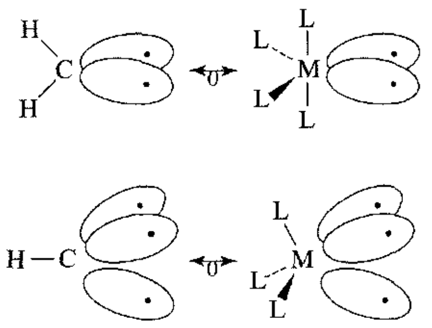
CHAPTER 15

Parallels Between Main Group and Organometallic Chemistry



It is common to treat organic and inorganic chemistry as separate topics and, within inorganic chemistry, to consider separately the chemistry of main group compounds and organometallic compounds, as we have generally done so far in this text. However, valuable insights can be gained by examining parallels between these different classifications of compounds. Such an examination may lead to a more thorough understanding of the different types of compounds being compared and may suggest new chemical compounds or new types of reactions. The objective of this chapter is to consider several of these parallels, especially between main group and organometallic compounds.

15-1 MAIN GROUP PARALLELS WITH BINARY CARBONYL COMPLEXES

Comparisons within main group chemistry have already been discussed in earlier chapters. These included the similarities (and differences) between borazine and benzene, the relative instability of silanes in comparison with alkanes, and differences in bonding in homonuclear and heteronuclear diatomic species (such as the isoelectronic N_2 and CO). In general, these parallels have centered around isoelectronic species. Similarities also occur between main group and transition metal species that are electronically equivalent, species that require the same number of electrons to achieve a filled valence configuration.[1] For example, a halogen atom, one electron short of a valence shell octet, may be considered electronically equivalent to $Mn(CO)_5$, a 17-electron species one electron short of an 18-electron configuration. In this section, we will discuss briefly some parallels between main group atoms and ions and electronically equivalent binary carbonyl complexes.

Much chemistry of main group and metal carbonyl species can be rationalized from the way in which these species can achieve closed shell (octet or 18-electron) configurations. These methods of achieving more stable configurations will be illustrated for the following electronically equivalent species:

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[1] J. E. Ellis, *J. Chem. Educ.*, **1976**, *53*, 2.

Electrons Short of Filled Shell	*Examples of Electronically Equivalent Species*	
	Main Group	*Metal Carbonyl*
1	Cl, Br, I	$Mn(CO)_5$, $Co(CO)_4$
2	S	$Fe(CO)_4$, $Os(CO)_4$
3	P	$Co(CO)_3$, $Ir(CO)_3$

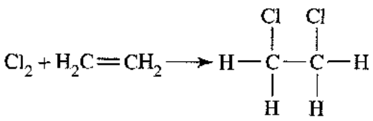
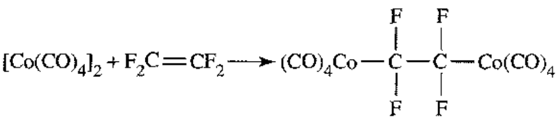
Halogen atoms, one electron short of a valence shell octet, exhibit chemical similarities with 17-electron organometallic species; some of the most striking are the parallels between halogen atoms and $Co(CO)_4$, as summarized in Table 15-1. Both can reach filled shell electron configurations by acquiring an electron or by dimerization. The neutral dimers are capable of adding across multiple carbon-carbon bonds and can undergo disproportionation by Lewis bases. Anions of both electronically equivalent species have a 1− charge and can combine with H^+ to form acids; both HX (X = Cl, Br, or I) and $HCo(CO)_4$ are strong acids in aqueous solution. Both types of anions form precipitates with heavy metal ions such as Ag^+ in aqueous solution. The parallels between 7-electron halogen atoms and 17-electron binary carbonyl species are sufficiently strong to justify extending the label *pseudohalogen* (Chapter 8) to these carbonyls.

Similarly, 6-electron main group species show chemical similarities with 16-electron organometallic species. As for the halogens and 17-electron organometallic complexes, many of these similarities can be accounted for on the basis of ways in which the species can acquire or share electrons to achieve filled shell configurations. Some similarities between sulfur and the electronically equivalent $Fe(CO)_4$ are listed in Table 15-2.

The concept of electronically equivalent groups can also be extended to 5-electron main group elements [Group 15 (VA)] and 15-electron organometallic species. For example, phosphorus and $Ir(CO)_3$ both form tetrahedral tetramers, as shown in Figure 15-1. The 15-electron $Co(CO)_3$, which is isoelectronic with $Ir(CO)_3$, can replace one or more phosphorus atoms in the P_4 tetrahedron, as also shown in this figure.

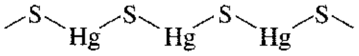
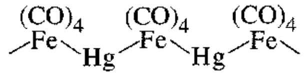
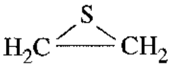
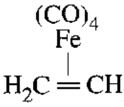
The parallels between electronically equivalent main group and organometallic species are interesting and summarize a considerable amount of their chemistry. The limitations of these parallels should also be recognized, however. For example, main group compounds having expanded shells (central atoms exceeding an electron count of 8) may not have organometallic analogues; organometallic analogues of such

TABLE 15-1
Parallels Between Cl and $Co(CO)_4$

Characteristic	*Examples*	*Examples*
Ion of 1− charge	Cl^-	$[Co(CO)_4]^-$
Neutral dimeric species	Cl_2	$[Co(CO)_4]_2$
Hydrohalic acid	HCl (strong acid in aqueous solution)	$HCo(CO)_4$ (strong acid in aqueous solution)[a]
Formation of interhalogen compounds	$Br_2 + Cl_2 \rightleftharpoons 2\,BrCl$	$I_2 + [Co(CO)_4]_2 \longrightarrow 2\,ICo(CO)_4$
Formation of heavy metal salts of low solubility in water	AgCl	$AgCo(CO)_4$
Addition to unsaturated species	 $Cl_2 + H_2C{=}CH_2 \longrightarrow H-\underset{H}{\overset{Cl}{C}}-\underset{H}{\overset{Cl}{C}}-H$	 $[Co(CO)_4]_2 + F_2C{=}CF_2 \longrightarrow (CO)_4Co-\underset{F}{\overset{F}{C}}-\underset{F}{\overset{F}{C}}-Co(CO)_4$
Disproportionation by Lewis bases	$Cl_2 + N(CH_3)_3 \longrightarrow [ClN(CH_3)_3]Cl$	$[Co(CO)_4]_2 + C_5H_{10}NH \longrightarrow [(CO)_4Co(C_5H_{10}NH)][Co(CO)_4]$ (piperidine)

NOTE: [a] However, $HCo(CO)_4$ is only slightly soluble in water.

TABLE 15-2
Parallels Between Sulfur and Fe(CO)$_4$

Characteristic	*Examples*	
Ion of 2− charge	S^{2-}	$[Fe(CO)_4]^{2-}$
Neutral compound	S_8	$Fe_2(CO)_9$, $[Fe(CO)_4]_3$
Hydride	H_2S: $pK_1 = 7.24^a$ $pK_2 = 14.92$	$H_2Fe(CO)_4$: $pK_1 = 4.44^a$ $pK_2 = 14$
Phosphine adduct	Ph_3PS	$Ph_3PFe(CO)_4$
Polymeric mercury compound		
Compound with ethylene	 (ethylene sulfide)	 (π complex)

NOTE: [a] pK values in aqueous solution at 25°C.

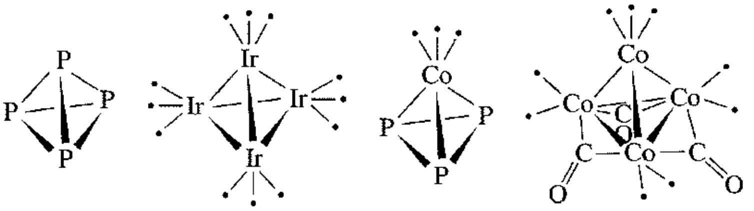

(• = terminal CO)

FIGURE 15-1 P_4, $[Ir(CO)_3]_4$, $P_3[Co(CO)_3]$, and $Co_4(CO)_{12}$.

compounds as IF_7 and XeF_4 are not known. Organometallic complexes of ligands significantly weaker than CO in the spectrochemical series may not follow the 18-electron rule and may consequently behave quite differently from electronically equivalent main group species. In addition, the reaction chemistry of organometallic compounds may be very different from main group chemistry. For example, loss of ligands such as CO is far more common in organometallic chemistry than in main group chemistry. Therefore, as in any scheme based on as simple a framework as electron counting, the concept of electronically equivalent groups, although useful, has its limitations. It serves as valuable background, however, for a potentially more versatile way to seek parallels between main group and organometallic chemistry, the concept of isolobal groups.

15-2
THE ISOLOBAL ANALOGY

An important contribution to the understanding of parallels between organic and inorganic chemistry has been the concept of isolobal molecular fragments, described most elaborately by Roald Hoffmann in his 1982 Nobel lecture.[2] Hoffmann defined molecular fragments to be isolobal

> if the number, symmetry properties, approximate energy and shape of the frontier orbitals and the number of electrons in them are similar—not identical, but similar.

To illustrate this definition, we will find it useful to compare fragments of methane with fragments of an octahedrally coordinated transition metal complex, ML_6. For simplicity, we will consider only σ bonding between the metal and the ligands in this complex.[3] The fragments to be discussed are shown in Figure 15-2.

[2] R. Hoffmann, *Angew. Chem., Int. Ed.* **1982**, *21*, 711; see also H-J. Krause, *Z. Chem.*, **1988**, *28*, 129.

[3] The model can be refined further to include π interactions between d_{xy}, d_{xz}, and d_{yz} orbitals with ligands having suitable donor and/or acceptor orbitals.

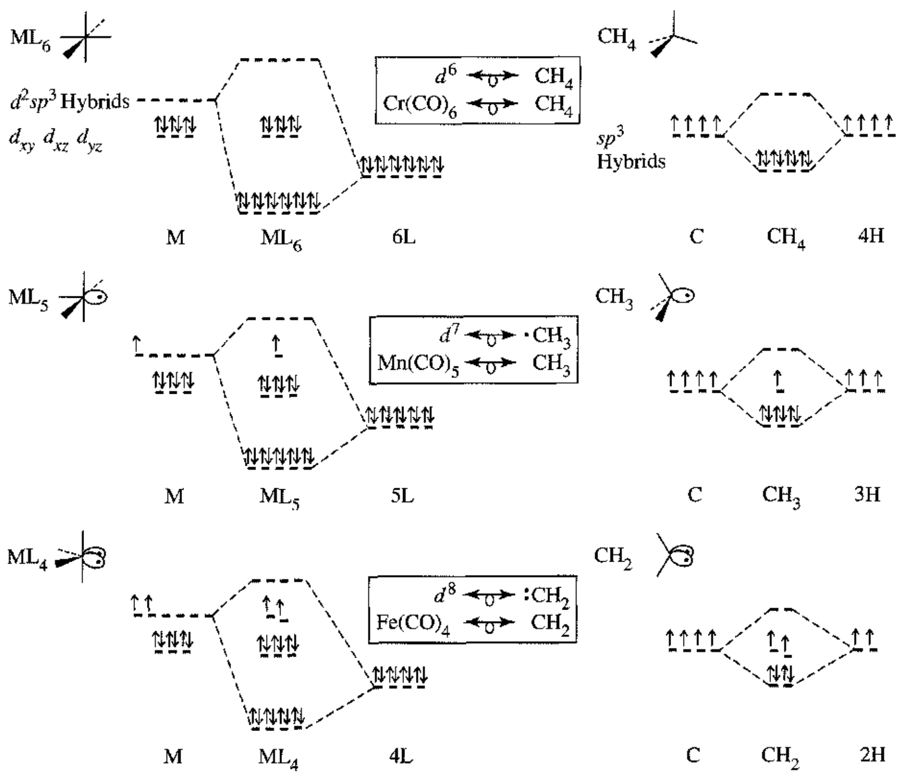


FIGURE 15-2 Orbitals of Octahedral and Tetrahedral Fragments.

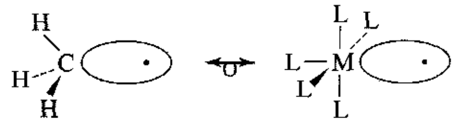
The parent compounds have filled valence shell electron configurations, an octet for CH_4, and 18 electrons for ML_6 [$Cr(CO)_6$ is an example of such an ML_6 compound]. Methane may be considered to use sp^3 hybrid orbitals in bonding, with 8 electrons occupying bonding pairs formed from interactions between the hybrids and $1s$ orbitals on hydrogen. The metal in ML_6, by similar reasoning, uses d^2sp^3 hybrids in bonding to the ligands, with 12 electrons occupying bonding orbitals and 6 essentially nonbonding electrons occupying d_{xy}, d_{xz}, and d_{yz} orbitals.

Molecular fragments containing fewer ligands than the parent polyhedra can now be described. For the purpose of the analogy, these fragments will be assumed to preserve the geometry of the remaining ligands.

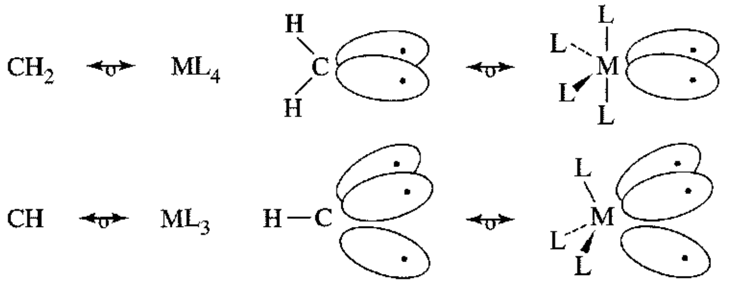
In the 7-electron fragment CH_3, three of the sp^3 orbitals of carbon are involved in σ bonding with the hydrogens. The fourth hybrid is singly occupied and at higher energy than the σ-bonding pairs of CH_3, as shown in Figure 15-2. This situation is similar to the 17-electron fragment $Mn(CO)_5$. The σ interactions between the ligands and Mn in this fragment may be considered to involve five of the metal's d^2sp^3 hybrid orbitals. The sixth hybrid is singly occupied and at higher energy than the five σ-bonding orbitals.

As Figure 15-2 shows, each of these fragments has a single electron in a hybrid orbital at the vacant site of the parent polyhedron. These orbitals are sufficiently similar to meet Hoffmann's isolobal definition. Using Hoffmann's symbol $\underset{\smile}{\leftrightarrow}$ to designate groups as isolobal, we may write

$CH_3 \underset{\smile}{\leftrightarrow} ML_5$



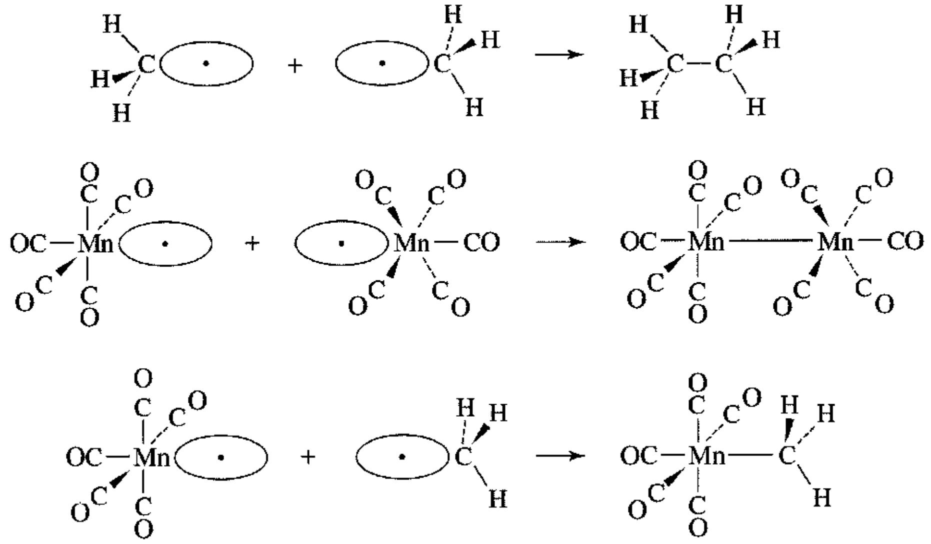
Similarly, 6-electron CH_2 and 16-electron ML_4 are isolobal. Both CH_2 and ML_4 are 2 electrons short of a filled shell octet or 18-electron configuration, so they are electronically equivalent; each has 2 single electrons occupying hybrid orbitals at otherwise vacant sites. Absence of a third ligand similarly gives a pair of isolobal fragments, CH and ML_3.



