

## Organometallic Chemistry

\*Organometallic chemistry:- The chemistry of compounds that contain one or more metal–carbon bonds.

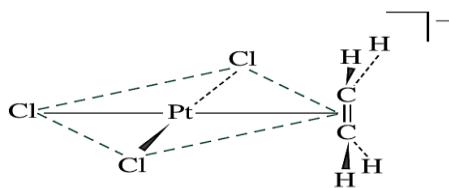
### \*Historical Background

\*In (1760) Cadet of Paris military pharmacy, works on invisible inks based on cobalt salt solutions. For their preparation, he uses cobalt minerals that contain arsenic.



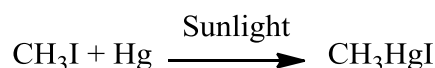
First organometallic compound

\* The first **olefin** complex synthesized in (1827) by **Zeise**, who obtained yellow needle-like crystals after refluxing a mixture of  $\text{PtCl}_4$  and  $\text{PtCl}_2$  in ethanol, followed by addition of  $\text{KCl}$  solution. Zeise's salt was the first compound identified as containing an organic molecule attached to a metal using the pi electrons of the organic molecule. It is an ionic compound of formula  $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]\cdot\text{H}_2\text{O}$  [**Potassium trichloro(ethene)platinate(II)**]; the structure of the anion, as shown bellow; is based on a square plane, with three chloro ligands occupying corners of the square and the ethylene occupying the fourth corner, but perpendicular to the plane.



### Anion of Zeise's Salt

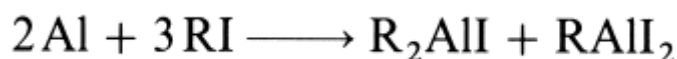
\* 1852 *Frankland* prepares the important alkylmercury halides.



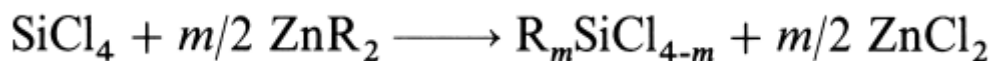
additionally:  $(\text{C}_2\text{H}_5)_4\text{Sn}$ ,  $(\text{CH}_3)_3\text{B}$  (1860). *Frankland* also introduced the concept of valency (“combining power”) and the term “organometallic”.

\*At (1852) *C. J. Löwig* and *M. E. Schweizer* in Zürich first prepare  $(\text{C}_2\text{H}_5)_4\text{Pb}$  from ethyl iodide and Na/Pb alloy. In a similar manner, they also obtain  $(\text{C}_2\text{H}_5)_3\text{Sb}$  and  $(\text{C}_2\text{H}_5)_3\text{Bi}$ .

\*In (1859) *W. Hallwachs* and *A. Schafarik* generate alkylaluminum iodides



\*In (1863) *C. Friedel* and *J. M. Crafts* prepare organochlorosilanes:



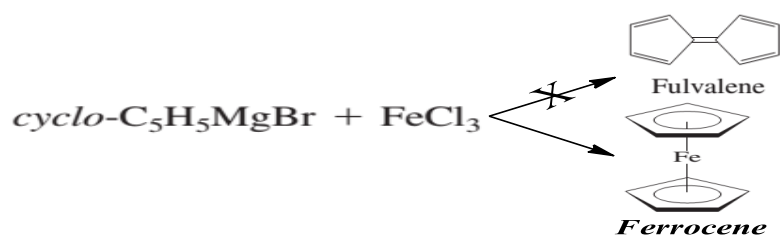
\* The first organometallic compound containing the carbonyl ligand,  $[\text{PtCl}_2(\text{CO})_2]$  was discovered by *P. Schützenberger* in (1868).

\* In (1890), *Mond* reported the preparation of the first binary metal carbonyl compound,  $\text{Ni}(\text{CO})_4$ , a compound that became commercially useful for the purification of nickel.

\* Reactions between magnesium and alkyl halides, performed by *Barbier* in (1898) and subsequently by *Grignard* led to the synthesis of alkyl magnesium complexes now known as *Grignard reagents*, which used extensively in organic synthesis.

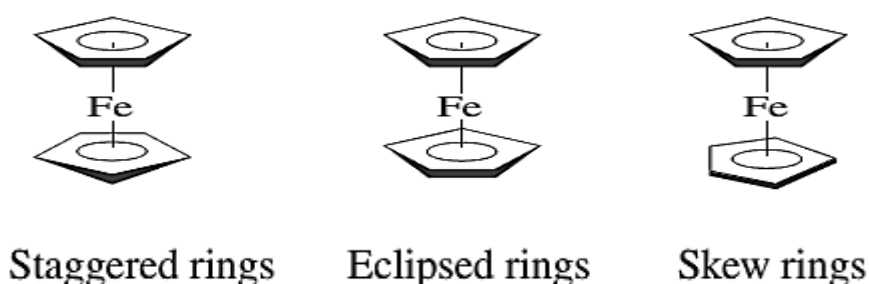
\*In (1909) *W. J. Pope*: prepared  $[(\text{CH}_3)_3\text{PtI}]$ , the first  $\sigma$ -**organotransition-metal** compound.

