollhardt, *Angew. Chem., Int. Ed.*, **23,** 539, 1984.
30. K. P. C. Vollhardt et al., *Tetrahedron,* **39,** 905, 1983.
31. (a) R. L. Funk and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, **101,** 215, 1979; **102,** 5253, 1980; (b) K. P. C. Vollhardt et al., *Tetrahedron,* **41,** 5791, 1985; (c) K. P. C. Vollhardt et al., *J. Org. Chem.*, **49,** 4786, 1984.
32. (a) P. L. Pauson, *Tetrahedron,* **41,** 585, 1985; (b) S. L. Schreiber, T. Sammakia, and W. E. Crowe, *J. Am. Chem. Soc.*, **108,** 3128, 1986; (c) T. R. Hoye et al., *ibid.*, **115,** 1154, 1993.
33. J. E. McMurry, *Acct. Chem. Res.*, **16,** 405, 1983.
34. (a) R. Noyori et al., *J. Am. Chem. Soc.*, **100,** 1786, 1978; (b) B. Bosnich et al., *Organometallics,* **11,** 2745, 1992; (c) J. W. Faller et al., *J. Am. Chem. Soc.*, **113,** 1579, 1991.
35. (a) R. F. Heck, *Acct. Chem. Res.*, **12,** 146, 1979; *Org. React.*, **27,** 345, 1982; (b) R. F. Heck et al., *J. Org. Chem.*, **43,** 2952, 1978; (c) L. S. Hegedus et al., *J. Am. Chem. Soc.*, **109,** 4335, 1987.
36. (a) J. P. Collman, *Acct. Chem. Res.*, **8,** 342, 1975; (b) J. E. McMurry et al., *J. Am. Chem. Soc.*, **101,** 1330, 1979.
37. E. Negishi, *Pure Appl. Chem.*, **64,** 323, 1992.
38. T. C. T. Chang and M. Rosenblum, *J. Org. Chem.*, **46,** 4626, 1981.
39. M. Rosenblum et al., *J. Org. Chem.*, **45,** 1984, 1980.
40. (a) B. M. Trost, *Acct. Chem. Res.*, **13,** 385, 1980; J. W. Faller et al., *Organometallics,* **3,** 927, 1231, 1984; (b) B. M. Trost et al., *J. Am. Chem. Soc.*, **100,** 3416, 1978.
41. J.-E. Backvall, *Acct. Chem. Res.*, **16,** 335, 1983.
42. J. E. McMurry et al., *Tetrahedron Lett.*, **23,** 1777, 1982.
43. B. M. Trost and T. P. Klun, *J. Am. Chem. Soc.*, **101,** 6756, 1979.

44. (a) A. J. Pearson and D. C. Rees, *J. Chem. Soc., Perkin I,* 619, 1983; (b) G. Jaouen, *Pure Appl. Chem.*, **58,** 597, 1986.
45. M. F. Semmelhack, *Ann. N.Y. Acad. Sci.*, **333,** 36, 1977.
46. C. Carganico et al., *Chem. Commun.*, 989, 1978.
47. M. Uemura, N. Nishiwaka, and Y. Hayashi, *Tetrahedron Lett.*, 2069, 1980.
48. D. H. R. Barton, S. G. Davies, B. Meunier, C. Pascard. et al., *Nouv. J. Chim.*, **4,** 369, 1980.
49. S. G. Davies, *Chem. Ind.*, 506, 1986.
50. J. R. Stille and R. H. Grubbs, *J. Am. Chem. Soc.*, **108,** 855, 1986.
51. M. P. Doyle et al., *J. Am. Chem. Soc.*, **115,** 958, 1993.

PROBLEMS

1. *o*-Iodoaniline and $CH_2{=}CHCH(OMe)_2$ give quinoline (1-azanaphthaline) with $Pd(PPh_3)_4$. Suggest a mechanism.

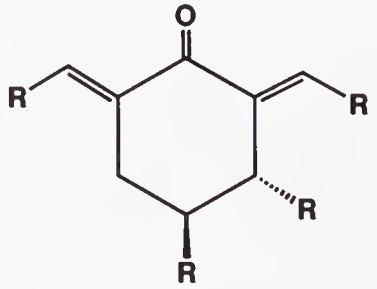
2. The epoxides from cis and trans 2-hexene are reduced to the parent alkenes with retention of stereochemistry by treatment with (i) Fp^-, (ii) H^+, and (iii) NaI/acetone. Suggest a mechanism.

3. $[CpFe(CO)_2]_2$ catalyzes the addition of CCl_4 to an alkene as shown below:

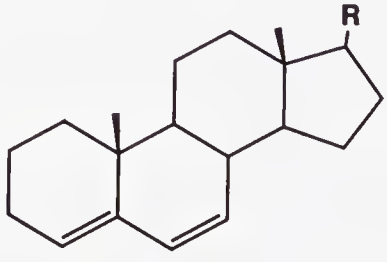
$$CCl_4 + RHC{=}CH_2 = RHCCl{-}CH_2CCl_3$$

The reaction is not affected by light, and running the reaction with mixed CCl_4 and CBr_4 gave no crossover products such as $RHCBr{-}CH_2CCl_3$, but only $RHCCl{-}CH_2CCl_3$ and $RHCBr{-}CH_2CBr_3$. Suggest a mechanism. (R. Davis et al., Chem. Commun., 1387, 1986.)

4. On treating compound **A** with $RhCl(CO)(PPh_3)_2$ an acidic compound is obtained. Treatment of **B** with $Fe(CO)_5$ gives a diene complex. What do you think these new species are?

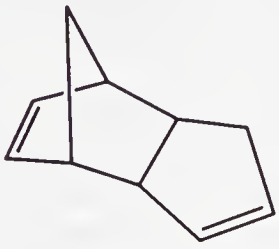


A

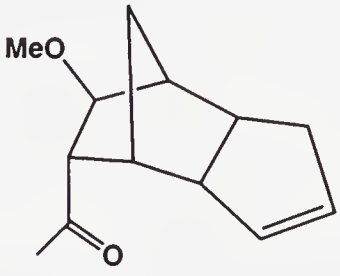


B

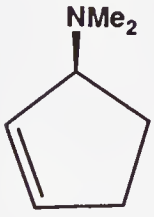
5. Compound **C** gives **D** on treatment with $PdCl_2$ and PPh_3 in methanol, followed by CO and then MeLi. Account for the stereochemistry of the product and explain the role of the PPh_3. In a related reaction, (cod)$PdCl_2$ is first treated with aqueous base, and then CO. The final product has the formula $C_9H_{12}O_2$. What is its structure and stereochemistry?



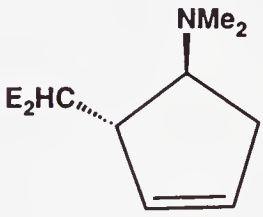
C



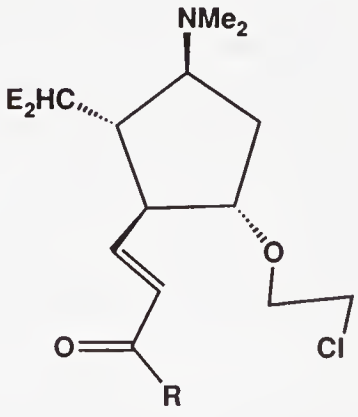
6. Compound **E** reacts with $PdCl_4^{2-}$ to give a complex. This, in turn, reacts with $NaCH(COOEt)_2$ and base to give **F**. Account for the formation of this product. In particular, why did the nucleophile attack where it did, and why is the double bond where it is in **F**? Compound **F** reacts with $PdCl_4^{2-}$ to give a new complex, which in turn reacts with (i) $ClCH_2CH_2OH$/base and (ii) CH_2=CHCOR, to give **G**, which can be converted to a number of prostaglandins. Account for the transformation of **F** to **G**.



E

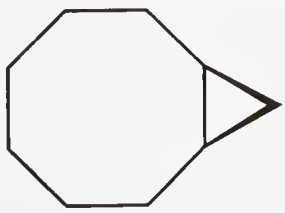


F



G

7. Fp^- reacts with $ClCH_2SMe$ to give a product that can be methylated with Me_3O^+. The methylation product reacts with cyclooctene to give **H**, shown below. Account for the formation of H.



H

8. Although aldehydes can be decarbonylated with $RhCl(PPh_3)_3$, ketones are unaffected. Why do you think this is so? What products, organic, and inorganic, do you think would be formed from RCOCl and $RhCl(PPh_3)_3$?

9. While decarbonylation of RCHO is not catalytic with $RhCl(PPh_3)_3$, they become catalytic using $RhCl(dpe)_2$ (dpe = 1,2-diphenylphosphinoethane) at 120°C or above. What is the origin of the difference in properties between $RhCl(dpe)_2$ and $RhCl(PPh_3)_3$?

10. Cyclohexene reacts with $HgCl_2$ and MeOH, followed by $PdCl_4^{2-}$ and CO, also in MeOH to give a compound $C_7H_{16}O_3$. What is this compound, what stereochemistry does it have, and how was it formed? Propargyl alcohol, $HC{\equiv}CCH_2OH$, gives a compound $C_5H_4O_3$ under similar conditions. What is the structure of this species?

11. In the Heck arylation of cyclohexene by an aryl bromide, what would you expect would be the stereochemistry of the insertion and β-elimination steps (syn or anti)? Given this stereochemistry, what regiochemistry would you expect for the C=C double bond in the final product (i.e., formation of the 1- 2- or 3-alkene)? (R. Semmelhack, *Pure Appl. Chem.*, **53,** 2379, 1981.)

12. Maleic anhydride (MA) reacts with $CoCl(PPh_3)_3$ to give an adduct $Co(MA)Cl(PPh_3)_2$. This adduct, in turn, reacts with 2-butyne to give 2,3-dimethylbenzoquinone. What structure do you propose for the adduct, and what methods might you use to test your suggestion? (L. N. Liebeskind et al., *Organometallics,* **5,** 1086, 1986; **1,** 771, 1982; *J. Am. Chem. Soc.*, **102,** 7397, 1980.)

CHAPTER 15

OXIDATION AND HIGH-OXIDATION-STATE COMPLEXES

Some of the work in organometallic chemistry is problem-driven (e.g., Chapter 12), but exciting and unexpected discoveries have always been made in curiosity-driven work. One approach is to ask what happens when one tries to go beyond the known classes of compound. For example, a very large fraction of organometallic chemistry has been developed with Cp, CO, and PR_3 as supporting ligands. Going to different ligands might have useful or interesting results. We saw one such effort in Section 5.4 with the search for N-, O- and S-donor analogs of Cp. In this chapter we look at high-oxidation-state compounds. This is largely descriptive chemistry because the patterns that underlie it are still emerging.

Organotransition metal chemistry has traditionally been associated with the lower oxidation states. The reason is that polyenes and CO tend to require back donation from the metal to bind well. As the oxidation state rises, back donation becomes less strong and the formation of a stable complex less likely. Few polyene or CO complexes are known for metals in an oxidation state higher than (II). Certain organometallic ligands, notably C_5H_5, C_5Me_5, carbenes, hydride, and alkyl groups, do form high-oxidation-state complexes, probably because they do not require so much back donation. Most are L_nX ligands, which as we saw in Section 5.7 are more tightly bound than L_n ligands.

Even in the 1960s, some high-oxidation-state organometallic compounds were known: Cp_2MX_2 (M = Ti, Zr, Hf), Cp_2MX_3 (M = V, Nb, Ta), $Cp_2Mo_2O_5$, and ReH_9^{2-}. The discovery of WMe_6 in 1972 was important because it suggested that unusual high-oxidation-state non-Cp and non-18e species might be isolable. As we saw in Section 11.1, it was an attempt to make

$TaNp_5$ (Np = neopentyl) that led to the Schrock carbene chemistry, one of the most important areas in high-valent organometallic chemistry. We also look at polyhydrides such as ReH_9^{2-} and then at some cyclopentadienyl complexes such as Cp^*ReO_3. These high-oxidation-state species offer the promise of giving new methods of oxidation.

The maximum oxidation state possible for any transition element is the Group number, N, because only N valence electrons are available for ionization or for forming covalent bonds. Re, in Group 7 and Os in Group 8 are the last elements that are able to attain their theoretical maximum oxidation states (e.g., ReF_7 and OsO_4); Ir and Pt only reach M(VI) in MF_6, and gold shows its highest oxidation state, Au(V), in $[AuF_6]^-$. It is therefore not surprising that most of the organometallic complexes having an oxidation state in excess of 4, come from the elements Ta, W, Re, Os, and Ir. While high oxidation states are usual for the earlier elements [e.g., Ti(IV), Ta(V)], high oxidation states are rare for the later elements, and it is here we might expect to see interesting oxidizing properties. Just as the study of low-valent organotransition metal complexes led to the development of methods for the selective reduction of organic compounds, we can anticipate that high-oxidation-state chemistry will lead to better methods of oxidation. We already looked at OsO_4 in Section 14.2. The higher oxidation states in general are more stable for the third-row transition metals (Section 2.8). We will see that this is also true for organometallic compounds.

As we saw in Section 2.6, the 18e rule is most likely to be obeyed by low-valent diamagnetic complexes. In this chapter, we will find many examples of stable species with electron counts less than 18e, but this is especially true of polyalkyls, some of which are paramagnetic. One reason is that an alkyl ligand occupies much space around the metal in exchange for a modest contribution to the electron count. Second, the high ∂^+ character of the metal leads to a contraction in its covalent radius, because the metal electrons are contracted by the positive charge. Note that this only leads to a slight decrease in the M—L bond lengths, because the ligands acquire ∂^- character and so their covalent radii increase. An increase in the ligand size and a decrease in the metal size makes it more difficult to fit a given number of ligands around a metal in the high-valent case. The low apparent electron count in such species as $MeReO_3$ may be augmented somewhat by contributions from the ligand (O, Cl, NR, etc.) lone pairs. Agostic interactions with the alkyl C—H bonds are probably not widespread in d^0 and high-valent complexes because this interaction needs back donation from the metal (Chapter 3). This means that electron counting in these species is not completely unambiguous. High-valent Cp complexes are more likely to be conventional 18e species, because Cp contributes many more electrons to the metal in proportion to the space it occupies than do alkyl groups. Polyhydrides are almost always 18e, as we might expect for what is one of the smallest, and one of the least electronegative ligands present in the complexes discussed in this section.

15.1 POLYALKYLS

Group 4 We saw in Section 14.1 how $MeTiCl_3$ is used in organic synthesis. The homoleptic $TiMe_4$ (a homoleptic complex contains only one type of ligand), was reported as early as 1959.[1] The bright yellow crystalline material decomposes above ~0°C to methane and a black powder containing Ti, C, and H. Adducts with such ligands as NMe_3, tmeda, or PMe_3 are thermally more stable. Note the hard character of the ligands that bind to $TiMe_4$; this suggests that the high formal oxidation state is real and that the electrophilic metal requires good σ-donor ligands but is incapable of significant back donation. Another clue that points in the same direction is the Grignard-like reactivity of the Ti(IV) alkyls (Section 14.1), which implies the presence of a ∂^- carbon. Since the electronegativity difference between C (2.5) and Ti (1.5) is considerable, the real charge on Ti must be quite positive. As we go to the right and down in the Periodic Table from Ti, we find that the electronegativity increases from 1.5 to about 2.2 for the heavy platinum metals, and so the M—C bond becomes less polar for these elements. This means the metal will be less positive and the alkyl groups less negatively charged in homoleptic alkyls of the later metals in a given oxidation state.

The red $Ti(CH_2Ph)_4$ has been studied crystallographically,[2] and it has been found that the Ti—C_a—C_b angle is only 84–86° (Fig. 15.1). Either the C_a—C_b bond or the C_b carbon of the aromatic ring must be interacting with the metal. The soft ligand CO does react with $Ti(CH_2Ph)_4$, although initial formation of a CO adduct has been proposed, but the final product is $Ti(COCH_2Ph)_2(CH_2Ph)_2$.[3] In contrast to the low thermal stability and high air and acid sensitivity of these alkyls, the bulky complexes **15.1** and **15.2** are

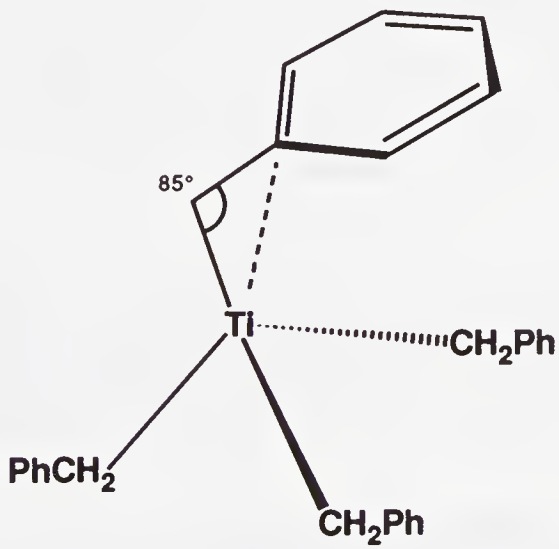
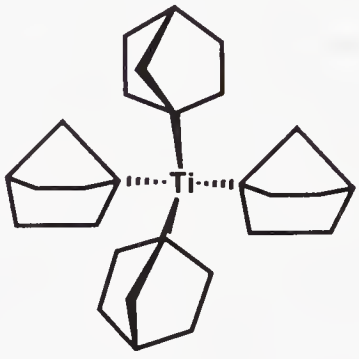
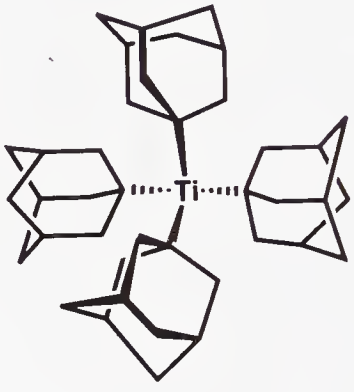


FIGURE 15.1 The structure of $Ti(CH_2Ph)_4$ showing the unusual distortion of the T—C_α—C_β bond.

unusually stable, thanks to steric protection of the metal. Complex **15.1** decomposes only over several days at 100°C, is stable to air even in solution, and decomposes only slowly in dilute H_2SO_4,[4] and **15.2** is stable enough to melt at 234°C.[5] The Zr and Hf alkyls are less well studied, but behave rather similarly to their Ti analogues.



15.1



15.2

Group 5 Even though vanadium has a stable (V) oxidation state, the only alkyls so far discovered are the dark paramagnetic VR_4 species, such as the green-black benzyl complex. The 1-norbornyl is the most stable, decomposing only slowly at 100°. Tantalum, the 3rd row element gives stable alkyls, such as $TaMe_5$, which forms a dmpe adduct.[6] As we go to the right in the Transition Series, the differences between the first-, second-, and third-row elements become more marked. An example is the increasing reluctance of the first- and second-row elements to give alkyls having the highest possible oxidation state, a feature that first appears in Group 5 and becomes dominant in Groups 6 and 7. $TaMe_5$ is trigonal bipyramidal, but attempts to make bulkier TaR_5 complexes always leads to α-elimination to carbenes.

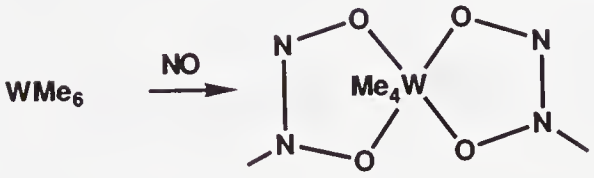
Group 6 A dark red Cr(IV) alkyl $[Cr(CH_2SiMe_3)_4]$ is known but Cr(III) is the common oxidation state (O.S.), as in the orange $Li_3[CrPh_6]$. WMe_6 was the first homoleptic alkyl of Group 6 having the maximum oxidation state allowed for the group. It can decompose explosively at room temperature, but the reactions shown in Eqs. 15.1–15.5 have been identified.[7]

$$WMe_6 \xrightarrow{O_2} W(OMe)_6 \qquad (15.1)$$

$$WMe_6 \xrightarrow{CO} W(CO)_6 + Me_2CO \qquad (15.2)$$

$$WMe_6 \xrightarrow{\text{heat}} 3MeH + C_2H_6(\text{traces}) \qquad (15.3)$$

$$WMe_6 \xrightarrow{Hal_2} WHal_6 + MeHal \qquad (15.4)$$



(15.5)

The reaction with CO may go by migratory insertion, then reductive elimination of species containing the W(COMe)Me unit. The reaction with NO may go via insertion to give W—O—N•—Me, the N-centered radical center may then bind a further NO to give the final product.

Schrock[8] has found that the hydrolysis of some of his alkylidyne complexes leads to oxo-alkyls, such as neopentyl tungsten trioxide, which is air-stable, and is hydrolyzed further only by strong acid or base. The $S(TMS)_2$ reagent (Eq. 15.6)[8] is a useful one for replacing oxygen with sulfur, because the formation of Si—O bonds provides a strong driving force. The mechanistic scheme proposed for the hydrolysis is also shown (Eq. 15.7). Note in Eq. 15.8 how the alkyl groups resist hydrolysis under conditions that would lead to cleavage of Ti—C bonds, a sign of the greater electronegativity of W compared to Ti.