To summarize:

	Organic	Inorganic	Organo-metallic Example	Vertices Missing from Parent Polyhedron	Electrons Short of Filled Shell
Parent	$\mathbf{CH_4}$	$\mathbf{ML_6}$	$\mathbf{Cr(CO)_6}$	0	0
Fragments	CH_3	ML_5	$Mn(CO)_5$	1	1
	CH_2	ML_4	$Fe(CO)_4$	2	2
	CH	ML_3	$Co(CO)_3$	3	3

These fragments can be combined into molecules. For example, two CH_3 fragments form ethane, and two $Mn(CO)_5$ fragments form $(OC)_5Mn—Mn(CO)_5$. Furthermore, these organic and organometallic fragments can be combined into $H_3C—Mn(CO)_5$, which is also a known compound.



The organic and organometallic parallels are not always this complete. For example, although two 6-electron CH_2 fragments form ethylene, $H_2C=CH_2$, the dimer of the isolobal $Fe(CO)_4$ is not nearly as stable; it is known as a transient species obtained photochemically from $Fe_2(CO)_9$.[4] However, both CH_2 and $Fe(CO)_4$ form three-membered rings, cyclopropane and $Fe_3(CO)_{12}$. Although cyclopropane is a trimer of

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[4] M. Poliakoff and J. J. Turner, *J. Chem. Soc., A*, **1971**, 2403.

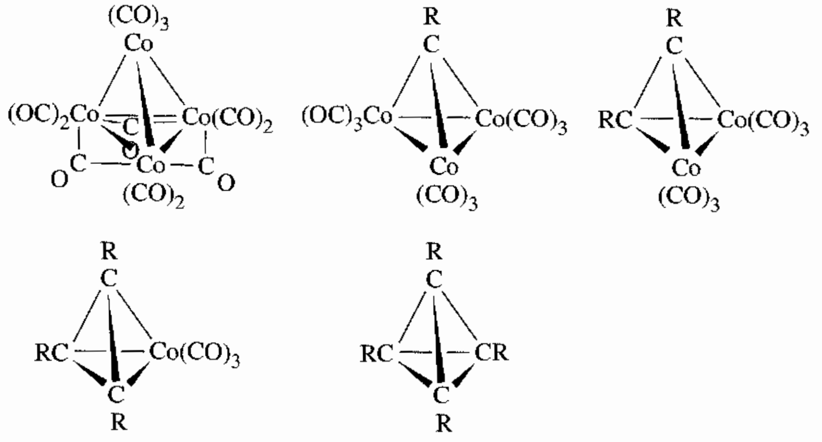
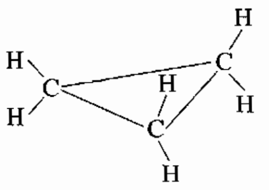
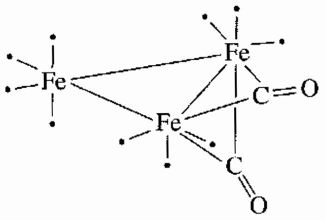


FIGURE 15-3 Structures Resulting from Combinations of Isolobal $Co(CO)_3$ and CR.

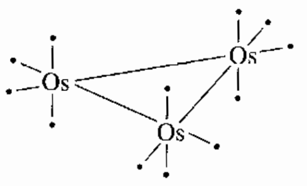
three CH_2 fragments, $Fe_3(CO)_{12}$ has two bridging carbonyls and is therefore not a perfect trimer of $Fe(CO)_4$. The isoelectronic $Os_3(CO)_{12}$, on the other hand, is a trimeric combination of three $Os(CO)_4$ fragments, which are isolobal with both $Fe(CO)_4$ and CH_2 and can correctly be described as $[Os(CO)_4]_3$.



C_3H_6



$Fe_3(CO)_{12}$
(• = terminal carbonyl)



$Os_3(CO)_{12}$

The isolobal species $Ir(CO)_3$, $Co(CO)_3$, CR, and P may also be combined in several different ways. As mentioned previously, $Ir(CO)_3$, a 15-electron fragment, forms $[Ir(CO)_3]_4$, which has T_d symmetry. The isoelectronic complex $Co_4(CO)_{12}$ has a nearly tetrahedral array of cobalt atoms, but has three bridging carbonyls and hence C_{3v} symmetry. Compounds are also known that have a central tetrahedral structure, with one or more $Co(CO)_3$ fragments [which are isolobal and isoelectronic with $Ir(CO)_3$] replaced by the isolobal CR fragment, as shown in Figure 15-3. This is similar to the replacement of phosphorus atoms in the P_4 tetrahedron by $Co(CO)_3$ fragments; P may also be described as isolobal with CR.

15-2-1 EXTENSIONS OF THE ANALOGY

The concept of isolobal fragments can be extended beyond the examples given so far to include charged species, a variety of ligands other than CO, and organometallic fragments based on structures other than octahedral. Some of the ways of extending the isolobal parallels can be summarized as follows:

1. The isolobal definition may be extended to isoelectronic fragments having the same coordination number. For example,

$$\begin{array}{cccc} & & \mathrm{Re(CO)_5} & \\ \text{Because } \mathrm{Mn(CO)_5} \leftarrow\!\!\circ\!\!\rightarrow & \mathrm{CH_3}, & \mathrm{[Fe(CO)_5]^+} & \leftarrow\!\!\circ\!\!\rightarrow \mathrm{CH_3} \\ & & \mathrm{[Cr(CO)_5]^-} & \\ \text{(17-electron fragment)} & \text{(7-electron fragment)} & \text{(17-electron fragments)} & \text{(7-electron fragment)} \end{array}$$

2. Gain or loss of electrons from two isolobal fragments yields isolobal fragments. For example,

Because $Mn(CO)_5$		CH_3,	$Cr(CO)_5$ $Mo(CO)_5$ $W(CO)_5$		CH_3^+
(17-electron fragment)	$\underset{\smile}{\longleftrightarrow}$	(7-electron fragment)	(16-electron fragments)	$\underset{\smile}{\longleftrightarrow}$	(6-electron fragment)
			$Fe(CO)_5$ $Ru(CO)_5$ $Os(CO)_5$	$\underset{\smile}{\longleftrightarrow}$	CH_3^-
			(18-electron fragments)		(8-electron fragment)

Note that all the examples shown above are one ligand short of the parent complex. $Fe(CO)_5$ is isolobal with CH_3^-, for example, because both have filled electron shells and both are one vertex short of the parent polyhedron. By contrast, $Fe(CO)_5$ and CH_4 are not isolobal. Both have filled electron shells (18 and 8 electrons, respectively), but CH_4 has all vertices of the tetrahedron occupied, whereas $Fe(CO)_5$ has an empty vertex in the octahedron.

3. Other 2-electron donors are treated similarly to CO:[5]

$$Mn(CO)_5 \underset{\smile}{\longleftrightarrow} Mn(PR_3)_5 \underset{\smile}{\longleftrightarrow} [MnCl_5]^{5-} \underset{\smile}{\longleftrightarrow} Mn(NCR)_5 \underset{\smile}{\longleftrightarrow} CH_3$$

4. η^5-C_5H_5 and η^6-C_6H_6 are considered to occupy three coordination sites and to be 6-electron donors:[6]

$$\begin{matrix}(\eta^5\text{-}C_5H_5)Fe(CO)_2\\(\eta^6\text{-}C_6H_6)Mn(CO)_2\end{matrix} \underset{\smile}{\longleftrightarrow} [Fe(CO)_5]^+ \underset{\smile}{\longleftrightarrow} Mn(CO)_5 \quad \text{(17-electron fragments)}$$

$$\begin{matrix}(\eta^5\text{-}C_5H_5)Mn(CO)_2\\(\eta^6\text{-}C_6H_6)Cr(CO)_2\end{matrix} \underset{\smile}{\longleftrightarrow} [Mn(CO)_5]^+ \underset{\smile}{\longleftrightarrow} Cr(CO)_5 \quad \text{(16-electron fragments)}$$

5. Octahedral fragments of formula ML_n (where M has a d^x configuration) are isolobal with square-planar fragments of formula ML_{n-2} (where M has a d^{x+2} configuration and L = 2-electron donor):

Octahedral Fragments		Square-planar Fragments
ML_n		ML_{n-2}
$Cr(CO)_5$ d^6	$\underset{\smile}{\longleftrightarrow}$	$[PtCl_3]^-$ d^8
$Fe(CO)_4$ d^8	$\underset{\smile}{\longleftrightarrow}$	$Pt(PR_3)_2$ d^{10}

The fifth of these extensions of the isolobal analogy is less obvious than the others and deserves explanation. We will consider two examples, the parallels between d^6 ML_5 (octahedral) and d^8 ML_3 (square-planar) fragments and the parallels between

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[5] Hoffmann uses electron-counting method A, in which chloride is considered a negatively charged, 2-electron donor.

[6] η^5-C_5H_5 is considered the 6-electron donor $C_5H_5^-$.

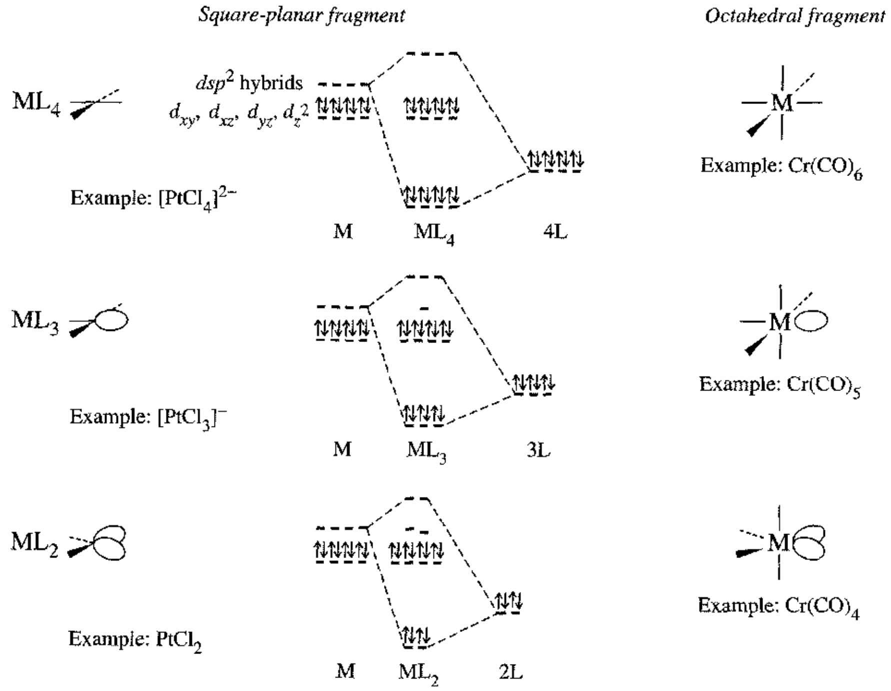
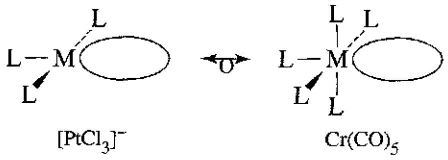


FIGURE 15-4 Comparison of Square-planar Fragments with Octahedral Fragments.

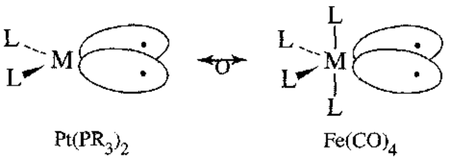
d^8 ML_4 (octahedral) and d^{10} ML_2 (square-planar) fragments. The ML_3 and ML_2 fragments of a square-planar parent structure are shown in Figure 15-4. They will be compared with the fragments of an octahedral ML_6 molecule shown in Figure 15-2.

A square-planar d^8 ML_3 fragment (such as $[PtCl_3]^-$) has an empty lobe of a nonbonding hybrid orbital as its LUMO. This is comparable to the LUMO of a d^6 ML_5 fragment of an octahedron (e.g., $Cr(CO)_5$):[7]



A d^8 fragment such as $[PtCl_3]^-$ would therefore be isolobal with $Cr(CO)_5$ and other ML_5 fragments provided the empty lobe in each case had suitable energy.[8]

A d^{10} ML_2 fragment such as $Pt(PR_3)_2$ would have 2 valence electrons more than the example of $PtCl_2$ shown in Figure 15-4. These electrons are considered to occupy two nonbonding hybrid orbitals. This situation is very comparable to the $Fe(CO)_4$ fragment (Figure 15-2); each complex has two singly occupied lobes:



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[7] Such a fragment would have one less electron than shown for $Mn(CO)_5$ in Figure 15-2.

[8] The highest occupied orbitals of ML_3 have similar energies. For a detailed analysis of the energies and symmetries of ML_5, ML_3, and other fragments, see M. Elian and R. Hoffmann, *Inorg. Chem.*, **1975**, *14*, 1058, and T. A. Albright, R. Hoffmann, J. C. Thibeault, and D. L. Thorn, *J. Am. Chem. Soc.*, **1979**, *101*, 3801.

Examples of isolobal fragments containing CO and η^5-C_5H_5 ligands are given in Table 15-3.

TABLE 15-3
Examples of Isolobal Fragments

Neutral hydrocarbons	$\boxed{CH_4}$	$\boxed{CH_3}$	$\boxed{CH_2}$	$\boxed{CH}$	$\boxed{C}$
Isolobal organometallic fragments (Cp = η^5-C_5H_5)	$Cr(CO)_6$ $[Mn(CO)_6]^+$ $CpMn(CO)_3$	$Mn(CO)_5$ $[Fe(CO)_5]^+$ $CpFe(CO)_2$	$Fe(CO)_4$ $[Co(CO)_4]^+$ $CpCo(CO)$	$Co(CO)_3$ $[Ni(CO)_3]^+$ CpNi	$Ni(CO)_2$ $[Cu(CO)_2]^+$
Anionic hydrocarbon fragments obtained by loss of H^+	$\boxed{CH_3^-}$	$\boxed{CH_2^-}$	$\boxed{CH^-}$		
Isolobal organometallic fragments	$Fe(CO)_5$	$Co(CO)_4$	$Ni(CO)_3$		
Cationic hydrocarbon fragments obtained by gain of H^+		$\boxed{CH_4^+}$	$\boxed{CH_3^+}$	$\boxed{CH_2^+}$	$\boxed{CH^+}$
Isolobal organometallic fragments		$V(CO)_6$	$Cr(CO)_5$	$Mn(CO)_4$	$Fe(CO)_3$

EXAMPLE

Propose examples of organometallic fragments isolobal with CH_2^+.

