Organometallic Chemistry of Transition Elements

for 4th Class

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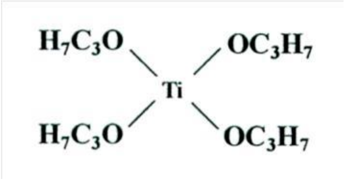
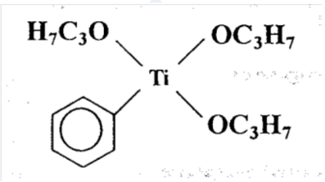
Introduction

Organometallic chemistry is the study of organometallic compounds, chemical compounds containing at least one chemical bond between a carbon atom of an organic molecule and a metal, including alkaline, alkaline earth, and transition metals, and some times broadened to include metalloids like boron, silicon, and tin, as well. For example, (OC_3H_7 = pentyl alkoxide). An alkoxide such as $(C_3H_7O)_4Ti$ is not considered to be an organometallic compound because the organic group is bound to Ti by oxygen, whereas $C_6H_5Ti(OC_3H_7)_3$ is, because a metal to carbon bond is present.





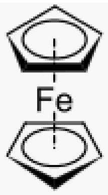
Aside from bonds to organyl fragments or molecules, bonds to 'inorganic' carbon, like carbon monoxide (metal carbonyls), cyanide, or carbide, are generally considered to be organometallic as well. Some related compounds such as transition metal hydrides and metal phosphine complexes are often included in discussions of organometallic compounds, though strictly speaking, they are not necessarily organometallic. The related term "metalorganic compound" refers to metal-containing compounds lacking direct metal-carbon bonds but which contain organic ligands. Metal β-diketonates, alkoxides, dialkyl amides, and metal phosphine complexes are representative members of this class. The field of organo metallic chemistry combines aspects of traditional inorganic and organic chemistry. Organometallic compounds are widely used both stoichiometrically in research and industrial chemical reactions, as well as in the role of catalysts to increase the rates of such reactions (e.g., as in uses of homogeneous catalysis), where target molecules include polymers, pharmaceuticals, and many other types of practical products.

Organometallic compounds are distinguished by the prefix "organo-" e.g. organo-palladium compounds. Examples of such organometallic compounds include all Gilman reagents, which contain lithium and copper. Tetracarbonyl nickel, and ferrocene are examples of organometallic compounds containing transition metals. Other examples include organomagnesium compounds like iodo(methyl)magnesium MeMgI, dimethyl magnesium (Me_2Mg), and all Grignard reagents; organolithium compounds such as *n*-

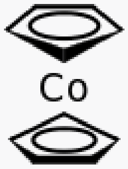
butyllithium (n-BuLi), organozinc compounds such as diethylzinc (Et_2Zn) and organo copper compounds such as lithium dimethylcuprate ($Li^+[CuMe_2]^-$).

In addition to the traditional metals, lanthanides, actinides, and semimetals, elements such as boron, silicon, arsenic, and selenium are considered to form organometallic compounds, e.g. organoborane compounds such as triethylborane (Et_3B).

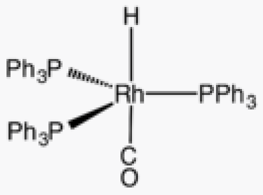
Representative Organometallic Compounds:



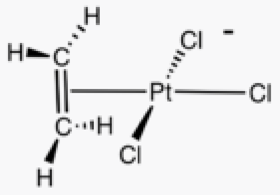
Ferrocene is an archetypal organoiron complex
It is an air-stable, sublimable compound.



Cobaltocene is a structural analogue
of ferrocene, but is highly reactive toward air.



Tris(triphenylphosphine)rhodium carbonyl hydride
is used in the commercial production of many
aldehyde-based fragrances.



Zeise's salt is an example of a
transition metal alkene complex.

Coordination compounds with organic ligands

Many complexes feature coordination bonds between a metal and organic ligands. The organic ligands often bind the metal through a heteroatom such as oxygen or nitrogen, in which case such compounds are considered coordination compounds. However, if any of the ligands form a direct M-C bond, then complex is usually considered to be organo metallic, e.g., $[(C_6H_6)Ru(H_2O)_3]^{2+}$. Furthermore, many lipophilic compounds such as metal acetylacetonates and metal alkoxides are called "metalorganics."

A naturally occurring transition metal alkyl complex is methylcobalamin (a form of Vitamin B_{12}), with a cobalt-methyl bond. This subset of complexes is often discussed within the subfield of bioorganometallic chemistry.

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 (CO, C_2H_4) are soft and can *π* bond. The structures of some typical organometallic compounds show many examples of such *π*-bonding ligands as butadiene, benzene, cyclopentadienyl (C_5H_5 or 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 characteristic of organometallic chemistry.

The 18 – electron rule:

The 18e rule 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, 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. To assign a formal oxidation state to carbon in an organic molecule, we impose an ionic model by artificially dissecting it into ions. 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, usually written C(-IV). Note that the net electron count always remains the same, whether we adopt the covalent (4e {C atom} + 4 × 1e {4H atoms} = 8e) or ionic (8e {C_4^- ion} + 4 × 0e {4H + ions} = 8e*)* model.

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 need 18e to fill all nine orbitals; some come from the metal, the rest from the ligands. Only a limited number of combinations of metal and ligand give an 18e count. The 18e fills the molecular orbital (MO) diagram of the complex ML_6 up to the $d\pi$ level, and leaves the M−L antibonding 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 (AO) on the metal that remains nonbonding will clearly give rise to one MO in the complex; each AO that interacts with a ligand orbital will give rise to one bonding MO, which will be filled in the complex, and one antibonding MO, which will normally be empty. Our nine metal orbitals therefore give rise to nine low-lying orbitals in the complex and to fill these we need 18 e.

Table 1 shows 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 from its lone pair; π back bonding makes no difference to the electron count for the metal. In the free atom, it had pairs of $d\pi$ electrons for back bonding; in the complex it still has them, now delocalized over metal and ligands. 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 such as 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.

Table 1 First-Row Carbonyls

$V(CO)_6$	17e; 18e $V(CO)_6^-$ also stable
$Cr(CO)_6$	Octahedral
$(CO)_5Mn{-}Mn(CO)_5$	M−M bond contributes 1e to each metal
$Fe(CO)_5$	Trigonal bipyramidal
$(CO)_3Co(\mu\text{-}CO)_2Co(CO)_3$	μ-CO contributes 1e to each metal, with M−M bond
$Ni(CO)_4$	Tetrahedral

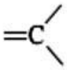
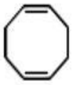
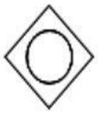
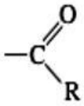
This completes the noble gas configuration for each metal as the unpaired electron in each fragment is shared with the other in forming the bond, much as the 7e methyl radical dimerizes to give the 8e compound, ethane. In the 17e fragment $Co(CO)_4$, dimerization via a metal–metal bond, but a pair of 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.

Ionic Versus Covalent Model:

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. Take $HMn(CO)_5$: 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, we can consider the complex as being 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.

Since all bonds between dissimilar elements have at least some ionic and some covalent character. 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. In classical coordination chemistry, the oxidation state model played a dominant role 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. 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 practice 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. Most commone ligand in organometalic chemistry shown below:-

Table – 2

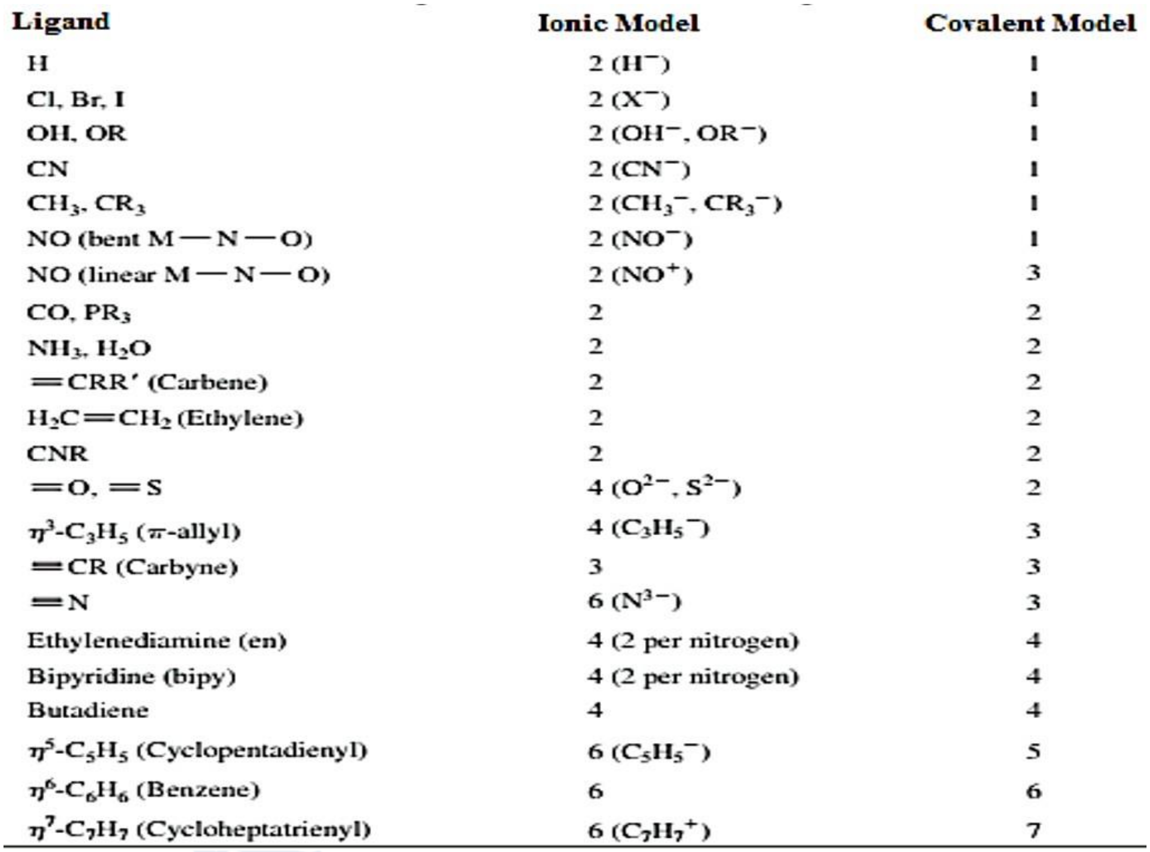
Ligand	Name	Ligand	Name
CO	Carbonyl		Benzene
	Carbene (alkylidene)		
$\equiv$C—	Carbyne (alkylidyne)		1,5-cyclooctadiene (1,5-COD) (1,3-cyclooctadiene complexes are also known)
	Cyclopropenyl (*cyclo*-C_3H_3)	$H_2C{=}CH_2$	Ethylene
		$HC{\equiv}CH$	Acetylene
	Cyclobutadiene (*cyclo*-C_4H_4)		π-Allyl (C_3H_5)
		$-CR_3$	Alkyl
	Cyclopentadienyl (*cyclo*-C_5H_5) (Cp)		Acyl

For ligands having all carbons bonded to a metal, sometimes the superscript is omitted. Ferrocene may therefore be written (η-C_5H_5)$_2$Fe and dibenzenechromium (η-C_6H_6)$_2$Cr. Similarly, π with no superscript may occasionally be used to designate that all atoms in the pi system are bonded to the metal; (for example, (π-C_5H_5)$_2$Fe).