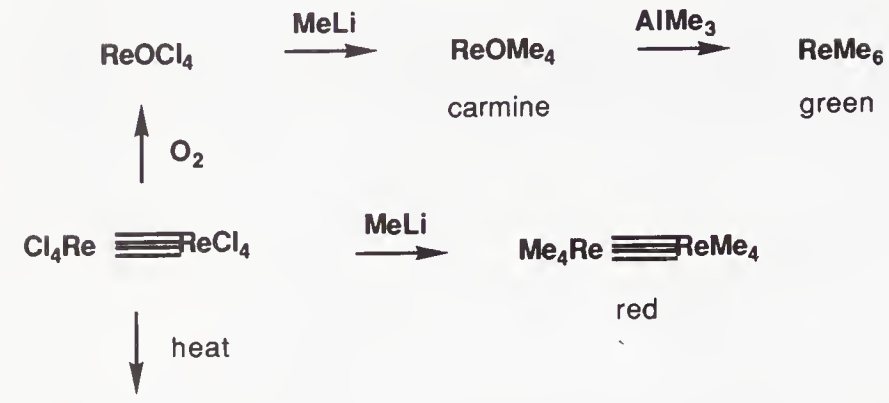
$$t\text{-BuC}{\equiv}\text{W(O}t\text{-Bu)}_3 \xrightarrow{OH^-} t\text{-BuCH}_2\text{—WO}_3 \xrightarrow{S(TMS)_2} t\text{-BuCH}_2\text{—WS}_3 \qquad (15.6)$$

$$\begin{aligned} t\text{-BuC}{\equiv}\text{W(O}t\text{-Bu)}_3 &\xrightarrow{OH^-} \{t\text{-BuC}{\equiv}\text{W(OH)(O}t\text{-Bu)}_3\}^- \xrightarrow{-t\text{-BuOH}} \\ &\{t\text{-BuCH}{=}\text{W(}{=}\text{O)(O}t\text{-Bu)}_2\}^- \xrightarrow{H_2O} \\ &\{t\text{-BuCH}_2\text{—W(}{=}\text{O)(OH)(O}t\text{-Bu)}_2\}^- \xrightarrow{H_2O} \\ &t\text{-BuCH}_2\text{—WO}_3 + 3t\text{-BuOH} \end{aligned} \qquad (15.7)$$

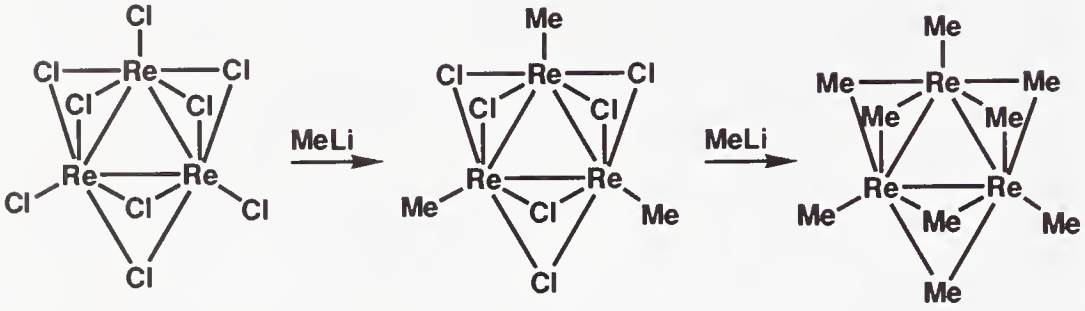
$$t\text{-BuC}{\equiv}\text{W(CH}_2t\text{-Bu)}_3 \xrightarrow{H_2O} \{(CH_2t\text{-Bu})_3W(=O)\}_2(\mu\text{-O}) \qquad (15.8)$$

Wilkinson has made an analogous series of M(VI) complexes of the type $M(=Nt\text{-Bu})_2(2,4,6\text{-}Me_3C_6H_2)_2$ for Cr, Mo, and W. The Cr complex is deep red and air-stable.[9]

Group 7 Only one Mn(IV) alkyl is known, the green Mn(1-norbornyl)$_4$, but rhenium has one of the most extensive series of high-oxidation-state alkyls, some of which are illustrated in Eq. 15.9.[10]



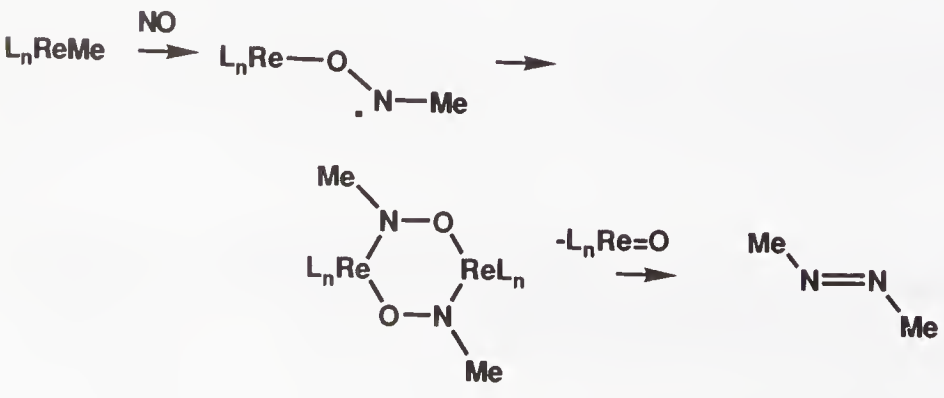
(15.9)



In contrast to the reactions of O_2 and NO with WMe_6 (Eqs. 15.1–15.5), interesting oxo-alkyls can be obtained by oxidation of $ReMe_6$ with these oxidants. The higher electronegativity of Re compared to W may make the Re alkyls generally more stable to air, acids, and attack by nucleophiles. $ReOMe_4$ fails to react with the Lewis bases that usually give complexes with the polyalkyls of the earlier metals. The dirhenium alkyls probably have the eclipsed structure characteristic of quadruply bonded metals (Section 13.1), and the trirhenium complexes are triangular clusters with Re—Re bonds and bridging halide or alkyl groups.[10]

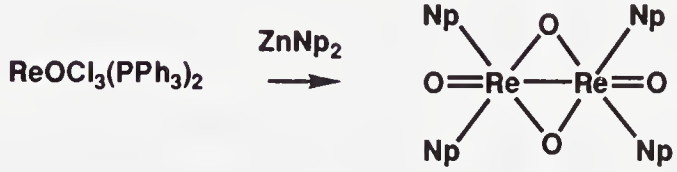
$$ReMe_6 \xrightarrow{O_2} ReOMe_4 \xrightarrow{NO} cis\text{-}ReO_2Me_3 \xrightarrow{O_2} ReO_3Me \qquad (15.10)$$

The NO reactions are said to go as follows:



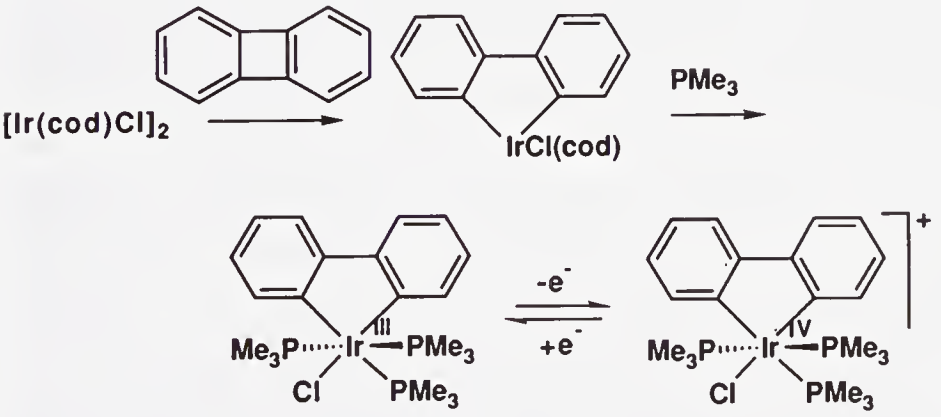
(15.11)

$ZnNp_2$ (Np = *t*-$BuCH_2$) and $ReOCl_3(PPh_3)_2$ give the unusual dirhenium tetraalkyl shown in Eq. 15.12.[11] The presence of a Re—Re bond is believed to account for the short intermetallic distance of 2.6 Å.



(15.12)

Groups 8–10 Purple Fe(IV) and brown Co(IV) norbornyls are known, but most alkyls of these groups are M(II) or M(III) such as the yellow $Li_2[FeMe_4]$ or *fac*-$[RhMe_3(PMe_3)_3]$. Co(III) alkyls have been studied in connection with coenzyme B_{12} chemistry (Section 16.2). Ir(IV) aryls have recently been reported by electrochemical oxidation of Ir(III) precursors.[12] The biphenyl-1,2-diyl ligand seems to be especially stabilizing for high oxidation states and is the C analog of the bipyridyl ligand that has proved so useful in coordination chemistry. Note how the strained ring in the biphenylene starting material helps drive the C—C bond cleavage reaction:



(15.13)

Nickel alkyls are always and Pd alkyls often M(II), such as the golden-yellow $Li_2[NiMe_4]$ or $PdMe_2$(bipy). In many organic synthetic applications of Pd, formation of a Pd(IV) alkyl had to be postulated, but for many years no isolable example was found.[13a] The first aryl, $PdCl_3(C_6F_5)$(bipy) (1975),[13b] and the first alkyl, $PdIMe_3$(bipy) (1986)[13c] (Eq. 15.14), both made use both of the stabilizing N-donor bipy group and the exceptionally strong M-C_6F_5 and M—Me bonds.

$$Pd(bipy)Me_2 \xrightarrow{MeI} Pd(bipy)Me_3I \qquad (15.14)$$

Of all polyalkyls, the longest known are the Pt(IV) species. The orange complex $[Me_3Pt(\mu^3\text{-}I)]_4$, which has a cubane structure with octahedral platinum, was described by Pope and Peachey in 1907–1909.[13d] Some of its reactions (Eqs. 15.15–15.17) illustrate how the chemistry resembles that for

aqueous high-valent metal ions, such as the Co(III) Werner compounds that we looked at in Chapter 1.

$$[Me_3Pt(\mu^3\text{-}I)]_4 \xrightarrow{L} Me_3PtIL_2 \qquad (15.15)$$

(L = NH_3, en, py, PMe_3)

$$\xrightarrow{\text{acacH}} [PtMe_3(acac)]_2 \qquad (15.16)$$

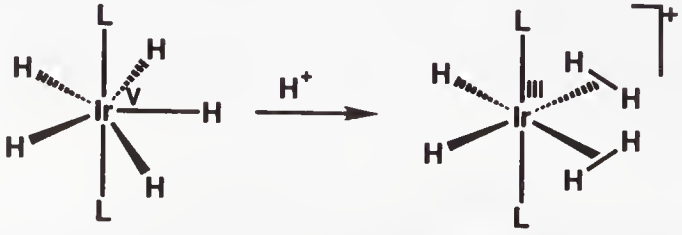
$$\xrightarrow{\text{water}} [PtMe_3(H_2O)_3]^+ \qquad (15.17)$$

Group 11 Cu and Ag give only M(I) alkyls, such as the bright yellow and explosive $[CuMe]_n$, but Au forms compounds from Au(I) to (III) such as $[Au(C_6F_5)_4]^-$. With many examples recently known, the reactions of high-valent alkyls now need to be investigated in more detail.

15.2 POLYHYDRIDES

Polyhydrides[14a] are complexes such as $FeH_4(PR_3)_3$, with a H:M ratio exceeding 3. Hydrogen is not as electronegative as carbon, and so the metal in a polyhydride is not as oxidized as in a polyalkyl. Polyhydrides therefore retain more of the properties of low-valent complexes than do polyalkyls. For example, many of them are 18e, and relatively soft ligands (in the vast majority of cases a phosphine or a cyclopentadienyl) are required to stabilize them. Rare examples of N-donor-stabilized polyhydrides are $[TpReH_6]$ and $[BpReH_7]$ (Tp = tris-pyrazolylborate (**5.37**) Bp = bis-pyrazolylmethane).[14b]

A second reason why the metal may not be as highly oxidized as is suggested by the high formal oxidation state is that not all polyhydrides have a *classical* structure, with all-terminal M—H bonds. Some are really dihydrogen complexes.[15] For example, $IrH_5(P\{C_6H_{11}\}_3)_2$ is classical and so authentically Ir(V), but $[IrH_6(P\{C_6H_{11}\}_3)_2]^+$ is in fact[16] $[Ir^{III}H_2(H_2)_2(P\{C_6H_{11}\}_3)_2]^+$, and so is Ir(III) not Ir(VII) because the dihydrogen ligand must be regarded as a 2e L-type ligand, contributing nothing to the oxidation state (Eq. 15.18).



(15.18)

$ReH_7(P\{p\text{-tolyl}\}_3)_2$ has the structure $ReH_5(H_2)L_2$ with a stretched H—H distance (1.357 Å[17a] instead of 0.8–1.0 Å in normal or unstretched H_2 complexes) and so the oxidation state is difficult to define because the structure is half

way between the Re(V) and Re(VII) extreme formulations. $Re^{VII}H_7(dppe)$ is classical, however.[17b] A related Re tetrahydride exists in a tautomeric equilibrium (Eq. 15.19).[18a]

$$[ReH_4(CO)(PMe_2Ph)_3]^+ \rightleftharpoons [ReH_2(H_2)(CO)(PMe_2Ph)_3]^+ \quad (15.19)$$

There is still doubt about the structures of some other polyhydrides, and this is an area in which X-ray crystallography is of limited use, because of the small X-ray scattering factor for H. Crystals of the size appropriate for neutron work can be difficult to grow (Section 10.10), and NMR spectroscopic data (Section 10.7) are not always definitive.

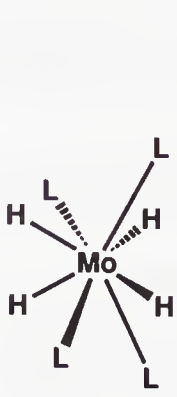
Polyhydrides often have coordination numbers in excess of 6, a consequence of the small size of the hydride ligand. Nine is the normal limit on the number of ligands imposed by the availability of nine orbitals, but if a polyhydride can adopt a nonclassical structure with an H_2 molecule bound via a single metal orbital, this limit can be exceeded. A rare example of such a complex is "$[WH_7(PPh(CH_2CH_2PPh_2)_2)]^+$" (Eq. 15.20), which is stable up to $-20°C$ in solution.[18b] Since **15.3** is classical with terminal M—H bonds, and therefore d^0, there are no metal lone pairs and so protonation must occur at the M—H bond to give an H_2 complex directly. If it were classical, **15.4** would exceed the maximum allowed oxidation state and coordination number for a transition metal.

$$\underset{\textbf{15.3}}{WH_6(triphos)} + H^+ \longrightarrow \underset{\textbf{15.4}}{\text{“}[WH_7(triphos)]^+\text{”}} \quad (15.20)$$

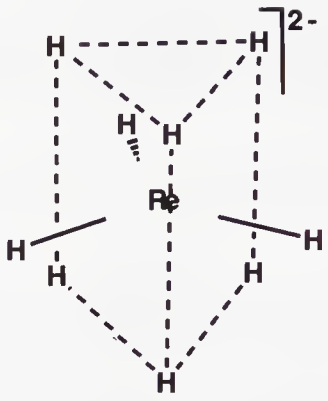
(triphos = $PPh(CH_2CH_2PPh_2)_2$)

Compound **15.4** must therefore have at least one H_2 ligand present but is probably $[WH_3(H_2)_2(triphos)]^+$. This d^2 formulation would allow for some back bonding to the H_2 ligands to help stabilize the M—(H_2) bond; d^0 H_2 complexes are unknown. Spectroscopic methods show that some H_2 ligands are present but do not tell the number. The 7-coordinate polyhydrides, such as $IrH_5(PEt_2Ph)_2$, have a pentagonal bipyramidal structure, rather than the much more usual capped octahedron. This is also a consequence of the small size of the hydride ligand, five of which can bind in the equatorial plane of the complex. The 8-coordinate examples (e.g., $MoH_4(PMePh_2)_4$, **15.5**) tend to be dodecahedral, with the H ligands in the more hindered A sites (see Table 2.5). Nine coordinate hydrides are always found in the tricapped trigonal prismatic geometry first seen for $[ReH_9]^{2-}$ (**15.6**), an unusual example of a homoleptic hydride.

Almost all polyhydrides are fluxional in the ^1H NMR, and show coupling to any phosphine ligands present. The number of hydrides present (n) can be predicted with some confidence from the 18e rule, but a useful experimental



15.5



15.6

method involves counting the multiplicity ($n + 1$) of the ^{31}P NMR peak, after the phosphine ligand protons have been selectively decoupled (Section 10.4).

The electron-rich character of polyhydrides is shown by the fact that many of them protonate, either to give stable cationic polyhydrides, or to lose H_2 to give coordinatively unsaturated species, which can bind any ligand available, such as the solvent (Eq. 15.21).[19] Other polyhydrides can lose H_2 and bind N_2 or CO (Eq. 15.23);[20] for nonclassical species this is especially easy. $ReH_7(PPh_3)_2$ is particularly interesting in that it can bind ligands such as pyridine,[21] phosphines,[22] and polyenes[23] to give substituted polyhydrides (Eq. 15.24).

$$MoH_4(PMePh_2)_4 \xrightarrow{HBF_4,\ MeCN} [MoH_2(MeCN)_3(PMePh_2)_3](BF_4)_2 \quad (15.21)$$

$$WH_4(PMePh_2)_4 \xrightarrow{HBF_4,\ thf} [WH_5(PMePh_2)_4]^+ \quad (15.22)$$

$$Ru(H_2)H_2(PPh_3)_2 \xrightarrow{L} RuLH_2(PPh_3)_2 \quad (15.23)$$

$$Re(H_2)H_5(PPh_3)_2 \xrightarrow{diene} (diene)ReH_3(PPh_3)_2 \quad (15.24)$$

Photochemical substitution is useful because it usually expels H_2 to generate one or more 2e sites at the metal (Eq. 15.25).[23]

$$MoH_4(PMePh_2)_4 \xrightarrow{h\nu,\ C_2H_4} Mo(C_2H_4)_2(PMePh_2)_4 \quad (15.25)$$

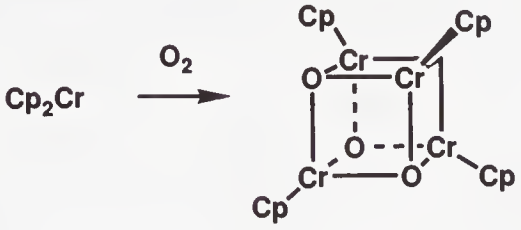
The importance of polyhydrides in the activation of alkanes has already been discussed (Eq. 12.31).

15.3 CYCLOPENTADIENYL COMPLEXES

The Cp and especially the Cp* ligands are very effective at stabilizing high oxidation states. While the Cp complexes can be polymeric and difficult to characterize, the Cp* species are often well-behaved, soluble complexes.

Several high-oxidation-state halo complexes have been known for many years, for example, Cp_2TiCl_2, Cp_2NbCl_3, Cp_2TaCl_3, and $[Cp_2MoCl_2]^+$. A well-known route to oxo and halo species is oxidation of the cyclopentadienyl carbonyls or the metallocenes.[24–27] The $[CpMO]_4$ complexes, of which the earliest (1960) was Fischer's $[CpCrO]_4$, have the cubane structure (**15.7**).[25]

$$CpV(CO)_4 \xrightarrow{HBr/O_2,\ or\ Cl_2} CpVOX_2 \qquad (15.26)^{24}$$



(15.27)

15.7

$$[CpMo(CO)_3]_2 \xrightarrow{O_2,\ h\nu} CpMoO_2Cl + (CpMoO)_2(\mu\text{-}O)_2$$
$$+ [(CpMoO_2)_2(\mu\text{-}O)] \xrightarrow{\text{hydrolysis}} [CpMoO]_4 \qquad (15.28)^{26}$$

$$CpMo(CO)_3Me \xrightarrow{PCl_5} CpMoCl_4 \qquad (15.29)^{27a}$$

Reaction of carbonyls with air or with PCl_5 seem to be general methods for preparing oxo and chloro complexes (Eqs. 15.28 and 15.29). These compounds can also react with organic peroxides; for example, $Cp^*W(=O)_2Me$ gives the very unusual η^2-peroxo complex, $Cp^*W(=O)(\eta^2\text{-}O_2)Me$.[27b]

Rhenium As one might perhaps expect, rhenium seems to have the most extensive oxo chemistry of this type. The early elements are so oxophilic that organometallic groups are unlikely to survive, when lower valent species are oxidized or hydrolyzed. Re is the last element, as we go to the right in the Periodic Table, for which the M=O bond is still reasonably stable. Herrmann[28] has shown how to make a whole series of oxo complexes of Cp^*Re. The Re=O vibrations show up very strongly in the IR spectrum, as for the yellow Cp^*ReO_3 at 878 and 909 cm^{-1}, and the IR provides useful data for the characterization of all the complexes shown.

$$Cp^*Re(CO)_3 \xrightarrow{O_2,\ h\nu\ or\ H_2O_2} Cp^*ReO_3 \qquad (15.30)^{28}$$

Partial reduction of Cp^*ReO_3 under various conditions can lead to the species shown in Fig. 15.2.[28] Note the selectivity of $SnMe_4$ alkylation versus MeMgBr. The binuclear species are interesting because the short M—M distances found indicate that M—M bonds are present, a somewhat unexpected feature for such high-valent metals. CO reduction gives an unusual oxocarbonyl; CO is characteristic of low-valent, and M=O of high-valent metals, and the two

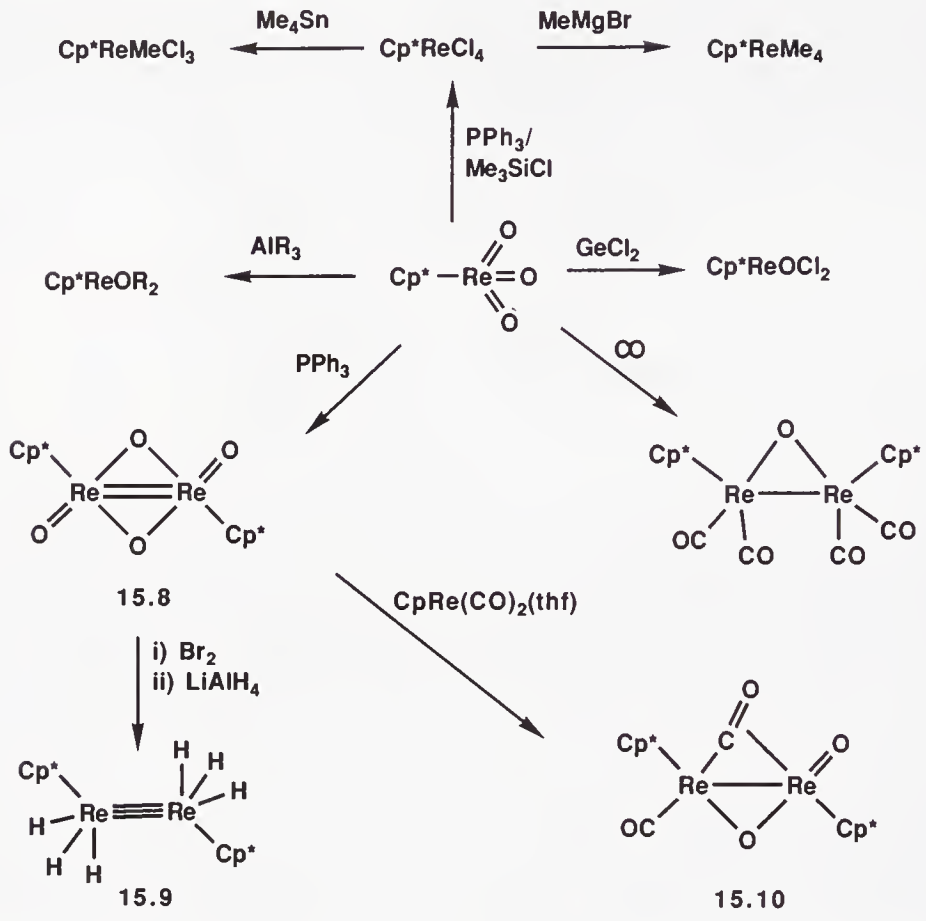


FIGURE 15.2 Some high-oxidation-state organometallic chemistry of the Cp*Re fragment.

ligands are rarely seen in the same complex. Compound **15.9** is interesting in being an unusual cluster hydride. Compound **15.10** is a mixed-valent species, the metal bearing the terminal CO being Re(II), and the one bearing the terminal oxo group being Re(IV); the semibridging CO is also a striking feature of the complex. The Cp^*ReX_4 systems in Fig. 15.2 all have low- and high-spin forms in equilibrium leading to unusual temperature dependent shifts in the ^1H NMR spectra, for example, the Re*Me* signal in Cp^*ReCl_3Me is broad and shifts from 13.5δ at −50°C to 36.5δ at +50°C in $CDCl_3$.