For the purpose of this example, we will limit ourselves to the ligand CO and first-row transition metals. Other ligands and other metals may be used with equally valid results.

CH_2^+ is two ligands and 3 electrons short of its parent compound (CH_4). The corresponding octahedral fragment will therefore be a 15-electron species with the formula ML_4 (two ligands and 3 electrons short of its parent $M(CO)_6$). If L = CO, the four carbon monoxides contribute 8 electrons, requiring that the metal contribute the remaining 7. The first-row d^7 metal is Mn. The overall result is $CH_2^+ \underset{o}{\longleftrightarrow} Mn(CO)_4$.

Other octahedral isolobal fragments can be found by changing the metal and the charge on the complex. A positive charge compensates for a metal with one more electron and a negative charge compensates for a metal with one less electron:

d^7: $Mn(CO)_4$ d^8: $[Fe(CO)_4]^+$ d^6: $[Cr(CO)_4]^-$

EXERCISE 15-1

For the following, propose examples of isolobal organometallic fragments other than those just above and in Table 15-3:

a. A fragment isolobal with CH_2^+.
b. A fragment isolobal with CH^-.
c. Three fragments isolobal with CH_3.

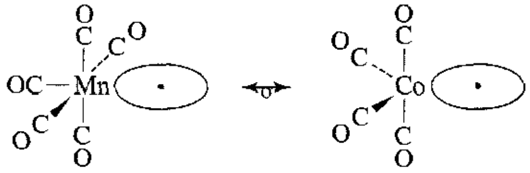
EXERCISE 15-2

Find organic fragments isolobal with each of the following:

a. $Ni(\eta^5$-$C_5H_5)$
b. $Cr(CO)_2(\eta^6$-$C_6H_6)$
c. $[Fe(CO)_2(PPh_3)]^-$

Analogies are by no means limited to octahedral and square-planar organometallic fragments; similar arguments can be used to derive fragments of different polyhedra.

For example, $Co(CO)_4$, a 17-electron fragment of a trigonal bipyramid, is isolobal with $Mn(CO)_5$, a 17-electron fragment of an octahedron:



Examples of electron configurations of isolobal fragments of polyhedra having five through nine vertices are given in Table 15-4.

TABLE 15-4
Isolobal Relationships for Fragments of Polyhedra

Organic Fragment	*Coordination Number of Transition Metal for Parent Polyhedron* 5	6	7	8	9	*Valence Electrons of Fragment*
CH_3	d^9-ML_4	d^7-ML_5	d^5-ML_6	d^3-ML_7	d^1-ML_8	17
CH_2	d^{10}-ML_3	d^8-ML_4	d^6-ML_5	d^4-ML_6	d^2-ML_7	16
CH		d^9-ML_3	d^7-ML_4	d^5-ML_5	d^3-ML_6	15

The interested reader is encouraged to refer to Hoffmann's Nobel Lecture for further information on how the isolobal analogy can be extended to include other ligands and geometries.

15-2-2 EXAMPLES OF APPLICATIONS OF THE ANALOGY

The isolobal analogy can be extended to any molecular fragment having frontier orbitals of suitable size, shape, symmetry, and energy. For example, the 5-electron fragment CH is isolobal with P and other Group 15 atoms. A potential application of this relationship is to seek phosphorus-containing analogues to organometallic complexes containing cyclic π ligands such as C_5H_5 and C_6H_6. Most of the examples developed to date have been with metallocenes, $[(C_5H_5)_2M]^n$. Not only can P_5^-, the analogue to the cyclopentadienide ion $C_5H_5^-$, be prepared in solution,[9] but sandwich compounds containing P_5 rings, such as those shown in Figure 15-5, have been synthesized. The first of these, $(\eta^5$-$C_5Me_5)Fe(\eta^5$-$P_5)$, was prepared, not directly from P_5^-, but rather from the reaction of $[(\eta^5$-$C_5Me_5)Fe(CO)_2]_2$ with white phosphorus (P_4).[10]

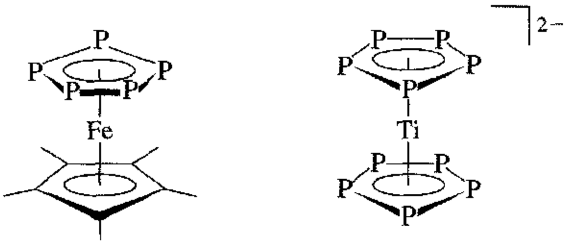


FIGURE 15-5 Metallocenes Containing P_5 rings.

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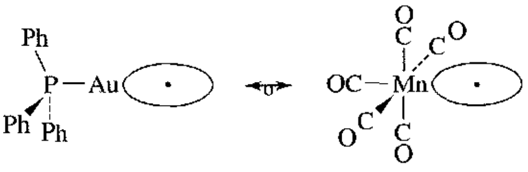
[9] M. Baudler, S. Akpapoglou, D. Ouzounis, F. Wasgestian, B. Meinigke, H. Budzikiewicz, and H. Münster, *Angew. Chem. Int. Ed.* **1988**, *27*, 280.

[10] O. J. Scherer and T. Brück, *Angew. Chem. Int. Ed.*, **1987**, *26*, 59.

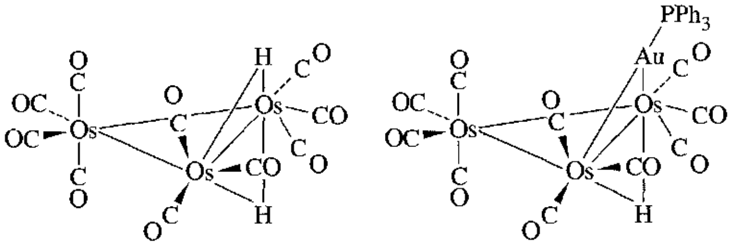
Perhaps the most interesting of all the phosphorus analogues of metallocenes is the first carbon-free metallocene, $[(\eta^5\text{-}P_5)_2Ti]^{2-}$. This complex, prepared by the reaction of $[Ti(naphthalene)_2]^{2-}$ with P_4, contains parallel, eclipsed P_5 rings.[11] The P_5 ligand in this and other complexes functions as a weaker donor but substantially stronger acceptor than the cyclopentadienyl ligand.

Another example, $Au(PPh_3)$, a 13-electron fragment, has a single electron in a hybrid orbital pointing away from the phosphine.[12] This electron is in an orbital of similar symmetry but of somewhat higher energy than the singly occupied hybrid in the $Mn(CO)_5$ fragment.



Nevertheless, $Au(PPh_3)$ can combine with the isolobal $Mn(CO)_5$ and CH_3 to form $(OC)_5Mn—Au(PPh_3)$ and $H_3C—Au(PPh_3)$.

Even a hydrogen atom, with a single electron in its 1*s* orbital, can in some cases be viewed as a fragment isolobal with such species as CH_3, $Mn(CO)_5$, and $Au(PPh_3)$. Hydrides of the first two are well known, and $Au(PPh_3)$ and H in some cases show surprisingly similar behavior, such as in their ability to bridge the triosmium clusters shown here.[13, 14]



Potentially, the greatest practical use of isolobal analogies is in the suggested syntheses of new compounds. For example, CH_2 is isolobal with 16-electron $Cu(\eta^5\text{-}C_5Me_5)$ (extension 4 of the analogy) and 14-electron PtL_2 ($L = PR_3$, CO; extension 5). Recognition of these fragments as isolobal has been exploited in the syntheses of organometallic compounds composed of fragments isolobal with fragments of known compounds.[15] Some of the compounds obtained in these studies are shown in Figure 15-6.

15-3 METAL-METAL BONDS

The isobal approach was used in the previous section to describe the formation of metal-metal bonds. These bonds differ from others only in the use of *d* orbitals on both atoms. In addition to the usual σ and π bonds, quadruple bonds are possible in transition metal compounds. Furthermore, bridging by ligands and the ability to form cluster compounds make for great variety in structures containing metal-metal bonds.

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[11] E. Urnezius, W. W. Brennessel, C. J. Cramer, J. E. Ellis, and P. von Ragué Schleyer, *Science*, **2002**, *295*, 832.

[12] D. G. Evans and D. M. P. Mingos, *J. Organomet. Chem.*, **1982**, *232*, 171.

[13] A. G. Orpen, A. V. Rivera, E. G. Bryan, D. Pippard, G. Sheldrick, and K. D. Rouse, *Chem. Commun.* (Cambridge), **1978**, 723.

[14] B. F. G. Johnson, D. A. Kaner, J. Lewis, and P. R. Raithby, *J. Organomet. Chem.*, **1981**, *215*, C33.

[15] G. A. Carriedo, J. A. K. Howard, and F. G. A. Stone, *J. Organomet. Chem.*, **1983**, *250*, C28.

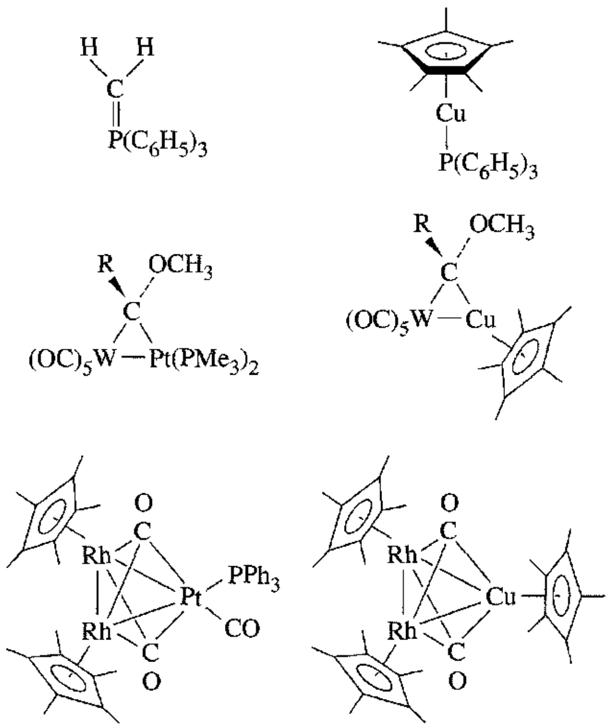
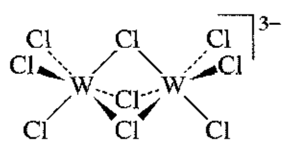


FIGURE 15-6 Compounds Composed of Isolobal Fragments.

Examples of compounds with carbon-carbon, other main group, and metal-metal single, double, and triple bonds, together with a metal-metal quadruple bond, are shown in Figure 15-7.

For nearly a century, compounds containing two or more metal atoms have been known. The first of these compounds to be correctly identified, by Werner, were held together by bridging ligands shared by the metals involved; X-ray crytallographic studies eventually showed that the metal atoms were too far apart to be likely participants in direct metal-metal orbital interactions.

Not until 1935 did X-ray crystallography demonstrate direct metal-metal bonding. In that year, Brosset reported the structure of $K_3W_2Cl_9$, which contained the $[W_2Cl_9]^{3-}$ ion. In this ion, the tungsten-tungsten distance (240 pm) was found to be substantially shorter than the interatomic distance in tungsten metal (275 pm):



The short distance between the metal atoms in this ion raised for the first time the serious possibility of direct bonding interactions between metal orbitals. However, little attention was paid to this interesting question for many years, even though several additional compounds having very short metal-metal distances were synthesized.

The modern development of the chemistry of metal-metal-bonded species was spurred by the crystal structures of $[Re_3Cl_{12}]^{3-}$ and $[Re_2Cl_8]^{2-}$.[16] $[Re_3Cl_{12}]^{3-}$, originally believed to be monomeric $ReCl_4^-$, was shown in 1963 to be a trimeric cyclic ion having very short rhenium-rhenium distances (248 pm). In the following year, during a

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[16] F. A. Cotton, *Chem. Soc. Rev.*, **1975**, *4*, 27.

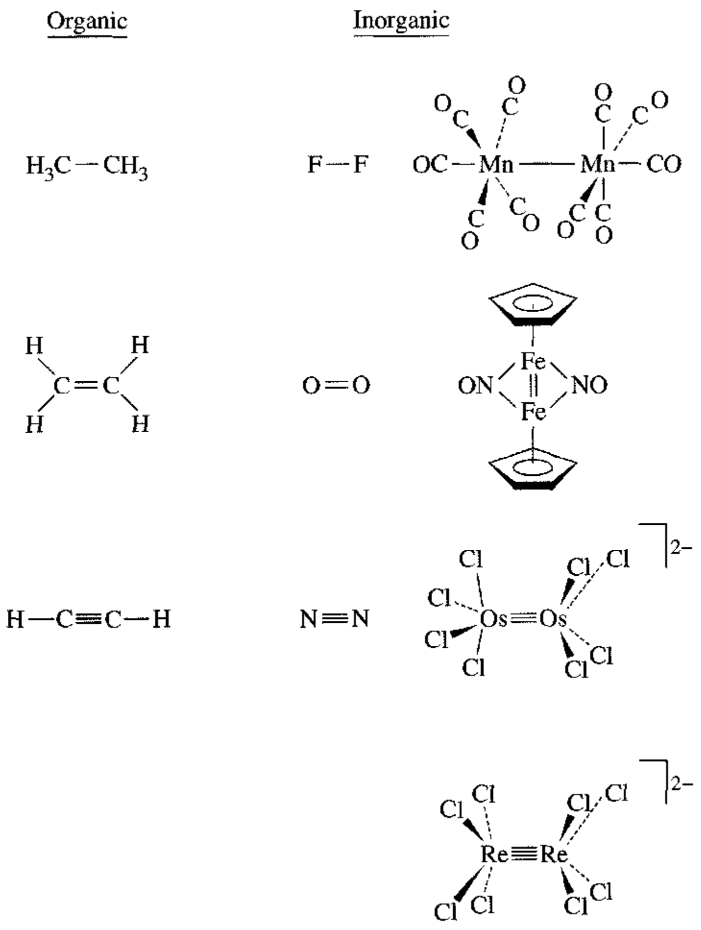
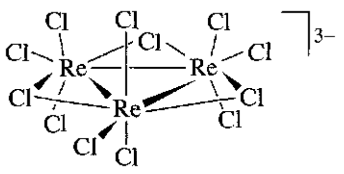
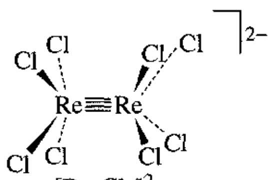


FIGURE 15-7 Single, Double, Triple, and Quadruple Bonds.

study on the synthesis of triruthenium complexes, the dimeric $[Re_2Cl_8]^{2-}$ was synthesized. This ion had a remarkably short metal-metal distance (224 pm) and was the first complex found to have a quadruple bond:



$[Re_3Cl_{12}]^{3-}$



$[Re_2Cl_8]^{2-}$

During the succeeding decades, many thousands of cluster compounds of transition metals have been synthesized, including hundreds containing quadruple bonds. Therefore, we need to consider briefly how metal atoms can bond to each other and, in particular, how quadruple bonds between metals are possible.