Electron Counts for Common Ligands and Hapticity:

In Table 3 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· 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 (1) can be considered as a combination of three C=C ligands. The allyl group can be considered as a combination of an alkyl and a C=C group. The two resonance forms (2) and (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 (4).

Table 3 Common Ligands and Their Electron Counts



Ligand	Ionic Model	Covalent Model
H	2 (H^-)	1
Cl, Br, I	2 (X^-)	1
OH, OR	2 (OH^-, OR^-)	1
CN	2 (CN^-)	1
CH_3, CR_3	2 (CH_3^-, CR_3^-)	1
NO (bent M—N—O)	2 (NO^-)	1
NO (linear M—N—O)	2 (NO^+)	3
CO, PR_3	2	2
NH_3, H_2O	2	2
=CRR′ (Carbene)	2	2
$H_2C{=}CH_2$ (Ethylene)	2	2
CNR	2	2
=O, =S	4 (O^{2-}, S^{2-})	2
η^3-C_3H_5 (π-allyl)	4 ($C_3H_5^-$)	3
≡CR (Carbyne)	3	3
≡N	6 (N^{3-})	3
Ethylenediamine (en)	4 (2 per nitrogen)	4
Bipyridine (bipy)	4 (2 per nitrogen)	4
Butadiene	4	4
η^5-C_5H_5 (Cyclopentadienyl)	6 ($C_5H_5^-$)	5
η^6-C_6H_6 (Benzene)	6	6
η^7-C_7H_7 (Cycloheptatrienyl)	6 ($C_7H_7^+$)	7

In such a case, the *hapticity* of the ligand, the number of ligand atoms bound to the metal, is three and so (5), referred to as "bis-π-allyl nickel" in the older literature, is now known as bis-η3-allyl nickel, or [Ni(η3-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 η3 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. The allyl group can also bind in another way (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 1.

Examples:

1- $[\pi\text{-}C_5H_5\,Fe(CO)_2\,C_2H_4]^+$

Fe^+	7
$\pi\text{-}C_5H_5$	5
$(CO)_2$	4
C_2H_4	2

	18e

2- $[Ni(CO)_4]$

Ni^0	10
$(CO)_4$	8
	-----
	18 e

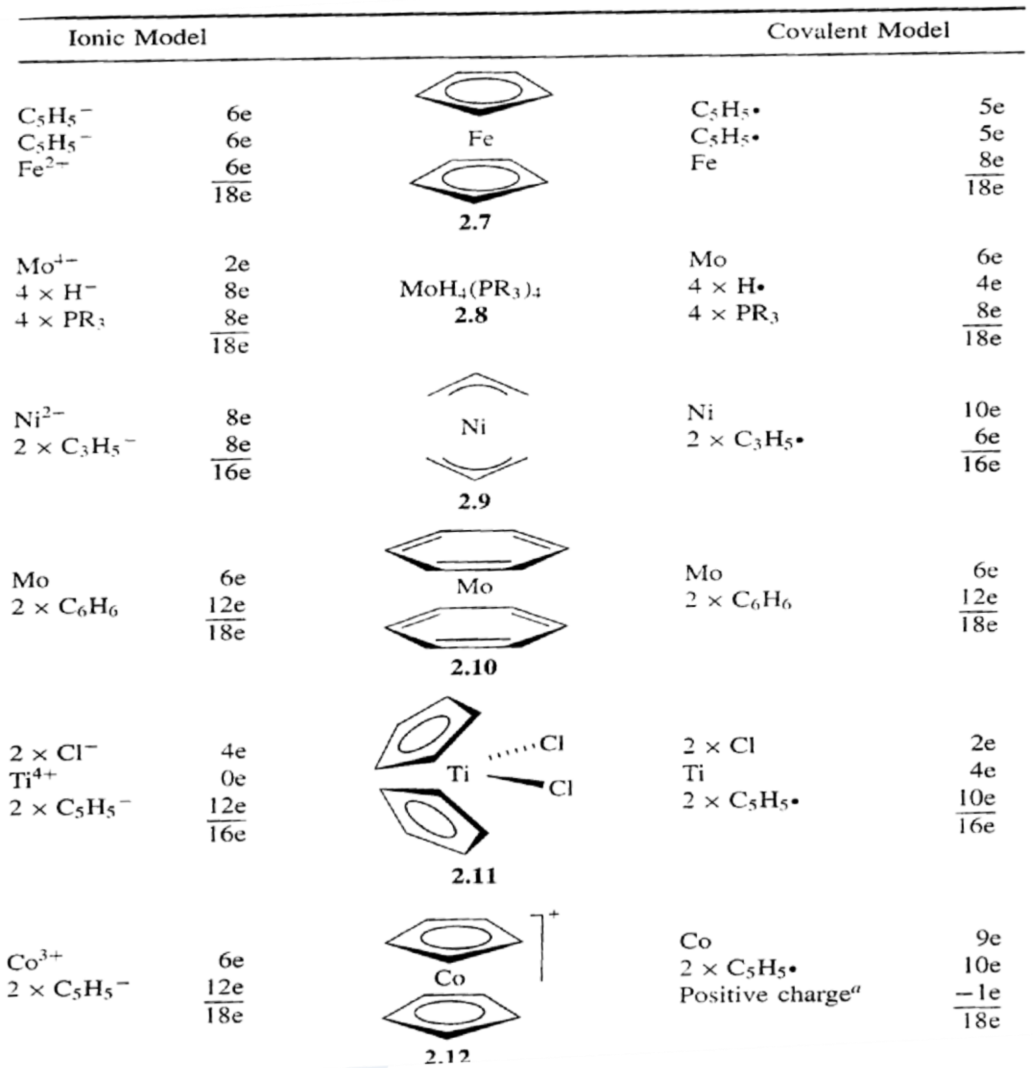
3- $Mn_2(CO)_{10}$ (Polynuclear carbonyls)

Mn^0	7
$(CO)_5$	10
Mn-Mn covalent bond	1
	-----
	18 e

4- $[\pi\text{-}C_3H_5Fe(CO)_2NO]$

Fe^0	8
$(CO)_2$	4
NO	3
π –allyl	3
	------
	18 e

Bridging ligands are very common and are prefixed by the symbol *μ*. Bridging CO ligands are usually counted as shown in Table 4. On the ionic model, a bridging Cl^- donates a pair of electrons to each of two LnM^+ groups. On the covalent model, we first form $L_nM{-}Cl$, the Cl of which 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.



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

Table 4 Electron counting on the covalent and ionic models.

For electron counting purposes, we can consider that the chlorine atom is a 1e donor to M and M−Cl is 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). A triply bridging Cl would donate 1e to the first and 2e each to the other two metals on the covalent model. 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.

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, $CoCp_2^+$ (Fig.1) is counted on the covalent model as follows. The neutral Co atom has 9e because it is group 9; from Table 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 $9 + 10 - 1 = 18e$.

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) 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 $6 + (2 \times 6) = 18$ electrons.

Limitation of the 18 – e 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 generally bind as are required to achieve 18e. With high-field ligands, for the complex will be large. This means that the $d^*\sigma$ 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 $d\pi$ orbitals that would have to give up electrons if the molecule had less than 18e and 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 $d\pi$ 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 $d^*\sigma$ or to remove them from the high-lying $d\pi$.

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 5). 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, but large distortions can occur.3 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).

Table 5 The d^8 Metals that can Adopt a 16e Square Planar Configuration

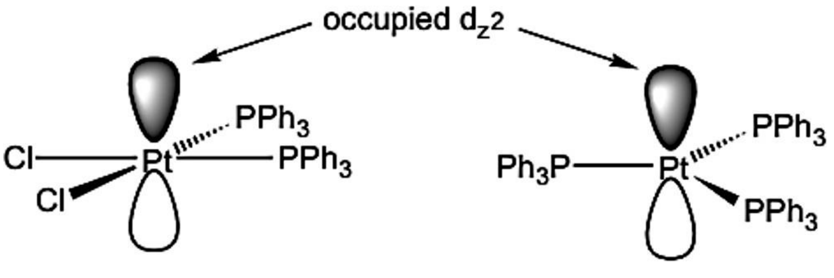
Group 8	 9	 10	 11
Fe(0)[a]	Co(I)[b]	Ni(II)	Cu(III)[c]
Ru(0)[a]	Rh(I)[b]	Pd(II)	—
Os(0)[a]	Ir(I)[b]	Pt(II)	Au(III)

[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.

Some high valent d^0 complexes have a lower electron count than 18. Sterically demanding bulky ligands force complexes to have less than 18 electrons. The 18 e rule fails when bonding of organometallic clusters of moderate to big sizes (6 Metal atoms and above) are considered. The rule is not applicable to organometallic compounds of main group metals as well as to those of lanthanide and actinide metals.

There are quite a few examples of organometallics which have 16 ve. As with all chemistry, the excuse is either ***electronic*** or ***steric*** (or both).

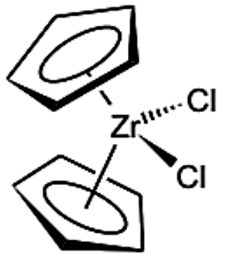
(i) Electronic effects: Late transition metals with d^8 electron configurations *e.g.* Rh(I), Ir(I), Pd(II), Pt(II) have a strong tendency to form square planar 16 ve complexes. Similarly, d^{10} complexes tend to form trigonal 16 ve complexes. As the atomic number Z increases, the d-shell is stabilized (lowers in energy). The occupied d_{z^2} orbital (perpendicular to the plane) is no longer involved in ligand bonding.



d^8 square planar

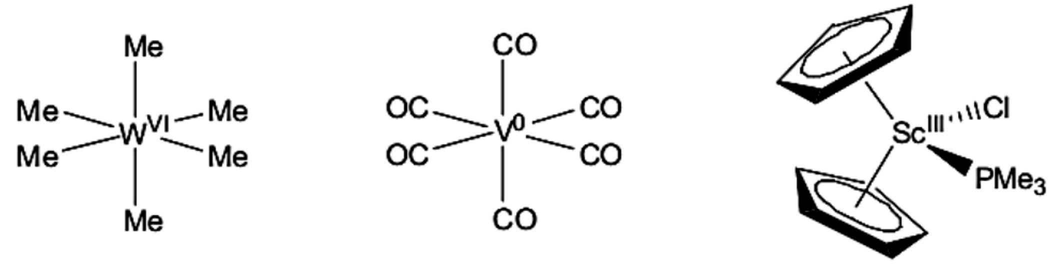
d^{10} trigonal

(ii) Steric Effects: Early transition metals have fewer d-electrons to start with than the middle and late transition metals, so they must achieve their 18e count by coordination of a larger number of ligands. If the ligands involved are too bulky, then low-electron count complexes are formed.



The 16e "Zirconocene dichloride."

Steric effects can produce low-coordinate (not many ligands) complexes which often have <18 electrons. For early transition metals (*e.g.* with d^0 metals) it is often not possible to fit the number of ligands necessary to reach 18 electrons around the metal.