\* In 1951, in an attempt to synthesize *fulvalene* from cyclopentadienyl bromide, *Kealy* and *Pauson* reacted the Grignard reagent *cyclo-* $(\text{C}_5\text{H}_5)\text{MgBr}$  with  $\text{FeCl}_3$ . This reaction did not yield *fulvalene* but an orange solid having the formula  $(\text{C}_5\text{H}_5)_2\text{Fe}$ , *ferrocene*. For each of the cyclopentadienyl rings, all five of the C atoms are equidistant from the metal ion, so that the two ring systems are parallel to each other just like the slices of bread in a sandwich, with the metal stuck in between them.



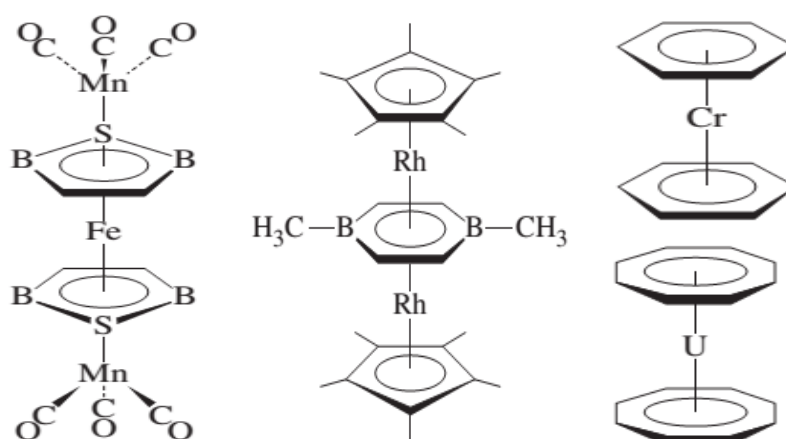
The initial study indicated that the rings were in a *staggered* conformation. Electron diffraction studies of gas-phase ferrocene, on the

other hand, showed the rings to be *eclipsed*, or very nearly so. More recent X-ray diffraction studies of solid ferrocene have identified several crystalline phases, with an eclipsed conformation at 98 K and with conformations having the rings slightly twisted (*Skew*) in higher-temperature crystalline modifications.

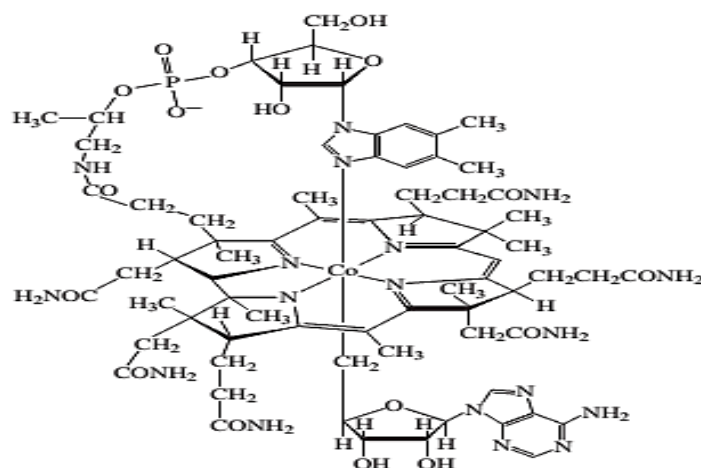


\* Fischer's group can also take credit for the discovery of the first metal–carbon double bond, or carbene compound,  $[(\text{CO})_5\text{W}=\text{C}(\text{OCH}_3)\text{Ph}]$ , in 1964 and the first metal–carbon triple bond, or carbyne,  $[(\text{CO})_4\text{XCr}\equiv\text{CPh}]$ , in 1973.

\*An other examples about sandwich compounds have been shown in the following figure;



\* The oldest organometallic compound known, vitamin B<sub>12</sub> coenzyme. This naturally occurring cobalt complex contains a cobalt–carbon sigma bond.