15-3-1 MULTIPLE METAL-METAL BONDS

Transition metals may form single, double, triple, or quadruple bonds (or bonds of fractional order) with other metal atoms. How are quadruple bonds possible? In main group chemistry, atomic orbitals in general can interact in a σ or π fashion, with the highest

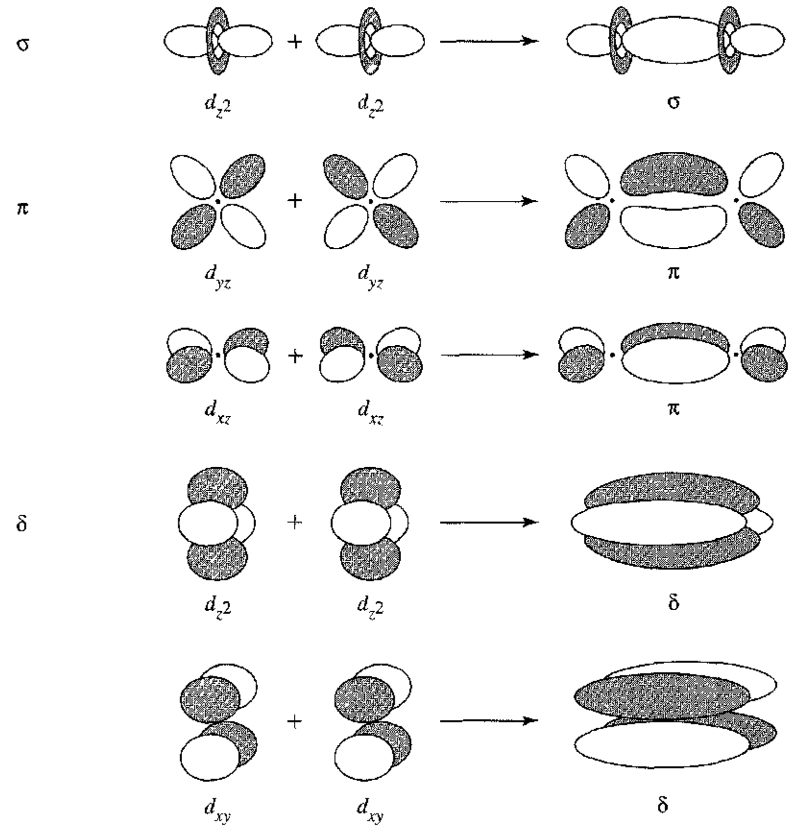


FIGURE 15-8 Bonding Interactions Between Metal *d* Orbitals.

possible bond order of 3 a combination of one σ bond and two π bonds. When two transition metal atoms interact, the most important interactions are between their outermost *d* orbitals. These *d* orbitals can combine to form not only σ and π orbitals, but also δ (delta) orbitals, as shown in Figure 15-8. If the *z* axis is chosen as the internuclear axis, the strongest interaction (involving greatest overlap) is the σ interaction between the d_{z^2} orbitals. Next in effectiveness of overlap are the d_{xz} and d_{yz} orbitals, which form π orbitals as a result of interactions in two regions in space. The last, and weakest, of these interactions are between the d_{xy} and $d_{x^2-y^2}$ orbitals, which interact in four regions in the formation of δ molecular orbitals.

The relative energies of the resulting molecular orbitals are shown schematically in Figure 15-9. In the absence of ligands, an M_2 fragment would have five bonding orbitals resulting from *d–d* interactions, with molecular orbitals increasing in energy in the order σ, π, δ, δ*, π*, σ*, as shown. In $[Re_2Cl_8]^{2-}$, our example of quadruple bonding, the configuration is eclipsed (D_{4h} symmetry). For convenience, we can choose the Re—Cl bonds to be oriented in the *xz* and *yz* planes. The ligand orbitals interact most strongly with the metal orbitals pointing toward them, in this case the δ and δ* orbitals originating primarily from the $d_{x^2-y^2}$ atomic orbitals.[17] The consequence of these interactions is that new molecular orbitals are formed, as shown on the right side of Figure 15-9. The relative energies of these orbitals depend on the strength of the metal-ligand interactions and therefore vary for different complexes.

In $[Re_2Cl_8]^{2-}$, each rhenium is formally Re(III) and has 4 *d* electrons. If the 8 *d* electrons for this ion are placed into the four lowest energy orbitals shown in Figure 15-9 (not including the low-energy orbital arising from the $d_{x^2-y^2}$ interactions,

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[17] Analysis of the symmetry of this ion shows that the *s*, p_x, and p_y orbitals are also involved.

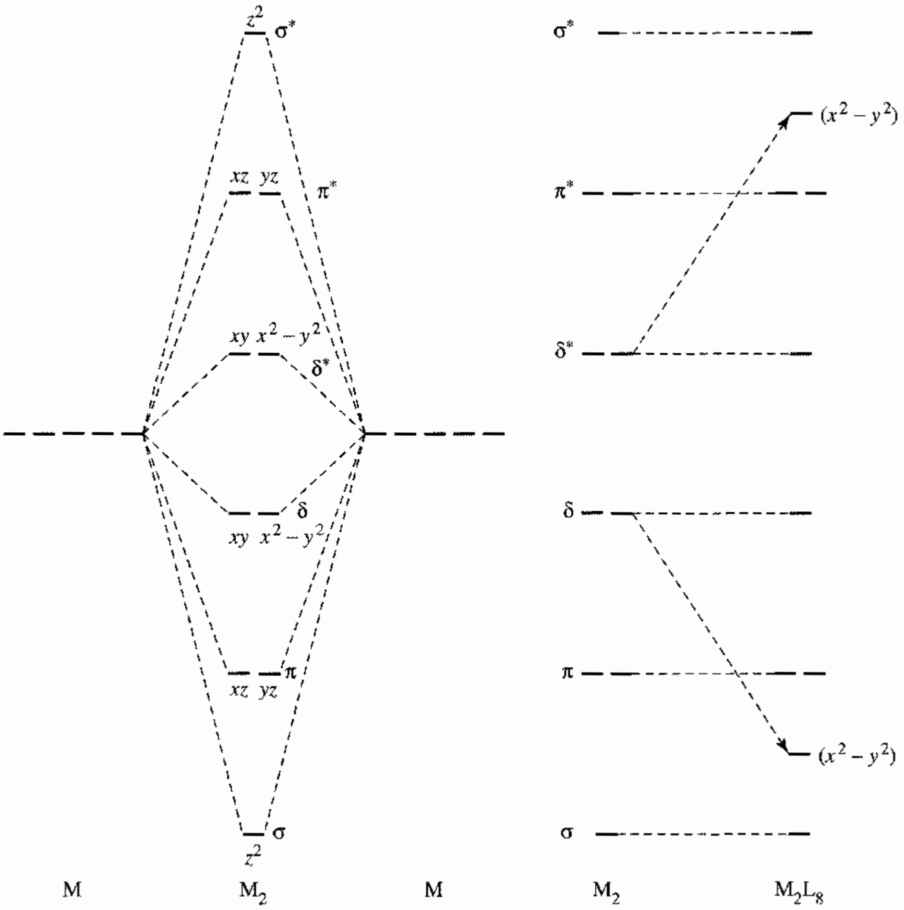
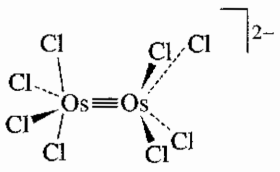


FIGURE 15-9 Relative Energies of Orbitals Formed from *d*-Orbital Interactions.

occupied by ligand electrons), the total bond order is 4, corresponding to (in increasing energy) one σ bond, two π bonds, and one δ bond. The δ bond is weakest; however, it is strong enough to maintain this ion in its eclipsed conformation. The weakness of the δ bond is illustrated by the small separation in energy of the δ and δ^* orbitals. This energy difference typically corresponds to the energy of visible light, with the consequence that most quadruply bonded complexes are vividly colored. For example, $[Re_2Cl_8]^{2-}$ is royal blue and $[Mo_2Cl_8]^{4-}$ is bright red. By comparison, main group compounds having filled π and empty π^* orbitals are often colorless (e.g., N_2 and CO), because the energy difference between these orbitals is commonly in the ultraviolet part of the spectrum.

Additional electrons populate δ^* orbitals and reduce the bond order. For example, $[Os_2Cl_8]^{2-}$, an osmium(III) species with a total of 10 *d* electrons, has a triple bond. The δ bond order in this ion is zero; in the absence of such a bond, the eclipsed geometry as found in quadruply bonded complexes such as $[Re_2Cl_8]^{2-}$ is absent. X-ray crystallographic analysis has shown $[Os_2Cl_8]^{2-}$ to be very nearly staggered (D_{4d} geometry), as would be expected from VSEPR considerations.



$[Os_2Cl_8]^{2-}$

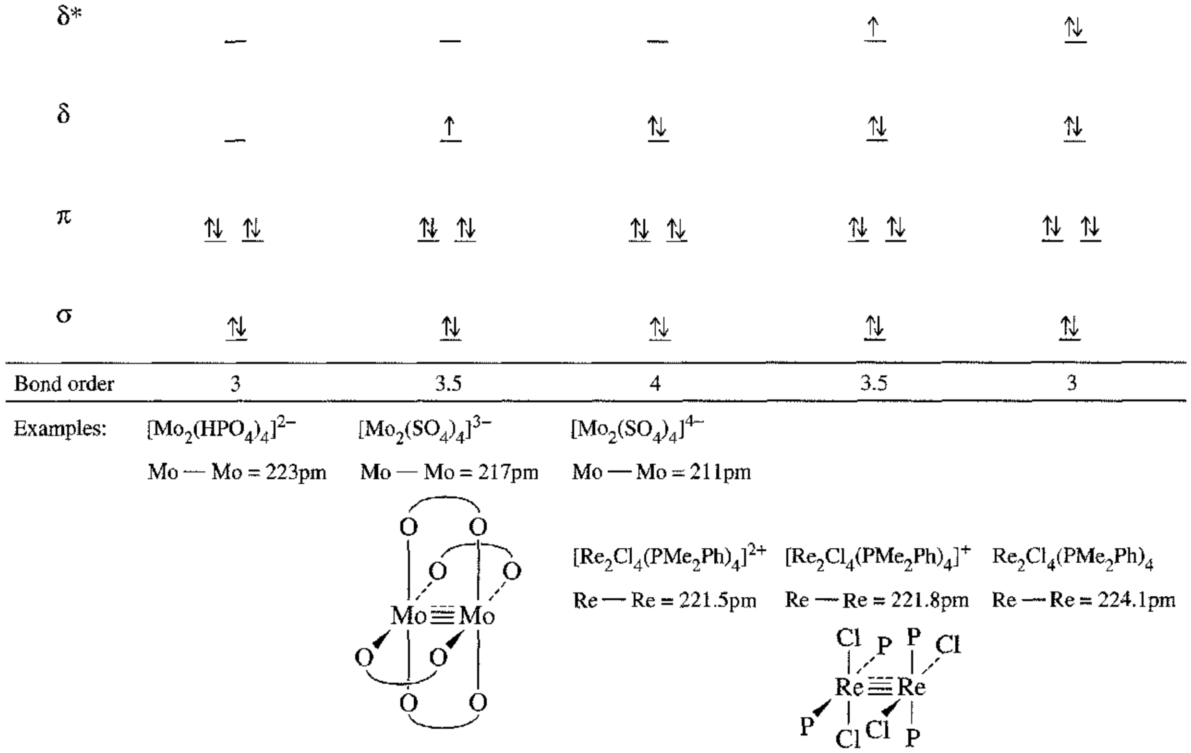


FIGURE 15-10 Bond Order and Electron Count in Dimetal Clusters. (From A. Bino and F. A. Cotton, *Inorg. Chem.*, **1979**, *18*, 3562; and F. A. Cotton, *Chem. Soc. Rev.*, **1983**, *12*, 35.)

Similarly, fewer than 8 valence electrons would also give a bond order less than 4. Examples of such complexes are shown in Figure 15-10.

Metal-metal multiple bonding can have dramatic effects on bond distances, as measured by X-ray crystallography. One way of describing the shortening of interatomic distances by multiple bonds is by comparing the bond distances in multiple bonds to the distances for single bonds. The ratios of these distances is sometimes called the **formal shortness ratio**. Values of this ratio are compared below for main group triple bonds and for some of the shortest of the measured transition metal quadruple bonds:

Multiple Bond Distance/Single Bond Distance			
Bond	*Ratio*	*Bond*	*Ratio*
C≡C	0.783	Cr≣Cr	0.767
N≡N	0.786	Mo≣Mo	0.807
		Re≣Re	0.848

The ratios found for several quadruply bonded chromium complexes are the smallest ratios found to date for any compounds. Considerable variation in bond distances has been observed. Mo-Mo quadruple bonds, for example, have been found in the range 203.7 to 230.2 pm.[18]

The effect of population of δ and δ* orbitals on bond distances can be sometimes be surprisingly small. For example, removal of δ* electrons on oxidation of

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[18] F. A. Cotton and R. A. Walton, *Multiple Bonds Between Metal Atoms*, John Wiley & Sons, New York, 1982, pp. 161–165.

TABLE 15-5
Effect of Oxidation on Re—Re Bond Distance in Re_2 Complexes

Complex	Number of d Electrons	Formal Re—Re Bond Order	Formal Oxidation State of Re	Re—Re Distance (pm)
$Re_2Cl_4(PMe_2Ph_4)_4$	10	3	2	224.1
$[Re_2Cl_4(PMe_2Ph_4)_4]^+$	9	3.5	2.5	221.8
$[Re_2Cl_4(PMe_2Ph_4)_4]^{2+}$	8	4	3	221.5

$Re_2Cl_4(PMe_2Ph_4)_4$ gives only very slight shortening of the Re—Re distances, as shown in Table 15-5.[19]

A possible explanation for the small change in bond distance is that, with increasing oxidation state of the metal, the *d* orbitals contract. This contraction may cause overlap of *d* orbitals in π bonding to become less effective. Thus, as δ^* electrons are removed, the π interactions become weaker; the two factors (increase in bond order and increase in oxidation state of Re) very nearly offset each other.

15-4 CLUSTER COMPOUNDS

Examples of cluster compounds have been given in previous sections of this chapter and in several earlier chapters. Transition metal cluster chemistry has developed rapidly since the 1980s. Beginning with simple dimeric molecules such as $Co_2(CO)_8$ and $Fe_2(CO)_9$,[20] chemists have developed syntheses of far more complex clusters, with some having interesting and unusual structures and chemical properties. Large clusters have been studied with the objective of developing catalysts that may duplicate or improve on the properties of heterogeneous catalysts; the surface of a large cluster may in these cases mimic the behavior of the surface of a solid catalyst.

Before discussing transition metal clusters in more detail, we will find it useful to consider compounds of boron, which has an extremely detailed cluster chemistry. As mentioned in Chapter 8, boron forms numerous hydrides (boranes) with interesting structures. Some of these compounds exhibit similarities in their bonding and structures to transition metal clusters.

15-4-1 BORANES

There are many neutral and ionic species composed of boron and hydrogen, far too many to describe in this text. For the purposes of illustrating parallels between these species and transition metal clusters, we will first consider of one category of boranes, *closo* (cagelike) boranes that have the formula $B_nH_n^{2-}$. These boranes consist of closed polyhedra with *n* corners and all triangular faces (triangulated polyhedra). Each corner is occupied by a BH group.

Molecular orbital calculations have shown that *closo* boranes have $2n + 1$ bonding molecular orbitals, including n B—H σ bonding orbitals and $n + 1$ bonding orbitals in the central core (described as **framework** or **skeletal** bonding orbitals).[21] A useful example is $B_6H_6^{2-}$, which has O_h symmetry. In this ion, each boron has four valence orbitals that can participate in bonding, giving a total of 24 boron orbitals for the

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[19] F. A. Cotton, *Chem. Soc. Rev.*, **1983**, *12*, 35.