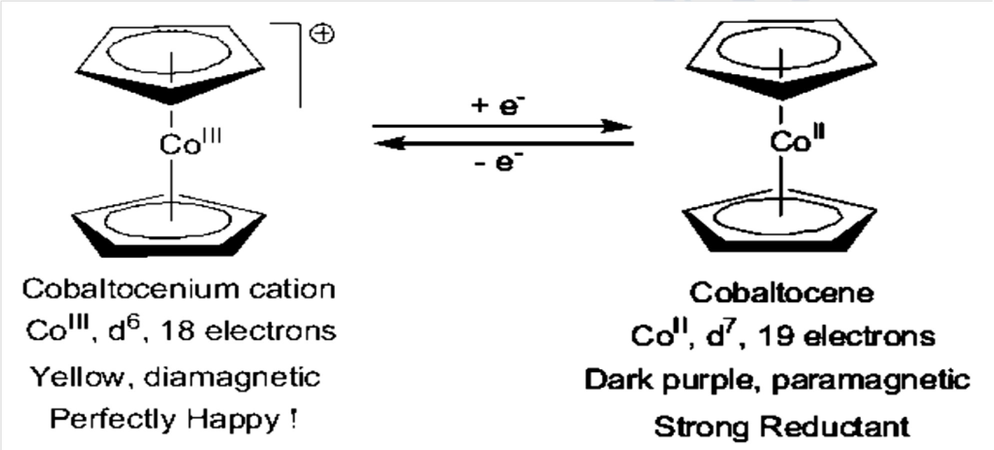
W^{6+} d^0 12 electrons V^0 d^5 17 electrons Sc^{3+} d^0 16 electrons

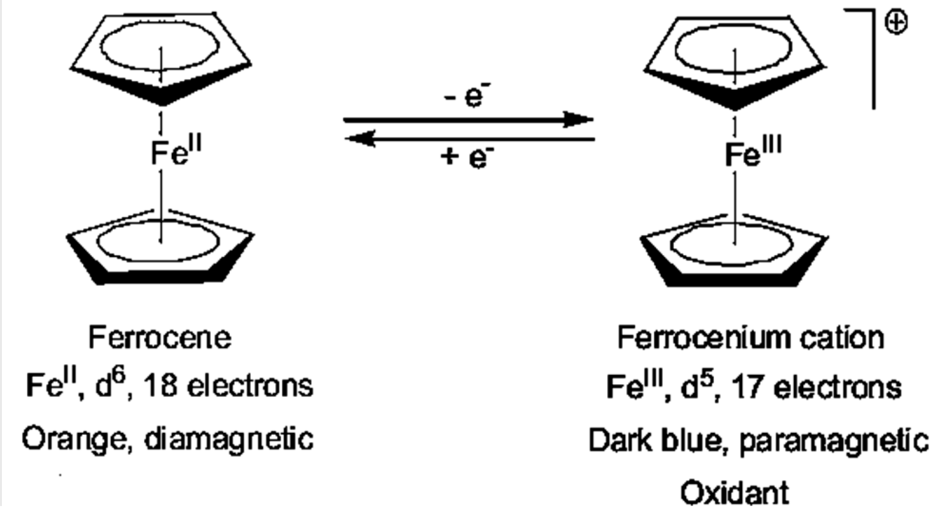
Linear complexes (d^{10}, 14 electrons): d^{10}-metals with 2 ligands, so 14-electron complexes. Common for Ag(I), Au(I) and Hg(II), Less for Cu(I), Zn(II) and Cd(II).

Explanation: For d^{10} compounds, there is a relatively small energy difference between the d, s and p orbitals (e.g. 5d, 6s and 6p for Au(I)). More common for group 11 (Cu, Ag, Au) than group 12 (Zn, Cd, Hg) because the energy difference between the d, s and p-orbitals is smaller for group 11.

More common for the heavier elements (Ag(I), Au(I), Hg(II). However, there are also lots of tetrahedral complexes of Ag(I), Au(I), Cu(I), Zn(II), Cd(II) and Hg(II) (*e.g.* 14 e- linear $[(R_3P)AuCl] + 2PR_3$ == 18 e- tetrahedral $[(R_3P)_3AuCl]$).

Strong oxidants or reductants: Many 18 electron compounds can be reduced or oxidised to give 17 or 19 electron compounds, respectively. Such compounds are often good oxidizing or reducing agents (i.e. they want to get back to being 18-electron compounds).





Why 18 Electrons?

A good example of a complex that obey to the 18-electron rule is $Cr(CO)_6$. The molecular orbitals of interest in this molecule are those that result primarily from interactions between the *d* orbitals of Cr and the σ-donor (HOMO) and π-acceptor orbitals (LUMO) of the six CO ligands. The relative energies of molecular orbitals resulting from these interactions are shown in below.

Chromium(0) has **6 electrons** outside its noble gas core. Each CO contributes a pair of electrons to give a total electron count of **18es.**. In the molecular orbital diagram, these 18 electrons appear as the (**12 σ**) electrons—the **σ** electrons of the CO ligands, stabilized by their interaction with the metal orbitals—and the (**6 t_2g)** electrons. Addition of one or more electrons to $Cr(CO)_6$ would populate the ***eg*** orbitals, which are antibonding; the consequence would be destabilization of the molecule. Removal of electrons from Cr(CO)6 would depopulate the ***t_2g*** orbitals, which are bonding as a consequence of the strong π-acceptor ability of the CO ligands (Figure 2) ; a decrease in electron density in these orbitals would also tend to destabilize the complex. The result is that the 18 electron configuration for this molecule is the most stable.

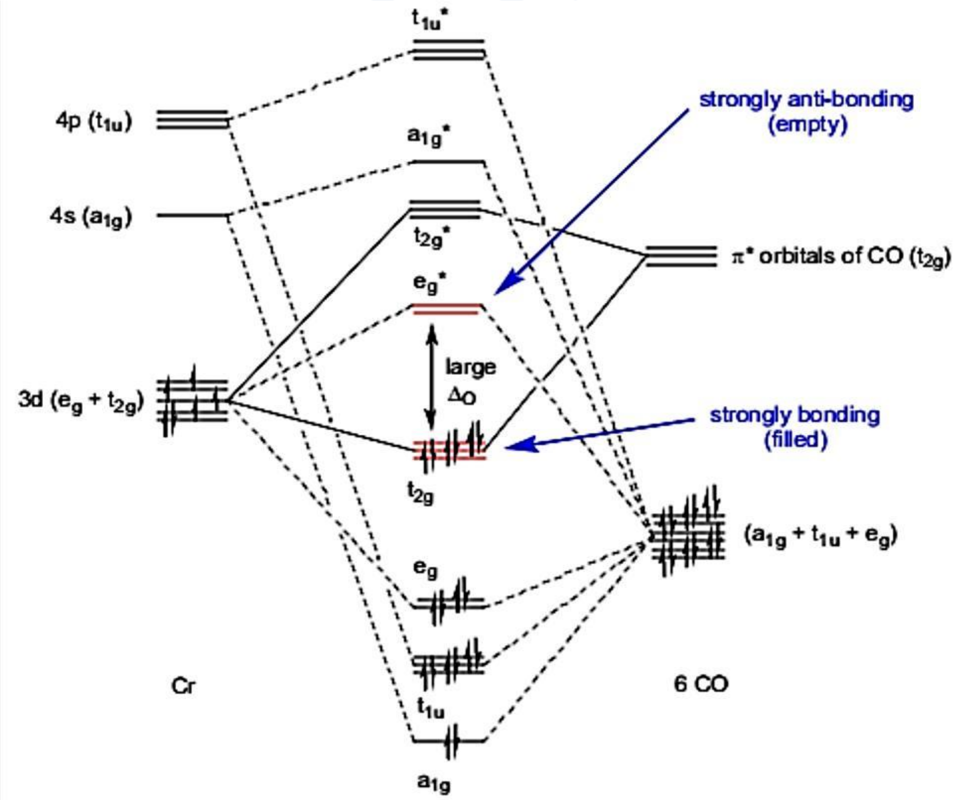


Figure 2

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 might be reluctant 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. 1). 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. **$Cp_2Fe + H^+ = [Cp_2FeH]^+$ (1)**

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. 1 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. 1. 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 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. **$W(CO)_5(thf) + Cl^- = [W(CO)_5Cl]^-$ (2)**

The reaction of Eq. 3 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 (such as Ph_3C^+) must be used. In this way the 18e rule helps us pick the right reagent.

$Cp(CO)_2Fe{-}CH(CH_3)_2 + Ph_3C^+ = [Cp(CO)_2Fe(\eta_2\text{-}CHMe{=}CH_2)]^+ + Ph_3CH$ (3)

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

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 (OS) 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. 4. 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 that corresponds to the oxidation state we have assigned. For Cp_2Fe^+ the OS 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 = 5e. Cp_2Fe^+ is therefore said to be a d^5 complex. Equation 5 gives the value of *n* in a general form. The significance of the *dn* configuration is that it tells us how to fill up the crystal field diagrams. For example, the odd number for Cp_2Fe^+ implies paramagnetism because in a mononuclear complex we cannot pair five electrons whatever the *d*-orbital splitting.

$$OS = c + a \qquad (4)$$

$$n = N - (c + a) = N - c - a \qquad (5)$$

Many organometallic compounds have low or intermediate formal oxidation states. High oxidation states are now gaining more attention, we look at these interesting species in detail. 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.

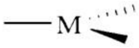
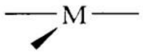
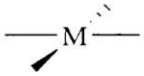
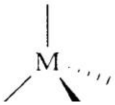
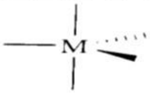
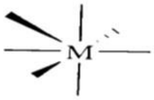
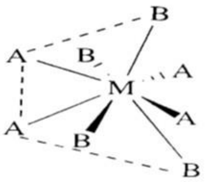
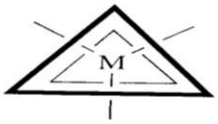
High oxidation states can be accessible if the ligands are small and non-π-bonding like H or Me, however, as in the d^0 species WMe_6 and $ReH_7(dpe)_2$. It is often useful to refer to the oxidation state and d^n configuration, but they are a formal classification only and do not allow us to deduce the 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 hexa hydride may even be more reduced and more electron rich than the W(0) carbonyl. 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. For this reason, the term *formal oxidation state* is often used for the value of OS as given by Eq. 4. The oxidation state of a complex can never be higher than the group number of the transition metal involved. Titanium can have no higher oxidation state than Ti(IV), for example, because Ti has only four valence electrons with which to form bonds and $TiMe_6$ therefore cannot exist.

Coordination number and geometry:

The coordination number (CN) 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., $[PtCl_4]^{2-}$, CN = 4, $W(CO)_6$, CN = 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 needs its own orbital. In most cases the CN is 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 6 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., $Pt(PCy_3)_2$], distance of the metal)? Most often, it is the second definition that is used, which is equivalent to counting up the number of lone pairs provided by the ligands on the ionic model. We use this as the CN in what follows.

Table 6 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		$ReH(PR_3)_3(MeCN)_3{}^{2+}$
	pentagonal bipyramid		$IrH_5(PPh_3)_2$
8	dodecahedral[a]		$MoH_4(PR_3)_4$
	square antiprism		$TaF_8{}^{3-}$
9	tricapped[b] trigonal prism		$ReH_9{}^{2-}$

Equations 6 – 9 summarize the different counting rules as applied to our generalized d^n transition metal complex $[MX^aL^b]^{c+}$, where N is the group number. In Eq. 6, the CN cannot exceed 9:

$$\textbf{Coordination number: } CN = a + b \leq 9 \qquad (6)$$

$$\textbf{Electron count: } N + a + 2b - c = 18 \qquad (7)$$

$$\textbf{Oxidation state: } OS = a + c \leq N \qquad (8)$$

$$d^n \textbf{ configuration: } d^n = d^{(N-OS)} = d^{(N-a-c)} \qquad (9)$$

d^n Configuration and Geometry

The d^n configuration of the metal is a good guide to the preferred geometry adopted, as indicated in Table.7, because of the ligand field effects specific to each configuration. The d^0, d^5 (hs), and d^{10} configurations are special because they have the same number of electrons (zero, one, or two) in each *d* orbital. This symmetric electron distribution means there are no ligand field effects and the ligand positions are sterically determined. The standard model for predicting geometries in main-group chemistry, VSEPR (valence shell electron pair repulsion), works reliably only when ligand field effects are absent. In transition metal systems, this means only for d^0, d^5 (hs), and d^{10} cases where the *d* electrons are not considered. For example, in d^{10} PtL_4, we consider only the four L lone pairs, which, in accordance with VSEPR, are arranged in a tetrahedral geometry.