Other Metals Maitlis[29] has described a number of Ir(V) alkyls, such as Cp^*IrMe_4. $M(\eta^3\text{-allyl})_4$ complexes also exist for Zr, Nb, Ta, Mo, and W.[30]

15.4 ALKYNE COMPLEXES

Alkynes have normally been considered as ligands that bind to low-valent metals. Several recent cases of binding to high-valent centers have changed

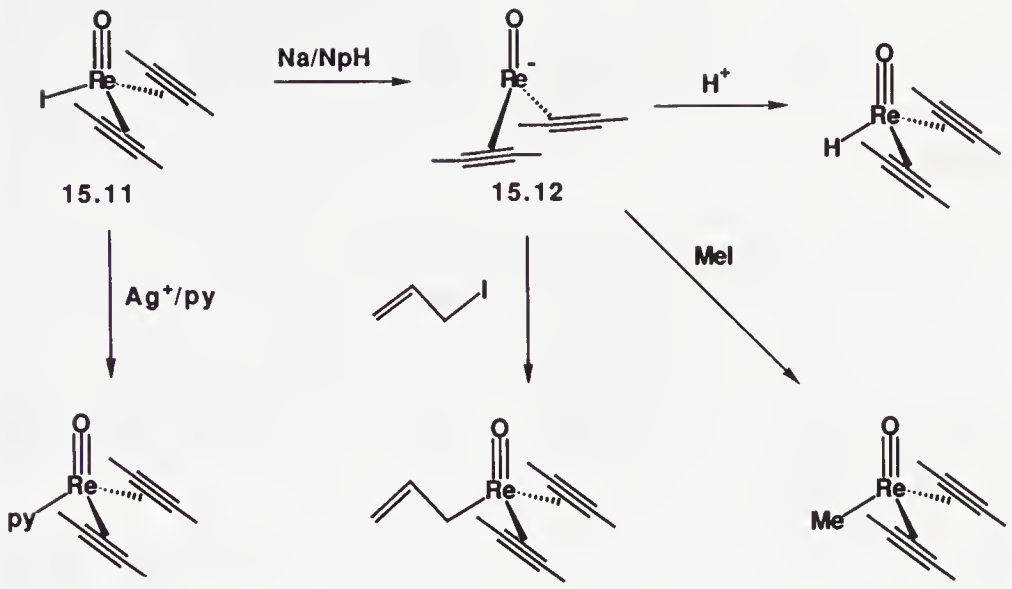


FIGURE 15.3 Some oxoalkyne chemistry of rhenium.

the picture. No d^0 metal has given such a complex to date because no back donation is possible in this case, but d^2 metals and higher are able to do so. C_2Cl_4 first reduces W(VI) in the reaction shown in Eq. 15.31, which shows how the unstable alkyne ClC≡CCl can bind to W(IV).[31]

$$ClC{\equiv}CCl + C_2Cl_4 + WCl_6 \longrightarrow (ClC{\equiv}CCl)WCl_4 \xrightarrow{PPh_4Cl} [(ClC{\equiv}CCl)WCl_5]^- \quad (15.31)$$

Rhenium The unusual species $ReO(RC{\equiv}CR)_2I$ (**15.11**) was prepared by Mayer by Eq. 15.32.[32a]

$$ReO_2I(PPh_3)_2 \xrightarrow{MeC{\equiv}CMe} ReOI(MeC{\equiv}CMe)_2 \quad (15.32)$$

This formally Re(III), d^4 compound is diamagnetic and is exceptional in having both an oxo ligand characteristic of high oxidation states and an alkyne, more common in low oxidation states. As we saw in Fig. 11.7, d^2 is expected to be the highest d^n configuration for an octahedral metal oxo complex; otherwise the extra electrons would have to go in M≡O π^* orbitals. This complex avoids the problem by adopting a tetrahedral structure with its "two-below-three" ligand field splitting pattern (Fig. 1.4). The two lowest energy orbitals can now accept four electrons in **15.11**. Reduction of **15.11** with sodium naphthalene at −80°C gives the salt **15.12** (Fig. 15.3), which is formally a Re(I) oxo species. The Re=O bond is long (1.76 Å in **15.12** vs. 1.7 Å in **15.11**) and has a low-energy Re=O stretch in the IR (824 cm^{-1} in **15.12** vs 975 cm^{-1} in **15.11**), consistent with the two extra electrons supplied by the reducing agent going into a Re≡O π^* orbital and so reducing the Re—O bond order from three to two. Compound **15.12** reacts with electrophiles to

give the very unusual oxo hydride and oxo alkyl shown in Fig. 15.3, and oxidation leads to the dimers also shown.[32b]

REFERENCES

1. K. Clauss and C. Beermann, *Angew. Chem.*, **71,** 627, 1959.
2. W. Bassi et al., *J. Am. Chem. Soc.*, **93,** 3788, 1971.
3. L. Marko et al., *J. Organometal. Chem.*, **199,** C31, 1980.
4. B. K. Bower and H. G. Tennent, *J. Am. Chem. Soc.*, **94,** 2512, 1972.
5. R. M. G. Roberts, *J. Organometal., Chem.*, **63,** 159, 1973.
6. G. Wilkinson et al., *Chem. Commun.*, 159, 1976; R. R. Schrock and P. Meakin, *J. Am. Chem. Soc.*, **96,** 159, 1974.
7. G. Wilkinson et al., *J. Chem. Soc., Dalton,* 872, 1973.
8. I. Feinstein-Jaffé, J. C. Dewan, and R. R. Schrock, *Organometallics,* **4,** 1189, 1985.
9. G. Wilkinson et al., *Chem. Commun.,* 1398, 1986.
10. (a) G. Wilkinson et al., *J. Chem. Soc., Dalton,* 607, 1975; 1488, 1976; 334, 1980; *Nouv. J. Chim.*, **1,** 389, 1977; I. R. Beattie and P. J. Jones, *Inorg. Chem.*, **18,** 2318, 1979; (b) W. A. Herrmann, *Angew. Chem., Int. Ed.*, **27,** 1297, 1988.
11. J. M. Huggins et al., *J. Organometal. Chem.*, **312,** C15, 1986.
12. Z. Lu and R. H. Crabtree, *Chem. Commun.*, 1994, in press.
13. (a) A. J. Canty, *Acct. Chem. Res.*, **25,** 83, 1992; (b) R. Usón et al., *J. Organometal. Chem.*, **96,** 307, 1975. (c) A. J. Canty et al., *Chem. Commun.*, 1722, 1986.
13. W. J. Pope and S. J. Peachey, *J. Chem. Soc.*, 571, 1909.
14. (a) G. G. Hlatky and R. H. Crabtree, *Coord. Chem. Rev.*, **65,** 1, 1985; (b) D. G. Hamilton, X.-L. Luo, and R. H. Crabtree, *Inorg. Chem.*, **28,** 3198–3203, 1989.
15. G. J. Kubas et al., *Acct. Chem. Res.*, **21,** 120, 1988; R. H. Crabtree, *Acct. Chem. Res.*, **23,** 95, 1990; *Angew. Chem., Int. Ed.*, **32,** 789, 1993.
16. R. H. Crabtree and M. Lavin, *Chem. Commun.*, 1661, 1985; *J. Am. Chem. Soc.*, **108,** 4032, 1986; R. H. Crabtree and D. Hamilton, *J. Am. Chem. Soc.*, **108,** 3124, 1986.
17. J. A. K. Howard et al., *Chem. Commun.:* (a) 241, 1991; (b) 1502, 1988.
18. (a) X. L. Luo and R. H. Crabtree, *J. Am. Chem. Soc.*, **112,** 6912, 1990; (b) D. Michos, X.-L. Luo, J. W. Faller, and R. H. Crabtree, *Inorg. Chem.*, **32,** 1370, 1993.
19. K. G. Caulton et al., *Inorg. Chem.*, **21,** 4185, 1982.
20. G. Wilkinson et al., *J. Chem. Soc., Dalton,* 1716, 1977; V. D. Makhaev, A. P. Borisov, et al., *Koord. Khim.*, **4,** 1274, 1978; **8,** 963, 1982.
21. R. O. Harris et al., *J. Organometal. Chem.*, **54,** 259, 1973.
22. D. Baudry, M. Ephritikine, H. Felkin, et al., *J. Organometal. Chem.*, **224,** 363, 1982.
23. M. S. Wrighton, G. L. Geoffroy, et al., *J. Am. Chem. Soc.*, **104,** 7526, 1982.
24. H. J. Leifde-Meijer et al., *Rec. Trav. Chem.*, **80,** 831, 1961; *Chem. Ind. (London)*, 119, 1960.

25. (a) E. O. Fischer et al., *Chem. Ber.*, **93,** 2167, 1960; (b) F. Bottomley et al., *J. Am. Chem. Soc.*, **104,** 5651, 1982.
26. M. L. H. Green et al., *J. Chem. Soc.*, 1567, 1964.
27. (a) R. R. Schrock et al., *Organometallics,* **4,** 953, 1985; (b) J. W. Faller and Y. Ma, *J. Organometal. Chem.*, **368,** 45, 1989.
28. W. A. Herrmann et al., *Angew. Chem., Int. Ed.*, **23,** 383, 515, 1983; **24,** 50, 860, 1984; *J. Organometal. Chem.*, **272,** 55, 287, 329, 1985; **300,** 111, 1986.
29. P. Maitlis et al., *Chem. Commun.*, 310, 1982.
30. G. Wilke, *Angew. Chem., Int. Ed.*, **2,** 105, 1963; **5,** 151, 1966.
31. K. Dehnicke, *Z. Anorg. Allg. Chem.*, **533,** 73, 1986.
32. (a) J. M. Mayer and T. H. Tulip, *J. Am. Chem. Soc.*, **106,** 3878, 1984; J. M. Mayer, D. L. Thorn, and T. H. Tulip, *J. Am. Chem. Soc.*, **107,** 7454, 1985; (b) J. M. Mayer et al., *J. Am. Chem. Soc.*, **109,** 157, 6896, 1987.

PROBLEMS

1. Suggest reasons why $Ti(CH_2Ph)_4$ does not form a stable CO adduct.

2. Given that an unstable CO adduct of $Ti(CH_2Ph)_4$ is an intermediate on the way to forming $Ti(COCH_2Ph)_2(CH_2Ph)_2$, suggest reasons why this adduct might be especially reactive.

3. Why do you think V only gives VR_4 as the highest-oxidation-state alkyl, but Ta can give TaR_5?

4. What mechanism is likely for Eq. 15.3, and would **15.1** and **15.2** be likely to give the same type of reaction?

5. The ethylenes in $Mo(C_2H_4)_2(PR_3)_4$ are mutually trans. What do you think the orientation of their C=C bonds would be with respect to one another? (Draw this looking down the principal axis of the molecule.)

6. Why are alkene polyhydrides so rare? Why is $Re(cod)H_3(PR_3)_2$ an exception, given that its stereochemistry is pentagonal bipyramidal, with the phosphines axial?

7. Why do you think Cr(1-norbornyl)$_4$ (with a structure analogous to **15.1**) is diamagnetic? Write a crystal field splitting diagram for the molecule. On the basis of your results, predict the magnetic behavior of Cr(1-norbornyl)$_4$.

8. Would you expect easy rotation of the alkynes in **15.11** about the alkyne–metal bond? Explain.

CHAPTER 16

BIOORGANOMETALLIC CHEMISTRY

In the future, chemistry will be increasingly influenced by biology as a result of the dramatic advances in our understanding of the chemical basis of life.[1] Both organic and inorganic compounds have long been known to be present in living things. Only very recently has it become clear that organometallic species also occur in biology, both as stable species and as reaction intermediates. Nature uses organometallic chemistry sparingly, but it has been suggested[2a] that the examples we see today are relics of early life forms, which had to live on simple molecules, such as H_2, CO, and CH_4 and may have used organometallic chemistry more extensively. The elements Co and Ni are rather unusual in biology, but when they are found, it is often in the context of organometallic chemistry. We will first review the basic aspects of biochemistry as they apply to enzymes.[1]

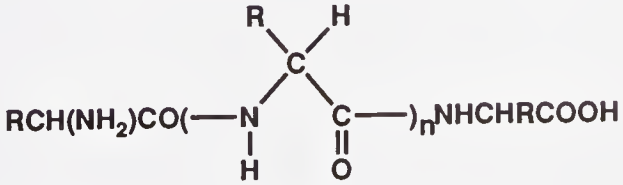
All the systems described in this chapter are organometallic in character. Coenzyme B_{12} has several forms with M—C or M—H bonds. In nitrogen fixation, CO binds competitively at the active site. The nickel enzymes are believed to operate via intermediates with M—H (H_2ase) or M—C bonds (CODH and MeCoM reductase).

16.1 INTRODUCTION

One of the important features of the chemistry of life is that biochemical reactions have to be kept under strict control. They must only happen as they are required, where they are required. One way of doing this is to employ

reactions that can only proceed when catalyzed. The organism now only has to turn the catalysts on and off to control its biochemistry. The catalysts of biology are called *enzymes,* and they can be soluble, or bound to a membrane, or even part of an enzyme complex, in which case they act as a cog in a larger piece of biochemical machinery.

Proteins Essentially all enzymes are *proteins;* that is, they are made up of one or more polypeptide chains having the structure shown in **16.1.** The value of n is usually from 20–100, and there may be several separate polypeptide chains or subunits in each enzyme. Sometimes two or more proteins must bind together to give the active enzyme. The monomers from which protein polymers are built up are the amino acids, $RCH(NH_2)COOH$, which always have the L configuration. There are more than 20 different amino acids commonly found in proteins, each having a different R group (see Table 16.1). The ordering of the R groups along the protein chain is its *primary structure,* and is of great significance. Each enzyme has its own specific ordering, which often differs in minor ways if we isolate the same enzyme from one species rather than another. Chains that have similar sequences are said to be *homologous.* In spite of minor sequence differences, the chains can fold in the same way in all cases to give an active enzyme. The sequence of the R groups is believed to decide the way in which the chain will fold, and the R groups also provide the chemical functional groups that enable the protein to perform its function. The problem of predicting the folding pattern of a polypeptide (usually found by X-ray diffraction) from its primary structure is still unsolved. Two types of *secondary structure* are common, the rod-like α helix and the flat β sheet. In each case the folding is decided by the patterns of many hydrogen bonds formed between N—H groups of one peptide bond and CO groups of another. *Tertiary structure* refers to the finer details resulting from H-bonding or other interactions between the R groups of the residues. Finally, *quarternary structure* refers to the way the subunits pack together. Greek letters are used to designate subunit structure; for example, an $(\alpha\beta)_6$ structure is one in which two different chains α and β form a heterodimer, which, in turn, associates into a hexamer in the native form of the protein.



16.1

Certain R groups are "greasy" and will tend to be found in the interior of the structure. Others are hydrophilic and are likely to be found at the surface.

TABLE 16.1 Some Common Amino Acids

Name	Symbol	R	Remarks
Glycine	Gly	H	Nonpolar R group
Alanine	Ala	Me	"
Valine	Val	*i*-Pr	"
Leucine	Leu	*i*-PrCH$_2$	"
Phenylalanine	Phe	PhCH$_2$	"
Glutamic acid	Glu	$^-$O$_2$CCH$_2$CH$_2$	Anionic R group[a]
Aspartic acid	Asp	$^-$O$_2$CCH$_2$	"
Lysine	Lys	$^+$H$_3$N(CH$_2$)$_4$	Cationic R group[a]
Arginine	Arg	$^+$H$_2$N=C(NH$_2$)NH(CH$_2$)$_3$	"
Tyrosine	Tyr	HO(C$_6$H$_4$)CH$_2$	Polar but not ionized
Serine	Ser	HOCH$_2$	"
Threonine	Thr	MeCH(OH)	"
Asparagine	Asn	H$_2$NOCCH$_2$	"
Methionine	Met	MeSCH$_2$CH$_2$	Soft nucleophile
Cysteine	Cys	HSCH$_2$	—[b]
Histidine	His	C$_3$N$_2$H$_4$CH$_2$	—[c]

[a]Predominant protonation state at pH 7.
[b]Binds metal ions and links polypeptide chains via an —CH$_2$S—SCH$_2$— group.
[c]Heterocyclic amine base that acts as a nucleophile or binds metal ions.

Some are sufficiently acidic or basic so as to be deprotonated or protonated at physiological pH (generally close to 7); these provide a positive or negative charge at the surface of the protein. When histidine is present, it usually serves one of two special functions: either as a nucleophile to attack the substrate, or to ligate any metal ions present. Similarly, cysteine either holds chains together by formation of a disulfide link (RS—SR) with a cysteine in another chain, or binds a metal ion as a thiolate complex (RS—ML$_n$). Any nonpolypeptide component of the protein required for activity (e.g., a metal ion, or an organic molecule) is called a *cofactor.* Sometimes two or more closely related protein conformations are possible. Which is adopted may depend on whether the substrate for the protein or the required cofactors are bound. Such a "conformational change" may turn the enzyme on or off or otherwise modify its properties. Proteins can lose the conformation required for activity if we heat, add urea (which breaks up the H-bond network) or salts, or move out of the pH range in which the native conformation is stable. This leads to denatured, inactive protein, which in certain cases can refold correctly when the favorable conditions of temperature, ionic strength and pH are reestablished.

Metalloenzymes More than half of all enzymes have metal ions in their structure; these are called *metalloenzymes.* In most cases, the metals are

essential to the action of the enzyme, and are often at the active site where the substrate for the biochemical reaction is bound. Most organisms require certain "trace elements" for growth. Some of these trace elements are the metal ions that the organism incorporates into its metalloenzymes. Of the inorganic elements, the following have been found to be essential for some species of plant or animal: Mg, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, B, Si, Se, F, Br(?), and I. New elements are added to the list from time to time, and the role of the established trace elements is gradually becoming more clear. In addition, Na, K, Ca, phosphate, sulfate, and chloride are required in bulk rather than trace amounts. Metal ions also play an important role in nucleic acid chemistry. The biochemistry of these elements has been termed *bioinorganic* chemistry.[2]

Modeling In addition to purely biochemical studies, bioinorganic chemistry also includes studies that try to elicit the chemical principles that are at work in biological systems. Two such areas are structural and functional modeling. In structural modeling, the goal is to prepare a small molecule, such as a metal complex, that can be structurally and spectroscopically characterized in order to compare the results with physical measurements on the biological system. This can help determine the structure, oxidation state, or spin state of a metal cofactor. It is often the case that a small molecule complex can reproduce many important physical properties of the target. Less common is functional modeling, where the goal is to reproduce some chemical property of the target in a small molecule complex and so try to understand what features of the structure promote the chemistry. Typical properties include the redox potential of a metal center or its catalytic activity. Functional models *with the correct metal and ligand set* that reproduce the catalytic activity of the target system are still rare. Many so-called models use the "wrong" metal or ligands and so provide less relevant information.

Molecular Recognition A key principle of biochemistry is the recognition of one molecule or fragment of a biochemical structure by another. One entity will bind strongly to another, whether it is binding of the substrate with its specific enzyme, or of a hormone with its receptor, or of a drug with its receptor. This happens as a result of complementarity between the two fragments with regard to shape, surface charges, and the possibility of forming hydrogen bonds. It is this chemical recognition that accounts for the astonishing specificity of biology; for example, only one enantiomer of a compound may be accepted by an enzyme, and only the human, but not the monkey, version of a given protein may be recognized by a suitable antibody (specific binding protein). It is largely the three-dimensional rigidity and the rich pattern of possible chemical functional groups in proteins that allows this to happen.

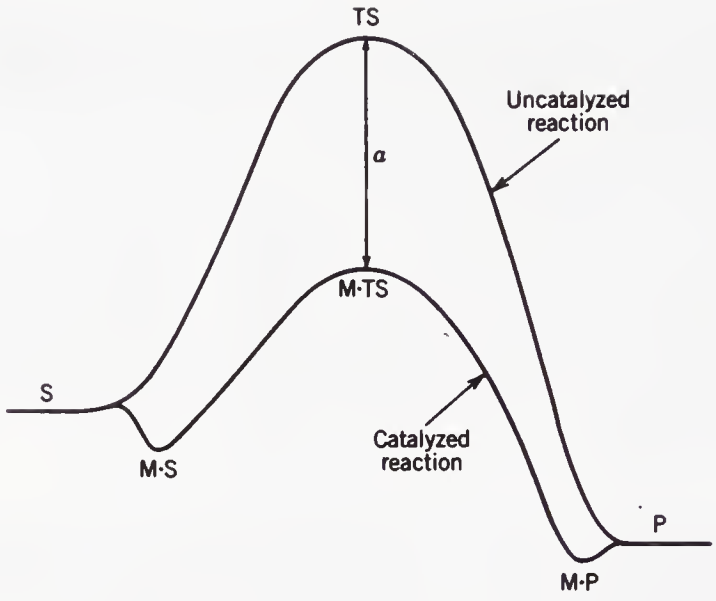
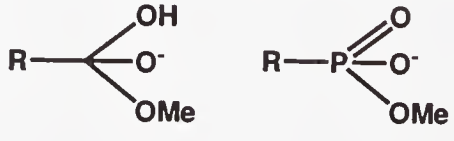


FIGURE 16.1 An enzyme lowers the activation energy for a reaction, often by binding the transition state (TS) for the reaction more tightly than the substrate (S) or product (P). The binding energy for the TS is represented as *a* in the figure.