[20] Some chemists define clusters as having at least three metal atoms.

[21] K. Wade, *Electron Deficient Compounds*, Thomas Nelson & Sons, London, 1971.

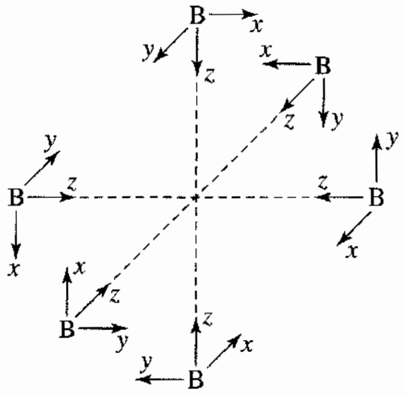

FIGURE 15-11 Coordinate System for Bonding in $B_6H_6^{2-}$

cluster. These orbitals can be classified into two sets. If the z axis of each boron atom is chosen to point toward the center of the octahedron (Figure 15-11), the p_z and s orbitals are a set of suitable symmetry to bond with the hydrogen atoms. A second set of orbitals, consisting of the p_x and p_y orbitals of the borons, is then available for boron-boron bonding.

The p_z and s orbitals of the borons collectively have the same symmetry (which reduces to the irreducible representations $A_{1g} + E_g + T_{1u}$; an analysis of the orbitals in terms of symmetry is left as an exercise in Problem 15-17 at the end of this chapter) and, therefore, may be considered to form sp hybrid orbitals. These hybrid orbitals, two on each boron, point out toward the hydrogen atoms and in toward the center of the cluster, as shown in Figure 15-12.

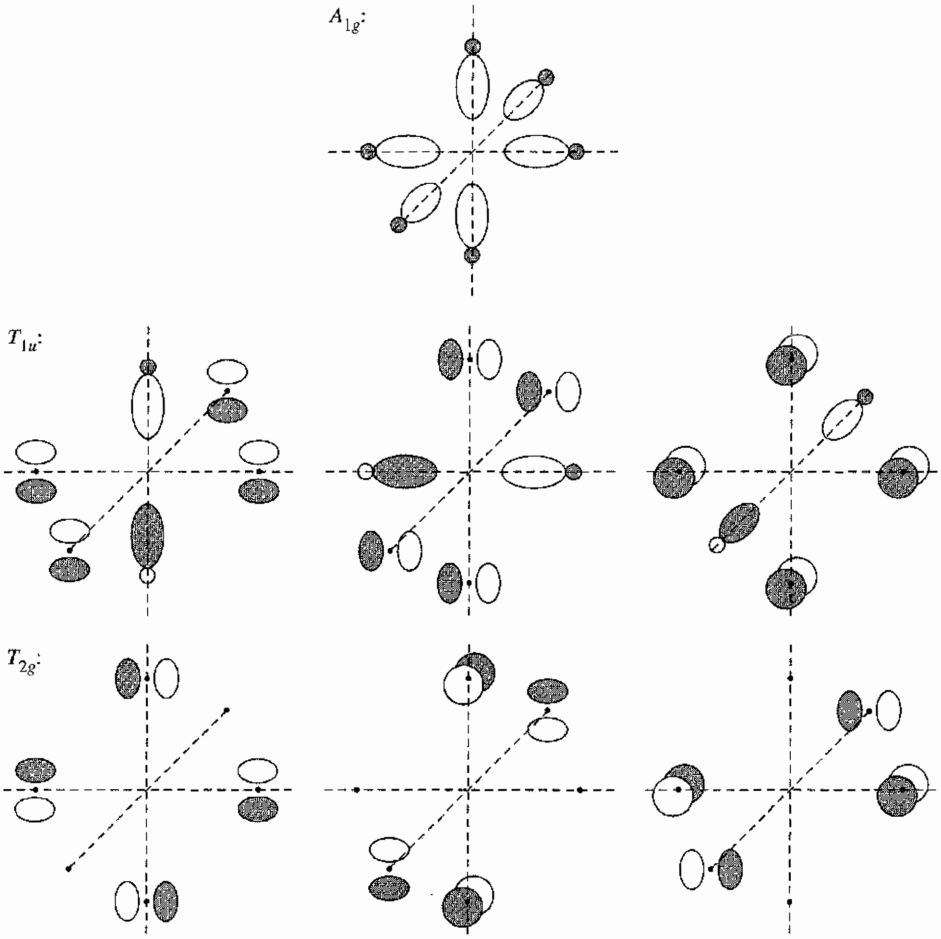

FIGURE 15-12 Bonding in $B_6H_6^{2-}$.

Six of the hybrids form bonds with the 1*s* orbitals of the hydrogens. The six remaining hybrids and the unhybridized 2*p* orbitals of the borons remain to participate in bonding within the B_6 core. Seven orbital combinations lead to bonding interactions; these are also shown in Figure 15-12. Constructive overlap of all six hybrid orbitals at the center of the octahedron yields a framework bonding orbital of A_{1g} symmetry; as its symmetry label indicates, this orbital is completely symmetric with respect to all symmetry operations of the O_h point group. Additional bonding interactions are of two types: overlap of two *sp* hybrid orbitals with parallel *p* orbitals on the remaining four boron atoms (three such interactions, collectively of T_{1u} symmetry) and overlap of *p* orbitals on four boron atoms within the same plane (three interactions, T_{2g} symmetry). The remaining orbital interactions lead to nonbonding or antibonding molecular orbitals. To summarize,

From the 24 valence atomic orbitals of boron are formed:

- 13 bonding orbitals ($= 2n + 1$), consisting of
  - 7 framework molecular orbitals ($= n + 1$), consisting of
    - 1 bonding orbital (A_{1g}) from overlap of *sp* hybrid orbitals
    - 6 bonding orbitals from overlap of *p* orbitals of boron with *sp* hybrid orbitals (T_{1u}) or with other boron *p* orbitals (T_{2g})
  - 6 boron-hydrogen bonding orbitals ($= n$)
- 11 nonbonding or antibonding orbitals

Similar descriptions of bonding can be derived for other *closo* boranes. In each case, one particularly useful similarity can be found: there is one more framework bonding pair than the number of corners in the polyhedron. The extra framework bonding pair is in a totally symmetric orbital (like the A_{1g} orbital in $B_6H_6^{2-}$) resulting from the overlap of atomic (or hybrid) orbitals at the center of the polyhedron. In addition, a significant gap in energy exists between the highest bonding orbital (HOMO) and the lowest nonbonding orbital (LUMO).[22] The numbers of bonding pairs for common geometries are shown in Table 15-6.

TABLE 15-6
Bonding Pairs for *closo* Boranes

		Framework Bonding Pairs		
Formula	*Total Valence Electron Pairs*	*A_1 Symmetry*[a]	*Other Symmetry*	*B—H Bonding pairs*
$B_6H_6^{2-}$	13	1	6	6
$B_7H_7^{2-}$	15	1	7	7
$B_8H_8^{2-}$	17	1	8	8
$B_nH_n^{2-}$	$2n + 1$	1	n	n

NOTE: [a] Symmetry designation depends on the point group (such as A_{1g} for O_h symmetry).

Together, the *closo* structures make up only a very small fraction of all known borane species. Additional structural types can be obtained by removing one or more corners from the *closo* framework. Removal of one corner yields a ***nido*** (nest-like) structure, removal of two corners an ***arachno*** (spiderweb-like) structure, removal of three corners a ***hypho*** (net-like) structure, and removal of four corners a ***klado*** (branched) structure.[23] Examples of three related *closo*, *nido*, and *arachno* borane structures are

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[22] K. Wade, "Some Bonding Considerations," in B. F. G. Johnson, ed., *Transition Metal Clusters*, John Wiley & Sons, New York, 1980, p. 217.

[23] *Hypho*- and *klado*- structures appear to be known only as derivatives. Additional details on naming boron hydrides and related compounds can be found in the IUPAC publication, G. J. Leigh, ed., *Nomenclature of Inorganic Chemistry: Recommendations 1990*, Blackwell Scientific Publications, Cambridge, MA, 1990, pp. 207–237.

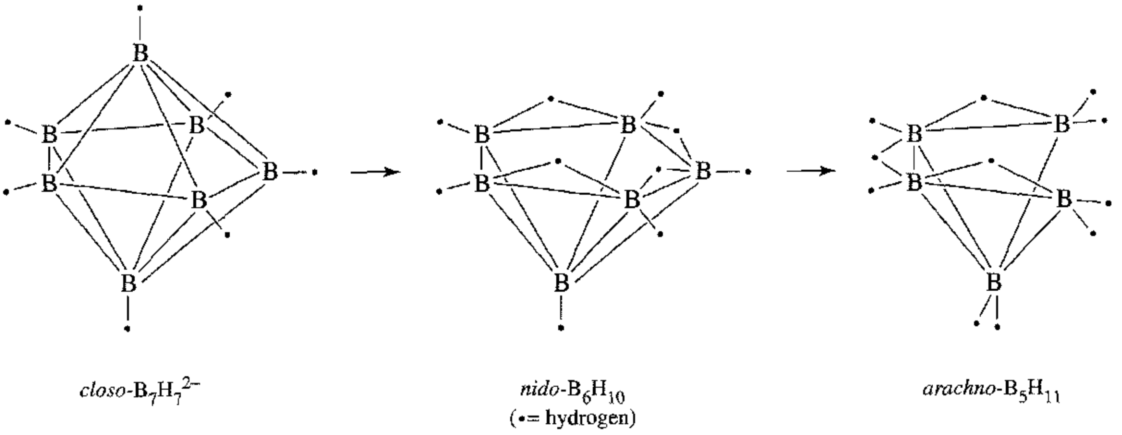

FIGURE 15-13 *Closo, nido,* and *arachno* Borane Structures.

shown in Figure 15-13, and the structures for these boranes having 6 to 12 boron atoms are shown in Figure 15-14.

The classification of structural types can often be done more conveniently on the basis of valence electron counts. Various schemes for relating electron counts to structures have been proposed, with most proposals based on the set of rules formulated by Wade.[24] The classification scheme based on these rules is summarized in Table 15-7. In this table, the number of pairs of framework bonding electrons is determined by subtracting one B—H bonding pair per boron; the $n + 1$ remaining framework electron pairs may be used in boron-boron bonding or in bonds between boron and other hydrogen atoms.

In addition, it is sometimes useful to relate the total valence electron count in boranes to the structural type. In *closo* boranes, the total number of valence electron pairs is equal to the sum of the number of vertices in the polyhedron (each vertex has a boron-hydrogen bonding pair) and the number of framework bond pairs. For example, in $B_6H_6^{2-}$ there are 26 valence electrons, or 13 pairs (= $2n + 1$, as mentioned previously). Six of these pairs are involved in bonding to the hydrogens (one per boron), and seven pairs are involved in framework bonding. The polyhedron of the *closo* structure is the parent polyhedron for the other structural types. Table 15-8 summarizes electron counts and classifications for several examples of boranes.

A method for classifying boranes

Boranes can conveniently be classified by considering the following:

closo boranes to have the formula $B_nH_n^{2-}$;
nido boranes to be derived from $B_nH_n^{4-}$ ions;
arachno boranes to be derived from $B_nH_n^{6-}$ ions;
hypho boranes to be derived from $B_nH_n^{8-}$ ions; and
klado boranes to be derived from $B_nH_n^{10-}$ ions.

The formulas of boranes can be related to these formulas by formally subtracting H^+ ions from the formula to make the number of B and H atoms equal. For example, to classify $B_9H_{14}^-$ we can formally consider it to be derived from $B_9H_9^{6-}$:

$$B_9H_{14}^- - 5\,H^+ = B_9H_9^{6-}$$

The classification for this borane is therefore *arachno*.

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[24] K. Wade, *Adv. Inorg. Chem. Radiochem.*, **1976**, *18*, 1–66.

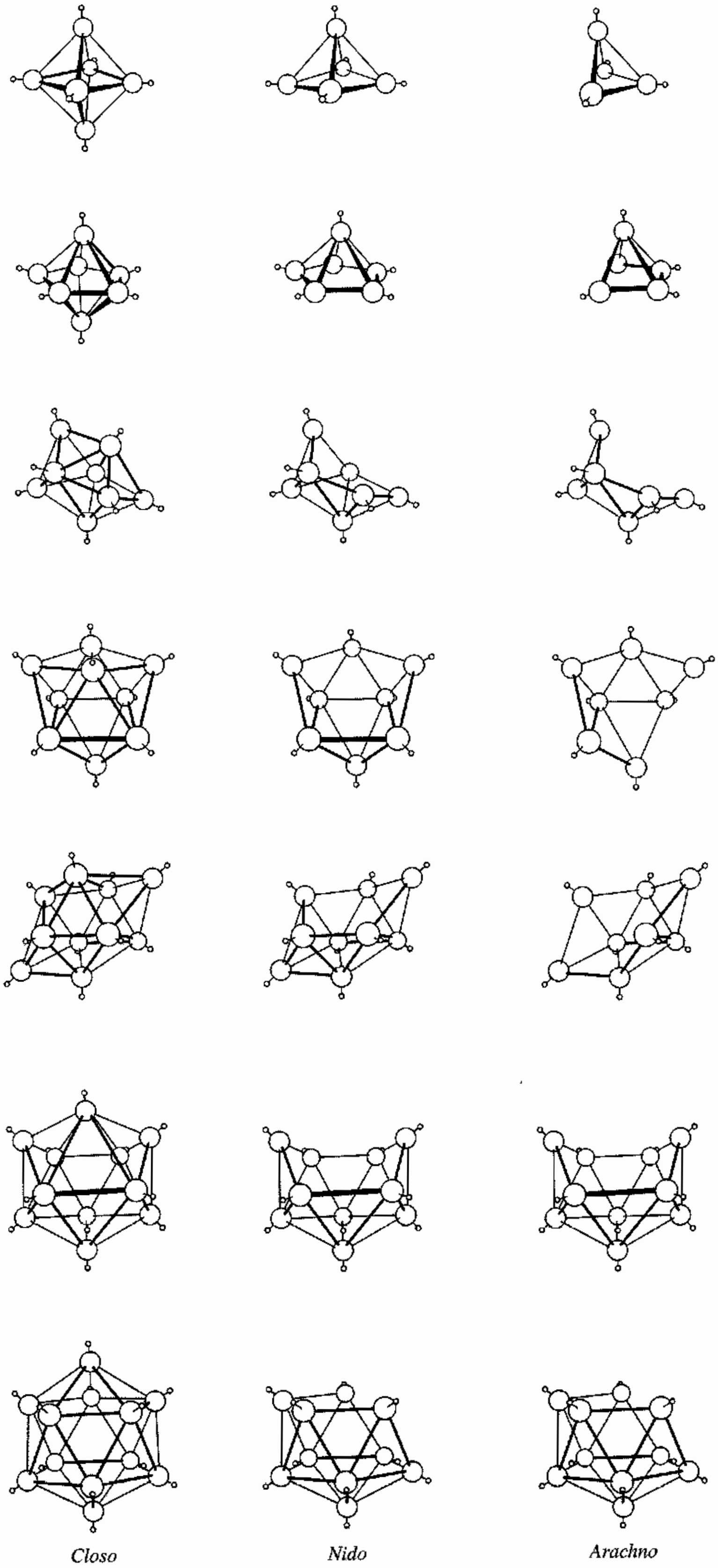


FIGURE 15-14 Structures of *closo*, *nido*, and *arachno* Boranes Having 6 to 12 Borons. (Reproduced and adapted with permission from R. W. Rudolph, *Acc. Chem. Res.*, **1976**, *9*, 446. © 1976 American Chemical Society.)