Steric Effects and Geometry

Large ligands favor low coordination numbers [e.g., $Pt(PCy_3)_2$]. These ligands also favor distortions from electronically preferred geometries. For example, $[CuBr_4]^{2-}$, $[Ni(CN)_4]^{2-}$, and $[PtI_4]^{2-}$ electronically prefer square planar, but steric effects cause a distortion toward the less hindered tetrahedral geometry.

Table 7 Common Geometries with Typical d^n Configuration

Coordination Number	Geometry	d^n Configuration	Example
3	T-shaped	d^8	$[Rh(PPh_3)_3]^+$
4	Tetrahedral	d^0, d^5(hs), d^{10}	$Pd(PPh_3)_4$
4	Square planar	d^8	$[RhCl(PPh_3)_3]$
5	Trigonal bipyramidal	d^8, $\{d^6\}^a$	$[Fe(CO)_5]$
6	Octahedral	d^0, d^3, d^5(ls), d^6	$[Mn(CO)_6]^+$
8	Dodecahedral	d^2	$WH_4(PMePh_2)_4$
9	TTP[b]	d^0	$[ReH_9]^{2-}$

[a] $\{d^6\}$ means that a distorted version of this geometry occurs for this *d* configuration.
[b] Tricapped trigonal prism. hs = high spin; ls = low spin.

Polarization:

Another important situation occurs 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. 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: $\mathbf{M - N^{\partial+} \Xi N^{\partial-}}$

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, nonpolar and notably unreactive. 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. Paradoxically, stronger binding does not always lead to stronger ligand activation. An excellent example is coordinated H_2 a ligand that is enormously acidified on binding.

Differences between 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. 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 these electrons 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. Ligands such as 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. This makes the ligand subject to attack by nucleophiles Nu^- and is the basis for important applications in organic synthesis. Table 8 shows that several types of changes all cause an increase in v(CO) values of metal carbonyls, corresponding to a reduction in the basicity of the metal and in the strength of back bonding to CO: (1) making the net ionic charge one unit more positive, (2) replacing one CO by a pure σ-donor amine ligand, and (3) moving to the right by one periodic group. All three changes seem to have approximately equal effects.

Table 8 Effects of Changing Metal, Net Charge, and Ligands on π Basicity of Metal, as Measured by v(CO) Values (cm^{-1}) of the Highest Frequency Band in i.r

Changing Metal Across the Periodic Table

$V(CO)_6$	$Cr(CO)_6$	$Mn_2(CO)_{10}$	$Fe(CO)_5$	$Co_2(CO)_8$	$Ni(CO)_4$
1976	2000	2013(av)	2023(av)	2044(av)	2057
$Cr(CO)_4$			$Fe(CO)_4$		
1938			1995		

Changing Metal down the Periodic Table

$[Cr(CO)_6]$	$[Mo(CO)_6]$	$W(CO)_6$
2000	2004	1998

Changing Net Ionic Charge in an Isoelectronic Series

$[Ti(CO)_6]^{2-}$	$[V(CO)_6]^-$	$Cr(CO)_6$	$[Mn(CO)_6]^+$
1747^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

The first series, going from $[Ti(CO)_6]^{2-}$ to $[Fe(CO)_6]^{2+}$, involves changes of metal as well as of ionic charge, but comparison with the series $Cr(CO)_4$ to $Ni(CO)_4$ suggests that about one half of the total effect is due to the change of metal and the other half to the change in ion charge. 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 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), (VI), 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.

Problems:

1. Give the electron counts, formal oxidation states, and *dn* configurations of the following: $[Pt(NH_3)_4]^{2+}$, $PtCl_2(NH_3)_2$, $PtCl_4^{2-}$, $(\eta^5\text{-}C_5H_5)_2Ni$, $[(R_3P)_3$, $Ru(\mu\text{-}Cl)_3Ru(PR_3)_3]^+$, $ReH_9{}^{2-}$, $CpIrMe_4$, $TaMe_5$, $(\eta^5\text{-}C_5H_5)_2TiCl_2$, 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 additional ligands?

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

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

5 – The electron counts of both $Mn(CO)_5$ and $Co(CO)_4$ were 17, how could they react to form more stabilized complexes or to obey 18e rule.

Carbonyls, Phosphine complexes and ligand substitution reactions

We first examine how CO, phosphines, and related species act as ligands, then look at ways in which one ligand can replace another in a *substitution* reaction:

$$L_nM{-}L + L^{\sim} = L_nM{-}L^{\sim} + L \qquad (10)$$

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.

Metal complexes of CO, RNC, CS, and NO:

A chance 1884 observation by Ludwig Mond led to an important advance in the nickel refining industry. When he found his nickel valves were being eaten away by CO, he deliberately heated Ni powder in a CO stream to form a volatile compound, $Ni(CO)_4$, the first metal carbonyl. The Mond refining process was based on the fact that the carbonyl can be decomposed to give pure nickel by further heating. Unlike a simple alkyl, CO is an unsaturated ligand, by virtue of the C−O multiple bond. Such ligands are soft because they are capable of accepting metal *dπ* 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). CO can act as a spectator or an actor ligand. We look first at the frontier orbitals of M and L because these usually dominate the M−L bonding.

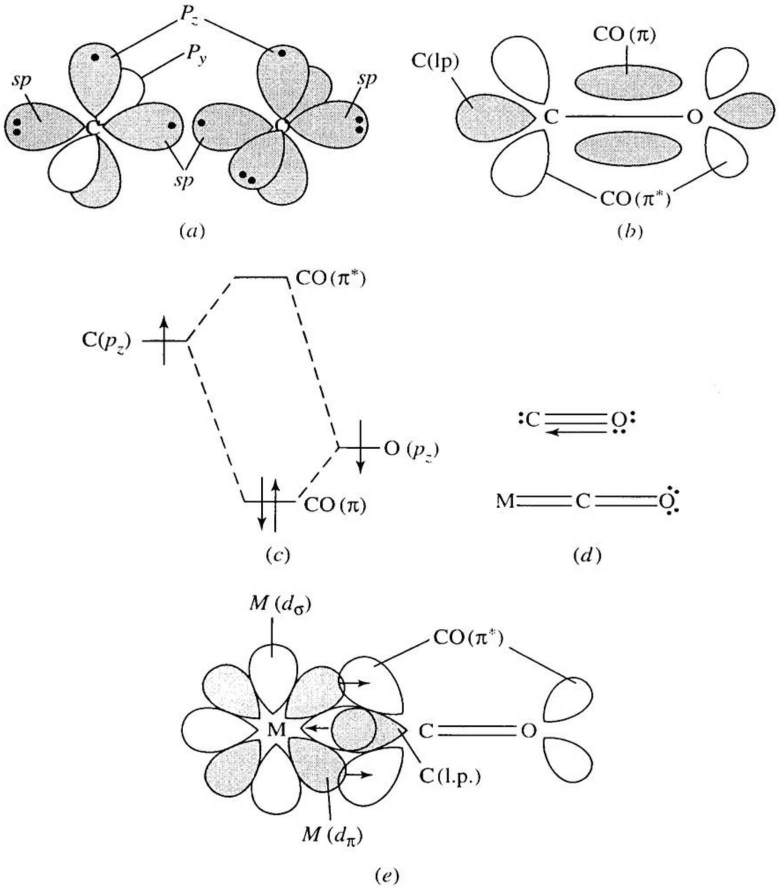


Figure2 Electronic structure of CO and carbonyl complexes. Shading represents occupied orbitals (*a*) and (*b*) building up CO from C and O, each atom having two *p* orbitals and two *sp* hybrids. In (*a*), the dots represent the electrons occupying each orbital in the C and O atoms. In (*b*), only one of the two mutually perpendicular sets of *π* orbitals is shown. (*c*) An MO diagram showing a *π* bond of CO. (*d*) Valence bond representations of CO and the MCO fragment. (*e*) An MO picture of the MCO fragment Again, only one of the two mutually perpendicular sets of *π* orbitals is shown.

The electronic structure of free CO is shown in Fig. 2*a* and 1*b*. We start with both the C and the O *sp* hybridized. The singly occupied *sp* and *pz* orbitals on each atom form a *σ* and a *π* bond, respectively. This leaves the carbon *py* orbital empty, and the oxygen *py* orbital doubly occupied, and so the second *π* bond is formed only after we have formed a dative bond by transfer of the lone pair of O*(py)* electrons into the empty *C(py)* 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.2*c* the reason for the polarization of the *πz* orbital is shown in MO terms. An orbital is always polarized so as to favor the AO that is closest in energy and so the C−O *π* MO has more O than C character. The valence bond picture of CO and one form of the MCO system is shown in Fig. 2*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 have lower energy. 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 2*e* shows how the CO HOMO, the carbon lone pair, donates electrons to the metal LUMO, the empty M(d^{σ}) orbital, and metal HOMO, the filled M*(dπ)* orbital, back donates to the CO LUMO. While the former removes electron density from C, the latter increases electron density at both C and 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 metal-induced polarization chemically activates the CO 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*n*M(CO), the CO carbon becomes 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 range can be represented in valence bond terms as **1**, * the extreme in which CO acts as a pure *σ* donor, through **2** and **3**, 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.

$$\begin{array}{ccc} \mathbf{M^{-}\longleftarrow C^{\partial +}\Xi\ O^{+}} & \mathbf{M = C = O} & \mathbf{M^{+}\ \ \Xi\ \ C\ \ -} \\ \mathbf{O^{-}\ 1} & \mathbf{2} & \mathbf{3} \end{array}$$

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 **1–3** is 2e. The same e count applies to all true resonance forms. We can tell where any particular CO lies on the continuum between **1** and **3**, by looking at the IR spectrum. Because **3** has a lower C=O bond order than **1**, the greater the contribution of **3** to the real structure, the lower the observed CO stretching frequency, *v(*CO*)*; the normal range is 1820–2150 cm^{-1}. The MO picture leads to a similar conclusion. As the metal to CO *π** back bonding becomes more important, we populate an orbital that is antibonding with respect to the C=O bond, and so we lengthen and weaken the CO 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 spectroscopy is extremely useful. From the band position, we can tell how good the metal is as a *π* base. From the number and pattern of the bands, we can tell the number and stereochemistry of the COs present.

Carbonyls bound to very poor *π*-donor metals, where **1** is the predominant contributor to the bonding, have very high *v*(CO) bands as a result of weak back donation. When these appear to high energy of the 2143 cm^{-1} band of free CO, the complexes are sometimes called *nonclassical carbonyls*.1a Even d^0 species can bind CO. One of the most extreme weak *π*-donor examples is $[Ir(CO)_6]^{3+}$ with *v*(CO) bands at 2254, 2276, and 2295 cm^{-1}. The X-ray structure of the related complex $[IrCl(CO)_5]^{2+}$ shows the long M−C [2.02(2)A°] and short C−O [1.08(2)A°] distances expected from structure **1**.1c The highest oxidation state carbonyl known is *trans*-$[OsO_2(CO)_4]^{2+}$ with *v(*CO*)* = 2253 cm^{-1}.1c Carbonyls with exceptionally low *v*(CO) frequencies are found for negative oxidation states (e.g., $[Ti(CO)_6]^{2-}$; *v(*CO*)* = 1747 cm^{-1}) or where a single CO is accompanied by non-π-acceptor ligands (e.g., $[ReCl(CO)(PMe_3)_4]$; *v(*CO*)* = 1820 cm^{-1}); these show short M−C and long C−O bonds. Although **1– 3** represent three ideal structures in the bonding range possible for CO, no one structure can be said to perfectly represent the situation for any particular case. There is therefore considerable looseness in the way carbonyls are represented in organometallic structures. Often, M−CO or M−C=O are used.