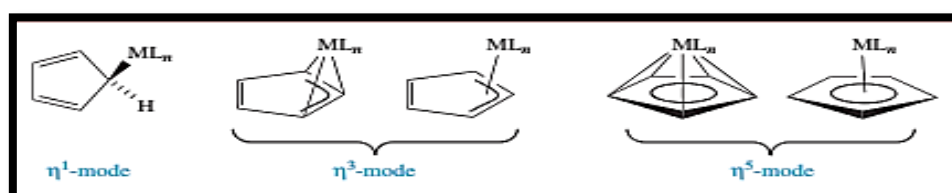
### \*Organic Ligands

Some common organic ligands are shown in Figure bellow. Special nomenclature has been devised to designate the manner in which some of these ligands bond to metal atoms; several of the ligands in Figure bellow may bond through different numbers of atoms. The number of atoms through which a ligand bonds is indicated by the Greek letter  $\eta$  (eta) followed by a superscript indicating the number of ligand atoms attached to the metal. For example, because the cyclopentadienyl ligands in ferrocene bond through all five atoms, they are designated  $\eta^5\text{-C}_5\text{H}_5$ . The formula of ferrocene may therefore be written  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$ . The  $\eta^5\text{-C}_5\text{H}_5$  ligand is designated the pentahaptocyclopentadienyl ligand. *Hapto* comes

from the Greek word for *fasten*; therefore, *pentahapto* means “*fastened in five places*”.

\*  $C_5H_5$ , 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                           | $\eta^1-C_5H_5$ | Monohaptocyclopentadienyl  |  |
| 3                           | $\eta^3-C_5H_5$ | Trihaptocyclopentadienyl   |  |
| 5                           | $\eta^5-C_5H_5$ | Pentahaptocyclopentadienyl |  |



\*The table below represents the most common ligand in organometallic chemistry:-

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

\* For ligands having all carbons bonded to a metal, sometimes the superscript is omitted. Ferrocene may therefore be written  $(\eta\text{-C}_5\text{H}_5)_2\text{Fe}$  and dibenzenechromium  $(\eta\text{-C}_6\text{H}_6)_2\text{Cr}$ . Similarly,  $\pi$  with no superscript may occasionally be used to designate that all atoms in the pi system are bonded to the metal; (for example,  $(\pi\text{-C}_5\text{H}_5)_2\text{Fe}$ ).

\***Hapticity**

\* The *hapticity* of the ligand, defined as the number of C atoms in the ligand that are directly bonded to the metal.

**The 18-Electron Rule**

In main group chemistry, we have encountered the *octet rule*, in which electronic structures can be rationalized on the basis of a valence shell requirement of *8 electrons*. Similarly, in organometallic chemistry, the electronic structures of many compounds are based on a total valence electron count of 18 on the central metal atom. As with the octet rule, there are many exceptions to the *18-electron rule*, but the rule nevertheless provides useful guidelines to the chemistry of many organometallic complexes, especially those containing strong  *$\pi$ -acceptor* ligands.

\*Because the transition metals can use their valence *d*-orbitals in their bonding, many (but not all) organometallic compounds follow the

*Effective Atomic Number (EAN)* rule of *Sidgwick*, otherwise known as the *18-electron rule*.

\*Just as some main group compounds violate the “octet rule” (for example,  $\text{BCl}_3$  is electron-deficient while  $\text{SF}_6$  is hypervalent),

\*Changes in the number of valence electrons has a profound influence on the bonding, structure, and reactions of a compounds.

\*low oxidation state organometallic complexes tend to obey the 18-electron rule via bonding with  $\pi$ -acceptor ligands.

\* This 18-electron rule often breaks down for *early* and *late* d-block metals. The majority of organometallic compounds with metals from the *middle* of the d-block obey the 18-electron rule.

\*16-electron complexes are common for e.g.  $\text{Rh(I)}$ ,  $\text{Ir(I)}$ ,  $\text{Pd(0)}$  and  $\text{Pt(0)}$ .

**\*Counting Electrons:-**

\*The group number represents the number of valence electron as shown in table below:-

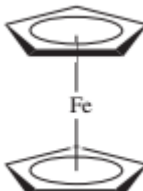

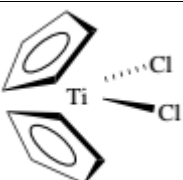
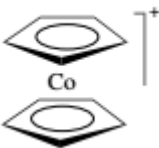
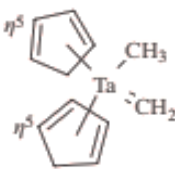
| 1-2     |    | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 | 11 | 12      | 13-18 |  |
|---------|----|----|----|----|----|----|----|----|----|----|---------|-------|--|
| s-block | Sc | Ti | V  | Cr | Mn | Fe | Co | Ni | Cu | Zn | p-block |       |  |
|         | Y  | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd |         |       |  |
|         | La | Hf | Ta | W  | Re | Os | Ir | Pt | Au | Hg |         |       |  |