TABLE 15-7
Classification of Cluster Structures

Structure Type	Corners Occupied	Pairs of Framework Bonding Electrons	Empty Corners
Closo	n corners of n-cornered polyhedron	$n + 1$	0
Nido	$(n - 1)$ corners of n-cornered polyhedron	$n + 1$	1
Arachno	$(n - 2)$ corners of n-cornered polyhedron	$n + 1$	2
Hypho	$(n - 3)$ corners of n-cornered polyhedron	$n + 1$	3
Klado	$(n - 4)$ corners of n-cornered polyhedron	$n + 1$	4

TABLE 15-8
Examples of Electron Counting in Boranes

Vertices in Parent Polyhedron	Classification	Boron Atoms in Cluster	Valence Electrons	Framework Electron Pairs	Examples	Formally Derived From
6	*Closo*	6	26	7	$B_6H_6^{2-}$	$B_6H_6^{2-}$
	Nido	5	24	7	B_5H_9	$B_5H_5^{4-}$
	Arachno	4	22	7	B_4H_{10}	$B_4H_4^{6-}$
7	*Closo*	7	30	8	$B_7H_7^{2-}$	$B_7H_7^{2-}$
	Nido	6	28	8	B_6H_{10}	$B_6H_6^{4-}$
	Arachno	5	26	8	B_5H_{11}	$B_5H_5^{6-}$
12	*Closo*	12	50	13	$B_{12}H_{12}^{2-}$	$B_{12}H_{12}^{2-}$
	Nido	11	48	13	$B_{11}H_{13}^{2-}$	$B_{11}H_{11}^{4-}$
	Arachno	10	46	13	$B_{10}H_{15}^{2-}$	$B_{10}H_{10}^{6-}$

EXAMPLES

Classify the following boranes by structural type.

$B_{10}H_{14}$

$B_{10}H_{14} - 4\,H^+ = B_{10}H_{10}^{4-}$ The classification is *nido*.

$B_2H_7^-$

$B_2H_7^- - 5\,H^+ = B_2H_2^{6-}$ The classification is *arachno*.

B_8H_{16}

$B_8H_{16} - 8\,H^+ = B_8H_8^{8-}$ The classification is *hypho*.

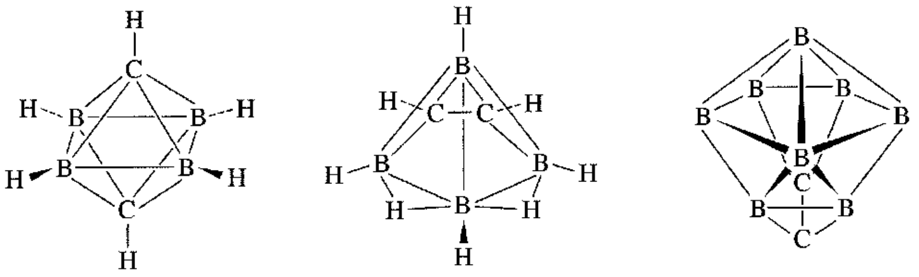
EXERCISE 15-3

Classify the following boranes by structural type:

a. $B_{11}H_{13}^{2-}$ b. $B_5H_8^-$ c. $B_7H_7^{2-}$ d. $B_{10}H_{18}$

15-4-2 HETEROBORANES

The electron-counting schemes can be extended to isoelectronic species such as the carboranes (also known as carbaboranes). The CH^+ unit is isoelectronic with BH; many compounds are known in which one or more BH groups have been replaced by CH^+ (or by C, which also has the same number of electrons as BH). For example, replacement of two BH groups by CH^+ in *closo*-$B_6H_6^{2-}$ yields *closo*-$C_2B_4H_6$, a neutral compound. *Closo*, *nido*, and *arachno* carboranes are all known, most commonly containing two carbon atoms; examples are shown in Figure 15-15.



$C_2B_4H_6$ *closo*

$C_2B_4H_8$ *nido*

$C_2B_8H_{10}^{4-}$ (has one terminal H on each B and C atom) *arachno*

FIGURE 15-15 Examples of Carboranes.

Chemical formulas corresponding to these designations are given in Table 15-9.

TABLE 15-9
Examples of Formulas of Boranes and Carboranes

Type	*Borane*	*Example*	*Carborane*	*Example*
Closo	$B_nH_n^{2-}$	$B_{12}H_{12}^{2-}$	$C_2B_{n-2}H_n$	$C_2B_{10}H_{12}$
Nido	B_nH_{n+4}[a]	$B_{10}H_{14}$	$C_2B_{n-2}H_{n+2}$	$C_2B_8H_{12}$
Arachno	B_nH_{n+6}[a]	B_9H_{15}	$C_2B_{n-2}H_{n+4}$	$C_2B_7H_{13}$

NOTE: [a] *Nido* boranes may also have the formulas $B_nH_{n+3}^-$ and $B_nH_{n+2}^{2-}$; *arachno* boranes may also have the formulas $B_nH_{n+5}^-$ and $B_nH_{n+4}^{2-}$.

Carboranes may be classified by structural type using the same method described previously for boranes. Because a carbon atom has the same number of valence electrons as a boron atom plus a hydrogen atom, formally each C should be converted to BH in the classification scheme. For example, for a carborane having the formula $C_2B_8H_{10}$,

$$C_2B_8H_{10} \longrightarrow B_{10}H_{12}$$

$$B_{10}H_{12} - 2\,H^+ = B_{10}H_{10}^{2-}$$

the classification of the carborane $C_2B_8H_{10}$ is therefore *closo*.

EXAMPLES

Classify the following carboranes by structural type:

$C_2B_9H_{12}^-$

$C_2B_9H_{12}^- \longrightarrow B_{11}H_{14}^-$

$B_{11}H_{14}^- - 3\,H^+ = B_{11}H_{11}^{4-}$ The classification is *nido*.

$C_2B_7H_{13}$

$C_2B_7H_{13} \longrightarrow B_9H_{15}$

$B_9H_{15} - 6H^+ = B_9H_9^{6-}$ The classification is *arachno*.

$C_4B_2H_6$

$C_4B_2H_6 \longrightarrow B_6H_{10}$

$B_6H_{10} - 4\,H^+ = B_6H_6^{4-}$ The classification is *nido*.

EXERCISE 15-4

Classify the following carboranes by structural type:

a. $C_3B_3H_7$ b. $C_2B_5H_7$ c. $C_2B_7H_{12}^-$

Many derivatives of boranes containing other main group atoms (designated heteroatoms) are also known. These heteroboranes may be classified by formally converting the heteroatom to a BH_x group having the same number of valence electrons, and then proceeding as in previous examples. For some of the more common heteroatoms, the substitutions are

Heteroatom	*Replace with*
C, Si, Ge, Sn	BH
N, P, As	BH_2
S, Se	BH_3

EXAMPLES

Classify the following heteroboranes by structural type:

SB_9H_{11}

$SB_9H_{11} \longrightarrow B_{10}H_{14}$

$B_{10}H_{14} - 4\,H^+ = B_{10}H_{10}{}^{4-}$ The classification is *nido.*

$CPB_{10}H_{11}$

$CPB_{10}H_{11} \longrightarrow PB_{11}H_{12} \longrightarrow B_{12}H_{14}$

$B_{12}H_{14} - 2H^+ = B_{12}H_{12}{}^{2-}$ The classification is *closo.*

EXERCISE 15-5

Classify the following heteroboranes by structural type:

a. SB_9H_9 b. $GeC_2B_9H_{11}$ c. $SB_9H_{12}{}^-$

Although it may not be surprising that the same set of electron-counting rules can be used to describe satisfactorily such similar compounds as boranes and carboranes, we should examine how far the comparison can be extended. Can Wade's rules, for example, be used effectively on compounds containing metals bonded to boranes or carboranes? Can the rules be extended even further to describe the bonding in polyhedral metal clusters?

15-4-3 METALLABORANES AND METALLACARBORANES

The CH group of a carborane is isolobal with 15-electron fragments of an octahedron such as $Co(CO)_3$. Similarly, BH, which has 4 valence electrons, is isolobal with 14-electron fragments such as $Fe(CO)_3$ and $Co(\eta^5\text{-}C_5H_5)$. These organometallic fragments have been found in substituted boranes and carboranes in which the organometallic fragments substitute for the isolobal main group fragments. For example, the organometallic derivatives of B_5H_9 shown in Figure 15-16 have been synthesized. Theoretical calculations on the iron derivative have supported the view that $Fe(CO)_3$ in this compound bonds in a fashion isolobal with BH.[25] In both fragments, the orbitals involved in framework bonding within the cluster are similar (Figure 15-17). In BH, the orbitals participating in framework bonding are an sp_z hybrid pointing toward the center of the polyhedron (similar to the orbitals participating in the bonding of A_{1g} symmetry in $B_6H_6{}^{2-}$; Figure 15-12) and p_x and p_y orbitals tangential to the surface of the

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[25] R. L. DeKock and T. P. Fehlner, *Polyhedron*, **1982**, *1*, 521.

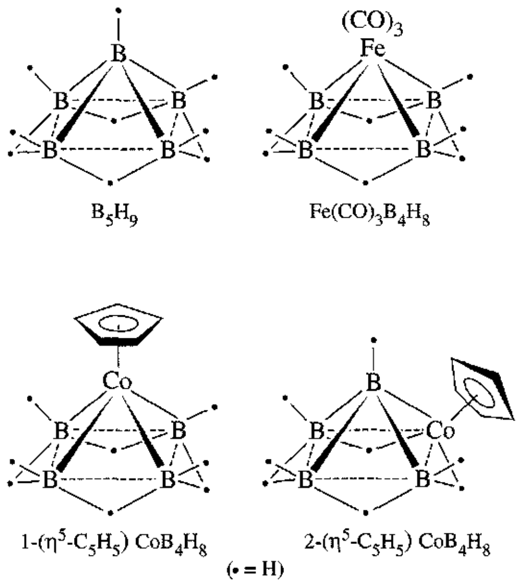

FIGURE 15-16 Organometallic Derivatives of B_5H_9.

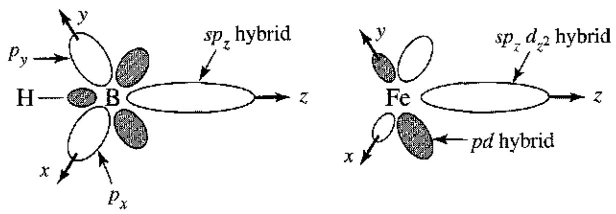

FIGURE 15-17 Orbitals of Isolobal Fragments BH and $Fe(CO)_3$.

cluster. In $Fe(CO)_3$, an sp_z hybrid points toward the center, and *pd* hybrid orbitals are oriented tangentially to the cluster surface.

There are many metalloboranes and metallocarboranes. Selected examples with *closo* structures are given in Table 15-10.

Anionic boranes and carboranes can also act as ligands toward metals in a manner resembling that of cyclic organic ligands. For example, *nido* carboranes of formula $C_2B_9H_{11}{}^{2-}$ have *p* orbital lobes pointing toward the "missing" site of the icosahedron (remember that the *nido* structure corresponds to a *closo* structure, in this case the 12-vertex icosahedron, with one vertex missing). This arrangement of *p* orbitals can be compared with the *p* orbitals of the cyclopentadienyl ring, as shown in Figure 15-18.

Although the comparison between these ligands is not exact, the similarity is sufficient that $C_2B_9H_{11}{}^{2-}$ can bond to iron to form a carborane analogue of ferrocene, $[Fe(\eta^5\text{-}C_2B_9H_{11})_2]^{2-}$. A mixed ligand sandwich compound containing one carborane and one cyclopentadienyl ligand, $[Fe(\eta^5\text{-}C_2B_9H_{11})(\eta^5\text{-}C_5H_5)]$, has also been made (Figure 15-19).[26] Many other examples of boranes and carboranes serving as ligands to transition metals are also known.[27]

Metallaboranes and metallacarboranes can be classified structurally by using a procedure similar to the method described previously for boranes and their main group derivatives. To classify borane derivatives with transition metal-containing fragments, it is convenient to determine how many electrons the metal-containing fragment needs to satisfy the requirement of the 18-electron rule. This fragment can be considered equivalent to a BH_x fragment needing the same number of electrons to satisfy the octet rule. For example, a 14-electron fragment such as $Co(\eta^5\text{-}C_5H_5)$ is 4 electrons short of 18;

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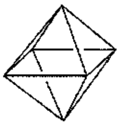
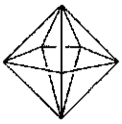
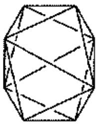
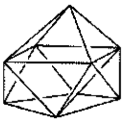
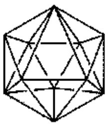
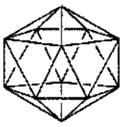
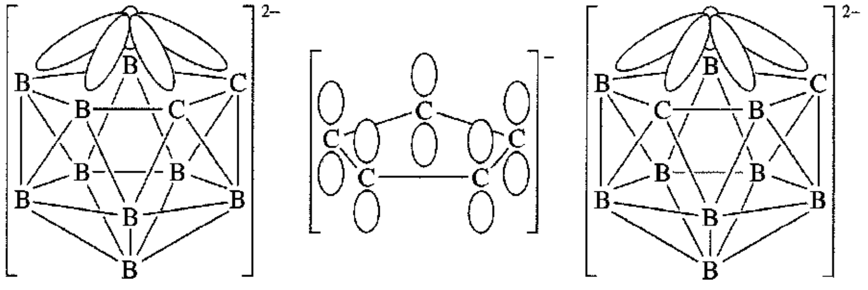
[26] M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Am. Chem. Soc.*, **1965**, *87*, 1818.

[27] K. P. Callahan and M. F. Hawthorne, *Adv. Organomet. Chem.*, **1976**, *14*, 145.

TABLE 15-10
Metallaboranes and Metallocarboranes with *closo* Structures

Number of Skeletal Atoms	*Shape*		*Examples*	
6	Octahedron		$B_4H_6(CoCp)_2$	$C_2B_3H_5Fe(CO)_3$
7	Pentagonal bipyramid		$C_2B_4H_6Ni(PPh_3)_2$	$C_2B_3H_5(CoCp)_2$
8	Dodecahedron		$C_2B_4H_4[(CH_3)_2Sn]CoCp$	
9	Capped square antiprism		$C_2B_6H_8Pt(PMe_3)_2$	$C_2B_5H_7(CoCp)_2$
10	Bicapped square antiprism		$[B_9H_9NiCp]^-$	$CB_7H_8(CoCp)(NiCp)$
11	Octadecahedron		$[CB_9H_{10}CoCp]^-$	$C_2B_8H_{10}IrH(PPh_3)_2$
12	Icosahedron		$C_2B_7H_9(CoCp)_3$	$C_2B_9H_{11}Ru(CO)_3$



nido-7, 8-$C_2B_9H_{11}^{2-}$ (η^5-C_5H_5)$^-$ *nido*-7, 9-$C_2B_9H_{11}^{2-}$

FIGURE 15-18 Comparison of $C_2B_9H_{11}^{2-}$ with $C_5H_5^-$. (Adapted with permission from N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford, 1984, p. 210. © 1984, Pergamon Press PLC.)