Preparations of CO Complexes: Typical examples are shown in Eqs. 11– 16:

1. From CO:

$Fe \xrightarrow{CO,\ 200\ atm.\ 200^{\circ}} Fe(CO)_5$ **(11)**

$IrCl(cod)L_2 + CO$---------- $IrCl(CO)L_2$ **(12)** $L = PMe_3$

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

$NiSO_4 + CO + S_2O_4^{2-}$--------- $Ni(CO)_4$ **(13)**

$Re_2O_7 + 17CO$ ---------- $(CO)_5Re\text{-}Re(CO)_5 + 7CO_2$ **(14)**

$Cr(CO)_4(tmeda)Na$-------- $Na_4[Cr(CO)_4]$ **(15)** tmeda= $Me_2NCH_2CH_2NMe_2$

3. From a reactive organic carbonyl compound:

$RhClL_3 + RCXO$ oxidative addition-----$\{XRhCl(COR)L_3\}$

$\{XRhCl(CO)RL_2\}$ reductive elimination----- $RX + RhCl(CO)L_2$ **(16)** $L = PPh_3$; X = H 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 5 illustrates the high tendency of CO groups to stabilize M−M bonds; not only are COs 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. The ability of CO to stabilize polyanionic species by acting as a strong π acceptor and delocalizing the negative charge over the CO oxygens. $Na_4[Cr(CO)_4]$ has the extraor dinarily low *v*(CO) of 1462 cm^{-1}, the extremely high anionic charge on the complex, and ion pairing of Na+ to the carbonyl oxygen contribute to the lowering by favoring the M≡C−ONa resonance form, which is related to **3**. 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. 16, the reaction requires three steps; the second step is the reverse of migratory insertion. The success of the reaction in any given instance relies in part 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 so 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.

Vibrational Spectra of Metal Carbonyls:

Infrared spectra have been widely used in the study of metal carbonyls since the C-O stretching frequencies give very strong sharp bond well separated from other vibrational modes of any other ligands that may also present. The CO molecule has a stretching frequency to 2143 cm^{-1} Terminal CO groups in neutral metal carbonyl molecules are found in the range 2125-1850 cm^{-1}. The most important use of IR spectra of CO compounds is in structural diagnosis, where bridging and terminal CO groups can be recognized. For terminal M-CO, the frequencies of C-O stretches range from 1860 to 2125 cm^{-1} but for bridging CO groups the range is 1750- 1850 cm^{-1}.

- When changes are made that should increase the extent of M-C back bonding, the CO frequencies are shifted to even lower values.

- Thus, if some CO groups are replaced by ligands with low or regligible back-accepting ability, those CO groups that remain must accept more d n electrons from the metal to prevent the accumulation of-ve charge on the metal atom.

e.g. : $Cr(CO)_6$ frequency 2000 cm^{-1}; $Cr(CO)_3$(dien), 1900 and 1760 Cm^{-1}

Similarly in $V(CO)_6$ where more -ve charge must be taken from the metal atom a band is found at 1860 cm^{-1} , while it is found at 2000 cm^{-1} in $Cr(CO)_6$. Conversely, a change that would tend to inhibit the shift of electrons from metal to CO σ orbital such as placing a +ve charge on the metal should cause the CO frequencies to rise.

e.g.: $Mn(CO)_6$,~ 2090; Mn (dien)$(CO)_3$, -2020, ~ 1900; $Cr(CO)_6$, ~ 2000 Cr dien $(CO)_3$, ~ 1900, ~1760; $V(CO)_6$,~ 1860. The frequency of terminal CO stretches can be quite low if:

a) There are a number of ligands present that are good donor but poor π -acceptors, or

There is a net -ve charge on the molecule. In either case, back- donation to CO group becomes very extensive thus increasing the **M-C** bond orders, decreasing the C-O bond orders and driving the CO stretching frequencies down.

Carbonylate anions and Carbonyl Hydrides

Carbonylate anions are formed when carbonyls are treated with aqueous or alcoholic alkali hydroxide or with amines, sulfoxides, or other Lewis bases, when M-M bonds are cleaved with sodium or when certain carbonlys are refluxed with salts in an ether, e.g. as mention above. The stoichiometrics of the simpler carbonylate ions obey the nobel-gas formalism, (octet configuration). Most of them are readily oxidized by air.

The alkali-metal salts are soluble in water from which they can be precipitated by large cations such as [Ph4As]+ . There are also many polynuclear species those of iron have been much studied. They are obtained by reactions such as

$$Fe_2 (CO)_9 + 40H^- \longrightarrow [Fe_2(CO)_8]^{2-} + 2H_2O + CO \qquad (17)$$

$$Fe(CO)_5 + Et_3N \xrightarrow{H_2O,\ 80^oC} [Et_3NH][HFe_3(CO)_{11}] \qquad (18)$$

- An important general reaction of carbonylate anions or substituted carbonylate ions is with halogen compounds. By this reaction M-C or M-M bonds can be formed.

- Typical examples are:

$$Mn(CO) + C1CH_2CH = CH_2 — (CO)_5MnCH_2CH = CH_2 + Cl^- \qquad (19)$$

$$Fe(CO) + 2Ph_3PauCl \qquad (Ph_3PAu)_2\ Fe\ (CO)_4 + 2Cl^- \quad (20)$$

$$Co(CO)_4 + Mn(CO)_5Br(OC)_4 \qquad CoMn(CO)_5 + Br^- \qquad (21)$$

Carbonyl hydrides:

In some cases, hydrides corresponding to carbonylate anions can be isolated.

- carbonyl hydrides are usually rather unstable.

- They can be obtained by acidification of appropriate alkali carbonylates or in other ways. **e.g**:

$$NaCo(CO)_4 + H^+aq \qquad HCo(CO)_4 + Na^+ (aq) \quad (22)$$

$$Fe(CO)_4I_2 + H_2 \qquad H_2Fe(CO)_4 \qquad (23)$$

$$[Mn_2(CO)_{10}] + H_2 \xrightarrow{200atm,\ 200^oC} 2HMn(CO)_5 \qquad (24)$$

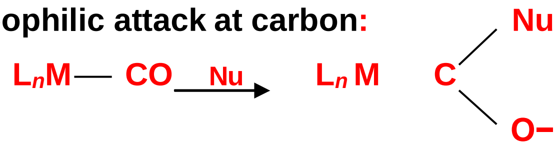
$$CO + 4CO + {}^1/_2H_2 \xrightarrow{50atm,\ 150^oC} HCO(CO)_4 \qquad (25)$$

The hydrides are slightly soluble in water where they behave as acids, ionizing to give the carbonylate ions. The carbonyl hydrides have sharp M-H stretching bands in the ir and proton magnetic resonanc (PMR) at very high x values (very low 8 values). The hydrogen atom occupies a regular place in the coordination polyhedron and the M-H distances are approximately equal to the values expected from the sum of single-bond covalent radii. A good example is afforded by the structure of $HMn(CO)_5$.

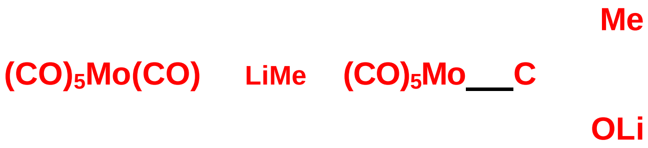
Reactions of Metal Carbonyls:

Typical reactions are shown in Eqs. 26 – 31. 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:



(26)



$$\mathrm{(CO)_5Mo(CO)} \quad \mathrm{LiMe} \quad \mathrm{(CO)_5Mo{-}C}\begin{matrix}\mathrm{Me}\\ \\ \mathrm{OLi}\end{matrix}$$

(27)

$[Cp(NO)(PPh_3)ReCO]^+$ $LiBHEt_3$ $Cp(NO)(PPh_3)Re(CHO)$ (28)

This reaction (Eq. 10) produces the unusual formyl ligand, which is important in CO reduction to MeOH. It is stable in this case because the 18e complex provides no empty site for rearrangement to a hydridocarbonyl complex.

2. Electrophilic attack at oxygen:

$Cl(PR_3)_4Re{-}CO$ $AlMe_3$ $[Cl(PR_3)_4Re{-}CO{\rightarrow}AlMe_3]$ (29)

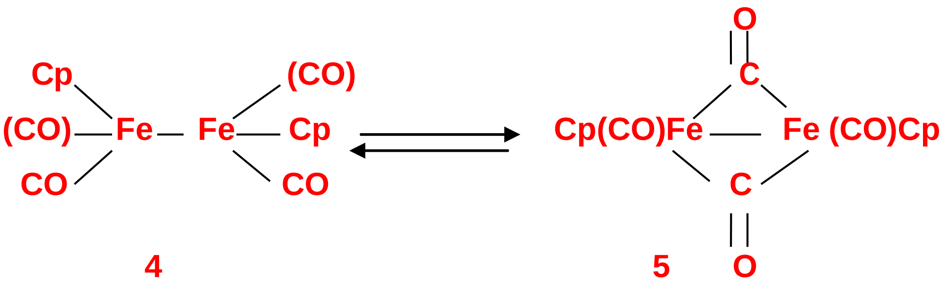
Protonation of this Re carbonyl occurs at the metal, as is most often the case, but the bulkier acid, $AlMe_3$, prefers to bind at the CO oxygen.

3. Finally, there is the migratory insertion reaction:

$MeMn(CO)_5$ PMe3 $(MeCO)Mn(CO)_4(PMe_3)$ (30)

Bridging CO Groups:

CO has a high tendency to bridge two metals (e.g., **4 and 5**):



(31)

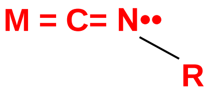
4 5

The electron count remains unchanged on going from **4** to **5**. The 15e CpFe(CO) fragment is completed in **4** by an M−M bond, counted as a 1e contributor to each metal, and a terminal CO counting as 2e. In **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 ketonelike 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. Triply and even quadruply bridging CO groups are also known in metal cluster compounds. These have CO stretching frequencies in the range of 1600–1730 cm^{-1}.