If a protein recognizes and binds the transition state for a reaction, then that reaction will be accelerated by catalysis. This is because a reaction will go faster if it becomes easier to reach the transition state, which will be the case if the transition state is stabilized more than is the substrate (note how TS is stabilized in this way in Fig. 16.1). An enzyme that hydrolyzes an ester RCOOMe as substrate may well recognize the transition state **16.2** for the attack of water on the ester. Such an enzyme may bind a transition state analogue, such as the phosphate **16.3** much more tightly than it binds the starting ester RCOOMe and inhibit the enzyme (poison the catalyst).



16.2

16.3

Coenzymes Just as a whole set of reactions may require a given reagent, sometimes a whole set of enzymes require a given *coenzyme*. The first organometallic system we shall study is coenzyme B_{12}, a small molecule containing Co, which is required for the activity of a number of enzymes, which are therefore said to be "B_{12}-dependent." Only when the coenzyme binds, does the enzyme become functional. The alternative strategy of incorporating

a Co into each mole of enzyme would make less efficient use of this rare element.

Protein Structure The structures of proteins are generally studied by crystallography,[3a] by no means a straightforward procedure for such large molecules. The structural data cannot reveal the oxidation state of any metal present, and for this we normally need to compare the UV–visible or EPR spectra of the protein with those of model compounds.[3b] If the natural enzyme has a metal such as Zn^{2+} that gives uninformative electronic spectra or is EPR-silent, it is sometimes possible to replace it with an unnatural but more informative metal, such as Co^{2+}.

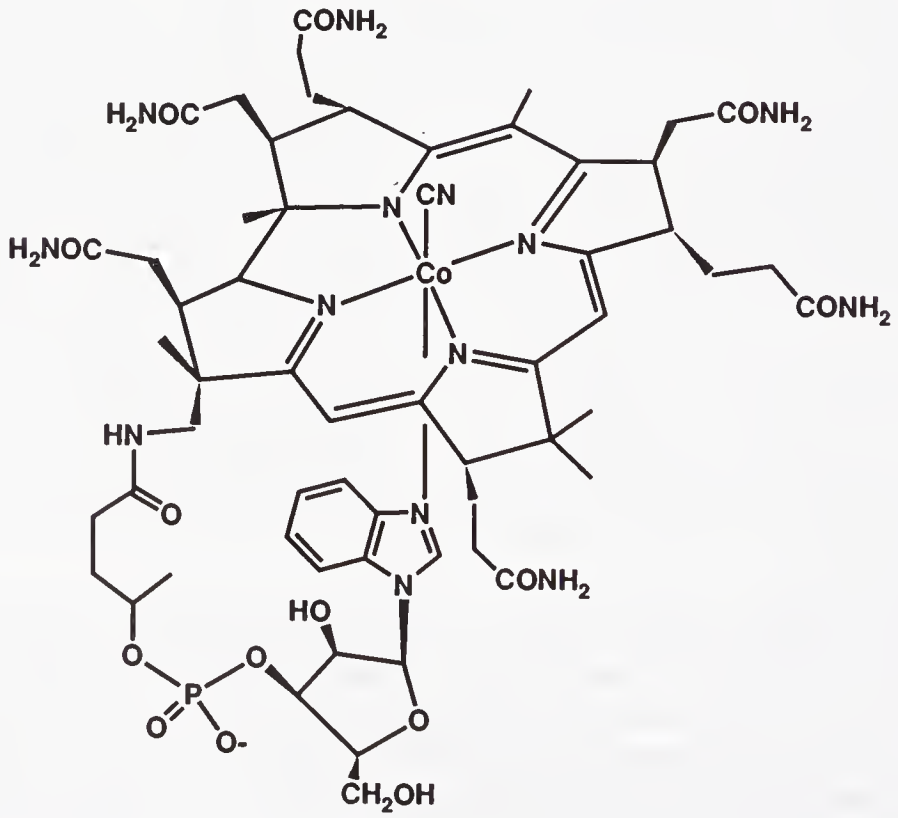
Many interesting metalloproteins are not yet crystallographically characterized, but it is always possible to use X-ray spectroscopy even in the absence of suitable crystals. For example, the fine structure on the X-ray absorbtion edge (EXAFS)[4] for the metal may reveal the number of ligand atoms, their distance, and whether they are first- (N,O) or second-row (S). The X-ray photon expels a photoelectron from the metal, if it has a certain minimum photon energy required to ionize electrons from a given shell (say, the 2s); an absorbtion edge appears at this energy in the X-ray absorbtion spectrum. As we go to slightly higher X-ray photon energies, the photoelectron leaves the metal atom with a certain small translational energy because of the slight excess energy of the X-ray photon relative to the absorbtion edge of the metal. The wavelength of the photoelectron will depend on the amount of excess energy of the X-ray photon. The backscattering of the electron from the ligands around the metal will also be wavelength-dependent and will affect the probability for absorbtion of the X-ray. Crudely speaking, the ligand atom may backscatter the photoelectron wave in such a way as to give a constructive or destructive interference and so raise or lower the probability of the electron leaving the vicinity of the metal; the probability of absorbtion of the X-ray photon will be raised or lowered in consequence. Interpretation of EXAFS data is not entirely straightforward and is considerably helped by making measurements on model complexes. Normally the M—L distance(s) can be extracted to an accuracy of ± 0.002 Å, but the number of ligands of a given type is much less well determined (e.g., ± 1). The energy of the X-ray absorbtion edge is related to the charge on the metal. Unfortunately, this is not related directly to the formal oxidation state for the reasons we considered in Section 2.6.

Another useful physical method is resonance Raman spectroscopy.[5a] It is found that if the exciting radiation in a Raman experiment is near an absorbtion feature of the metal ion in the electronic spectrum, then Raman scattering involving bonds in the immediate vicinity of the metal is greatly enhanced. This selectivity for the vicinity of the active site is very useful in bioinorganic studies, because the absorbtions from the active site would otherwise be buried under the multitude of absorbtions from the rest of the

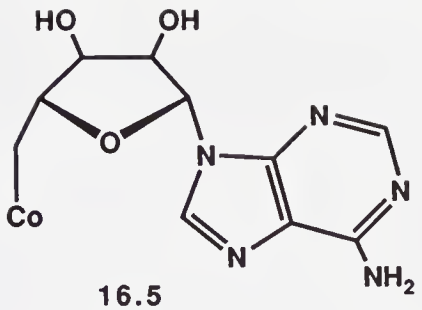
protein. For iron proteins, Mössbauer measurements[5b] can help determine oxidation state and help distinguish 4- from 5- and 6-coordinate metals.

16.2 COENZYME B_{12}[6]

The story begins with the observation, made early in the century, that raw liver is a cure for the otherwise uniformly fatal disease, pernicious anemia. The active component of liver extract was first separated and finally crystallized in 1948. In 1965 Dorothy Hodgkin[7] determined the structure **16.4** crystallographically. This showed that the molecule is an octahedral cobalt complex with a 15-membered 4-nitrogen ring L_3X ligand, called a *corrin,* occupying the equatorial plane. Connected to the corrin is a side chain containing a benzimidazole, which can bind as an axial ligand. The sixth site of the octahedron can be occupied by a number of different ligands. As a result of the isolation procedure commonly used, cyanide binds at the sixth site, and the final product is cyanocobalamin, the species studied by Hodgkin. In nature, several other ligands can be present including water (aquocobalamin or B_{12a}), or methyl (methylcobalamin) or adenosyl groups, **16.5** (the vitamin B_{12} coenzyme). Other than B_{12a}, all these species have a Co—C bond, the first M—C bonds of any sort to be recognized in biology.



16.4



16.5

The coenzyme acts in concert with a variety of enzymes that catalyze reactions of three main types. In the first, two substituents on adjacent carbon atoms, -X and -H, are permuted; this is called the *isomerase reaction.* The generalized process is shown in Eq. 16.1 and specific examples are given in Eq. 16.2–4. Note that CoA has nothing to do with cobalt, but is the biochemical symbol for coenzyme A, a thiol that activates carboxylic acids by forming a thioester.

$$R'CHX—CH_2R \xrightarrow{\text{enzyme, } B_{12} \text{ coenzyme}} R'CH_2—CHXR \qquad (16.1)$$

$$\underset{\text{succinyl coenzyme A}}{HOOCCH_2—CH_2COS(CoA)} \xrightarrow[B_{12} \text{ coenzyme}]{\text{methylmalonyl CoA mutase,}} \underset{\text{methylmalonyl coenzyme A}}{HOOCCHCOS(CoA)—CH_3} \qquad (16.2)$$

In the second general type, methylcobalamin methylates a substrate, as in the conversion of homocysteine to methionine, for example.

$$\underset{\text{homocysteine}}{HSCH_2CH_2CH(COOH)NH_2} \xrightarrow[\text{methylcobalamin}]{\text{methionine synthetase,}} \underset{\text{methionine}}{MeSCH_2CH_2CH(COOH)NH_2} \qquad (16.3)$$

Finally, B_{12} is also involved in the conversion of the ribose ring of the ribonucleotides that go to make RNA to the deoxyribose ring of the deoxyribonucleotides that go to make DNA. The schematic reaction is shown in Eq. 16.4.

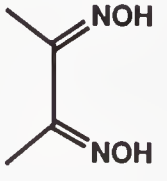
$$—CHOH—CHOH— \xrightarrow[B_{12} \text{ coenzyme}]{\text{deoxyribose synthetase,}} —CHOH—CH_2— \qquad (16.4)$$

The coenzyme is required only in small amounts; 2–5 mg is present in the average human, for example, and one of the first signs of deficiency is the

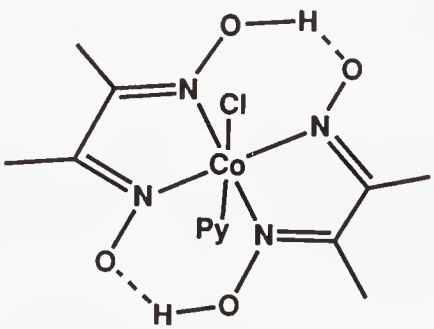
failure to form red blood cells. Hence the anemia, but the disease is not treated successfully by the methods that work for the usual iron-deficiency anemia, which explains the term "pernicious" anaemia.

The B_{12a} system was found to be easily reducible, first to B_{12r}, and then to B_{12s} (r stands for reduced and s for superreduced). Physical studies showed that B_{12r} contains Co(II), and by comparison with model compounds, B_{12s} was shown to contain Co(I), probably in a 4- or 5-coordinate form. The B_{12s} state turns out to be one of the most powerful nucleophiles known, and it reacts rapidly with MeI, or the natural Me^+ donor, N^5-methyl tetrahydrofolate, to give methylcobalamin.

Model Studies Is this chemistry unique to the natural system, or is it a general property of cobalt in a 5-nitrogen ligand environment? At the time that the original model studies were carried out (1960s), it was believed that transition metal alkyls were stable only with very strong ligand field ligands, such as CO or PPh_3. This problem was better understood by studying model systems. Schrauzer[6] found that the simple ligand dimethylglyoxime (dmgH) **16.6** gives a series of Co(III) complexes (called *cobaloximes*) **16.7** that have much in common with the natural system. Two dmg ligands model the corrin, a pyridine models the axial base, and the sixth position can be an alkyl group or water. It was found that these alkyls are stable when the equatorial ligand had some, but not too much electron delocalization. Neither fully saturated ligands, nor the more extensively delocalized porphyrin system, common in other metalloenzymes, allow cobalt to form alkyls easily. The second interesting point is that the longer-chain alkyls, such as -Et or -adenosyl, do not β-eliminate easily. We can now see that this is because the equatorial ligand prevents a vacant site from being formed cis to the alkyl in this 18e system. Such a site would be needed for β elimination to take place by a concerted mechanism (Section 6.5).



16.6



16.7

The nature of the B_{12r} and B_{12s} states was made clearer when it was found that cobaloxime could be reduced to Co(II) and Co(I) oxidation states. The

Co(I) form, $[Co(dmg)_2py]^-$, proved to be a supernucleophile, reacting very fast with MeI to give $[MeCo(dmg)_2py]$ (Eq. 16.5).

$$[Co(dmg)_2py]^- + MeI \longrightarrow [MeCo(dmg)_2py] + I^- \qquad (16.5)$$

Homolytic Mechanisms The mechanism of the isomerase reactions involving the coenzyme is believed to start with reversible homolysis of the Co(III)—C bond to generate the Co(II) "radical," B_{12r}, and the adenosyl radical, $RCH_2\bullet$. This carbon radical abstracts a hydrogen atom from the substrate, QH, to give RCH_3, and the substrate radical, Q•. This radical is believed to undergo a 1,2 shift of the X group (see Eq. 16.8), to give the product radical. Hydrogen atom transfer from RCH_3 to the product radical gives the final product:

$$L_nCo—CH_2R \longrightarrow L_nCo\bullet + \bullet CH_2R \qquad (16.6)$$

$$R'HCX—CH_2R + \bullet CH_2R \longrightarrow R'HCX—\bullet CHR + CH_3R \qquad (16.7)$$

$$R'HCX—\bullet CHR \longrightarrow R'HC\bullet—CXHR \qquad (16.8)$$

$$R'HC\bullet—CXHR + CH_3R \longrightarrow R'CH_2—CXHR + \bullet CH_2R \qquad (16.9)$$

This mechanism implies that the Co—C bond in the coenzyme is not particularly strong, because Eq. 16.6 requires that it must be spontaneously homolyzing at ambient temperatures at a rate fast enough to account for the rapid turnover observed for the B_{12}-dependent enzymes ($\sim 10^2$ sec^{-1}). Halpern[8] has estimated Co—C bond strengths in B_{12} models by two methods. The first involves measuring the equilibrium constant for Eq. 16.10. From the ΔH and ΔS values, and given the known heats of formation of $PhCH{=}CH_2$ and $PhCH\bullet—CH_3$, the ΔH and ΔS for Eq. 16.6 can be deduced.

$$(py)dmg_2Co—CHMePh \rightleftharpoons (py)dmg_2Co\bullet + PhCH{=}CH_2 + \tfrac{1}{2}H_2$$
$$(\Delta H = 22.1 \text{ kcal/mol } \{\text{measured}\}) \qquad (16.10)$$

$$PhCH{=}CH_2 + \tfrac{1}{2}H_2 \rightleftharpoons PhCH\bullet—CH_3$$
$$(\Delta H = -2.2 \text{ kcal/mol } \{\text{calculated}\}) \qquad (16.11)$$

$$(py)dmg_2Co—CHMePh \rightleftharpoons (py)dmg_2Co\bullet + PhCH\bullet—CH_3$$
$$(\Delta H = 19.9 \text{ kcal/mol } \{\text{calculated}\}) \qquad (16.12)$$

Note that Eq. 16.10 looks like a β elimination of the sort that we said should be prevented by the unavailability of a 2e vacant site at the metal. In fact, the reaction probably goes by Co—C bond homolysis, followed by abstraction of a hydrogen atom from the carbon radical by the Co(II) (Eqs. 16.13–16.15), not by a concerted mechanism at all.

$$(py)dmg_2Co—CHMePh \rightleftharpoons (py)dmg_2Co\bullet + PhCH\bullet—CH_3 \quad (16.13)$$

$$(py)dmg_2Co\bullet + PhCH\bullet—CH_3 \rightleftharpoons (py)dmg_2CoH + PhCH{=}CH_2 \quad (16.14)$$

$$2(py)dmg_2CoH \rightleftharpoons 2(py)dmg_2Co\bullet + H_2 \quad (16.15)$$

Halpern's second method of determining the Co—C bond strength is to trap the R• intermediate using a second Co(II) complex as the trap. The $\Delta H^{\ddagger}$ found for this process should be a measure of the Co—C bond strength. In the case above where we already know the Co—C bond strength is approximately 20 kcal/mol, the answer by the kinetic method comes out to be 22 kcal/mol. The extra 2 kcal probably represents the activation energy for the homolysis. Applying the method to coenzyme B_{12} itself gives a figure of 28.6 kcal/mol for the Co—CH_2R bond strength. This figure is too high to account for the rate of turnover of the B_{12}-dependent enzymes, because the rate of the homolysis of such a strong bond would be much slower than 10^2 sec^{-1}. On reflection, however, this Co—C bond strength is indeed reasonable, because the coenzyme must be under control. It must not liberate a radical until required to do so. Very likely, when the coenzyme binds to the B_{12}-dependent enzyme, part of the binding energy of the B_{12} to the enzyme is used to deform the coordination sphere around Co in such a way[9] that the Co—C bond is made slightly weaker, and when the substrate also binds, the coenzyme may be further activated so that it is now able to homolyze at the appropriate rate.

Halpern has also looked at the rearrangement step itself by making the proposed substrate-derived radical independently in the absence of metal by a standard method, the action of Bu_3SnH on the corresponding halide. He finds that for the methylmalonyl mutase reaction, the rate of rearrangement is 2.5 sec^{-1}, only slightly slower than the 10^{-2}-sec^{-1} turnover rate for the enzyme. This difference is small enough to be accounted for by saying that the radical involved in the natural system is not free, but bound to the enzyme, which will hold it in the conformation most favorable for the rearrangement. All this does not prove that the substrate radical does not bond to cobalt in the course of the rearrangement, but at least we can say for the moment that a viable pathway exists without any such binding being necessary. The same goes for some of the other proposals that have been made for the rearrangement, notably redox reactions between the radical and the Co(II) to generate a putative carbonium ion or carbanion, either of which might also rearrange. The role of coenzyme B_{12} in the mechanism of the deoxyribose synthetase reaction, however, still remains obscure.

Bioalkylation and Biodealkylation Methylcobalamin is important in certain bacteria. In some cases it has been found that Hg(II) in the sea can be methylated by these bacteria to give $MeHg^+$. This water-soluble organometallic species can be absorbed by shellfish, which can then become toxic

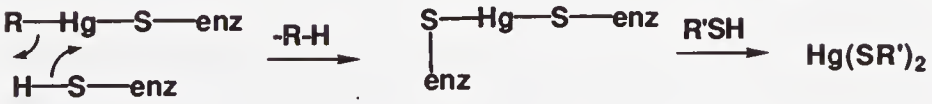
to humans. Mercury is naturally present in small quantities in seawater, but the concentration can be dramatically increased by pollution. A notorious poisoning episode of this sort occurred at Minimata in Japan, where an abnormally high amounts of mercury were found in the sea, as a result of industrial activity. Certain bacteria even have a pair of enzymes, organomercury lyase, and mercuric ion reductase, that detoxify organomercury species via the processes shown in Eqs. 16.16–16.17. The lyase cleaves the R—Hg bond and the reductase reduces the resulting Hg(II) ion to the metallic state; in this form it evaporates from the organism. The mechanisms involved have been studied by Walsh.[10] The retention of configuration observed in the lyase reduction of *Z*-2-butenylmercury chloride and the failure of radical probes such as **16.8** to give a radical rearrangement (to norbornadiene) led to the

16.8

proposal that the reaction goes by an S_E2 mechanism in which a cysteine SH group of the protein cleaves the bond (Eq. 16.18; enz = lyase). The reduction of the Hg^{2+} to Hg(0) is believed to go via initial formation of a dithiolate that loses disulfide (Eq. 16.19; enz′ = reductase).

$$R—Hg—Cl \xrightarrow{\text{organomercury lyase}} RH + Hg^{2+} \qquad (16.16)$$

$$Hg^{2+} \xrightarrow{Hg^{2+}\ \text{reductase}} Hg(0) \qquad (16.17)$$



(16.18)

(16.19)

In the early nineteenth century, certain green wallpapers contained copper arsenite (Scheele's green) as a dyestuff. In damp conditions, moulds, such as *Scopulariopsis bevicaulis,* are able to convert the arsenic to the very toxic $AsMe_3$, by a B_{12}-dependent pathway, and many people died before the problem was recognized. It has even been argued[11a] that in 1821 Napoleon was accidentally poisoned in this way, when he was held at St. Helena by the British; others have blamed the British for deliberately poisoning him.[11b]

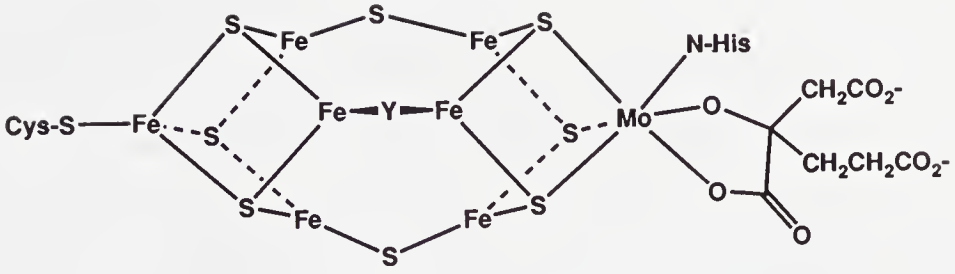
16.3 NITROGEN FIXATION[12]

It has been noticed by farming communities since antiquity that the presence of certain plants encourages the growth of crops. The presence of a fertility goddess in the plant was a colorful explanation developed in early times to account for this phenomenon. The truth is only slightly less remarkable: the roots of the plant in question are infected by various species of soil bacteria, which, provided in their new home with the necessary energy input by the plant, "fix" atmospheric N_2 to NH_3, by means of a metalloenzyme, nitrogenase. The resulting ammonia not only fertilizes the host plant but also escapes into the surroundings, where the growth of crop plants is stimulated. Before the advent of fertilizers, almost all the nitrogen required in human nutrition was obtained by biological nitrogen fixation; now, some of it also comes from N_2 fixed by the Haber process (Eq. 16.20):

$$N_2 + H_2 \xrightarrow{\text{Fe catalyst}} 2NH_3 \qquad (16.20)$$

As early as 1930, it was realized that molybdenum was normally essential for biological nitrogen fixation; iron and magnesium are also required. More recently, alternative nitrogenases have been described that contain no Mo, but either V and Fe or Fe alone instead. The Mo—Fe N_2ase is the best studied and this is the system referred to below, unless specifically stated. Ammonia is the first reduction product released by the enzyme, and there is no evidence for other species, such as hydrazine. The enzyme, like many organometallic complexes, is air-sensitive, and CO and NO are strong inhibitors. It is believed that the CO or NO coordinate to the N_2 binding site, and that this site is a low-valent metal, Fe or Mo. Apart from N_2, the enzyme also reduces some other substrates very efficiently, such as C_2H_2 (but only to C_2H_4), MeNC (to MeH and $MeNH_2$), and N_3^-. Acetylene reduction is used as the standard assay for the enzyme. Since the V—Fe N_2ase reduces C_2H_2 to C_2H_6, its presence escaped detection by the classic assay.