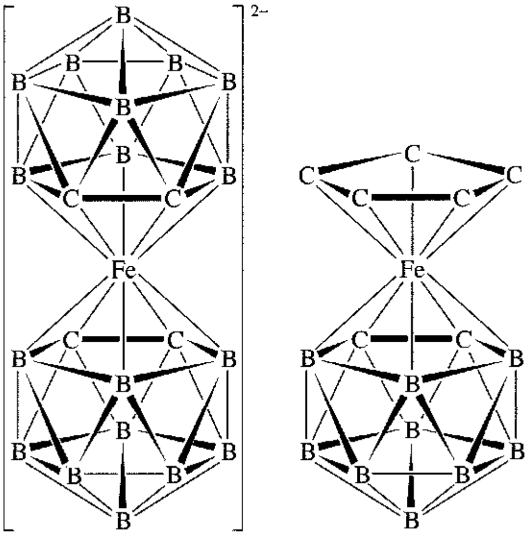


FIGURE 15-19 Carborane Analogs of Ferrocene. (Adapted with permission from N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford, 1984, pp. 211–212. © 1984, Pergamon Press PLC.)

this fragment may be considered the equivalent of the 4-electron fragment BH, which is 4 electrons short of an octet. Shown here are examples of organometallic fragments and their corresponding BH_x fragments:

Valence Electrons in Organometallic Fragment	*Example*	*Replace with*
13	$Mn(CO)_3$	B
14	CoCp	BH
15	$Co(CO)_3$	BH_2
16	$Fe(CO)_4$	BH_3

EXAMPLES

Classify the following metallaboranes by structural type:

$B_4H_6(CoCp)_2$

$B_4H_6(CoCp)_2 \longrightarrow B_4H_6(BH)_2 = B_6H_8$

$B_6H_8 - 2\,H^+ = B_6H_6^{2-}$ The classification is *closo*.

$B_3H_7[Fe(CO)_3]_2$

$B_3H_7[Fe(CO)_3]_2 \longrightarrow B_3H_7[BH]_2 = B_5H_9$

$B_5H_9 - 4\,H^+ = B_5H_5^{4-}$ The classification is *nido*.

EXERCISE 15-6

Classify the following metallaboranes by structural type:

a. $C_2B_7H_9(CoCp)_3$ b. $C_2B_4H_6Ni(PPh_3)_2$

15-4-4 CARBONYL CLUSTERS

The structures of several carbonyl cluster compounds were shown in Chapter 13. Many carbonyl clusters have structures similar to boranes; it is therefore of interest to determine to what extent the approach used to describe bonding in boranes may also be applicable to bonding in carbonyl clusters and other clusters.

According to Wade, the valence electrons in a cluster can be assigned to framework and metal-ligand bonding:[28]

Total number of valence electrons in cluster = number of electrons involved in framework bonding + number of electrons involved in metal-ligand bonding

As we have seen previously, the number of electrons involved in framework bonding in boranes is related to the classification of the structure as *closo*, *nido*, *arachno*, *hypho*, or *klado*. Rearranging this equation gives

Number of electrons involved in framework bonding = total number of valence electrons in cluster − number of electrons involved in metal-ligand bonding

For a borane, one electron pair is assigned to one boron-hydrogen bond on each boron. The remaining valence electron pairs are regarded as framework bonding pairs.[29] For a transition metal carbonyl complex, on the other hand, Wade suggests that 6 electron pairs per metal are involved either in metal-carbonyl bonding (to all carbonyls on a metal) or are nonbonding and therefore unavailable for participation in framework bonding. A metal-carbonyl cluster has 5 more electron pairs per framework atom, or 10 more electrons, than the corresponding borane. A metal-carbonyl analogue of *closo*-$B_6H_6^{2-}$, which has 26 valence electrons, would therefore need a total of 86 valence electrons to adopt a *closo* structure. An 86-electron cluster that satisfies this requirement is $Co_6(CO)_{16}$, which has an octahedral framework similar to $B_6H_6^{2-}$. As in the case of boranes, *nido* structures correspond to *closo* geometries from which one vertex is empty, *arachno* structures lack two vertices, and so on.

A simpler way to compare electron counts in boranes and transition metal clusters is to consider the different numbers of valence orbitals available to the framework atoms. Transition metals, with nine valence orbitals (one *s*, three *p*, and five *d* orbitals), have five more orbitals available for bonding than boron, which has only four valence orbitals; these five extra orbitals, when filled as a consequence of bonding within the framework and with surrounding ligands, give an increased electron count of 10 electrons per framework atom. Consequently, a useful rule of thumb is to increase the electron requirement of the cluster by 10 per framework atom when replacing a boron with a transition metal atom. In the example cited previously, replacing the six borons in *closo* $B_6H_6^{2-}$ with six cobalts should, therefore, increase the electron count from 26 to 86 for a comparable *closo* cobalt cluster. $Co_6(CO)_{16}$, an 86-electron cluster, meets this requirement.

The valence electron counts corresponding to the various structural classifications for main group and transition metal clusters are summarized in Table 15-11.[30] In this table, *n* designates the number of framework atoms.

TABLE 15-11
Electron Counting in Main Group and Transition Metal Clusters

Structure Type	*Main Group Cluster*	*Transition Metal Cluster*
Closo	$4n + 2$	$14n + 2$
Nido	$4n + 4$	$14n + 4$
Arachno	$4n + 6$	$14n + 6$
Hypho	$4n + 8$	$14n + 8$

---

[28] K. Wade, *Adv. Inorg. Chem. Radiochem.*, **1980**, *18*, 1.

[29] For structures involving bridging hydrogen atoms, the bridging hydrogens are considered to be involved in framework bonding.

[30] D. M. P. Mingos, *Acc. Chem. Res.*, **1984**, *17*, 311.

TABLE 15-12
Closo, nido, and *arachno* Borane and Transition Metal Clusters

Atoms in Cluster	Vertices in Parent Polyhedron	Framework Electron Pairs	Valence Electrons (Boranes)				Valence Electrons (Transition Metal Cluster)			
			Closo	*Nido*	*Arachno*	*Example*	*Closo*	*Nido*	*Arachno*	*Example*
4	4	5	18				58			
	5	6		20		$B_4H_7^-$		60		$Co_4(CO)_{12}$
	6	7			22	B_4H_{10}			62	$[Fe_4C(CO)_{12}]^{2-}$
5	5	6	22			$C_2B_3H_5$	72			$Os_5(CO)_{16}$
	6	7		24		B_5H_9		74		$Os_5C(CO)_{15}$
	7	8			26	B_5H_{11}			76	$[Ni_5(CO)_{12}]^{2-}$
6	6	7	26			$B_6H_6^{2-}$	86			$Co_6(CO)_{16}$
	7	8		28		B_6H_{10}		88		$Os_6(CO)_{17}[P(OMe)_3]_3$
	8	9			30	B_6H_{12}			90	

Examples of *closo, nido,* and *arachno* borane and transition metal clusters are given in Table 15-12. Transition metal clusters formally containing seven metal-metal framework bonding pairs are among the most common; examples illustrating the structural diversity of these clusters are given in Table 15-13 and Figure 15-20.

The predictions of structures of transition metal-carbonyl complexes, using Wade's rules are often, but not always, accurate. For example, the clusters $M_4(CO)_{12}$ (M = Co, Rh, Ir) have 60 valence electrons and are predicted to be *nido* complexes ($14n + 4$ valence electrons). A *nido* structure would correspond to a trigonal bipyramid

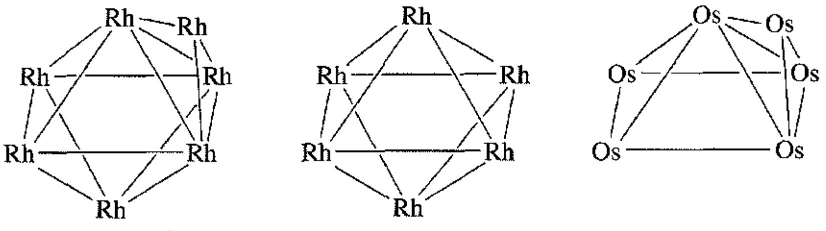
TABLE 15-13
Clusters Formally Containing Seven Metal-Metal Framework Bond Pairs

Number of Framework Atoms	Cluster Type	Shape	Examples
7	Capped *closo*[a]	Capped octahedron	$[Rh_7(CO)_{16}]^{3-}$ $Os_7(CO)_{21}$
6	*Closo*	Octahedron	$Rh_6(CO)_{16}$ $Ru_6C(CO)_{17}$
6	Capped *nido*[a]	Capped square pyramid	$H_2Os_6(CO)_{18}$
5	*Nido*	Square pyramid	$Ru_5C(CO)_{15}$
4	*Arachno*	Butterfly	$[Fe_4(CO)_{13}H]^{-}$[b]

SOURCE: K. Wade, "Some Bonding Considerations," in B. F. G. Johnson, ed., *Transition Metal Clusters*, John Wiley & Sons, 1980, p. 232.

NOTE: [a] A capped *closo* cluster has a valence electron count equivalent to neutral B_nH_n. A capped *nido* cluster has the same electron count as a *closo* cluster.

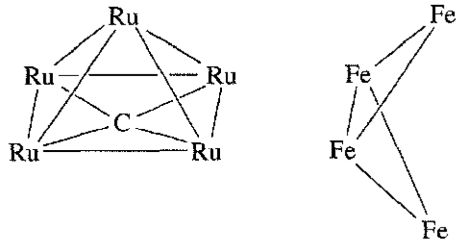
[b] This complex has an electron count matching a *nido* structure, but it adapts the butterfly structure expected for *arachno*. This is one of the many examples in which the structure of metal clusters is not predicted accurately by Wade's rules. Limitations of Wade's rules are discussed in R. N. Grimes, "Metallacarboranes and Metallaboranes," in G. Wilkinson, F. G. A. Stone, and W. Abel, eds., *Comprehensive Organometallic Chemistry*, Vol. 1, Pergamon Press, Elmsford, NY, 1982, p. 473.



$[Rh_7(CO)_{16}]^{3-}$
Capped octahedron

$Rh_6(CO)_{16}$
Octahedron

$H_2Os_6(CO)_{18}$
Capped square pyramid



$Ru_5C(CO)_{15}$
Square pyramid

$[Fe_4(CO)_{13}H]^-$
Butterfly

FIGURE 15-20 Metal Cores for Clusters Containing Seven Skeletal Bond Pairs.

(the parent structure) with one position vacant. X-ray crystallographic studies, however, have shown these complexes to have tetrahedral metal cores.

Ionic clusters of main group elements can also be classified by a similar approach to that used for other clusters. Many such clusters are known;[31] they are sometimes called **Zintl ions**. Examples are shown in Figure 15-21.

EXAMPLES

Classify the following main group clusters:

a. Pb_5^{2-}: the total valence electron count is 22 (including each of the 4 valence electrons per Pb, plus 2 electrons for the charge). Because $n = 5$, the total electron count $= 4n + 2$; the classification is *closo*. (See Table 15-11.)

b. Sn_9^{4-}: total number of valence electrons $= 40$. For $n = 9$, the electron count $= 4n + 4$; the classification is *nido*. The structure, as shown in Figure 15-21, has one missing vertex.

a. Sb_4^{2-}: total number of valence electrons $= 22 = 4n + 6$. The classification is *arachno*. The square structure of this ion (Figure 15-21) corresponds to an octahedron with two vertices missing.

EXERCISE 15-7

Classify the following main group clusters:

a. Ge_9^{2-}

b. Bi_5^{3+}

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[31] J. D. Corbett, *Angew. Chem. Int. Ed.*, **2000**, *39*, 670.

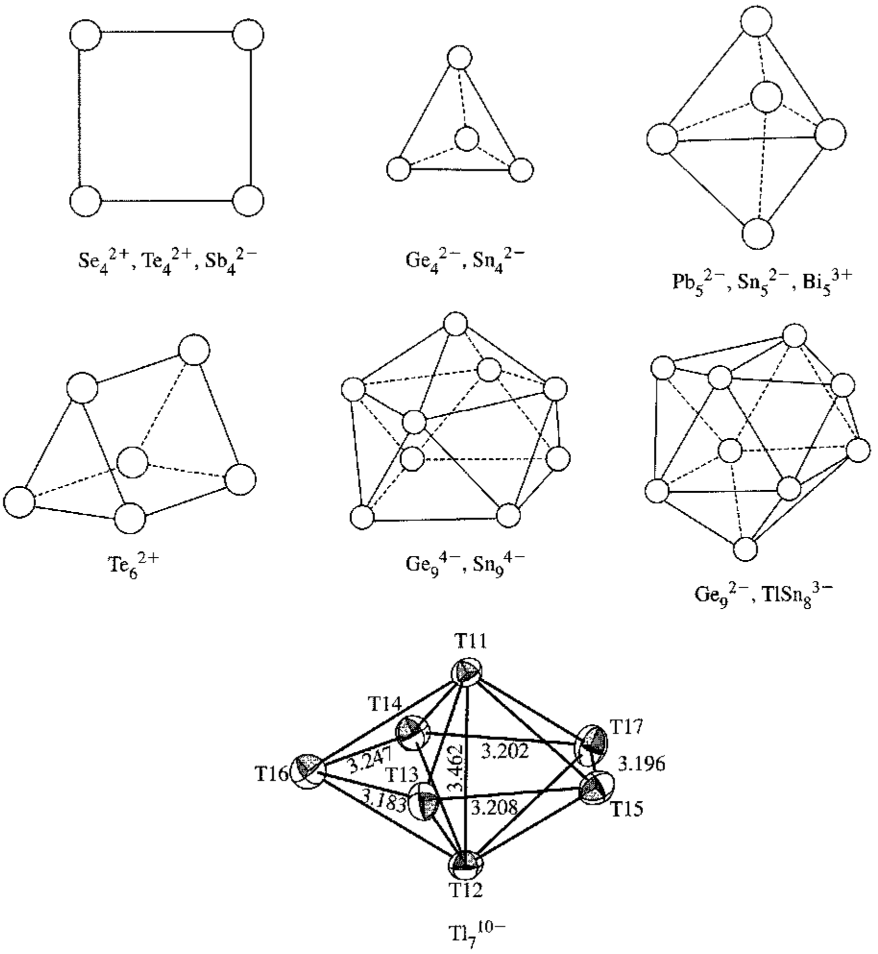

FIGURE 15-21 Ionic Clusters of Main Group Elements (Zintl Ions). (Tl_7^{10-} diagram reprinted with permission from S. Kaskel and J. D. Corbett, *Inorg. Chem.* **2000**, *39*, 778. © 2000, American Chemical Society.)

Recently, an extension of Wade's rules has been described for electron counting in boranes, heteroboranes, metallaboranes, other clusters, and even metallocenes.[32] This approach called the ***mno*** **rule**, states that for a closed cluster structure to be stable, there must be $m + n + o$ skeletal electron pairs, where

m = number of condensed (linked) polyhedra

n = total number of vertices

o = number of single-atom bridges between two polyhedra

A fourth term, p, must be added for structures with missing vertices:

p = number of missing vertices (e.g., $p = 1$ for *nido*, $p = 2$ for *arachno*.)

This approach has been particularly developed for application to macropolyhedral structures, clusters involving linked polyhedra, and many examples have been described in detail.[33]

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[32] E. D. Jemmis, M. M. Balakrishnarajan, and P. D. Pancharatna, *J. Am. Chem. Soc.*, **2001**, *123*, 4313.