\*The table below represents Electron Counting Schemes for Common Ligands:-

| <b>Electron Counting Schemes for Common Ligands</b> |                           |                       |
|---|---------------------------|-----------------------|
| <b>Ligand</b>                                       | <b>Ionic Model</b>        | <b>Covalent Model</b> |
| 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                     |
| $\eta^3-C_3H_5$ ( $\pi$ -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                     |
| $\eta^5-C_5H_5$ (Cyclopentadienyl)                  | 6 ( $C_5H_5^-$ )          | 5                     |
| $\eta^6-C_6H_6$ (Benzene)                           | 6                         | 6                     |
| $\eta^7-C_7H_7$ (Cycloheptatrienyl)                 | 6 ( $C_7H_7^+$ )          | 7                     |

\*There are two models of electron counting; *Covalent* and *ionic* models.

| Compound  | Covalent Model   | Ionic Model  |
|---|--|--|
|    | $\text{Fe}(0) = 8$ valence es.<br>$2 \text{Cp}^{\cdot} = 10$ electrons<br><hr/> Total = 18 es.                                 | $\text{Fe(II)} = 6$ valence es.<br>$2 \text{Cp}^{-} = 12$ electrons<br><hr/> Total = 18 es.                                    |
| $\text{MoH}_4(\text{PR}_3)_4$   | $\text{Mo}(0) = 6$ v. es.<br>$4 \text{H}^{\cdot} = 4$ es.<br>$4 \text{PR}_3 = 8$ es.<br><hr/> Total = 18 es.                   | $\text{Mo(IV)} = 2$ v. es.<br>$4 \text{H} = 8$ es.<br>$4 \text{PR}_3 = 8$ es.<br><hr/> Total = 18 es.                          |
|    | $\text{Ni}(0) = 10$ v. es.<br>$2 \text{C}_5\text{H}_5^{\cdot} = 6$ es.<br><hr/> Total = 16 es.                                 | $\text{Ni(II)} = 8$ v. es.<br>$2 \text{C}_5\text{H}_5^{-} = 8$ es.<br><hr/> Total = 16 es.                                     |
| $\text{Mo}(\text{C}_6\text{H}_6)_2$   | $\text{Mo}(0) = 6$ v. es.<br>$2 \text{C}_6\text{H}_6^{\cdot} = 12$ es.<br><hr/> Total = 18 es.                                 | $\text{Mo(II)} = 4$ v. es.<br>$2 \text{C}_6\text{H}_6^{-} = 14$ es.<br><hr/> Total = 16 es.                                    |
|  | $\text{Ti}(0) = 4$ v. es.<br>$2 \text{Cl} = 2$ es.<br>$2 \text{C}_5\text{H}_5^{\cdot} = 10$ es.<br><hr/> Total = 16 es.        | $\text{Ti(V)} = 0$ v. es.<br>$2 \text{Cl}^{-} = 4$ es.<br>$2 \text{C}_5\text{H}_5^{-} = 12$ es.<br><hr/> Total = 16 es.        |
|  | $\text{Co}(0) = 9$ valence es.<br>$2 \text{Cp}^{\cdot} = 10$ es.<br>positive charge = -1 e.<br><hr/> Total = 18 es.            | $\text{Co(III)} = 6$ valence es.<br>$2 \text{Cp}^{-} = 12$ es.<br><hr/> Total = 18 es.   |
| $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Cl}$                      | $\text{Fe}(0) = 8$ valence es.<br>$\text{Cp}^{\cdot} = 5$ es.<br>$2$ terminal CO = 4 es.<br>Cl = 1 e.<br><hr/> Total = 18 es.  | $\text{Fe(II)} = 6$ valence es.<br>$\text{Cp}^{-} = 6$ es.<br>$2$ terminal CO = 4 es.<br>Cl = 2 es.<br><hr/> Total = 18 es.    |
|  | $\text{Ta}(0) = 5$ valence es.<br>$2 \text{Cp}^{\cdot} = 10$ es.<br>1 alkyl = 1 e.<br>1 Carbene = 2 e.<br><hr/> Total = 18 es. | $\text{Ta(III)} = 2$ valence es.<br>$2 \text{Cp}^{-} = 12$ es.<br>1 alkyl = 2 es.<br>1 Carbene = 2 es.<br><hr/> Total = 18 es. |

\*According to **18-electron Rule** The central transition metal can accommodate electrons in the s, p, and d orbitals. s (2) , p (6) , and d (10) = maximum of 18 es.