The Mo enzyme consists of two components: (1) the Fe protein (molecular weight 57,000 daltons), which contains iron and sulfur (4 atoms of each per protein); and (2) the Mo—Fe protein (220,000 daltons, $\alpha_2\beta_2$ subunits), which contains both metals (1 atom Mo, 32 atoms Fe). Each also contains S^{2-} ions (ca. one per iron), which act as bridging ligands for the metals. The protein contains special Fe—S clusters called "P clusters" that have epr resonances like those of no other Fe—S cluster. A soluble protein-free molybdenum and iron containing cluster can be separated from the enzyme. This iron–molybdenum cofactor, or FeMo-co, was known to have approximately 1 Mo, 7–8 Fe, 4–6 S^{2-} and one molecule of homocitrate ion. As for the P cluster, there was no agreement on the structure of FeMo-co for many years. In purified form FeMo-co does crystallize, and it can restore N_2 reducing activity to samples of mutant N_2ase that are inactive because they lack FeMo-co.[13] On



FeMo-co

FIGURE 16.2 The structure of the FeMo-co of *A. vinelandii* nitrogenase, as revealed by the crystallographic work of Kim and Rees.[14] Y is probably S^{2-}.

the other hand, no crystal structure of FeMo-co proved possible, and no synthetic model complex was found that could activate the mutant enzyme.

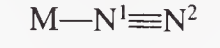
The crystal structure of the entire enzyme obtained by Kim and Rees[14] in 1992 has been very important in clearing up some of the mysteries surrounding the system. FeMo-co proves to have the structure shown in Fig. 16.2. One surprise is that the Mo is 6-coordinate, making it less likely to be the N_2 binding site. Model studies had for many years concentrated on this element. The possible noninvolvement of the Mo in binding N_2 illustrates one hazard of bioinorganic model chemistry: that the data on the biological system may undergo a reinterpretation that alters the significance or relevance of any model studies. The current state of the refinement suggests that six Fe atoms of the cofactor have the very low coordination number of 3, making it possible that the N_2 may bind to one or more of them, perhaps even from within the cluster.

The isolated enzyme will reduce N_2 and the other substrates if a source of the electrons required by Eq. 16.21, such as $Na_2S_2O_4$, is provided. In addition, ATP is also consumed, even though the overall process of Eq. 16.21 is exoergonic under physiological conditions, so the ATP must provide additional driving force to increase the rate. The Mo-Fe protein binds the N_2, and the Fe protein accepts electrons from the external reducing agent and passes them on to the Mo—Fe protein. In the absence of N_2, N_2ase acts as a hydrogenase in reducing protons to H_2; indeed, H_2 is also formed even in the presence of N_2.

$$N_2 + 6H^+ + 6e^- \longrightarrow 2NH_3 \qquad (16.21)$$

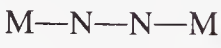
Dinitrogen and N_2 Complexes Dinitrogen is a very inert molecule, and no one has yet been able to reduce it catalytically under the mild conditions employed by nitrogenase. N_2 will react with Li and Mg to give nitrides, but the only other nonbiological reaction of N_2 under mild conditions is the formation of N_2 complexes. More than 100 examples are now known, of

which many contain Fe or Mo. In most cases, the N_2 is terminal and bound by one N atom, as in **16.9**. N_2 is isoelectronic with CO, so a comparison between the two ligands is useful. CO has a filled σ-lone pair orbital located on carbon, with which it forms a σ-bond to the metal, and an empty π^* orbital for back bonding. N_2 also has a filled σ-lone pair, but it lies at lower energy than the corresponding orbital in CO, probably because N is more electronegative than C, and so N_2 is the weaker σ donor. N_2 also has an empty π^* orbital. Although it is lower in energy, and so more accessible than the CO π^* orbital, it is equally distributed over N^1 and N^2 and therefore the M—N π^* overlap is smaller than for M—CO, where the π^* is predominantly located on carbon. The result is that N_2 binds very much less efficiently than CO. Of the two M—N interactions, the back donation is the more important for stability, and only strongly π-basic metals bind N_2. Because the two ends of N_2 are the same, the molecule can relatively easily act as a bridging ligand between two metals (**16.10**). If the back donation is large, the N_2 can be reduced to a hydrazide complex. The two forms **16.11** and **16.12**, shown below, are really resonance contributors to the real structure, which may more closely resemble **16.11** or **16.12**. The side-on bonding mode is rare.



terminal

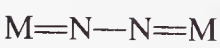
16.9



bridging

16.10

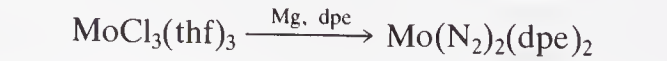
16.11



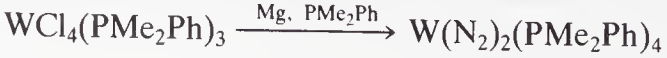
16.12

The first dinitrogen complex to be recognized, $[Ru(NH_3)_5(N_2)]^{2+}$, was isolated in 1965 by Allen and Senoff[15] during the attempted synthesis of $[Ru(NH_3)_6]^{2+}$ from $RuCl_3$ and hydrazine. The N—N distance of this and related N_2 complexes is only slightly different (1.05–1.16 Å) from that of free N_2 (1.1 Å). An important property of the mononuclear complexes is the strong IR absorbtion due to the N—N stretch at 1920–2150 cm^{-1}. Free N_2 is inactive in the IR, but binding to the metal causes a strong polarization of the molecule (see Section 2.6), with N^1 becoming positively charged and N^2 negatively charged. This contributes both to making the N—N stretch IR active and to the chemical activation of the N_2 molecule.

Common preparative routes are reduction of a phosphine substituted metal halide in the presence of N_2, degradation of a nitrogen-containing ligand, and displacement of a labile ligand by N_2.



$$MoCl_3(thf)_3 \xrightarrow{Mg,\ dpe} Mo(N_2)_2(dpe)_2 \qquad (16.22)$$



$$WCl_4(PMe_2Ph)_3 \xrightarrow{Mg,\ PMe_2Ph} W(N_2)_2(PMe_2Ph)_4 \qquad (16.23)$$

$$ReCl_2(PPh_3)_2(N_2COPh) + PMe_2Ph \xrightarrow{MeOH}$$

$$ReCl(N_2)(PMe_2Ph)_4 + PhCOOMe + HCl \quad (16.24)$$

$$FeH_2(H_2)(PEtPh_2)_3 \xrightarrow{N_2} FeH_2(N_2)(PEtPh_2)_3 \quad (16.25)$$

Only on rare occasions is it possible to synthesize and purify a whole series of N_2 complexes with different ligands; the Mo, W, and Re systems shown above are perhaps the most versatile in this respect. N_2 can often displace η^2-H_2, as shown in Eq. 16.25; if this were the last step in the catalytic cycle, it would explain why N_2ase always produces at least one mole of H_2 per mole of N_2 reduced.

Some examples of complexes in which the N_2 bridges two metals are shown in Eqs. 16.26 and 16.27. In the ruthenium case, the system resembles **16.11**, and the μ-N_2 is little different in length from the terminal N_2 in $[Ru(NH_3)_5(N_2)]^{2+}$ itself. Some dinitrogen complexes are appreciably basic at N^2, showing once again the strong polarization of the N_2. These can bind Lewis acids at N^2 to give adducts, some of which have very low N—N stretching frequencies, and these seem to resemble **16.12**.

$$[Ru(NH_3)_5(N_2)]^{2+} + [Ru(NH_3)_5(H_2O)]^{2+} \longrightarrow [\{Ru(NH_3)_5\}_2(\mu\text{-}N_2)]^{4+} \quad (16.26)$$

$$ReCl(PMe_2Ph)_4(N_2) + MoCl_4(OEt_2)_2 \longrightarrow$$

yellow [$\nu(N_2) = 1925\ cm^{-1}$]

$$Cl(PMe_2Ph)_4Re(\mu\text{-}N_2)MoCl_4(\mu\text{-}N_2)ReCl(PMe_2Ph)_4 \quad (16.27)$$

blue-black [$\nu(N_2) = 1680\ cm^{-1}$]

Reactions of N_2 Complexes Only the most basic N_2 complexes, notably the bis-dinitrogen Mo and W complexes, can be protonated. According to the exact conditions, various N_2H_x complexes are obtained, and even, in some cases, free NH_3 and N_2H_4. As strongly reduced Mo(0) and W(0) complexes, the metal can apparently supply the six electrons required by Eq. 16.21, and so the metals are oxidized during the process. Note, too, that in Eq. 16.28, the loss of the very strong N—N triple bond is compensated by the formation of two N—H bonds and a metal nitrogen multiple bond.

$$W(N_2)_2(dpe)_2 \xrightarrow{2HCl} WCl_2(=N—NH_2)(dpe)_2 \xrightarrow{\text{base, } (-HCl)}$$

$$WCl(=N—NH)(dpe)_2 \quad (16.28)^{12a}$$

$$W(N_2)_2(PMe_2Ph)_4 \xrightarrow{H_2SO_4,\ MeOH} N_2 + 2NH_3 + W(VI) \quad (16.29)^{12a}$$

The mechanism shown in Eq. 16.30 has been proposed for the N_2 reduction observed in these experiments. N_2 is a net electron acceptor from the metal, and so loss of the first N_2 leads to the metal acquiring a greater negative

charge, and thus back donating more efficiently to the remaining N_2, which is therefore polarized and activated even further. Note that the final N—N bond breaking is again accompanied by the formation of a metal nitride; such species are known to hydrolyze easily to give ammonia. It is possible that the natural system may also go by similar intermediates.

$$L_nM(N_2)_2 \xrightarrow{-N_2} L_nM(N_2) \xrightarrow{H_2SO_4}$$
$$L_{n-1}M(SO_4)(=N—NH_2) \xrightarrow{H+} L_{n-1}M(SO_4)(=N—NH_3)^+ \longrightarrow$$
$$L_{n-2}M(SO_4)(\equiv N) + NH_3 \xrightarrow{H+} M(VI) + 2NH_3 \quad (16.30)$$

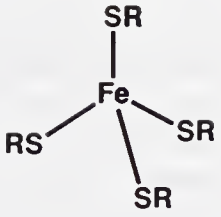
The greatest weakening of the N—N bond might be expected for early d^2 metals, which back-bond the most strongly to π-acceptor ligands. Cp_2^*Ti reacts with N_2 as shown in Eq. 16.31, where $Cp_2^*Ti(N_2)$ seems to have η^1 and η^2 forms and protonates with HCl to give N_2H_4. These show different $\nu(N_2)$ frequencies in the IR (2056 and 2023 cm^{-1}, respectively) and, most significantly, the ^{15}N NMR shows two mutually coupled (J = 7 Hz) resonances for the η^1 and a single resonance for the η^2 form.[16]

$$Cp_2^*Ti \xrightarrow{N_2} Cp_2^*Ti(\eta^1\text{-}N_2) \rightleftharpoons Cp_2^*Ti(\eta^2\text{-}N_2) \xrightarrow{Cp_2^*Ti}$$
$$Cp_2^*Ti(NN)TiCp_2^* \quad (16.31)$$

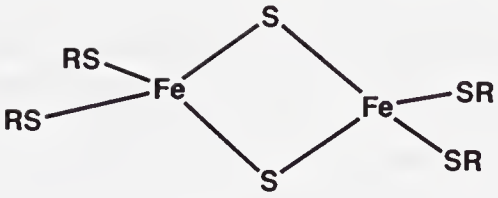
Schrock[17] has made $Cp^*Me_3M{=}N—N{=}MMe_3Cp^*$ (M = Mo or W) where the back donation is so strong that the N_2 is now effectively reduced to a hydrazide tetraanion, as shown by the N—N distance of 1.235 Å (Mo). Ammonia is formed with lutidine hydrochloride as proton source and Zn/Hg as reductant.

In spite of much effort, no one has yet succeeded in making an N_2 complex using only thiolate and S^{2-}, ligands closer to those that are present in the enzyme. Indeed, the chemistry of sulfur ligands is plagued by their high tendency to bridge, and so soluble and characterizable materials can often be obtained only with thiolates having very bulky R groups. The binding site for N_2 in the enzyme may be one or more Fe atoms of the FeMo-co cluster.

Fe—S Clusters The other surprise in the N_2ase structure, apart from the FeMo-co structure, is the nature of the P clusters. To understand this result, we must briefly look at iron–sulfur proteins, which have been known for many years, but the structures of the active sites having become clear only relatively recently. Structures **16.13–16.15** show some the main cluster types that had been recognized.[18] There are also a number of triiron clusters.[19] In each case the R groups represent the cysteine residues by which the metal is bound to the protein chain. In the cases in which there is more than one iron atom, S^{2-} ions are also present and bridge the metals. The ferredoxin proteins contain Fe_4S_4 or Fe_2S_2 cores, and these have been extruded apparently intact



16.13



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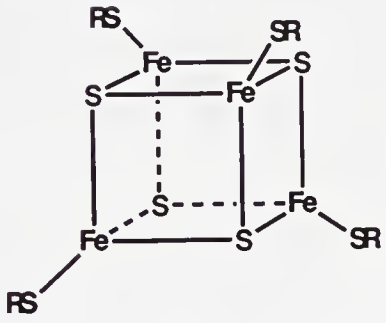


16.15

from the enzyme by the addition of suitable thiols that can chelate the metal, to give a fully characterizable complex. The metal-free enzyme (the apoenzyme) can then be made active once again simply by adding Fe^{2+} and S^{2-}. These clusters are said to have the property of self-assembly; that is, they can form readily in solution on mixing the components (apoenzyme + metal ions or, for the model compounds, ligands + metal ions) under the correct conditions. This contrasts with FeMo-co, which as yet cannot be formed either from the apoenzyme and metal ions or in models from ligands and metal ions. At least three genes are present in nitrogen fixing organisms whose role has been identified as the inorganic synthesis of the FeMo-co cluster.

It has been possible to synthesize model complexes with core geometries similar to those present in the natural Fe–S clusters. Some examples are shown in Eq. 16.32 and 16.33. Normally, adding an oxidizing metal like Fe^{3+} to RSH simply leads to oxidation to RSSR, and so the choice of reaction conditions is critical. Millar and Koch have shown that metathesis from the phenoxide is very useful (Eq. 16.34), which allows synthesis of $Fe^{III}(SPh)_4^-$, an apparently very simple compound, but one that long resisted attempts to make it.[20]

$$FeCl_3 + RSH \xrightarrow{NaSH,\ NaOMe} (RS)_4Fe_4(\mu_2\text{-}S)_4 \qquad (16.32)$$

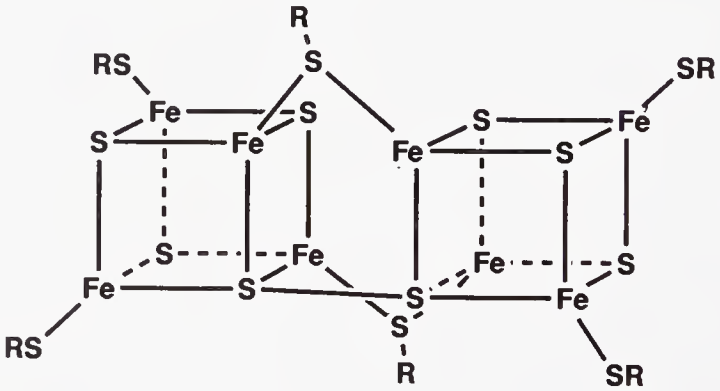
$$FeCl_3 + o\text{-}C_6H_4(CH_2SH)_2 \xrightarrow{NaSH,\ NaOMe} C_6H_4(CH_2S)_2Fe(\mu\text{-}S)_2Fe(SCH_2)_2C_6H_4 \qquad (16.33)$$

$$Fe^{III}(OPh)_4^- \xrightarrow{PhSH} Fe^{III}(SPh)_4^- \qquad (16.34)$$

The oxidation states present in the natural systems can be determined by comparison of the spectral properties of the natural system in its oxidized and reduced states with those of the synthetic models; the latter can be prepared in almost any desired oxidation state by electrochemical means. The result show that the monoiron systems indeed shuttle between Fe(II) and Fe(III) as expected. The diiron enzymes are Fe(III), Fe(III) in the oxidized state, and Fe(II), Fe(III) in the reduced state. The mixed-valence species are fully delocalized in all cases. There is also a superreduced state, Fe(II), Fe(II), which is probably not important in vivo. The 4-iron proteins shuttle between 3Fe(II), Fe(III), and 2Fe(II), 2Fe(III), such as in the ferredoxins (Fd). One class of 4-iron proteins have an unusually high oxidation potential (HIPIP, or high potential iron protein), because the system shuttles between 2Fe(II), 2Fe(III), and Fe(II), 3Fe(III).

$$\begin{array}{lll} 3Fe(II),\ Fe(III) & 2Fe(II),\ 2Fe(III) & Fe(II),\ 3Fe(III) \\ Fd_{red} & Fd_{ox} & Fe_{superox} \\ HIPIP_{superred} & HIPIP_{red} & HIPIP_{ox} \end{array} \qquad (16.35)$$

The N_2ase crystal structure, apart from showing FeMo-co, also revealed the structure of the P clusters (**16.16**), which consist of a pair of Fe_4S_4 cubanes bridged by an S-S group. This is a new type of Fe—S cluster.



16.16

16.4 THE NICKEL ENZYMES[21]

Urease is famous in enzymology for being the first enzyme to be purified and crystallized (1926). At the time enzymes were widely viewed as being too ill-defined for detailed chemical study. Sumner argued that its crystalline character meant that urease was a single defined substance and the fact that he could not find any cofactors led to the conclusion that polypeptides could have catalytic activity on their own. The existence of two essential Ni^{2+} ions

per mole of urease was not proved until 1975. Sumner's conclusion that cofactors are not always required for catalytic activity is correct, but we now know that urease is not a good example. Nickel has only recently been recognized as a significant catalytic element in a series of metalloenzymes.[21] In three of these, hydrogenase (H_2ase), CO dehydrogenase (CODH), and MeCoM reductase (MCMR), organometallic Ni species are thought to be involved.

Archaebacteria This group of bacteria, including the methanogens, the thermoacidophiles and the halobacteria are sufficiently different from all other forms of life that it has been proposed that they be assigned to their own natural kingdom, the archaebacteria.[22a] The name indicates that they are believed to be very early organisms in an evolutionary sense. One of the signs of this antiquity is the fact that many archaebacteria can live on the simple gases, such as H_2 and CO or CO_2, both as energy and carbon source, and on N_2 via nitrogen fixation as nitrogen source.[22b] Higher organisms have more sophisticated nutritional requirements, humans, for example, have to have such complex compounds as ascorbic acid (vitamin C) and vitamin B_{12} as part of the diet in order to survive; these compounds can only come from other life forms. Few, if any, other life forms must have existed when archaebacteria evolved, and they therefore had literally to live on air and water. A life form that can synthesize all its carbon constituents from CO_2 is called an *autotroph;* one that requires other C_1 compounds, such as methane or methanol, is called a *methylotroph.*

The archaebacteria are very rich in nickel-containing enzymes, and coenzymes, and Nature has clearly chosen this element to bring about the initial steps in the biochemical utilization of H_2, CO, CH_4, and other C_1 compounds, at least in an anaerobic environment. These steps almost certainly involve organonickel chemistry, although how this happens in detail is only just beginning to be understood.

CO Dehydrogenase CODH is unusual in that it can bring about two reactions (e.g., Eqs. 16.37 and 16.39) that are particularly interesting to the organometallic chemist because they are analogous to ones we have seen before in this book: the water–gas shift reaction (Eq. 16.36), and the Monsanto acetic acid synthesis (Eq. 16.38). In the equations, the familiar organometallic reaction is shown first, and the biological analog, second. The analogy between the first pair of equations is very close, $2H^+ + 2e^-$ being equivalent to H_2. In the second case, the natural Me donor, methyl tetrahydrofolate, or MeTHF, stands in for MeOH, and the product is acetyl coenzyme A, the natural acetic acid equivalent (CoA is a thiol, so acetylCoA is a thiol ester). The enzyme contains two Ni centers; one is part of a cluster containing Ni, Fe, and a substrate CO, because the corresponding epr signal shows coupling to ^{61}Ni, ^{57}Fe, and ^{13}C (of CO) in CODH labeled with these spin-active isotopes. This Ni can be removed from the protein, in which case

the acetylCoA synthesis activity (Eq. 16.39) but not CO oxidation activity (Eq. 16.37) is abolished. A second Ni, remote from the first, is believed to be responsible for the CO oxidation. Both Ni are present in an N-, O-, S-ligand environment from EXAFS data.

An important detail emphasizes the difference in the behavior of enzymes and of simple compounds: although the NiFeC site always contains a full mole of nickel, the epr integration suggested only 0.1–0.35 spins were present per cluster. The addition of phenanthrene (phen) removes 0.1–0.35 Ni per enzyme and abolishes 100% of both the epr signal and the acetyl CoA synthase activity. Although the protein is pure by all the usual criteria, some of the enzyme molecules appear to contain catalytically- and epr-inactive NiFeC clusters in which the Ni cannot be removed by phen.[23] Biological systems are not always so well defined as chemical compounds.