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 in many cases 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 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 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 v(CO) but raises v(CN). Back bonding lowers both v(CO) and v(CN). Depending on the balance of σ versus π bonding, v(CN) is raised for weak π-donor metals, such as Pt(II), and lowered for strong π-donor metals, such as Ni(O). Cases such as $NbCl(CO)(CNR)(dmpe)_2$ have been found in which back bonding to an isonitrile is so strong that this normally linear ligand becomes bent at N (129° –144°), indicating that the resonance form **6** has become dominant. The M−C bond is also unusually short (2.05 °A compared to 2.32 A° for an Nb−C single bond) in the bent isonitrile case, and the v(CN) is unusually low (1750 cm^{-1} compared to ~ 2100 cm^{-1} for the linear type), again consistent with the structure **7.** 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.



$$M = C= N^{\bullet\bullet}\!\!-R \qquad (6)$$

Thiocarbonyls:

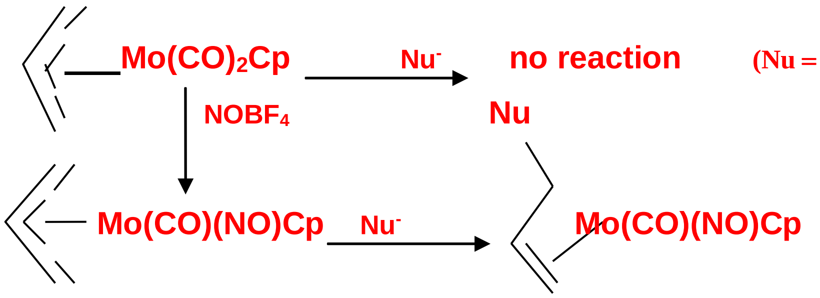
CS is not stable above −160°C in the free state, but a number of complexes are known, such as $RhCl(CS)(PPh_3)$ (Eq. 32) and $Cp(CO)Ru(\mu^2\text{- }CS)_2RuCp(CO)$, but so far no “pure” or *homoleptic* examples of $M(CS)_n$. They are usually made from CS_2 or by conversion of a CO to a CS group. Perhaps 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 **3** 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.

$$RhCl(PPh_3)_3 + \quad CS_2 \quad \text{--------} \quad \textit{trans}\text{-}RhCl(CS)(PPh_3)_2 + SPPh_3 \qquad (32)$$

Typical $v(CS)$ ranges for CS complexes are 1273 cm^{-1} for free CS, 1040–1080 cm^{-1} for $M_3(\mu_3\text{-}CS)$, 1100–1160 cm^{-1} for $M_2(\mu_2\text{-}CS)$, and 1160–1410 cm^{-1} for M−CS.

Nitrosyls:

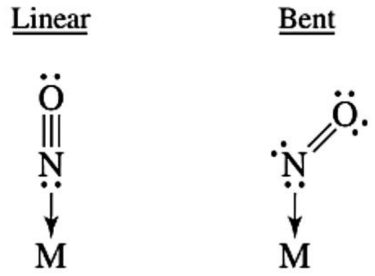
Free NO is a stable free radical because the ON−NO bond in the dimer is very weak. In a surprising development, NO was found to be important in biological signaling having a biosynthetic pathway and specialized sensor proteins. It forms an extensive series of diamagnetic nitrosyl complexes by binding to odd-electron metal fragments. As an alternative to using free NO for the synthesis of nitrosyl complexes, 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 ligand on the covalent model. NO^+ is isoelectronic with CO and thus binds in a linear fashion. 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 for such a reaction (e.g., Eq. 33.)



(Nu = enamine or PhMgBr)

(33)

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. 3). In bringing $CpMo(CO)_2$ and NO together to form $CpMo(CO)_2$(*lin*-NO), we first remove the unpaired electron 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.



M—N—O angle	165°–180°	119°–140°
ν (N-O) in neutral molecules	1610–1830 cm^{-1}	1520–1720 cm^{-1}
Electron donor count	2 (as NO^+) 3 (as neutral NO)	2 (as NO^-) 1 (as neutral NO)

The formal oxidation state of the metal is obtained by considering a linear NO as NO^+ and a bent NO as NO^-, for example Cr(*lin*-NO)$_4$ is formally Cr(-IV) with the tetrahedral geometry appropriate for d^{10}. The conversion of a linear to a bent NO is considered to lead to an increase in the formal oxidation state by two units (Eq. 34). Raising the e 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^-.

For example, the Fe(III) center in the oxidized form of myoglobin, an iron protein found in muscle, forms a linear NO complex, but on reduction to Fe(II) the NO switches to the bent form. On the covalent model, a linear NO is a 3e ligand. In this case there is no need to rehybridize. The metal has a singly occupied $d\pi$ orbital, which binds with the singly occupied NO(π^*) to give an M−N π bond, and the N(lp) (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 such as 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.

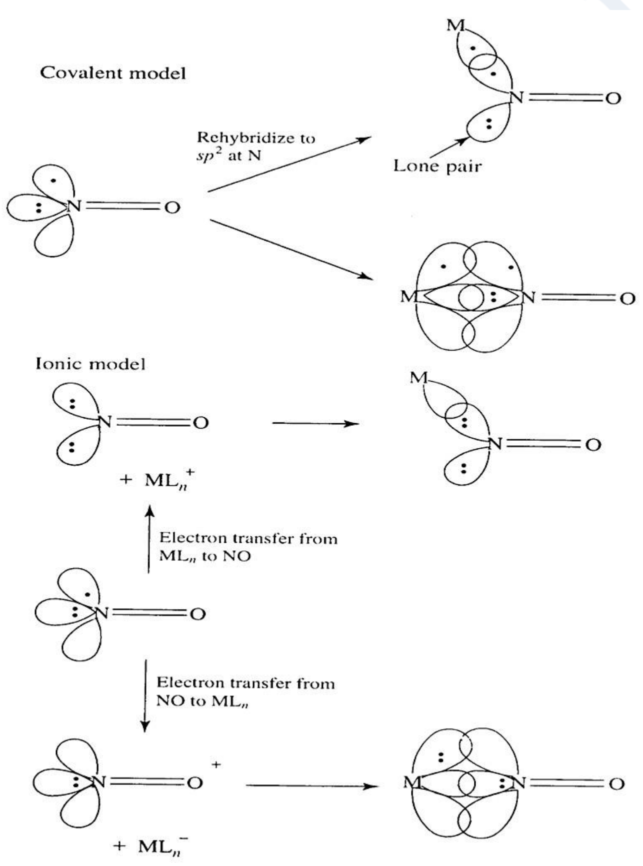


Figure 3 Electronic structure of NO and its binding to a metal fragment on the covalent and ionic models.

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. The 16e bent NO complexes are not uncommon. Some complexes have both bent and linear NO: for example, ClL_2Ir(*lin*-NO)(*bent*-NO). Equations 34 and 35 show examples where the linear and bent nitrosyl isomers are in equilibrium. For the Co case, the linear complex has v(NO) at 1750 cm^{-1} and the bent NO has v(NO) at 1650 cm^{-1}; unfortunately, the typical v(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 Eq. 36, can we safely assign a bent structure.

$$\underset{\text{18e, Co(I)}}{CoCl_2L_2(\textit{lin}\text{-}NO)} \rightleftarrows \underset{\text{16e, Co(III)}}{CoCl_2L_2(\textit{bent}\text{-}NO)} \qquad (34)$$

$$\underset{\text{18e, Ir(I)}}{(o\text{-}C_6H_4O_2)_2L_2Ir(\textit{lin}\text{-}NO)} \rightleftharpoons \underset{\text{16e, Ir(III)}}{(o\text{-}C_6H_4O_2)_2L_2Ir(\textit{bent}\text{-}NO)} \qquad (35)$$

$$(L = PPh_3)$$

$$\underset{\text{18e, Co(I)}}{[Co(\textit{lin}\text{-}NO)(diars)_2]^{2+} + X^-} \rightleftharpoons \underset{\text{18e, Co(III)}}{[CoX(\textit{bent}\text{-}NO)(diars)_2]^+} \qquad (36)$$

The discovery that NO and CO are important messenger molecules in the mammalian brain and exert their effect by binding to metalloprotein receptors will certainly provoke increased interest in the area.

Typical nitrosyls, together with some preparative routes, are shown in Eqs. 37 – 42. The first two cases show linear–bent equilibria. Equation 36 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 (Eq. 41). The resulting higher-oxidation-state ions cannot usually bind NO, however.

$$Cr(CO)_6 + NO + h\nu = Cr(\textit{lin}\text{-}NO)_4 \qquad (37)$$

$$Mn(CO)_5I + NO = Mn(\textit{lin}\text{-}NO)_3(CO) \qquad (38)$$

$$IrH_5(PR_3)_2 + NO = (R_3P)(\textit{lin}\text{-}NO)_2Ir{-}Ir(\textit{lin}\text{-}NO)_2(PR_3) \qquad (39)$$

$$(toluene)Cr(CO)_3 + NO^+ + MeCN = \textit{trans}\text{-}[Cr(\textit{lin}\text{-}NO)_2(MeCN)_4]^{2+} \qquad (40)$$

$$Pd + 2NO^+ + MeCN = [Pd(MeCN)_4]^{2+} + 2NO \qquad (41)$$

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

$$[CpCo(NO)]^- \xrightarrow{RI} [CpCoR(NO)] \xrightarrow{PPh3} [CpCo(NOR)PPh_3] \qquad (42)$$

Dinitrogen

Dinitrogen (N_2) is a ligand of great importance in connection with biological nitrogen fixation (conversion to ammonia), It binds to metals much less strongly than CO because it is both a weaker σ donor and a weaker π acceptor.

- *Back bonding to CO strengthens the M−C but weakens the C−O bond lowering ν(CO) in the IR spectrum.*
- *M−CO is subject to nucleophilic attack at C particularly when the metal is incapable of strong back bonding.*

Phosphine and related 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 $(R_3P)_nM-L$. Phosphines are more commonly spectator than actor ligands.

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 the π^* orbital accepts electrons from the metal. The σ^* orbitals of the P−R bonds play the role of acceptor in PR_3. Whenever the R group becomes more electro negative, the orbital that the R fragment uses to bond to phosphorus becomes more stable (lower in energy). 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 to σ^*). Both of these factors make the empty σ^* more accessible for back donation. The final order of increasing π-acid character is

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

$P(NR_2)_3$ is a better donor than it should be probably because the basic N lone pairs compete with the metal $d\pi$ orbitals in donating to PR σ^*. Occupation of the P−R 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. 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 M−P distance and a shorter P−O distance. 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.

Tolman Electronic Parameter and Cone Angle

The electronic effect of various PR_3 ligands can be adjusted by changing the R group as, quantified by Tolman, who compared the v(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.

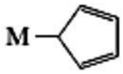
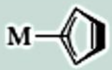
The second important feature of PR_3 as a ligand is the variable steric size, which can be adjusted by changing R. COs are so small that as many can bind as are needed to achieve 18e. In contrast, the same is rarely true for phosphines, where only a certain number of phosphines can fit around the metal. This can be a great advantage in that by using bulky PR_3 ligands, we can favor forming low-coordinate metals or we can 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 to a single metal 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 $W(PMe_3)_6$, a rare case of a hexakis–phosphine complex.

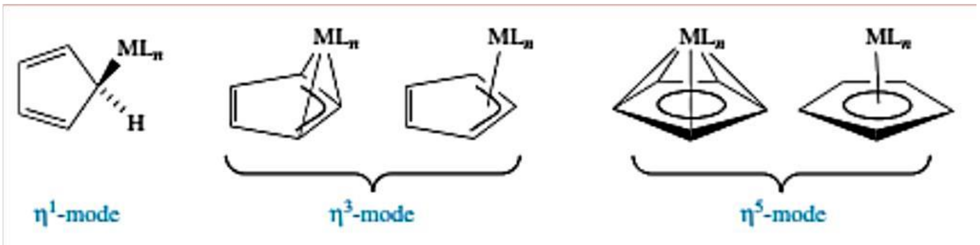
An important part of organometallic chemistry consists in the steric and electronic nature of the ligand environment of a complex to promote whatever properties are desired: activity or selectivity in homogeneous catalysis, reversible binding of a ligand, facile decomposition, or high stability. A key feature of the PR_3 series of ligands is that we can relatively easily change electronic effects without changing steric effects [e.g., by moving from PBu_3 to $P(O\mathit{i}Pr)_3$] or change steric effects without changing electronic effects [e.g., by moving from PMe_3 to P(*o*-tolyl)$_3$]. One outcome of increasing the ligand electron donor strength, for example, might be to perturb an oxidative addition/reductive elimination equilibrium in favor of the oxidative addition product. Likewise, increasing the steric bulk is expected to favor low-coordination-number species. We can therefore expect the chemistry of a phosphine-containing complex to vary with the position of the phosphine in the Tolman map.