\*Many stable organometallic compounds have an electron count other than 18; otherwise, most non-18e structures have <18e, such as [MeTiCl<sub>3</sub>, (8e)]; [Me<sub>2</sub>NbCl<sub>3</sub>, (10e)]; [WMe<sub>6</sub>, (12e)]; [Pt(PCy<sub>3</sub>)<sub>2</sub>, (14e)]; [M(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> (M = V, 15e; Cr, 16e; Mn, 17e; Fe, 18e)]. Much rarer are *d* block examples with >18e: CoCp<sub>2</sub>, 19e; and NiCp<sub>2</sub>, 20e are prominent cases.

### Exceptions to the 18 electron rule

\*Square planar organometallic complexes of the late transition metals (16e).

- Some organometallic complexes of the early transition metals (e.g. Cp<sub>2</sub>TiCl<sub>2</sub>, WMe<sub>6</sub>, Me<sub>2</sub>NbCl<sub>3</sub>, CpWOC<sub>3</sub>) [ A possible reason for the same is that some of the orbitals of these complexes are too high in energy for effective utilization in bonding or the ligands are mostly  $\sigma$  donors.

\* Some high valent *d*<sup>0</sup> complexes have a lower electron count than 18.

\* Sterically demanding bulky ligands force complexes to have less than 18 electrons.

\* The 18 electron rule fails when bonding of organometallic clusters of moderate to big sizes (6 Metal atoms and above) are considered.

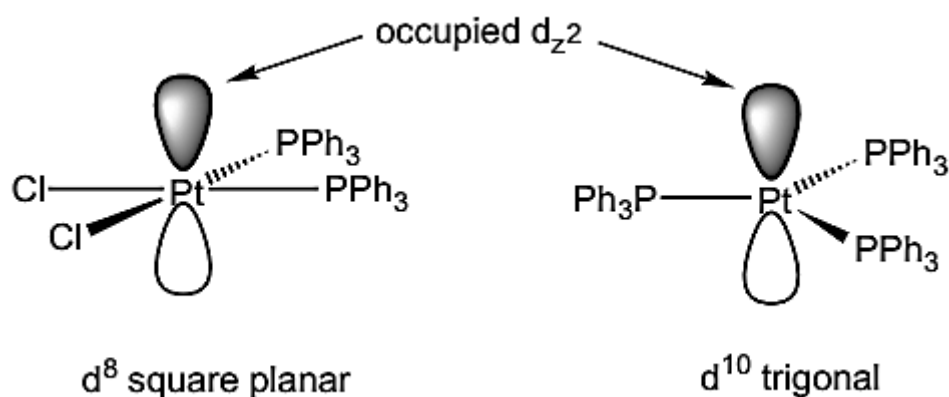
\* The rule is not applicable to organometallic compounds of main group metals as well as to those of lanthanide and actinide metals.

\*\*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).

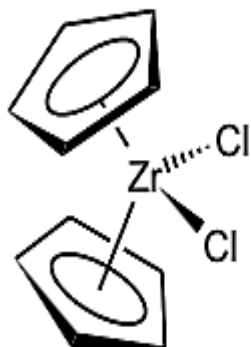
(i) *Electronic effects*

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.



(ii) *Steric Effects*

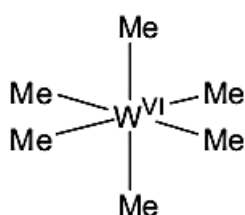
Early transition metals have fewer d-electrons to start with than the middle and late transition metals, so they must achieve their 18e count by coordination of a larger number of ligands. If the ligands involved are too bulky, then low-electron count complexes are formed.



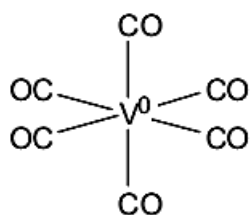
The 16e "Zirconocene dichloride."

\* Steric effects can produce low-coordinate (not many ligands) complexes which often have <18 electrons.

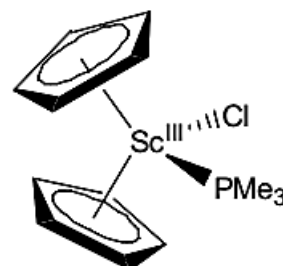
\* For early transition metals (*e.g.* with  $d^0$  metals) it is often not possible to fit the number of ligands necessary to reach 18 electrons around the metal.