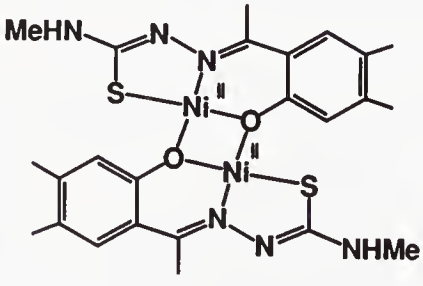
$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{16.36}$$

$$CO + H_2O \rightleftharpoons CO_2 + 2H^+ + 2e^- \tag{16.37}$$

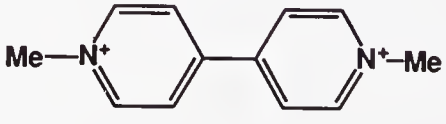
$$MeOH + CO \longrightarrow MeCOOH \tag{16.38}$$

$$MeTHF + CoA + CO \longrightarrow MeCOCoA + THF \tag{16.39}$$

A fully functional model for the second Ni in CODH has been found: **16.17**.[24] This complex has the appropriate metal, Ni^{2+}, as well as an N-, O-, S-ligand environment and catalyzes the reaction shown in Eq. 16.37. The CO_2 is detected by precipitation with $Ca(OH)_2$, the H^+ production with a pH meter, and the electrons formed are transferred to the electron acceptor MV^{2+} (**16.18**) and gives the dark blue radical anion, $MV^{\bullet+}$. The reaction probably



16.17



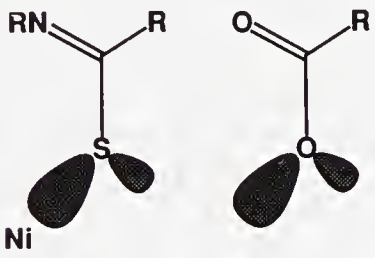
16.18

goes by CO splitting the Ni_2O_2 bridge to give LNiCO because the CO analog CN^- does so to give a stable complex $[LNiCN]^-$; CN^- is an inhibitor in both model and enzyme. Because Ni(II) is weakly back bonding, it would normally not bind CO at all (the S-ligand environment probably raises the basicity of the Ni d_π electrons in this case), but once bound, the CO should be very sensitive to nucleophilic attack because a CO bound to a weak π donor should

be very ∂^+ at C. A possible scheme based on analogy with the water–gas shift reaction is as follows:

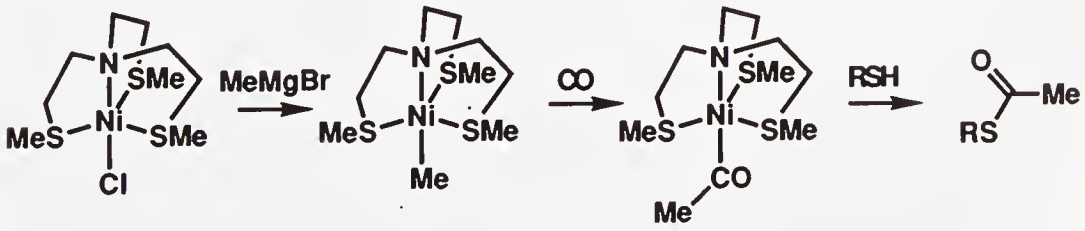
$$LNi^{II}—CO + OH_2 \xrightarrow{-H^+} [LNi^{II}COOH]^- \xrightarrow{-2e,-H^+} LNi^{II} + CO_2 \quad (16.40)$$

Note the iminothiolate S-donor group in **16.17**. An S-ligand environment is difficult to achieve while retaining an open site for catalytic activity because nickel thiolates have a very high tendency to bridge. This tends to remove any labile sites and prevents binding of the substrate CO. In **16.17** this problem is avoided by using an iminothiolate, which has two lone pairs on S, only one of which is strongly basic (see **16.19**). This is similar to the situation in acetate, where the lone pair syn to the C=O group is known to be less basic (see **16.20**). The other less basic S lone pair anti to the C=N group is only weakly basic, and so **16.17** prefers to bridge via phenolate O to give a weak bridge, easily opened up by ligands analogous to CO, like CN^-.



16.19 **16.20**

A stoichiometric model system by Holm[25] for the acetylCoA synthase activity of CODH is shown in Eq. 16.41. This reaction is a property of the NiFeC cluster, of unknown structure, present in CODH. The enzyme brings about exchange between ^{14}CO and $Me^{12}COCoA$, which implies that formation of the C—S and Me—CO bonds is reversible.[26] This is consistent with CO insertion into a Ni—Me bond, and nucleophilic attack on the resulting Ni(COMe), both of which can be reversible.



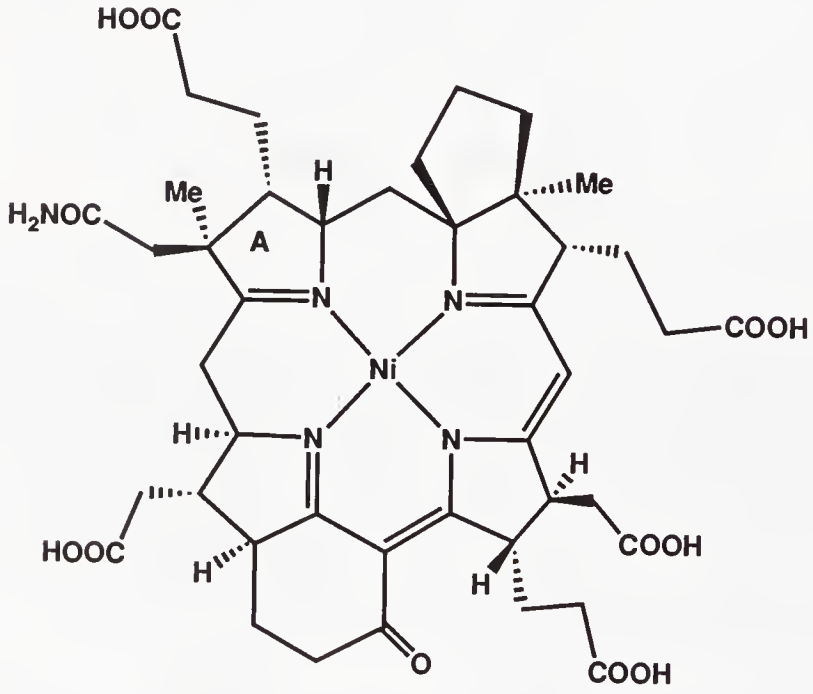
(16.41)

Methanogenesis The methanogens reduce CO_2 to CH_4 and extract the resulting free energy. In the last step, methylcoenzyme M, **16.21**, is hydro-

genolyzed to methane by a thiol cofactor HS—HTP (= R′SH), catalyzed by the Ni enzyme, MCMR.

$$\underset{\text{methylcoenzyme M}}{\underset{\textbf{16.21}}{CH_3SCH_2CH_2SO_3^-}} + \underset{\text{HS-HTP}}{R'SH} \xrightarrow{\text{MCMR}} CH_4 + R'S{-}SCH_2CH_2SO_3^- \qquad (16.42)$$

A coenzyme, Factor F_{430} (**16.22**), is bound to MCMR and is believed to be the site at which Eq. 16.42 is brought about, perhaps via binding of the Me group from methylcoenzyme M to Ni.[27] If so, the macrocycle might have to distort to accommodate a 5-coordinate geometry. The structure of the enzyme is unknown, however. Various distortions of F_{430} have been discussed,[28a] but one attractive one which is suggested by molecular mechanics is for the A ring to fold out of the plane of the macrocycle to accommodate a trigonal bipyramidal Ni.[28b]



16.22
Factor F_{430}

At first it was thought that F_{430} might be reduced to its Ni(I) form, a reduction possible in isolated, enzyme-free F_{430},[29] and then undergo methylation by MeCoM. The reduced form of F_{430} does not react with MeCoM in solution, however, so either the F_{430} or the MeCoM must be activated in some way when bound to the enzyme.

An interesting mechanistic suggestion by Berkessel[30] for this activation is shown in Eq. 16.43. The HTP thiolate anion is thought to reduce the Ni(II)

form of F_{430} to Ni(I). The resulting S-centered radical attacks MeCoM to give **16.23**, which, on the basis of analogy with organic sulfur chemistry, should be a very good Me• donor to Ni(I). This scheme has the additional merit of rationalizing the formation of the observed heterodisulfide product HTP—S—S—CoM:

$$\text{HTP—S}^- \xrightarrow{\text{Ni(II)—F}_{430}} \text{HTP—S}\bullet \xrightarrow{\text{CH}_3\text{SCoM}}$$

$$[\text{HTP—S—(•SMe)—CoM}] \xrightarrow{\text{Ni(I)-F}_{430}}$$

16.23

$$\text{HTP—S—S—CoM} + \text{MeNi}^{\text{II}}\text{-F}_{430} \xrightarrow{\text{H}^+} \text{MeH} \quad (16.43)$$

Hydrogenase The hydrogenases bring about Eq. 16.44, which allow certain bacteria to live on H_2, and others to get rid of excess electrons as H_2. The [NiFe] hydrogenases are the largest class. The number of metals vary with the species studied, but the minimum cofactor composition is one Ni and one Fe_4S_4 cluster. There is some evidence[21b] that Ni is the binding site for H_2 in the [NiFe] hydrogenases. All-iron hydrogenases do exist, but these contain a special H cluster of unknown structure containing about 6 Fe and about 6 S that could have a structure broadly similar to FeMo-co (Fig. 16.2), since N_2ase acts as a hydrogenase in the absence of N_2.

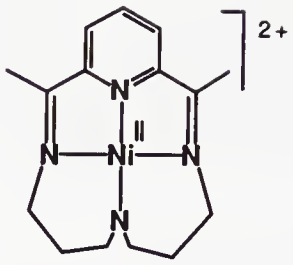
$$H_2 \rightleftharpoons 2H^+ + 2e^- \quad (16.44)$$

The nickel has been shown by EXAFS to have a predominantly sulfur ligand environment.[31] The epr active, odd-electron oxidized form, perhaps Ni(III), can be reduced to an epr inactive form, perhaps Ni(II), a more reduced, odd-electron form, perhaps Ni(I), accessible[32] by H_2 reduction, and an even more reduced even-electron form.* The balance of probability is that the Ni(III) state may be formed as part of a mechanism for protecting the enzyme against exposure to air and that the catalytic cycle involves Ni(II) and more reduced states. Hydrogen activation by the enzyme is heterolytic because D_2 exchanges with solvent protons, as shown here:

$$D_2 + ROH \rightleftharpoons HD + ROD \quad (16.45)$$

It has been suggested[33a] that H_2 may bind to the Ni as a dihydrogen complex, which easily lose protons (Section 3.5), and so could account for the isotope exchange seen in Equation 16.45. Dihydrogen complexes do indeed catalyze the reaction in Eq. 16.45.[33b] Some Ni(II) complexes are now known that electrocatalytically release H_2 from protic solvents and so can be considered functional models of H_2ase. Complex **16.24**[33c] requires acidic (pH 4) solutions to protonate the reduced form, but a thioamide derivative related to **16.17** is active at pH7.[33d]

*Ni(I) and (III) are convenient labels implying that the oxidation or reduction are *at least in part* metal-centered. The reader should be warned that inorganic chemists enjoy arguing about whether oxidation states such as these are valid descriptions of the species involved.

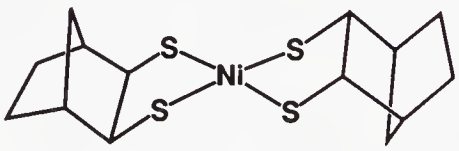


16.24

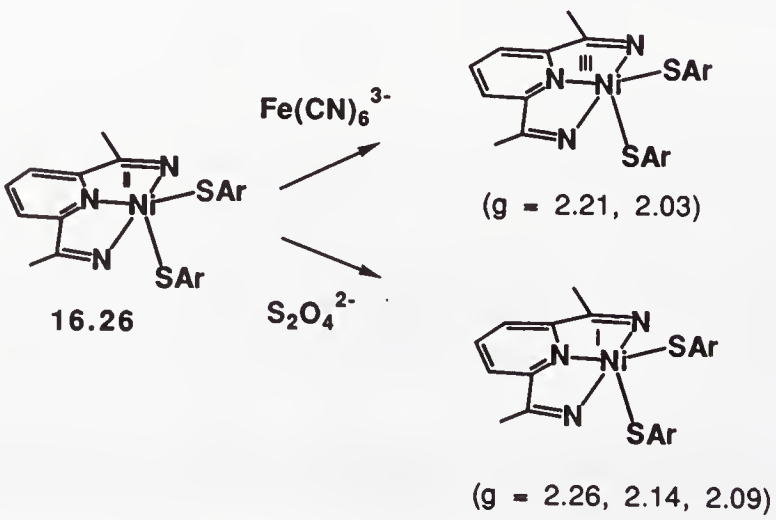
The reaction is first order in Ni, and so the sequence of Eq. 16.46 has been proposed.

$$\text{Ni(II)} \xrightarrow{e^-} \text{Ni(I)} \xrightarrow{H^+} \text{Ni(III)(H)} \xrightarrow{e^-,\ H^+} \text{Ni(II)(H}_2\text{)} \longrightarrow \text{Ni(II)} + \text{H}_2 \tag{16.46}$$

Ni(III) is an unusual oxidation state, especially in a S environment, and so it is not surprising that a large amount of work has gone into looking for model compounds. The most easily oxidized Ni(II) species of this type is Millar's complex, **16.25**, for which the redox potential is -0.76 V.[34] Note the ingenious use of the cage structure to protect the metal and inhibit disulfide formation. Complex **16.26** is an interesting system in that all three oxidation states, I, II, and III are accessible without rearrangement or decomposition.[35] The g values seen in the epr, also shown in the equation, are very different from those seen for organic radicals, which are always close to 2.0. This is the evidence that the reduction and oxidation are at least in large part metal-centered, where g values different from two are common.



16.25



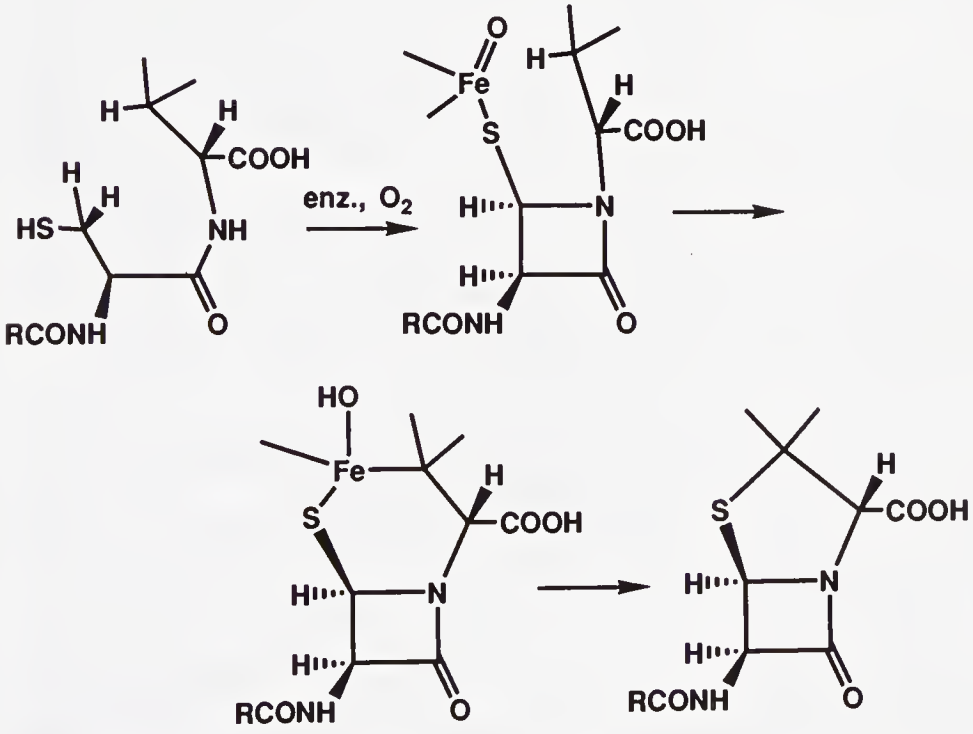
16.26

(16.47)

Other Enzymes Insufficient is still known about other enzymes that may also operate via M—C bonds. Lipoxgenases convert polyunsaturated fatty acids, such as arachidonic acid, to hydroperoxides. These can go on to form prostaglandins, which are known to regulate a variety of processes, such as inflammation. Corey[36] has proposed that certain lipoxygenases deprotonate one of the central protons in a segment of arachidonic acid to give a pentadienyl iron intermediate that reacts with O_2 to give the hydroperoxide product.

$$\begin{aligned} &\text{—CH=CH—CH}_2\text{—CH=CH—} \xrightarrow{\text{base, Fe(III)}} \\ &\qquad \text{—CH=CH—CH=CH—CH\{Fe(III)\}—} \xrightarrow{O_2,\ H^+} \\ &\qquad\qquad \text{—CH=CH—CH=CH—CH(OOH)—} + \text{Fe(III)} \end{aligned} \quad (16.48)$$

Baldwin[37] has suggested that a C—H activation involving the formation of Fe—C bonds may be important in the biosynthesis of penicillin. In one model, the enzyme first forms the four-membered ring of penicillin. Then an iron oxo species abstracts an H atom from the substrate to leave a carbon-centered radical that in turn binds to the metal. A reductive elimination of a thiolate with the alkyl leads to the formation of the penicillin ring:



(16.49)

Gif Chemistry Barton[38] has reported an interesting series of oxidation catalysts, based on Fe(II) and Zn/O_2 or Fe(II) and ROOH, which are referred to as the *Gif, Gif-Orsay,* and *Go-Agg* system. The unusual selectivity for hydroxylation and ketonization of alkanes led to the rejection of the typical radical-based mechanisms often seen in metal ion–O_2–alkane reactions. One of the suggestions currently under discussion is the formation of direct Fe—C

and Fe=C bonds. If this is true, then organometallic chemistry could also play a role in the many Fe-based monooxygenase enzymes that may be related to Gif chemistry.

It is likely that the few organometallic systems we currently recognize in biology represent a small fraction of the total, and that many others remain to be discovered. We can therefore anticipate growing interest in this new area.

REFERENCES

1. J. Darnell, H. Lodish, and D. Baltimore, *Molecular Cell Biology,* 2nd ed., Scientific American Books, New York, 1990; L. Stryer, *Biochemistry,* 3rd. ed; Freeman, New York, 1988.
2. (a) J. J. R. F. da Silva and R. J. P. Williams, *The Biological Chemistry of the Elements,* Oxford Univ. Press, 1991; (b) R. W. Hay, *Bioinorganic Chemistry,* Ellis Horwood, Chichester (UK), 1984; (c) H. Sigel, *Metal Ions in Biological Systems,* 20 vols., Marcel Dekker, New York.
3. (a) F. A. Quicho and W. N. Lipscomb, *Adv. Protein Chem.*, **25,** 1, 1971; (b) R. S. Alger, *Electron Paramagnetic Resonance,* Wiley Interscience, New York, 1968.
4. S. P. Cramer and K. O. Hodgson, *Prog. Inorg. Chem.*, **25,** 1, 1979.
5. (a) T. G. Spiro, in B. Moore (ed), *Chemical and Biological Applications of Lasers,* Academic Press, New York, 1974; (b) T. C. Gibbs, *Principles of Mössbauer Spectroscopy,* Chapman, Hall, London, 1976.
6. G. N. Schrauzer et al., *J. Am. Chem. Soc.*, **93,** 1503 and 1505, 1971; B. T. Golding, *Chem. in Brit.*, 950, 1990; D. Dolphin, B_{12}, Wiley, New York, 1982.
7. D. C. Hodgkin, *Proc. Roy. Soc. A,* **288,** 294, 1965.
8. J. Halpern, *Pure Appl. Chem.*, **55,** 1059, 1983; *Acct. Chem. Res.*, **15,** 231, 1982; *J. Am. Chem. Soc.*, **106,** 8317, 8319, 1984.
9. J. M. Pratt, *Chem. Soc. Rev.*, **14,** 161, 1985.
10. P. G. Schultz, K. G. Au, and C. T. Walsh, *Biochemistry*, **24,** 6840, 1985; T. P. Begley and C. T. Walsh, *Biochemistry,* **25,** 7186, 7192, 1986.
11. (a) D. Jones, *New Scientist,* Oct. 14, 1982, p. 101; (b) S. Forshufvud, *Who Killed Napoleon?,* Hutchinson, London, 1962.
12. (a) J. Chatt, *Chem. Soc. Rev.*, **1,** 121, 1972; *J. Organometal. Chem.*, **100,** 17, 1975; J. Chatt, J. R. Dilworth, and R. L. Richards, *Chem. Rev.*, **78,** 589, 1978; (b) R. W. F. Hardy, F. Bottomley, and R.C. Burns, *A Treatise on Nitrogen Fixation,* Wiley, New York, 1977; W. E. Newton and W. H. Orme-Johnson, *Nitrogen Fixation,* University Park Press, Baltimore, 1980.
13. V. K. Shah and W. J. Brill, *Proc. Natl. Acad. (USA)*, **74,** 3249, 1977.
14. J. Kim and D. C. Rees, *Science,* **257,** 1677, 1992; ibid., **260,** 792, 1993; *Nature,* **360,** 553, 1992.
15. A. D. Allen and F. Bottomley, *Acct. Chem. Res.*, **1,** 360, 1968.
16. J. E. Bercaw, *J. Am. Chem. Soc.*, **96,** 5087, 1974.