[33] E. D. Jemmis, M. M. Balakrishnarajan, and P. D. Pancharatna, *Chem. Rev.*, **2002**, *102*, 93.

This approach is best illustrated by some examples.

EXAMPLES

Determine the number of skeletal electron pairs predicted by the *mno* rule for the following:

$B_{12}H_{12}{}^{2-}$ (see Figure 15-14)

m:	This structure consists of a single polyhedron.	$m = 1$
n:	Each boron atom in the polyhedron is a vertex.	$n = 12$
o:	There are no bridges between polyhedra.	$o = 0$
p:	The structure is *closo*, so $p = 0$.	
		$m + n + o =$ **13** electron pairs

$(\eta^5\text{-}C_2B_9H_{11})_2Fe^{2-}$ (see Figure 15-19)

m:	This structure has two linked polyhedra.	$m = 2$
n:	All carbons, borons, and the Fe are vertices.	$n = 23$
o:	The Fe atom serves to bridge the polyhedra.	$o = 1$
p:	The structure is *closo*, so $p = 0$.	
		$m + n + o =$ **26** electron pairs

Ferrocene, $(\eta^5\text{-}C_5H_5)_2Fe$ (see Figure 13-5)

m:	The structure may be viewed as two linked polyhedra (pentagonal pyramids).	$m = 2$
n:	Each atom in the structure is a vertex.	$n = 11$
o:	The iron atom bridges the polyhedra.	$o = 1$
p:	The structure is *not* closo; the top or bottom may be viewed as a pentagonal bipyramid lacking one vertex; the classification is *nido*.	$p = 2$ (one open face per polyhedron)
		$m + n + o + p =$ **16** electron pairs

EXERCISE 15-8

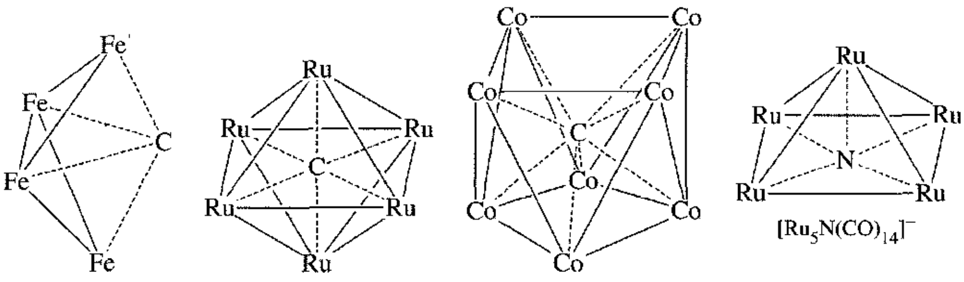
Determine the number of skeletal electron pairs predicted by the *mno* rule for the following:

a. $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_2B_9H_{11})Fe$ (see Figure 15-19)

b. *nido*-7,8-$C_2B_9H_{11}{}^{2-}$ (see Figure 15-18)

15-4-5 CARBIDE CLUSTERS

Many compounds have been synthesized, often fortuitously, in which one or more atoms have been partially or completely encapsulated within metal clusters. The most common of these cases have been the carbide clusters, with carbon exhibiting coordination numbers and geometries not found in classic organic structures. Examples of these unusual coordination geometries are shown in Figure 15-22.



$Fe_4C(CO)_{13}$ $Ru_6C(CO)_{17}$ $[Co_8C(CO)_{18}]^{2-}$ $[Ru_5N(CO)_{14}]^-$ An example of a nitride cluster

FIGURE 15-22 Carbide Clusters. CO ligands have been omitted for clarity.

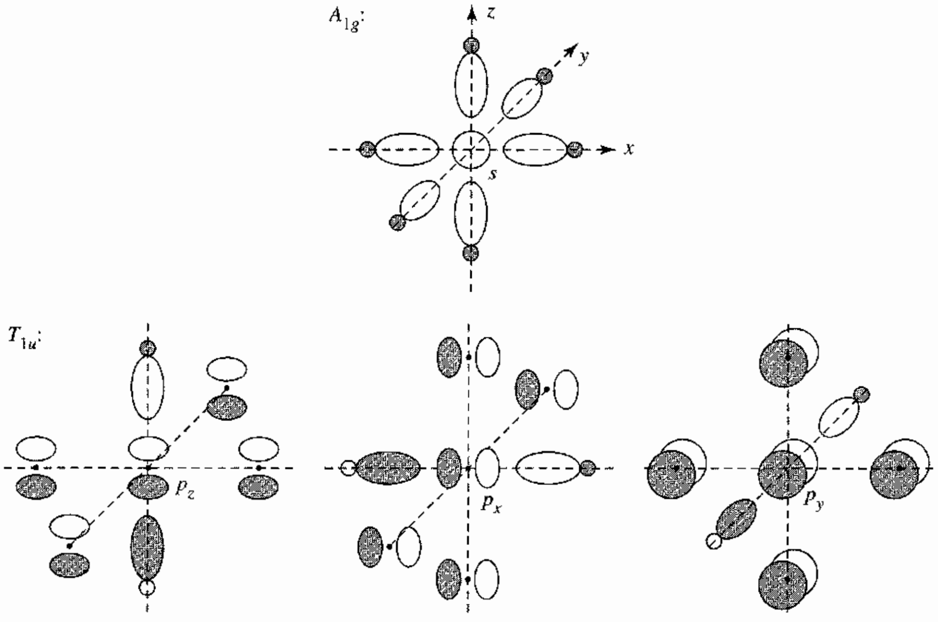


FIGURE 15-23 Bonding Interactions Between Central Carbon and Octahedral Ru_6.

Encapsulated atoms contribute their valence electrons to the total electron count. For example, carbon contributes its 4 valence electrons in $Ru_6C(CO)_{17}$ to give a total of 86 electrons, corresponding to a *closo* electron count (Table 15-12).

How can carbon, with only four valence orbitals, form bonds to more than four surrounding transition metal atoms? $Ru_6C(CO)_{17}$, with a central core of O_h symmetry, is a useful example. The $2s$ orbital of carbon has A_{1g} symmetry and the $2p$ orbitals have T_{1u} symmetry in the O_h point group. The octahedral Ru_6 core has framework bonding orbitals of the same symmetry as in $B_6H_6^{2-}$ described earlier in this chapter (see Figure 15-12): a centrally directed A_{1g} group orbital and two sets of orbitals, oriented tangentially to the core, of T_{1u} and T_{2g} symmetry. Therefore, there are two ways in which the symmetry match is correct for interactions between the carbon and the Ru_6 core, the interactions of A_{1g} and T_{1u} symmetry shown in Figure 15-23 (the T_{2g} orbitals participate in Ru—Ru bonding but not in bonding with the central carbon). The net result is the formation of four C—Ru bonding orbitals, occupied by electron pairs in the cluster, and four unoccupied antibonding orbitals.[34]

EXERCISE 15-9

Classify the following clusters by structural type:

a. $[Re_7C(CO)_{21}]^{3-}$ b. $[Fe_4N(CO)_{12}]^-$

15-4-6 ADDITIONAL COMMENTS ON CLUSTERS

As we have seen, transition metal clusters can adopt a wide variety of geometries and can involve metal-metal bonds of order as high as 4. Clusters may also include much larger polyhedra than shown so far in this chapter, polyhedra linked through vertices,

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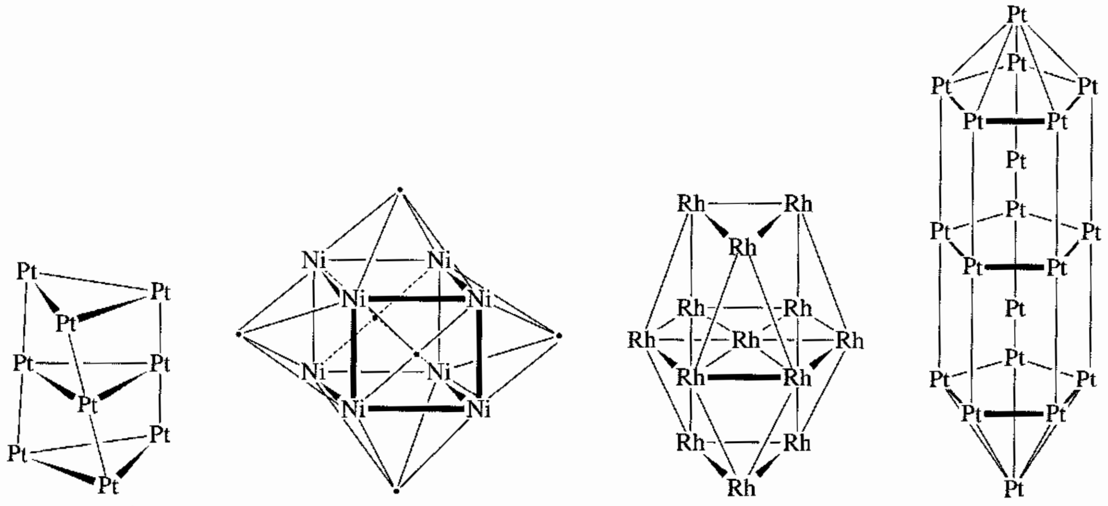
[34] G. A. Olah, G. K. S. Prakash, R. E. Williams, L. D. Field, and K. Wade, *Hypercarbon Chemistry*, John Wiley & Sons, New York, 1987, pp. 123–133.



$[Pt_9(CO)_{18}]^{2-}$ $Ni_8(CO)_8(PPh_3)_6$ (• = PPh) $[H_2Rh_{13}(CO)_{24}]^{3-}$ $[Pt_{19}(CO)_{22}]^{4-}$

FIGURE 15-24 Examples of Large Clusters. CO and hydride ligands have been omitted to show the metal-metal bonding more clearly.

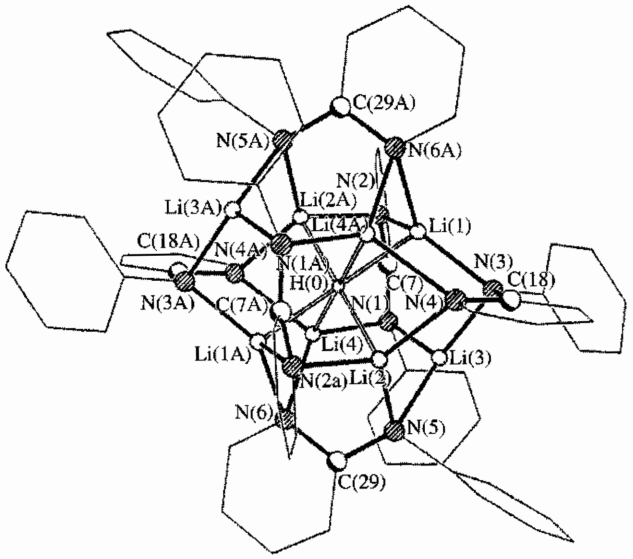


FIGURE 15-25 A Hydride Ion in a Cage of Eight Lithium Ions. (Reproduced with permission from D. R. Armstrong, W. Clegg, R. P. Davies, S. T. Liddle, D. J. Linton, P. R. Raithby, R. Snaith, and A. E. H. Wheatley, *Angew. Chem., Int. Ed.*, **1999**, *38*, 3367. © 1999, Wiley-VCH and A. E. H. Wheatley.)

edges, or faces, and extended three-dimensional arrays. Examples of these types of clusters are given in Figure 15-24. Even an example of a hydride-centered cluster, with a hydride ion within a cage of eight lithium ions, has been reported (Figure 15-25).

GENERAL REFERENCES

The best reference on parallels between main group and organometallic chemistry is Roald Hoffmann's 1982 Nobel Lecture, "Building Bridges Between Inorganic and Organic Chemistry," in *Angew. Chem., Int. Ed.*, **1982**, *21*, 711–724, which describes in detail the isolobal analogy. Another very useful paper is John Ellis's "The Teaching of Organometallic Chemistry to Undergraduates," in *J. Chem. Educ.*, **1976**, *53*, 2–6. K. Wade, *Electron Deficient Compounds*, Thomas Nelson, New York, 1971, provides detailed descriptions of bonding in boranes and related compounds. Metallacarboranes have been reviewed extensively by R. N. Grimes in E. W. Abel, F. G. A. Stone, and G. Wilkinson, eds., *Comprehensive Organometallic Chemistry II*, Pergamon Press, Oxford, 1995, Vol. 1, Chapter 9, pp. 373–430. Topics related to multiple bonds between metal atoms are discussed in detail in F. A. Cotton and R. A. Walton, *Multiple Bonds Between Metal Atoms*, John Wiley & Sons, New York, 1982. Two articles in *Chemical and Engineering News* are recommended for further discussion of applications of cluster chemistry: E. L. Muetterties, "Metal Clusters," *Chem. Eng. News*, Aug. 20, 1982, pp. 28–41, and F. A. Cotton and M. H. Chisholm, "Bonds Between Metal Atoms," *Chem. Eng. News*, June 28, 1982, pp. 40–46.

PROBLEMS

15-1 Predict the following products:

a. $Mn_2(CO)_{10} + Br_2 \longrightarrow$
b. $HCCl_3$ + excess $[Co(CO)_4]^- \longrightarrow$
c. $Co_2(CO)_8 + (SCN)_2 \longrightarrow$
d. $Co_2(CO)_8 + C_6H_5\text{-}C{\equiv}C\text{-}C_6H_5$ (product has single Co—Co bond)
e. $Mn_2(CO)_{10} + [(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2 \longrightarrow$

15-2 Find organic fragments that are isolobal with

a. $Tc(CO)_5$
b. $[Re(CO)_4]^-$
c. $[Co(CN)_5]^{3-}$
d. $[CpFe(\eta^6\text{-}C_6H_6)]^+$
e. $[Mn(CO)_5]^+$
f. $Os_2(CO)_8$ (find organic molecule isolobal with this dimeric molecule)

15-3 Propose two organometallic fragments not mentioned in this chapter that are isolobal with

a. CH_3
b. CH
c. CH_3^+
d. CH_3^-
e. $(\eta^5\text{-}C_5H_5)Fe(CO)_2$
f. $Sn(CH_3)_2$

15-4 Propose an organometallic molecule that is isolobal with each of the following:

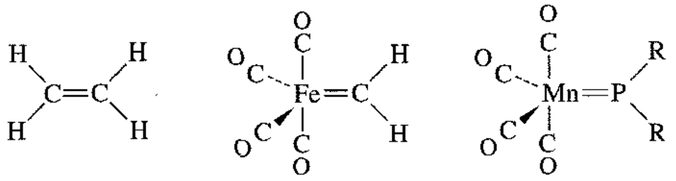
a. Ethylene
b. P_4
c. Cyclobutane
d. S_8

15-5 Hydrides such as $NaBH_4$ and $LiAlH_4$ have been reacted with the complexes $[(C_5Me_5)Fe(C_6H_6)]^+$, $[(C_5H_5)Fe(CO)_3]^+$, and $[(C_5H_5)Fe(CO)_2(PPh_3)]^+$. (Reference: P. Michaud, C. Lapinte, and D. Astruc, *Ann. N. Y. Acad. Sci.*, **1983**, *415*, 97).

a. Show that these complexes are isolobal.
b. Predict the products of the reactions of these complexes with hydride reagents.

15-6 Hoffmann has described the following molecules to be composed of isolobal fragments. Subdivide the molecules into fragments, and show that the fragments are isolobal.

a.



b.