$W^{6+} d^0$  12 electrons



$V^0 d^5$  17 electrons



$Sc^{3+} d^0$  16 electrons

**\*\* Linear complexes ( $d^{10}$ , 14 electrons)**

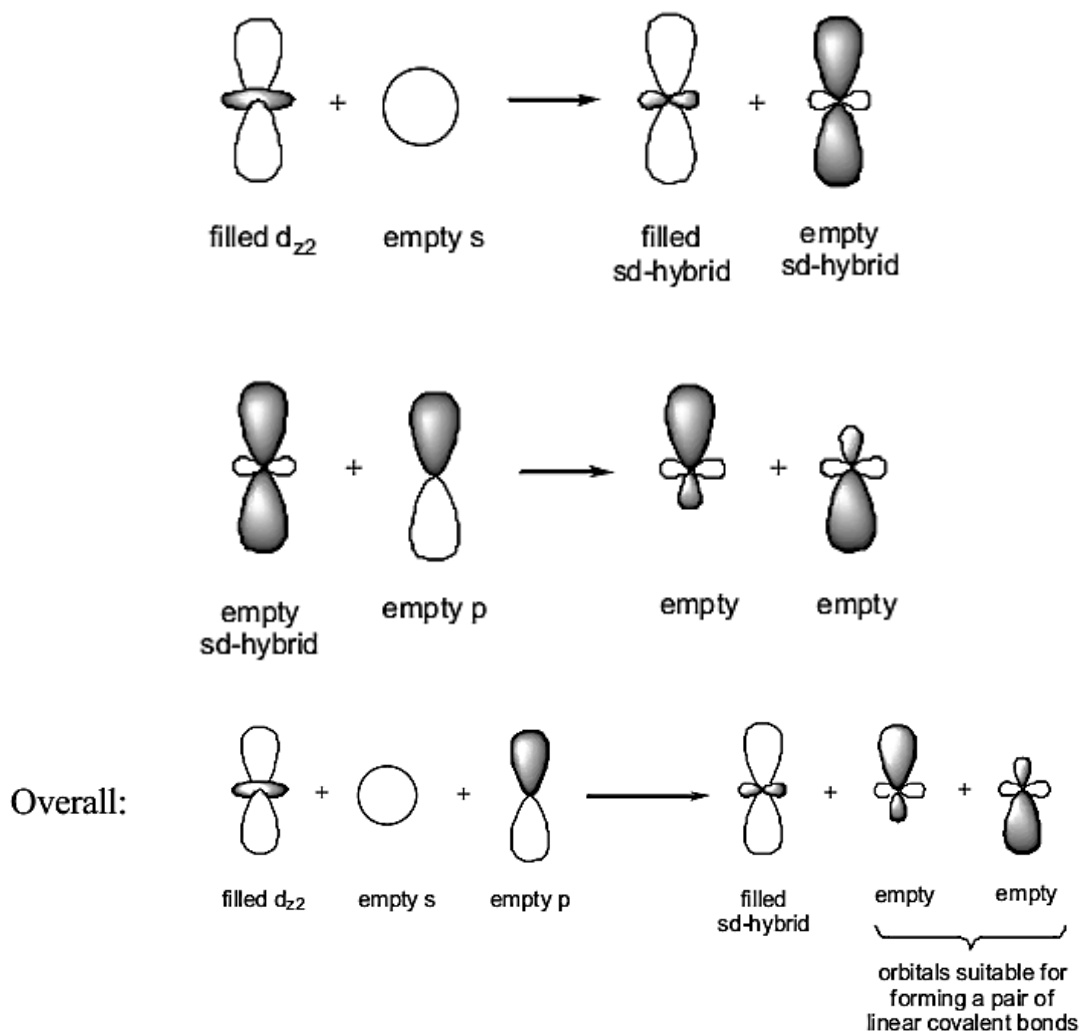
\*  $d^{10}$ -metals with 2 ligands, so 14-electron complexes.

\* Common for Ag(I), Au(I) and Hg(II), Less common 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)).

\* This permits extensive hybridization between the  $dz^2$ , s and p orbitals as shown below:

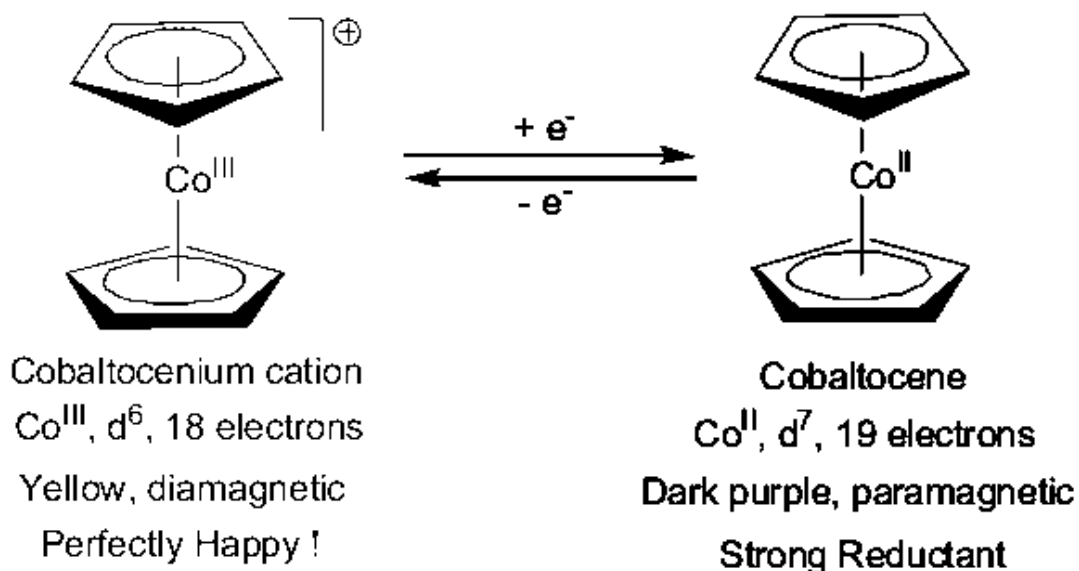
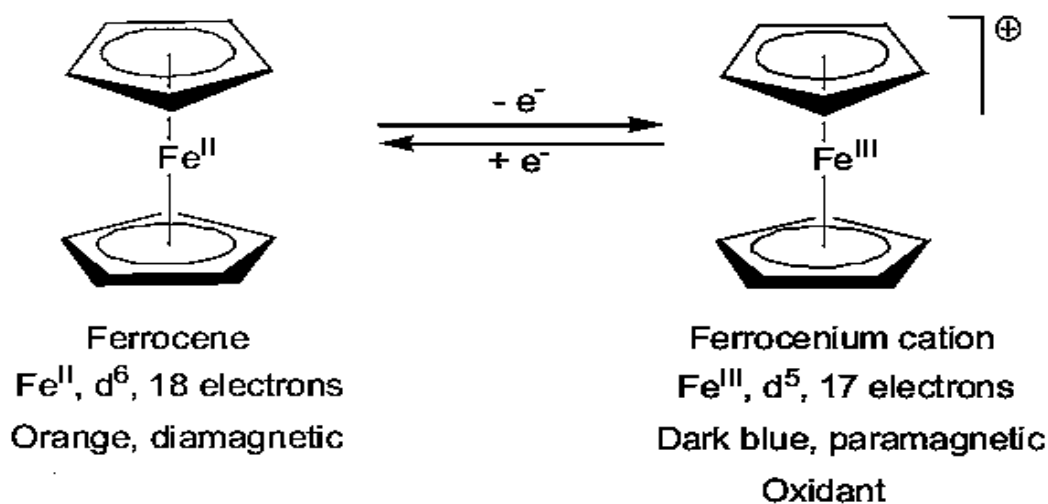


\* More common for group 11 (Cu, Ag, Au) than group 12 (Zn, Cd, Hg) because the energy difference between the d, s and p-orbitals is smaller for group 11.

\* 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  $[(R_3P)AuCl] + 2 PR_3 \rightleftharpoons 18 e-$  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).