Ligands Having Extended π-Systems

Cyclopentadienyl (Cp) Complexes

The cyclopentadienyl group, C_5H_5, may bond to metals in a variety of ways, with many examples known of the η^1-, η^3-, and η^5-bonding modes. The discovery of the first cyclopentadienyl complex, ferrocene, was a landmark in the development of organometallic chemistry and stimulated the search for other compounds containing π-bonded organic ligands. Substituted cyclopentadienyl ligands are also known, such as $C_5(CH_3)_5$, often abbreviated Cp*, and C_5(benzyl)$_5$. C_5H_5, probably the second ligand in organometallic chemistry (after CO), most commonly bonds to metals through five positions, but under certain circumstances, it may bond through only one or three positions. As a ligand, C_5H_5 is commonly abbreviated Cp. The corresponding formulas and names are designated as follows;

Number of Bonding Positions	Formula	Name	
1	η^1-C_5H_5	Monohaptocyclopentadienyl	
3	η^3-C_5H_5	Trihaptocyclopentadienyl	
5	η^5-C_5H_5	Pentahaptocyclopentadienyl	



Ferrocene, (η^5-$C_5H_5)_2$Fe: Ferrocene is the prototype of a series of sandwich compounds, the metallocenes, with the formula $(C_5H_5)_2M$. Electron counting in ferrocene can be viewed in two ways. One possibility is to consider it an iron(II) complex with two 6-electron cyclopentadienide (C_5H_5-) ions, another to view it as iron(0) coordinated by two neutral, 5-electron C_5H_5 ligands. The actual bonding situation in ferrocene is more complicated and requires an analysis of the various metal–ligand interactions.

As usual, we expect orbitals on the central Fe and on the two C_5H_5 rings to interact if they have appropriate symmetry; furthermore, we expect interactions to be strongest if they are between orbitals of similar energy. Ferrocene and other cyclopentadienyl complexes can be prepared either by direct and indirect methods as below:

i) Direct method: by reacting of metal salts with cyclopentadiene in the presence of amine.

$$MCl_2 + 2C_5H_6 + 2RNH_2 \longrightarrow M(C_5H_5)_2 + 2RNH_3^+Cl^- \quad (43)$$

ii) Indirect method: by reacting of cyclopentadiene with NaCl or TlCl to get NaCp or TlCp, which can react with transition metal salts to produce cyclopentadiene of transition metals.

$$NaCl + C_5H_6 \longrightarrow NaC_5H_5 + HCl \quad (44)$$

$$2NaC_5H_5 + FeCl_2 \longrightarrow (C_5H_5)_2Fe + 2NaCl \quad (45)$$

other reactions as below.

1. From a source of Cp^- :

$$TlCp + Mn(CO)_5Cl \longrightarrow CpMn(CO)_3 \quad (46)$$

$$MoCl_5 + NaCp \xrightarrow{NaBH_4,\ -100^\circ C} Cp_2MoH_2 \quad (47)$$

2. From a source of Cp^+ :

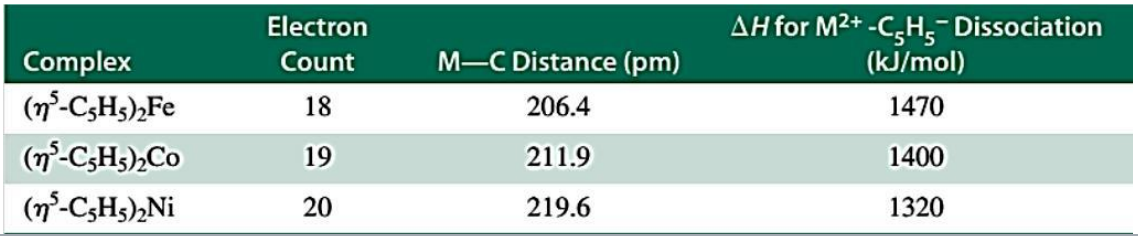
$$CpFe(CO)_2^- + C_5H_5Br \xrightarrow{heat,\ -CO} FeCp_2 \quad (48)$$

3. From the diene or a related hydrocarbon:

$$C_5Me_5H + MeRe(CO)_5 \longrightarrow CpRe(CO)_3 \quad (49)$$

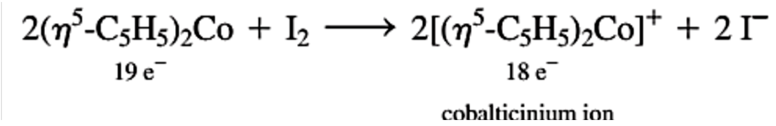
Other Metallocenes and Related Complexes

Other metallocenes have similar structures but do not necessarily obey the rule. For example, cobaltocene and nickelocene are structurally similar 19- and 20-electron species.



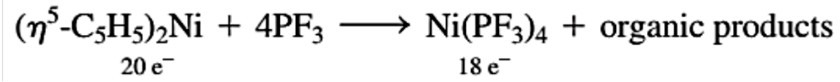
Complex	Electron Count	M—C Distance (pm)	ΔH for M^{2+}-$C_5H_5^-$ Dissociation (kJ/mol)
$(\eta^5$-$C_5H_5)_2$Fe	18	206.4	1470
$(\eta^5$-$C_5H_5)_2$Co	19	211.9	1400
$(\eta^5$-$C_5H_5)_2$Ni	20	219.6	1320

The extra electrons have chemical and physical consequences, as can be seen from comparative data in **Table** above. Electrons 19 and 20 of the metallocenes occupy slightly antibonding orbitals; as a consequence, the metal–ligand distance increases, and Δ*H* for metal–ligand dissociation decreases. Ferrocene shows much more chemical stability than **cobaltocene** and **nickelocene**; many of the chemical reactions of the latter are characterized by a tendency to yield 18-electron products. For example, ferrocene is unreactive toward iodine and rarely participates in reactions in which other ligands substitute for the cyclopentadienyl ligand. However, cobaltocene and nickelocene undergo reactions to give 18-electron products:



$$\underset{19\,e^-}{2(\eta^5\text{-}C_5H_5)_2Co} + I_2 \longrightarrow \underset{\substack{18\,e^-\\ \text{cobalticinium ion}}}{2[(\eta^5\text{-}C_5H_5)_2Co]^+} + 2\,I^-$$

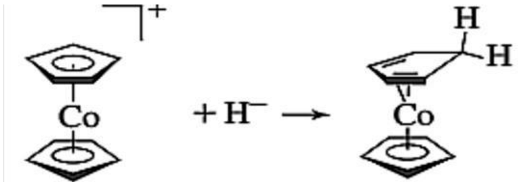
(50)



$$\underset{20\,e^-}{(\eta^5\text{-}C_5H_5)_2Ni} + 4PF_3 \longrightarrow \underset{18\,e^-}{Ni(PF_3)_4} + \text{organic products}$$

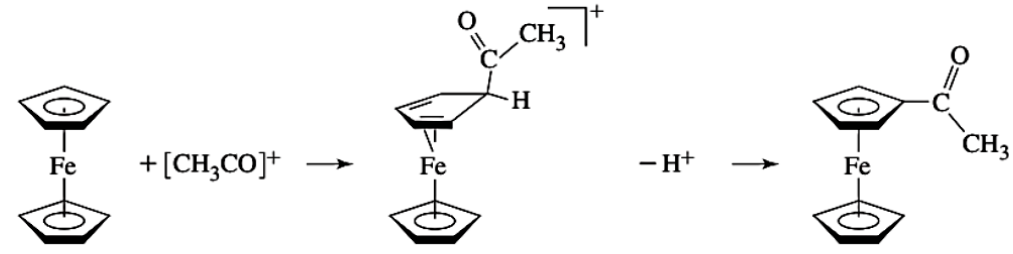
(51)

Cobaltocins reacts with hydride to give a neutral, 18-electron sandwich compound in which one cyclopentadienyl ligand has been modified into η^4-C_5H_6 (**Figure below)**



(52)

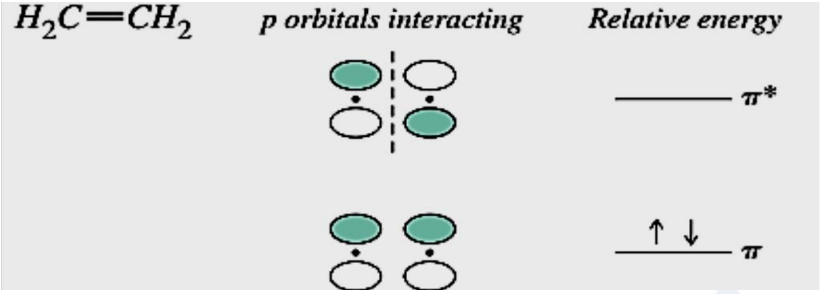
Ferrocene,. It undergoes a variety of reactions, including many on the cyclopentadienyl rings. A good example is that of electrophilic acyl substitution (**Figure below**), a reaction paralleling that of benzene and its derivatives. In general, electrophilic aromatic substitution reactions are much more rapid for ferrocene than for benzene, an indication of greater concentration of electron density in the rings of the sandwich compound.



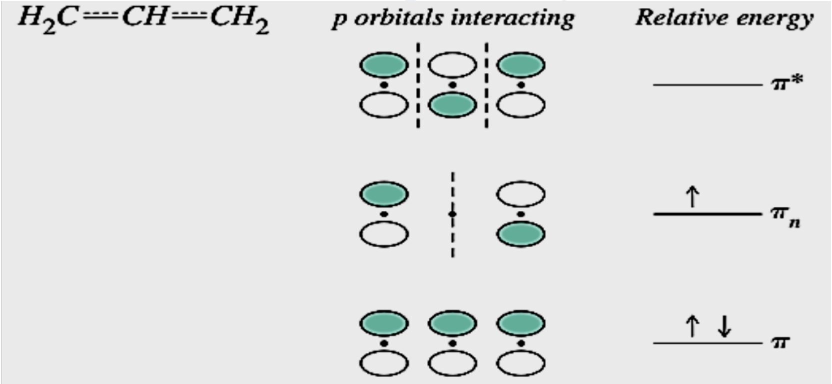
(53)

Many complexes are known containing both Cp and CO ligands. These include “**half-sandwich**” compounds such as **(η^5-C_5H_5)Mn(CO)$_3$** and dimeric and larger cluster molecules.

Linear π-Systems: The simplest case of an organic molecule having a linear π-system is ethylene, which has a single π-bond resulting from the interactions of two 2*p* orbitals on its carbon atoms. Interactions of these *p* orbitals result in one bonding and one antibonding π-orbital, as shown:



The anti-bonding interaction has a nodal plane perpendicular to the internuclear axis, but the bonding interaction has no such nodal plane. Next is the three-atom π-system, the π-allyl radical, C_3H_5. In this case, there are three 2*p* orbitals to be considered, one from each of the carbon atoms participating in the π-system. The possible interactions are as follows:

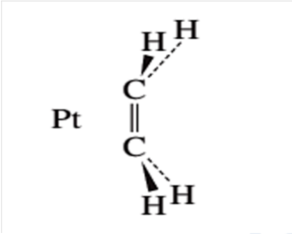


Lowest energy π-molecular orbital for this system has all three *p* orbitals interacting constructively, to give a bonding molecular orbital. Higher in energy is the nonbonding orbital ($\boldsymbol{\pi}^{n}$), in which a nodal plane bisects the molecule, cutting through the central carbon atom. In this case, the *p* orbital on the central carbon does not participate in the molecular orbital; a nodal plane passes through the center of this π-orbital and thereby cancels it from participation. Highest in energy is the antibonding π* orbital, in which there is an antibonding interaction between each neighboring pair of carbon *p* orbitals.