17. R. R. Schrock et al., *J. Am. Chem. Soc.*, **112,** 4331, 4338, 1990.
18. R. H. Holm, *Prog. Inorg. Chem.*, **38,** 1, 1990; *Chem. Soc. Rev.*, **10,** 455, 1981; *Iron-Sulfur Proteins,* W. Lovenberg (ed.), 3 vols., Academic Press, New York, 1973–1977.
19. H. Beinert and A. J. Thompson, *Arch. Biochem. Biophys.*, **222,** 333, 1983.
20. M. Millar and S. A. Koch, *Inorg. Chem.*, **31,** 4594, 1992.
21. (a) J. A. Kovacs, *Advances in Inorganic Biochemistry,* G. L. Eichhorn (ed.), Prentice-Hall, N.Y., 1993, Vol 9, Chapter 5. (b) J. R. Lancaster (ed.), *The Bioinorganic Chemistry of Nickel,* VCH, Weinheim, 1988.
22. C. Anthony, *Biochemistry of Methylotrophs,* Academic Press, Orlando, Fla., 1982; *Microbial Gas Metabolism,* R. K. Poole and C. S. Dow (eds.), Academic Press, Orlando, Fla., 1985; *Microbial Growth on C_1 Compounds,* H. Dalton (ed.), Academic Press, Orlando, Fla., 1981.
23. W. Shin and P. A. Lindahl, *J. Am. Chem. Soc.*, **114,** 9718, 1992.
24. Z. Lu, C. White, A. L. Rheingold, and R. H. Crabtree, *Angew. Chem., Int. Ed.*, **32,** 92, 1993.
25. R. H. Holm et al., *J. Am. Chem. Soc.*, **112,** 5385, 1990.
26. S. W. Ragsdale and H. G. Wood, *J. Biol. Chem.*, **260,** 3970, 1985.
27. A. Eschenmoser et al., *Helv. Chim. Acta,* **68,** 1338, 1985.
28. (a) J. Fajer et al., *J. Am. Chem. Soc.*, **113,** 6891, 1991; (b) M. Zimmer and R. H. Crabtree, *J. Am. Chem. Soc.*, **112,** 1062, 1990.
29. B. Jaun and A. Pfaltz, *Chem. Commun.*, 1327, 1986.
30. A. Berkessel, *Bioorgan. Chem.*, **19,** 101, 1991.
31. B. K. Teo, C. T. Walsh, W. H. Orme-Johnson, et al., *J. Am. Chem. Soc.*, **106,** 3062, 1984.
32. R. A. Scott et al., *J. Am. Chem. Soc.*, **106,** 6864, 1984.
33. (a) R. H. Crabtree, *Inorg. Chim. Acta.*, **125,** L7, 1986; (b) A. C. Albeniz, D. M. Heinekey, and R. H. Crabtree, *Inorg. Chem.*, **30,** 3632, 1991; (c) L. E. Efros, H. H. Thorp, G. W. Brudvig and R. H. Crabtree, *Inorg. Chem.*, **31,** 1722, 1992. (d) T. Richardson and R. H. Crabtree, unpubl. data.
34. M. Millar et al., *J. Am. Chem. Soc.*, **112,** 3218, 1990.
35. P. K. Mascharak et al., *J. Am. Chem. Soc.*, **114,** 9666, 1992.
36. E. J. Corey, *Pure Appl. Chem.*, **59,** 269, 1987.
37. J. Baldwin et al., *Chem. Commun.*, 1305, 1986.
38. D. H. R. Barton and D. Doller, *Acct. Chem. Res.*, **25,** 504, 1992.

PROBLEMS

1. Why do you think Nature uses first-row transition metals in most of the transition metalloenzymes?

2. The oxidation states found in the metal centers we have been discussing in this chapter, Fe(II), Fe(III), Ni(III), and Co(III), are often higher than

those usually present in organometallic species we discussed in Chapters 1–14. Why do you think this is so?

3. Those mononuclear N_2 complexes, which have the lowest N—N stretching frequency in the IR, are in general also the complexes in which N_2 is most easily protonated. Explain.

4. Would you expect the following R groups to dissociate more or less readily as R• from cobaloxime than does $\bullet CH_2Ph$: $—CH_3$, $—CF_3$, $—CPh_2H$? Explain.

5. Many N_2 complexes protonate. In the case of $ReCl(N_2)(PMe_2Ph)_4$, the protonated form $HReCl(N_2)(PMe_2Ph)_4^+$ (A) is relatively stable. What might happen to the N—N stretching frequency on protonation? Most N_2 complexes simply lose N_2 on protonation. Given that a complex of type A is the intermediate, explain why N_2 is lost.

USEFUL TEXTS ON ALLIED TOPICS

Bioinorganic Chemistry

J. J. R. Frausto da Silva and R. J. P. Williams, *The Biological Chemistry of the Elements,* Oxford, 1991.

Homogeneous Catalysis

P. A. Chaloner, *Handbook of Coordination Catalysis in Organic Chemistry,* Butterworth, London, 1986.

Encyclopedias

R. B. King (ed.), *Encyclopedia of Inorganic Chemistry,* Wiley, New York, 1994.

G. Wilkinson, F. G. A. Stone, and E. Abel (eds.), *Comprehensive Organometallic Chemistry,* Pergamon Press, Oxford, 1982, 9 vols.

G. Wilkinson, R. D. Gillard, and J. E. McCleverty (eds.), *Comprehensive Coordination Chemistry,* Pergamon Press, Oxford, 1987, 7 vols.

Gmelin, *Handbook of Inorganic Chemistry,* Springer Verlag, Berlin, n.d.

Group Theory and Spectroscopy

F. A. Cotton, *Chemical Applications of Group Theory,* Wiley, New York, 1967.

R. S. Drago, *Physical Methods in Chemistry,* Saunders, Philadelphia, 1977.

Inorganic Chemistry

F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry,* 3rd ed., Wiley, 1973.

J. E. Huheey, *Inorganic Chemistry—Principles of Structure and Reactivity,* 3rd. ed., Harper & Row, New York, 1983.

K. F. Purcell and J. C. Kotz, *Inorganic Chemistry,* Saunders, Philadelphia, 1977.

Kinetics and Mechanism

K. J. Laidler, *Chemical Kinetics,* 3rd. ed., Wiley, New York, 1987.

J. E. Espenson, *Chemical Kinetics and Reaction Mechanisms,* McGraw-Hill, New York, 1981.

F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions,* 2nd ed., Wiley, N.Y., 1967.

C. H. Langford and H. B. Gray, *Ligand Substitution Processes,* Benjamin, New York, 1966.

R. B. Jordan, *Reaction Mechanisms of Inorganic and Organometallic Systems,* Oxford, 1991.

R. G. Wilkins, *Kinetics and Mechanism of Reactions of Transition Metal Complexes,* 2nd ed., VCH, Weinheim, 1991.

NMR

W. Kemp, *NMR in Chemistry,* 1st ed., Macmillan, London, 1986.

K. A. McLaughlan, *Magnetic Resonance,* Clarendon Press, Oxford, 1982.

J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance,* Pergamon Press, Oxford, 1966.

J. A. Pople, W. G. Schneider, and H. J. Bernstein, *High Resolution Nuclear Magnetic Resonance Spectroscopy,* McGraw-Hill, New York, 1959.

P. S. Pregosin and R. W. Kunz, *31P and 13C NMR Spectroscopy of Transition Metal Complexes,* Springer Verlag, Heidelberg, 1979.

G. N. Lamar, W. D. Horrocks, and R. H. Holm, *NMR of Paramagnetic Molecules,* Academic Press, New York, 1973.

Organic Chemistry, Organometallics in

S. G. Davies, *Organotransition Metal Chemistry: Applications to Organic Synthesis,* Pergamon Press, Oxford, 1982.

P. J. Harrington, *Transition Metals in Total Synthesis,* Wiley, NY, 1990.

P. A. Chaloner, *Handbook of Coordination Catalysis in Organic Chemistry,* Butterworth, London, 1986.

Organometallic Chemistry

P. Collman, L. S. Hegedus, J. R. Norton, and R. G. Finke, *Principles and Applications of Organometallic Chemistry,* 2nd. ed., University Science Books, Mill Valley, Calif., 1987.

C. M. Lukehart, *Fundamental Organometallic Chemistry,* Brooks, Cole, Monterey, Calif., 1985.

A. Yamamoto, *Organotransition Metal Chemistry,* Wiley, N.Y., 1990.

P. Powell, *Principles of Organometallic Chemistry,* 2nd. ed., Chapman & Hall, London, 1988.

G. E. Coates, M. L. H. Green, and K. Wade, *Organometallic Compounds,* 3rd. ed. Methuen, London, 1967.

P. S. Braterman, (ed.), *Reactions of Coordinated Ligands,* Plenum Press, New York, 1986.

Photochemistry

G. L. Geoffroy and M. S. Wrighton, *Organometallic Photochemistry,* Academic Press, New York, 1979.

Preparative Techniques

D. F. Shriver, *The Handling of Air-Sensitive Compounds,* McGraw-Hill, New York, 1969.

Special Topics

W. A. Nugent and J. M. Mayer, *Metal–Ligand Multiple Bonds,* Wiley, New York, 1988.

Structure

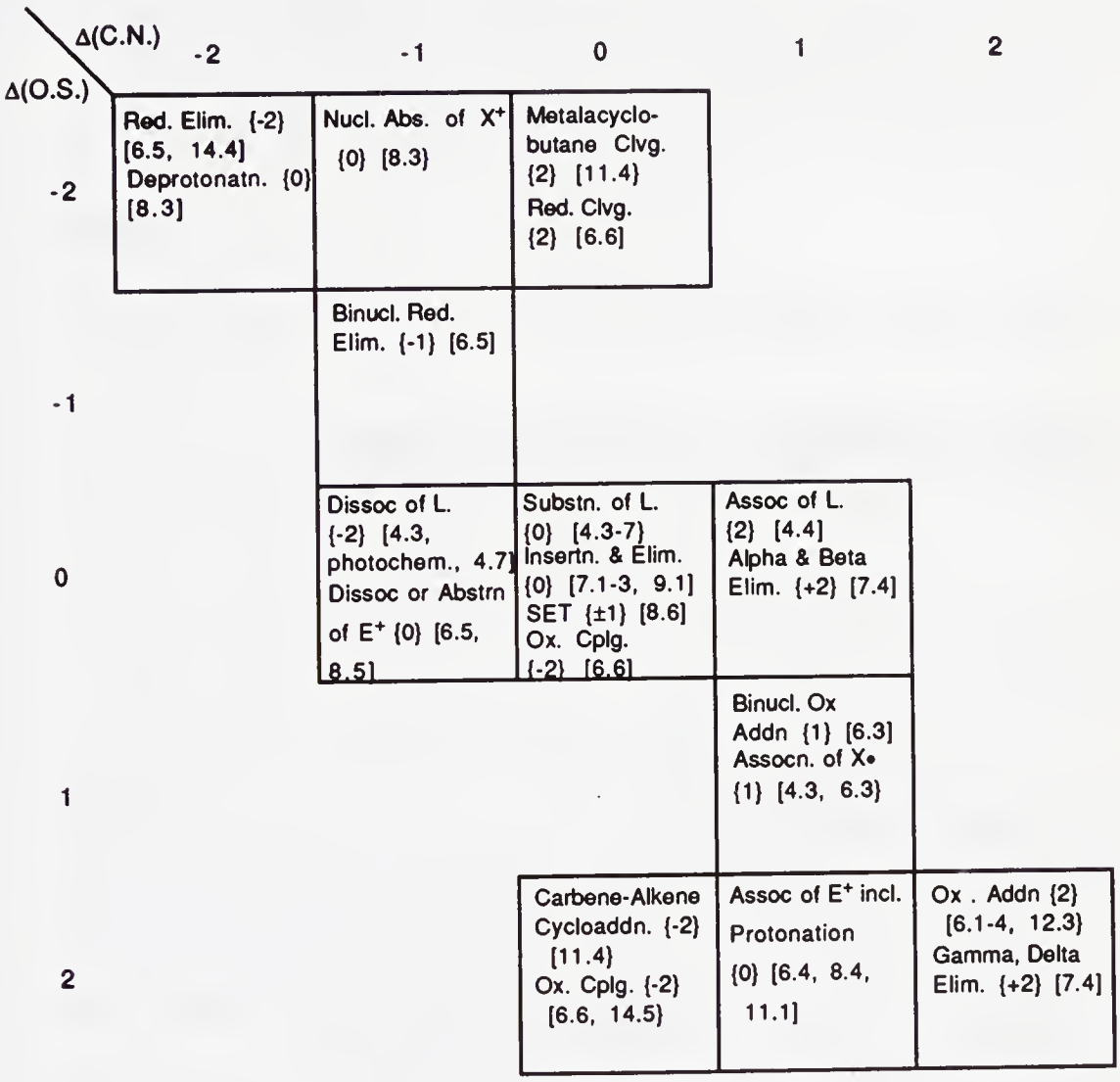
E. A. V. Ebsworth, D. W. H. Rankin, and S. Cradock, *Structural Methods in Inorganic Chemistry,* Blackwell, Oxford, 1987.

MAJOR REACTION TYPES

Alphabetical List of Reaction Types and Where to Find Them in the Text

Reaction Type	Section
α Elimination	7.4
Abstraction of E^+	6.5, 8.3, 8.5
Alkene–carbene cycloaddition	11.4
Association of E^+	6.4, 8.4, 11.1
Association of L	4.4
Association of X·	4.3, 6.3
β Elimination	7.4
Binuclear oxidative addition	6.3
Binuclear reductive elimination	6.5
Carbene–alkene cycloaddition	11.4
γ Elimination	7.4
∂ Elimination	7.4
Deprotonation	8.3
Dissociation of E^+	6.5, 8.5
Dissociation of L	4.3
Eliminations and insertions	7.1–7.3, 9.1–9.5
Insertions and eliminations	7.1–7.3, 9.1–9.5
Ligand substitution	4.3–4.7
Metalacyclobutane cleavage	11.4
Nucleophilic abstraction of X^+	8.3
Oxidative coupling of RNC, CO	6.6
Photochemical dissociation of L or X_2	4.7
Reductive cleavage	6.6
Single-electron transfer	8.6

The major reaction types presented in this book are listed in Fig. A.1.



{} = Δ(e count) [] = Section number

FIGURE A1 Master list of reaction types. *Key:* Abs. = abstraction, Addn. = addition, Assoc. = association, Binucl. = binuclear, Cplg. = coupling, Dissoc. = dissociation, E^+ = electrophile, Elim. = elimination, Fragtn. = fragmentation. L = 2e ligand, Ox. = oxidative, SET = single electron transfer, Substn. = substitution, X· = free radical. {encloses electron count change in the reaction} (encloses section number for the topic)

SOLUTIONS TO PROBLEMS

Chapter 1

1. 4 (if you thought 2, you forgot structures like $[PtL_4]^{2+}$ $[PtCl_4]^{2-}$).
2. A cubane with $PtMe_3$ and I at alternate corners to give the octahedral geometry required by Pt(IV).
3. The first diamine ligand gives a favorable five-membered ring on chelation, while the second gives an unfavorable four-membered ring. The second lone pair of water repels and destabilizes the d_π electrons.
4. $[PtCl_4]^{2-}$ + (i) tu, 1 equiv. which must give $[Pt(tu)Cl_3]^-$; (ii) NH_3, which replaces the Cl trans to the high trans effect tu ligand.
5. The Ti complex is a hard acid so the order is: N > P > C (hard base best); the W complex is a soft acid so: C > P > N (soft base best).
6. The tetrahedral structure with a two-below-three orbital pattern will be paramagnetic because in a d^8 ion the lower set of three orbitals will take six electrons, leaving two for the upper set of two orbitals; these must go in with parallel spin, so there will be two unpaired electrons.
7. Measure ν(CO), the better donors will cause the greater lowering because they will cause a greater charge buildup on the metal which will lead to increased $M(d_\pi) \rightarrow CO(\pi^*)$ back donation and a lower C—O bond order.
8. The d orbitals are stabilized by the higher nuclear charge and so back donation (required to form a strong M—CO bond) is reduced. Cu(I) rather than Cu(II) would be best because it would be a stronger π donor.

9. Reduced complexes will easily lose electrons to O_2 in an oxidation reaction but will not tend to bind a π donor like H_2O.

10. Assume an octahedral three-below-two splitting pattern, then $MnCp_2$ has 5 unpaired electrons one in each of the five orbitals; $MnCp_2^*$ has 4e paired up in the lower pair of orbitals and 1 unpaired electron in the upper set of orbitals; Cp* has the higher ligand field because it causes spin pairing.

Chapter 2

1. The first three are 16e, Pt(II), d^8, then 20e, Ni(II), d^8, 18e, Ru(II), d^6; 18e, Re(VII), d^0; 18e, Ir(V), d^4; 10e, Ta(V), d^0; 16e, Ti(IV), d^0, 14e, Re(VII), d^0.

2. $[\{(CO)_3Re\}(\mu_3\text{-}Cl)]_4$. A triply bridging Cl^- in a cubane structure allows each Cl^- to donate 5 electrons (6e ionic model).

3. $(\eta^6\text{-}PhC_6H_5)Cr(CO)_3$, with a π-bound arene ring.

4. Ti(0) if both ligands are considered as being 4e L_2, but Ti(II) if one is considered as being X_2 and bound via the two N atoms in the MeN—CH=CH—NMe form, and Ti(IV) if both are considered as being in the X_2 form.

5. The complex is 12e, 10e and 8e in the Ti(0), (II), and (IV) forms.

6. M—M counts one for each metal. This rule allows the Os compound to reach 18e. The Rh compound has a tetrahedron of mutually bonded Rh atoms for a total of six Rh—Rh bonds is also 18e.

7. 8e C for $H_3C^+ \leftarrow\!:NH_3$ (three X ligands, one L and a positive charge) and 8e for $H_2C \leftarrow\!:CO$ (two X ligands and one L).

8. Counting only one lone pair gives an 18e count in both cases.

9. 2e either way. A σ-acid metal favors the η^1 form in which the important bonding interaction is L $\rightarrow$ M σ-donation and a π-basic metal favors the η^2 form where back donation into the C=O π^* is the most important interaction.

10. W, η^3 and η^5 gives an 18e count. If each triphos is η^2 we get a 16e count which is appropriate for Pd(II) and this is the true structure; an η^2-η^3 structure would be 18e and cannot be ruled out, but an η^3-η^3 would be 20e and is unreasonable.

11. The left hand complex has six L type ligands, so we have 18e, d^6, W(0); the right hand complex has five L and two X ligands, so we have 18e, d^4, W(II).

Chapter 3

1. Protonation of the Pt or oxidative addition give a Pt—H into which the acetylene inserts.
2. M—CF_2—Me (σ-acceptor substituents, especially F strongly stabilize an alkyl).
3. Oxidative addition of MeCl, followed by reaction of the product with LiMe, which acts as a Me^- donor and replaces the Ir—Cl by Ir—Me.
4. 18e in all cases; both structures have the same electron count because (H_2) is a 2e L ligand and $(H)_2$ consists of two 1e X ligands, so no change. Both structures are in fact classical.
5. If X or Y have lone pairs they may compete for binding. Y—H—M allows close approach of YH to M.
6. It is easier to reduce a more oxidized complex.
7. (a) To maximize M → Ph back bonding from the out of plane d_{z^2} orbital, the Ph will have to be in the square plane so the π cloud of the Ph ring is lined up with the d orbital. (b) To minimize steric repulsion, Ph will be out of the plane.
8. 17e, Ru(III), d^5; 18e, Cr(0), d^6; 12e, W(VI), d^0.
9. Initial formation of Ir—(*i*-Pr) with RMgX acting as source of R^- to replace the Br^- initially bound to Ir. The alkyl then β eliminates to give propene as the other product.
10. Insertion of the alkene into the M—H bond to give M—CHMe(nPr), followed by β elimination to give MeCH=CHMe; insertion requires prior binding of the alkene and so does not happen in the 18e case.

Chapter 4

1. (a) Halide dissociation is bad for two reasons: the product is 16e and cationic, while for proton dissociation the product is 18e and anionic; 16e species are less favorable and cations are less well stabilized by the π-acceptor CO groups than anions. (b) Solvent likely to bind only to the 16e cation.
2. The NO can bend to accommodate the incoming ligand.
3. The more ∂^+ the CO carbon, the easier the reaction, so the order is: $Mn(CO)_6^+$ > $Mo(CO)_3(NO)_2$ > $Mo(CO)_6$ > $Mo(CO)_4$(dpe) > $Mo(CO)_2(dpe)_2$ > $Mo(CO)_5^{2-}$. [This order is decided by (1) cations > neutrals > anions, and (2) within each class, complexes with the better π-acceptor ligands > complexes with less good π-acceptor ligands].

4. The ν(CO) in the IR or the ease of oxidation as measured electrochemically.

5. $CpWH_2$: 18e, W(IV), 8; $\{Cp_2W\}_2$: same; $ReCl(N_2)L_4$: 18e, Re(I), d^6; Re dimer: same; FeL_4: 16e, Fe(0), 4; cyclometalated form: 18e, Fe(II), 6; W compounds: 18e, W(0), 6.

6. NR_3 lacks significant π-acid character, but NF_3 should bind better thanks to its N—F σ^* orbital, which should be polarized toward the metal and could act as π acceptor; this resembles the cases of CH_3 versus CF_3, where the same applies.

7. As a highly reduced metal, Ni(0) prefers π-acceptor ligands like $P(OMe)_3$. PMe_3 as a poor π acceptor causes the electron density on the metal to rise so much that the NiL_3 fragment is a poor σ-acceptor.

8. D, A, D, D, A, A. D for 18e, A for 16e species.

9. Eighteen electron structures (or 16e where appropriate) can be achieved as follows: η^6-Ph or BPh_4; η^3 and η^5-Ind groups; $[Me_3Pt(\mu\text{-}I)]_4$, cot must be η^4 to two $PtCl_2$ groups; μ-Cl required.

10. *trans*-$L'_2Mo(CO)_4$ — L′ labilizes the CO trans to itself; *cis*-$L'_2Mo(CO)_4$ — CO preferentially labilizes a CO trans to itself.

11. Six positive ionic charges on the complex rules it out because the metal would not retain enough π-donor power to bind NO. Very few complexes exceed a net ionic charge of ± 2.

12. Protonation at the metal (always allowed even for 18e complexes) should weaken M—CO and put a high trans effect ligand on the metal.

Chapter 5

1. The poorer π-back bonding centers will have the highest reactivity: Pd > Pt; cation > neutral; phosphite > phosphine.

2. Nucleophilic attack on a halide or tosylate (the latter may be better because the halide may dehydrohalogenate) $2L_nM^- + TsOCH_2CH_2OTs$. ^{13}C NMR should show two equivalent carbons with coupling to two directly-attached H, and coupling to $2n$ L and 2 M nuclei (if these have $I \neq 0$).

3. Oxidative coupling of two alkynes to give the metallole, followed by CO insertion and reductive elimination.

4. From $Cp_2MoClMe$ by abstraction of Cl^- with Ag^+ in the presence of ethylene. C—C should be parallel to Mo—Me for the best back donation because the back bonding orbital lies in the plane shown in Figure 5.6. NMR should show inequivalent CH_2 groups, one close to the methyl and one far from this group.

5. We expect more LX_2 character as L becomes more donor, so C_2C_3 should shorten.

6. The allyl mechanism of Figure 9.2b to give $[(1,5\text{-cod})IrCl]_2$ and removal of the cod with the phosphite. 1,5-Cod is less stable because it lacks the conjugated system of the 1,3-isomer. The formation of two strong M—P bonds provides the driving force.

7. Two optical isomers are possible: the 2-carbon of propene has four different substituents: CH_3, H, CH_2 and Cl_3Pt.

8. The allene complex $Fp(\eta^2\text{-}CH_2{=}C{=}CH_2)^+$ is formed.

9. The first complex is the 18e species, $[(\eta^6\text{-indane})IrL_2]^+$ formed by hydrogenation of the C=C bond by the IrH_2 group, and the second is $[(\eta^5\text{-indenyl})IrHL_2]^+$, formed by oxidative addition of an indane C—H bond, β elimination, then loss of H_2 from the metal and oxidative addition of an indane C—H bond. Substitution only of the arene complex by CO is possible because loss of arene is easier than loss of the Cp-like η^5-indenyl (see Section 5.7).

10. An 18e structure is $(\eta^6\text{-}PhBPh_3)Rh(cod)$.

Chapter 6

1. **A** reacts by S_N2, **B** by a radical route. *i*-PrI is an excellent substrate for radical reactions and MeOTs for S_N2 (see Section 6.3).

2. Assuming steric effects are not important, only the bond strengths change, so these are in the order Me—Me < M-Ph < M-H < M—SiR_3, favoring silane addition and disfavoring methane addition.

3. True oxidative addition is more likely for e-releasing ligands, good π-donor third row elements, and better π-donor reduced forms. Dewar–Chatt binding is favored for a weak π-donor site that binds H_2 as a molecule.

4. For HCl the steps must be: (1) oxidative addition of HCl; (2a) a second oxidative addition of HCl followed by reductive elimination of H_2 and binding of Cl^- or (2b) electrophilic abstraction of H^- by H^+ and coordination of the second Cl^- to the empty site so formed. In either case H_2 is also formed. For *t*-BuCl: (1) SET to give •PtClL and *t*-Bu•. *t*-Bu• may abstract H from a second molecule of *t*-BuCl to give $Me_2C{=}CH_2$ and Cl•. In the final step, Cl• adds to $PtClL_2$• to give the product. A Pt(*t*-Bu) intermediate is also possible, but less likely (M—*t*-Bu is very rare).

5. Oxidative coupling to give the metallacycle followed by β elimination to give $L_nM(H)(CH_2CH_2CHCH_2)$, followed by reductive elimination of 1-butene.

6. C > D > B > A. The ν(CO) frequencies increase in the reverse order and lower ν(CO) correlates with a more reduced metal and so faster oxidative addition. After oxidative addition the frequencies should rise, because oxidation of the metal should reduce its π basicity.

7. Reductive elimination of MeH and PhH are thermodynamically favored relative to reductive elimination of HCl.

8. Oxidative addition is not possible for d^0 species, so sigma bond metathesis must be implicated in the first step, probably via formation of H_2 complex, which is allowed in a 12e species. PMe_3 then displaces H_2 from intermediate MH_2 species to give the final product. The final H_2 is not lost because $W(PMe_3)_6$ is a rather unstable species, for the same reasons we saw for the Ni(0) analog in Q.7 of Chapter 4.

9. The two Hs must be cis in the products. If we run the rearrangement under D_2, D incorporation into products will be seen if H_2 is lost.

10. PhCN has an unusually unhindered C—C bond, an intermediate η^2-arene complex is possible and this may help bring the metal close to the C—C bond. Finally, M—CN is unusually strong for a C—C bond because of the π-bonding possible with this CO analog.

Chapter 7

1. (a) Migratory insertion should give the acyl [CpRu(CO)(COMe)(PPh_3)]; (b) insertion into M—H should give the allyl product; (c) attack at an 18e complex is allowed for SO_2 (see Section 7.3), so the [$CpFe(CO)_2(MeSO_2)$] is formed; (d) no reaction is expected because the M—CF_3 bond is too strong.

2. Cyclometallation of the amine with loss of HCl gives **A**, followed by insertion of the cyclopropene to give **C** or oxidative addition of the strained C—C single bond of the cyclopropene followed by rearrangement to give **D**. Cyclometallation of the amine is not possible for $PhNMe_2$ because of the wrong ring size in this case.

3. α Elimination of CH_3 leaves M=CH_2 groups which couple to give $H_2C{=}CH_2$.

4. (1) RNC must bind, undergo migratory insertion and the resulting imine undergo another insertion with the second hydride. (2) Migratory insertion twice over gives a bis-acyl that in its carbenoid canonical form (**7.2**) couples to give the new double bond. (3) Migratory insertion once, followed by alkyl migration from the metal to the carbene carbon in the carbenoid canonical form of the cyclic acyl. (4) Insertion to give $MPh(O_2CPh)$ is probably followed by a cyclometallation by a sigma bond metathesis pathway with loss of PhH.

5. Oxidative addition of MeI is followed by reductive elimination. The possibility of binuclear reductive elimination is suggested from the label crossover data.

6. Ethylene displaces the agostic C—H to give $MEt(C_2H_4)$. Insertions of ethylene gives an agostic butyl with no β elimination of the growing chain. The process is repeated. The presence of an agostic C—H points to a weakly π-donor metal, which is unable to carry out a β elimination. In the Rh system, neutral Rh(I) is a better π donor and so β elimination is fast in the first formed butyl complex.

7. Possibilities are $—CH_2—CMe(OMe)_2$ or $—CH_2—CMePh_2$. For C—C bond breaking we need a strained ring system such as $—CH_2—CMe(CH_2CH_2)$, or $—CH_2—CMe(CH_2CH_2CH_2)$.

8. More strongly ligating solvents, more electron-withdrawing ligands, and a poorer π-basic metal will all favor the reaction. The solvent stabilizes the product and the ligands and metal make the CO more ∂^+ at carbon and so more reactive.

9. Cyclometallation should give $PtHClL_2$; the phosphine must cyclometallate in the $—CH_2Nb$ case, this would release CH_3Nb and leave a cyclometallated Pd complex.

10. The α-CH is β to the second metal, M_2, in a $Me\text{-}M_1\text{-}M_2$ cluster.

Chapter 8

1. The rules of Section 8.2 predict attack at: (1) ethylene, (2) the terminal position, (3) the butadiene.

2. (1) Protonation gives MeH and FpCl, (2) SET and nucleophilic abstraction gives MeCl, (3) electrophilic abstraction gives MeHgCl, (4) protonation gives MeH and $CpL_2Fe(thf)^+$.

3. Reduction of Pd(II) to Pd(0) by nucleophilic attack of the amine on the diene complex is followed by oxidative addition of PhI and then insertion of the diene into the Pd—Ph bond to give a Pd(II) allyl. This can either β eliminate to give the free diene or undergo nucleophilic attack by the amine to give the allylic amine.

4. The high ν(CO) and 2+ charge imply weak π-back donation and means the CO carbon is very δ+ in character and very sensitive to nucleophilic attack.

5. The arene is activated for nucleophilic attack by coordination because the $Cr(CO)_3$ group is so electron withdrawing. The product should be $[(\eta^6\text{-PhOMe})Cr(CO)_3]$.

6. The H^- group abstracted should be anti to the metal, but in β elimination, expected for a 16e complex, the metal abstracts the syn H.

7. We need to make the metal a better σ acid and π base, use a noncoordinating anion, sterically protect the site to prevent dimerization or binding of a solvent C—H bond, and use a poor donor solvent to prevent displacement.

8. Nucleophilic attack of MeOH to give the 2-methoxy-5-cyclooctene-1-yl complex is followed by a PR_3-induced β elimination to give **C** and the hydride. The 1,4-diene might also be formed.

9. Nucleophilic attack of Me^- to give a vinyl complex is followed by electrophilic abstraction of the vinyl with I_2.

10. The P=O bond is too strong and the oxygen is less nucleophilic; dppe increases the back donation and so lowers the δ+ charge at C making it less sensitive to nucleophilic attack; peroxysulfate or PhIO are more powerful reagents.

Chapter 9

1. Isomerization should bring all three double bonds together in the right hand ring to give a phenol, a compound known to be acidic; the reaction is driven by the aromatic stabilization in the product.

2. Dissociation of L, required for activity, is unlikely for triphos because of chelation, but Cl^- abstraction by BF_3 or Tl^+ opens the required site.

3. The initial terminal cyanation step should be followed by isomerization of the remaining internal C=C group to the terminal position and so should give the 1,5-dinitrile as the final product.

4. Successive H transfers to the ring are followed by oxidative addition of H_2 and further H transfers. The first H transfer to the arene will be difficult because the aromatic stabilization will be disrupted; this should be easier with naphthalene, where the aromatic stabilization is lower per ring and we only disrupt one ring.

5. Oxidative addition of the aldehyde C—H bond to Rh is followed by C=C insertion into the M—H to give a metallacycle; this gives the product shown after reductive elimination. Oxidative addition of the strained C—O bond is followed by β-elimination and reductive elimination to give the enol which tautomerizes to acetone.

6. The first and second are thermodynamically unfavorable unless we find reagents to accept the H_2 or O_2, respectively. The third reaction is favorable but it will be difficult to prevent over-oxidation because the MeOH is usually much more reactive than MeH.

7. $H_2[PtCl_6]$ (i.e., an acid not a hydride).

8. Insertion into the M—Si rather than the M—H bond would give M—CR=CHSiR_3 and β elimination can now give the unsaturated product. This β elimination produces an MH_2 species which could hydrogenate some alkene to alkane, which is the third product.

9. Oxidative coupling, followed by β elimination and reductive elimination. If the β elimination were suppressed by avoiding β-H substituents the metallacycle might be isolable. A 1,6-heptadiene is another possibility, where the bicyclic structure of the oxidative coupling product might make the metallacycle isolable.

10. Oxidative addition of H_2 is possible after the arene slips to the η^4 form. The substrate can displace the arene to give $M(CO)_3$(diene)H_2. If we consider that the diene adopts an LX_2 form, the observed product can be formed by two successive reductive eliminations. The cis product reflects the conformation of the bound diene and the monoene is a much poorer ligand in this system and so does not bind and is therefore not reduced.

Chapter 10

1. The cis form has a doublet of quartets in the hydride region, because of the presence of three P nuclei cis to each H and one P trans to H. The trans form has a quintet, because of the presence of four P nuclei cis to each H. Using the HD complex will give a 1:1:1 triplet from H coupling to the I = 1 D nucleus and after dividing J(H,D) by six to adjust for the lower γ of the D isotope, we get the J(H,H) which is not observed in the dihydride because equivalent Hs do not couple.

2. MH_3 and $MH(H_2)$ are the most likely. T_1(min) data or ^1J(H,D) in the H_2D complexes would be useful. The trihydride should have a long T_1 and a low J(H,D) (see Section 10.7).

3. One Ind could be η^3, in which case we should see two distinct sets of Ind resonances. If the two rings were rapidly fluxional, exchanging between η^3 and η^5 forms, one set of C resonances would be seen but the presence of an IPR effect (see Section 10.8) in this case should make it distinguishable.

4. The presence of an IPR effect (see Section 10.8) would suggest the η^4 form.

5. 31 sec^{-1}, 2500 × $\pi\sqrt{2}$ sec^{-1}.

6. (1) c,a; (2), b,d; (3) d; (4) d; (5) d; (6) b.

7. Using Equation 10.17 gives an angle close to 120°, consistent with a TBP structure with the COs equatorial.

8. The CO bond order falls when bridging as μ_2 and falls even further when bridged as μ_3.

9. 6-coordination is expected in both cases, and so loss of Cl^- is necessary to produce an η^2 form; the conductivity should be high for the ionic species and the IR of the two acetate binding modes are also different. Comparison of the IR with literature examples would be needed to distinguish the two cases.

10. If the plane of the pyridine ring is orthogonal to the square plane (as expected if steric effects dominate) we expect diastereotopy of the phosphine methyls because the methyl group of the pyridine breaks the plane of symmetry.

Chapter 11

1. Two moles of Tebbe's reagent should convert the ketone first to methylene cyclohexane and via that intermediate to product.

2. Initial intramolecular metalacycle formation, presumably with initial reversible CO loss, with metathesis-like cleavage leads to the product.

3. Initial oxidative coupling of the two ethylenes would have to be followed by β elimination and reductive elimination. The resulting 1-butene would have to resist displacement by ethylene (unlikely) but give an oxidative coupling of butene with ethylene, with the Et group always in the 1-position of the metalacycle and the β-elimination would have to occur only at the former ethylene end of the metalacycle.

4. (a) $Ph_3P{=}CH_2$ has strong Schrock-like character, judging from the strongly nucleophilic character of the methylene group. This is consistent with Figure 11.1 because C is more electronegative than P. (b) O is more electronegative than C, so Re=O should be more nucleophilic than $Re{=}CH_2$.

5. Initial metathesis of the substrate C=C bond gives MeCH=CR(OR) and a C=W carbene intermediate. This forms a metalacycle with the nearby alkyne and metathesis-like steps lead to product.

6. The β elimination of the linear alkyl gives a 1-alkene as the kinetic product. Clearly, the SHOP catalyst cannot be a good isomerization catalyst otherwise the 1-alkene would be isomerized.

7. A pairwise mechanism would give cdd, but a nonpairwise mechanism should give polymer.

8. Oxidation to Mo(VI), the active catalyst.

9. The key to polymerization is avoiding β elimination. Ti, as a d^0 metal, does this well. If the chain is transferred to a Ni cocatalyst it will β

eliminate and so a shorter chain will result. Fe should work too but V is probably too early and Hg too late to β eliminate rapidly.

10. The CH_2 group lines up with the Cp—M—Cp direction to benefit from back donation from W. The two extra electrons of the anion would have to go into the CH_2 *p*-orbital. the CH_2 orientation would be at right angles to that in cation to minimize repulsion between the two filled orbitals.

Chapter 12

1. The reverse process should go by the reverse mechanism, which implies (see Figure 12.2) that H_2 will oxidatively add to Pt(0) and then CO_2 will insert into the Pt—H bond.

2. Os(0) is a better π base than Ir(III) and the Os is also neutral and the Ir cationic. Perhaps the most important factor is the low steric hindrance for side-on bonding in formaldehyde versus acetone.

3. Cyclometalation of a PMe group in preference to a PPh group is very unusual; perhaps the RLi deprotonates PMe, the CH_2^- group of which then binds to the metal.

4. As an 18e species, an η^1-*C*O_2 adduct is expected; for the indenyl case, slip could generate a site to allow η^2-*OC*O binding; the 18e complex could only plausible react by H^- abstraction from the metal by CO_2, which would produce an η^1-*O*CHO complex. The Re anion is probably the best case because of the negative charge (after all, CO_2 reacts easily with OH^-).

5. Cyclometallation of the $ArCH_3$ group followed by CO insertion.

6. Loss of PhH by reductive elimination, binding of substrate via the isonitrile C, cyclometallation of the $ArCH_3$ group, migratory insertion involving the isonitrile, isomerization and reductive elimination of the product.

7. Transfer of *endo*-Et to the metal, rotation of Cp, migration of Et back to a different point on the Cp ring, a 1,3 H shift on the *exo*-face to bring an H into the endo position from which H transfer to the metal is possible.

8. Reductive elimination to form a cyclopropane which immediately oxidatively adds back to the metal.

9. Binding of formate as η^1-*O*CHO, followed by β elimination to deliver H^- to the metal and release CO_2. This can be a good synthetic route to hydrides.

10. CO_2 insertion into the terminal M—C bond to give an η^4-*O*C*O*CH_2CHCHCH_2 carboxylato-allyl complex. Oxidation then leads to the coupling of the allyls by binuclear reductive elimination.

11. 112 kcal/mol. Yes.

12. Oxidative addition of Si—H, followed by coordination and insertion of the alkyne into M—H or M—Si, followed by reductive elimination. The extra products could be formed by insertion of the alkyne into the M—Si bond, followed by isomerization of the vinyl intermediate so as to put the β-C—H endo to the metal, then β elimination to give the silaalkyne and MH_2. Formation of the alkene would be the result of hydrogenation of the substrate by the dihydride L_nMH_2.

Chapter 13

1. Any bridging CO complex with L_nM isolobal with CH, for example, $Cp_2Ni_2(CO)$. This might be formed from $NiCp_2$ and CO.

2–3. (1) 48e, 3 M—M bonds; (2) 50e, 2 M—M bonds; (3) 52e, 1 M—M bond. The S are counted as vertex atoms—they retain their lone pair as shown by easy methylation.

4. This 60e cluster is 2e short of the 62e system expected; Wades rules give 14 skeletal electrons appropriate for an octahedron counting each of the EtC carbons as vertices.

5. **B** is isolobal with tetrahedrane, **C** with cyclopropane.

6. The Fe_4 species is 60e and should be tetrahedral. Four $Fe(CO)_3$ groups are likely, which leaves a single CO, which might be bridging but we cannot tell from counting electrons. The Ni_5 structure is 76e and so a square pyramid with one Ni—Ni bond opened up is most likely. The 36e Cr_2 system is expected to have no M—M bond but be held together by the bridging phosphine.

7. Two W≡C bonds bind to Pt in the cluster just as two alkynes should bind to Pt in the alkyne complex, so $n = 2$. On an 18e rule picture, the alkynes are 4e donors. The unsaturated ligands are orthogonal so that each X≡C bond (X = W or C) can back bond to a different set of d_π orbitals.

8. The most symmetrical structure is a square pyramid with Fe at the apex and four Bs at the base; $(\eta^4\text{-}C_4H_4)Fe(CO)_3$ is the carbon analogue.

9. Elements to the left of C are electron-deficient, elements to the right are electron-rich. As long as electron deficient elements dominate a structure, a cluster product can be formed.

10. An $\eta^2\text{-}\mu\text{-}CH_2CO$ complex with the ligand bridging two Os atoms which have lost their direct M—M bond.

Chapter 14

1. Oxidative addition of ArI is followed by insertion of the alkene, β-elimination gives a new alkene, nucleophilic attack on which by the N lone pair is followed by loss of MeOH to aromatize the system.

2. Nucleophilic attack at C with displacement of the epoxide as an $—O^-$ group, is followed by protonation to give the alcohol, loss of water, formation of $Fp(alkene)^+$ and displacement of the alkene with I^-.

3. Possibly an oxidative addition of $Cl—CCl_3$, insertion of C=C and reductive elimination, but this could also be a radical chain reaction initiated by the metal. In this case $•CCl_3$ would add to the free alkene to give $RCH•CH_2CCl_3$, which would abstract Cl from another mole of CCl_4. If the latter were true, however, we would see crossover, so we can rule out the radical pathway.

4. The phenol is formed by isomerization. Treatment with the iron carbonyl forms a diene complex in which the double bonds have been shifted by isomerization so that they are in the same (A) ring.

5. Chelation of the diene is followed by nucleophilic attack of MeOH on the exo face, then CO insertion and nucleophilic attack of MeLi on the resulting acyl.

6. The NMe_2 group binds to the metal and so directs Pd to the front face, CHE_2^- attacks from the back to give a 5-membered ring intermediate which then β-eliminates. The second sequence is similar but includes a Heck reaction.

7. $FpCH_2SMe$ is formed first, then $FpCH_2SMe_2^+$. Loss of Me_2S gives the carbene which cyclopropanates the alkene.

8. Ketones lack a reactive C—H bond. After oxidative addition of RCO—Cl, retromigratory insertion and reductive elimination of RCl, $RhCl(CO)L_2$ is formed.

9. The 16e $RhCl(CO)L_2$ does not lose CO easily, but the dpe complex gives $Rh(dpe)_2(CO)$, which being 18e loses CO more easily because Rh(I) prefers 16e to 18e.

10. Trans-2-methoxycyclohexane carboxylic ester is formed by trans methoxymercuration (Figure 14.2) transfer of the alkyl to Pd, CO insertion and hydrolysis.

Chapter 15

1–2. The metal is d^0 and therefore CO does not bind well enough to give a stable complex, but weak binding is possible and the absence of back

donation increases δ^+ character of CO carbon and speeds up migratory insertion in the weakly-bound form.

3. The third row element prefers the higher oxidation state and has longer M—C bonds, allowing a greater number of R groups to fit around the metal.

4. Electrophilic abstraction is likely for Equation 15.3, but this is unlikely for **15.1–15.2** because the M—C carbons are sterically protected in these two compounds.

5. The two alkenes are orthogonal to allow the metal to back donate efficiently to both alkenes by using different sets of d_π orbitals.

6. Alkene hydrogenation normally occurs in the presence of many hydride ligands. The stereochemistry of the Re compound makes the (C=C) groups of the bound alkene orthogonal to the M—H bonds and prevents insertion.

7. Rotation is not easy because the alkynes would lose the back donation component from the metal.

Chapter 16

1. These are the most abundant metals in the biosphere.

2. Most organisms live in an oxidizing environment and proteins have mostly hard ligands.

3. A low $\nu(N_2)$ implies strong back donation which also means that the terminal N will also have a large ∂^- charge and therefore be readily protonated.

4. The stability of radicals R• is measured by the R—H bond strength, which is the ΔH for splitting the bond into R• and H•. For these species this goes in the order $HCN > CF_3H > CH_4 > PhCH_3 > Ph_2CH_2$. C—H bonds to *sp* carbons are always unusually strong because of the high *s* character while pH groups weaken C—H bonds by delocalizing the unpaired electron in the resulting radical. This is the reverse of the order of ease of loss of R•.

5. Protonation lowers the electron density on Re and reduces the back donation to N_2, resulting in an increase in $\nu(N_2)$ and weaker M—N_2 binding, making the N_2 more easily lost.

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