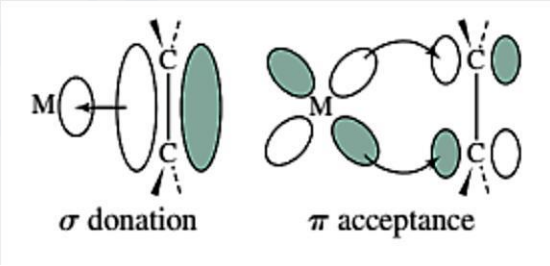
The number of nodes perpendicular to the carbon chain increases in going from lower energy to higher energy orbitals; for example, in the π-allyl system, the number of nodes increases from zero to one to two from the lowest to the highest energy orbital. This is a trend that will also appear in the following examples. The term “linear” is used broadly to include not only ligands that have carbons in a straight line but acyclic ligands that are bent at inner *sp*^{2} carbons.

π–Ethylene Complexes

Many complexes involve ethylene, C_2H_4, as a ligand, including the anion of Zeise’s salt, **$[Pt(\eta_2\text{-}C_2H_4)Cl_3]^-$**. In such complexes, ethylene commonly acts as a sidebound ligand with the following geometry with respect to the metal:



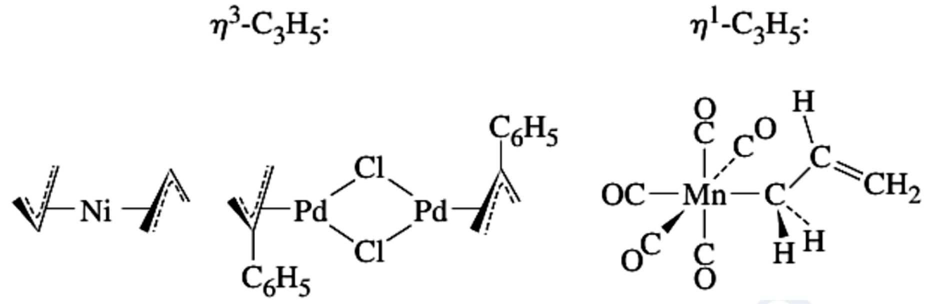
Hydrogens in ethylene complexes are bent back away from the metal, as shown. Ethylene donates electron density to the metal in a sigma fashion, using its π-bonding electron pair, as shown in **Figure below**. At the same time, electron density can be donated back to the ligand in a pi fashion from a metal *d* orbital to the empty π* orbital of the ligand. This is another example of the synergistic effect of s donation and π-acceptance.



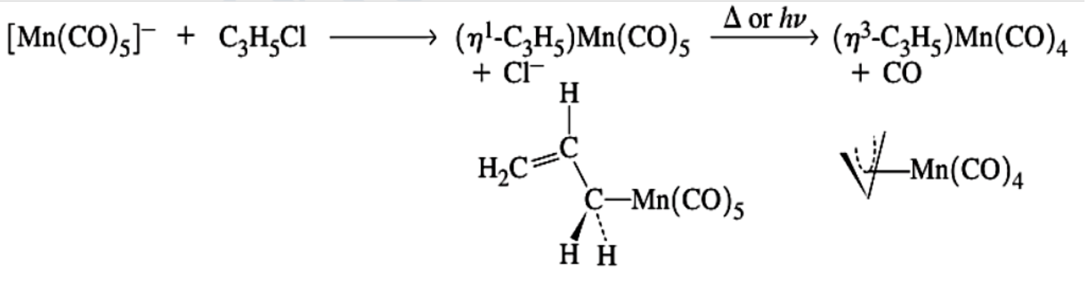
The **C-C** distance in Zeise’s salt is **137.5 pm** in comparison with **133.7 pm** in free ethylene. The lengthening of this bond can be explained by a combination of the two factors involved in the synergistic **σ-donor**, **π-acceptor** nature of the ligand: donation of electron density to the metal in a sigma fashion reduces the π-bonding electron density within the ligand, weakening the **C-C bond**. The net effect weakens and lengthens the **C-C** bond in the C_2H_4 ligand.

π–Allyl Complexes

The allyl group most commonly functions as a trihapto ligand, using delocalized π-orbitals as described previously, or as a monohapto ligand, primarily σ-bonded to a metal. Examples of these types of coordination are in **Figure below**.

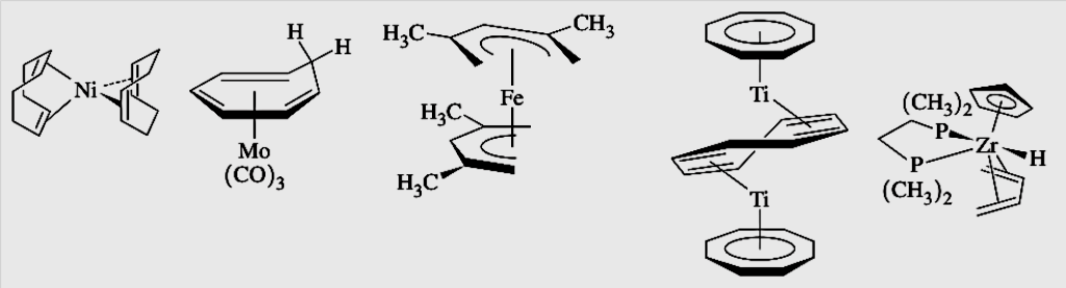


The lowest energy π-orbital can donate electron density in a sigma fashion to a suitable orbital on the metal. The next orbital, nonbonding in free allyl, can act as a donor or acceptor, depending on the electron distribution between the metal and the ligand. The highest energy π-orbital acts as an acceptor; thus, there can be synergistic **sigma** and **pi** interactions between allyl and the metal. The **C-C-C** angle within the ligand is generally near 120°, consistent with *sp*^{2} hybridization. Allyl complexes (or complexes of substituted allyls) are intermediates in many reactions, some of which take advantage of the capability of this ligand to function in both a **η^3 and η^1** fashion. Loss of CO from carbonyl complexes containing **η^1-allyl** ligands often results in conversion of **η^1**-allyl to **η^3-allyl**. For example,



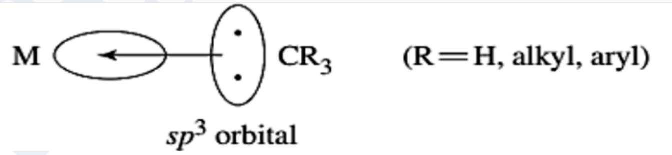
(54)

The **[Mn(CO)$_5$]$^-$** ion displaces **Cl-** from allyl chloride to give an 18-electron product containing **η^1-C$_3$H$_5$**. The allyl ligand switches to trihapto when a CO is lost, preserving the 18-electron count. Many other such systems are known; several examples of organic ligands having longer π-systems are in Figure below. **Butadiene** and longer conjugated π-systems have the possibility of isomeric ligand forms (*cis* and *trans* for butadiene). Larger cyclic ligands may have a π-system extending through part of the ring. An example is **cyclooctadiene (COD)**; the 1,3-isomer has a 4-atom π-system comparable to butadiene; 1,5-cyclooctadiene has two isolated double bonds, one or both of which may interact with a metal in a manner similar to ethylene.



Alkyl and Related Complexes

Some of the earliest known organometallic complexes were those having **σ-bonds** between main group metal atoms and alkyl groups. Examples include Grignard reagents, having magnesium–alkyl bonds, and alkyl complexes with alkali metals, such as methyllithium. Stable transition metal alkyls were initially synthesized in the first decade of the twentieth century; many such complexes are now known. The metal–ligand bonding in these complexes may be viewed as primarily involving covalent sharing of electrons between the metal and the carbon in a sigma fashion:



In terms of electron counting, the alkyl ligand may be considered a **2**-electron donor **:CR_3-** (Ionic model) or a **1-**electron donor **.**CR_3 (covalent model). Significant ionic contribution to the bonding may occur in complexes of highly electropositive elements, such as the alkali metals and alkaline earths. Many synthetic routes to transition-metal alkyl complexes have been developed. Two of the most important of these methods are:

1- Reaction of a transition-metal halide with organolithium, organomagnesium, or organoaluminum reagent

$$ZrCl_4 + 4\,PhCH_2MgCl \longrightarrow Zr(CH_2Ph)_4\,(Ph = \text{phenyl}) + 4\,MgCl_2 \qquad (55)$$

2- Reaction of a metal carbonyl anion with an alkyl halide

$$Na[Mn(CO)_5]^- + CH_3I \longrightarrow CH_3Mn(CO)_5 + NaI \quad (56)$$

Although many complexes contain alkyl ligands, transition-metal complexes that contain alkyl groups as the only ligands, are relatively rare. Examples include **$Ti(CH_3)_4$**, **$W(CH_3)_6$**, and **$Cr[CH_2Si(CH_3)_3]_4$**. Alkyl complexes have a tendency to be kinetically unstable; their stability is enhanced by structural crowding, which protects the coordination sites of the metal. The 6-coordinate **$W(CH_3)_6$** can be melted at **30 °C** without decomposition, whereas the 4-coordinate **$Ti(CH_3)_4$** is subject to decomposition at approximately **–40 °C**.

Arenes usually bind to transition metals in the 6e, η^6-form, but η^4 and η^2 structures are also known. 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 in the free arene. Arenes are much more reactive than Cp groups, and they are also more easily lost from the metal so arenes are normally actor, rather than spectator, ligands.

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

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

$$Cr(CO)_6 + C_6H_6 \quad ^{n\text{-}Bu_2O} \quad (\eta^6\text{-}C_6H_6)Cr(CO)_3 \qquad (57)$$

$$Ti(atoms) + PhMe \rightarrow (\eta^6\text{-}PhMe)_2Ti \qquad (58)$$

$$FeCp_2 + C_6H_6 + AlCl_3 \rightarrow [CpFe(\eta^6\text{-}C_6H_6)] + [AlCl_4] \qquad (59)$$

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

$$3CrCl_3 + 2Al + AlCl_3 + 6C_6H_6 \rightarrow 3[Cr(\eta^6\text{-}C_6H_6)_2]^{+\ reduction}\ 3[Cr(\eta^6\text{-}C_6H_6)_2] \quad (60)$$

3. From the diene:

$$1,3\text{-cyclohexadiene} + RuCl_3 \rightarrow [(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2 \qquad (61)$$

The MO picture is similar to that for Cp, but the arene ligand is a weaker net donor to the metal. The shift in *v*(CO) of only 50 cm−1 to lower energy on going from Cr(CO)6 to *(*C6H6*)*Cr(CO)3 confirms this picture. Binding depletes the electron density on the ring, which becomes subject to nucleophilic attack.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 back bonding to the CO groups.

Problems:

1. $Ni(CO)_4$ and C_O(*lin*-NO)$(CO)_3$ are both tetrahedral. The Ni compound undergo dissociative substitution while Co compound undergo associative substitution. Why?

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

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

4. Ligand 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.

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