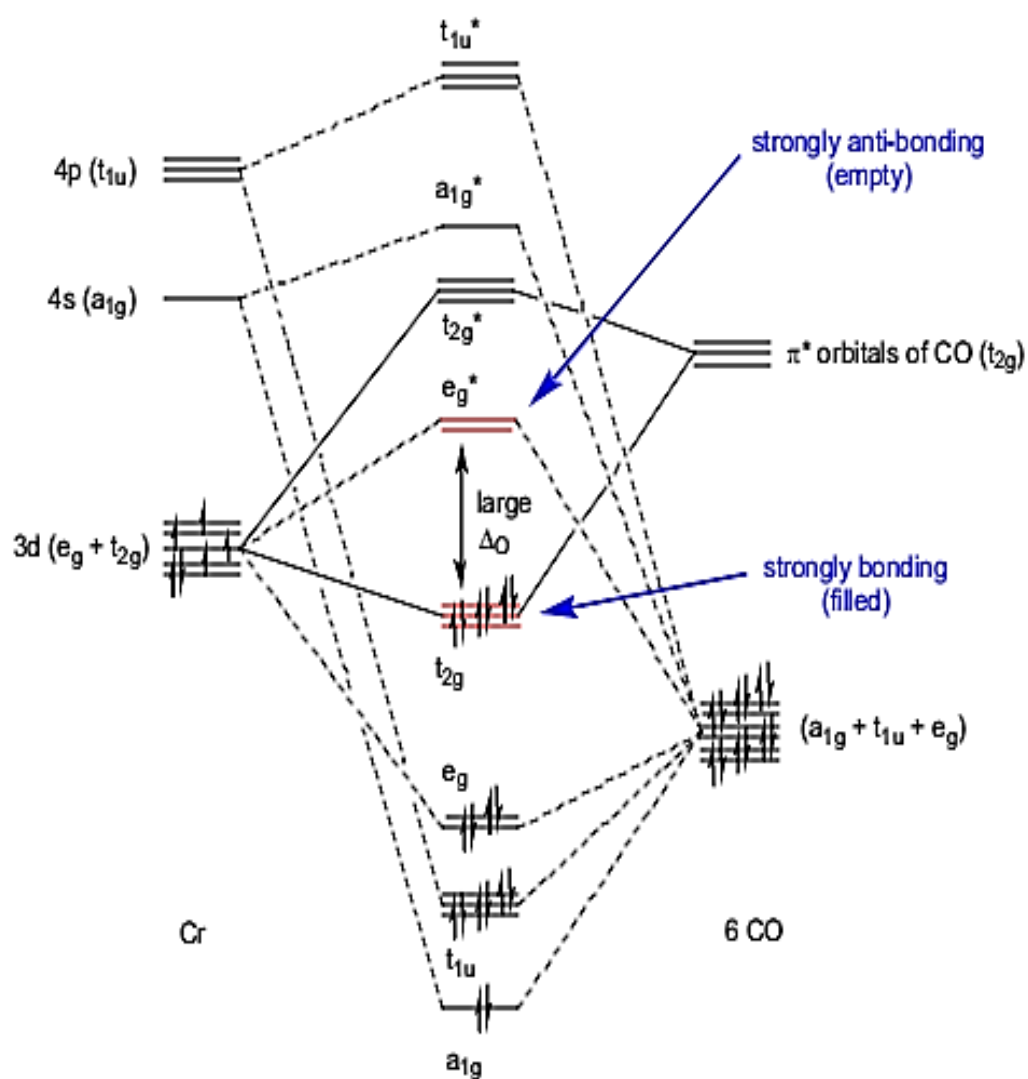


**\*Why 18 Electrons?**

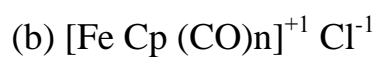
A good example of a complex that obeys the 18-electron rule is  $\text{Cr}(\text{CO})_6$ . The molecular orbitals of interest in this molecule are those that result primarily from interactions between the  $d$  orbitals of Cr and the  $\sigma$ -donor (HOMO) and  $\pi$ -acceptor orbitals (LUMO) of the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

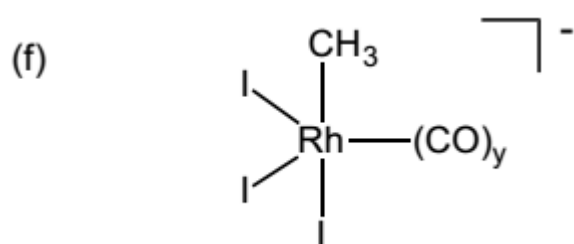
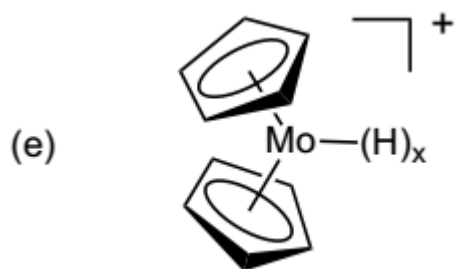
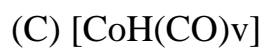
Chromium(0) has **6 electrons** outside its noble gas core. Each CO contributes a pair of electrons to give a total electron count of **18es.** In the molecular orbital diagram, these 18 electrons appear as the (**12  $\sigma$** ) electrons—the  $\sigma$  electrons of the CO ligands, stabilized by their interaction with the metal orbitals—and the (**6  $t_{2g}$** ) electrons. Addition of one or more electrons to  $\text{Cr}(\text{CO})_6$  would populate the  $eg$  orbitals, which are antibonding; the consequence would be destabilization of the molecule. Removal of electrons from  $\text{Cr}(\text{CO})_6$  would depopulate the  $t_{2g}$  orbitals, which are bonding as a consequence of the strong  $\pi$ -acceptor ability of the CO ligands; 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.



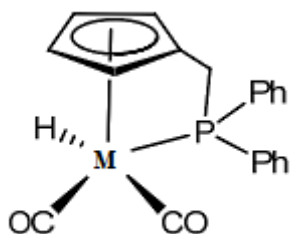
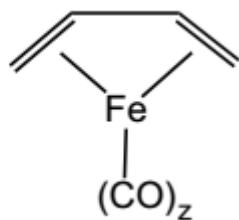


\*Exercise :- Assuming the eighteen electron rule is obeyed, what are the values of t-z and the oxidation state of the metal in (a)-(g)?





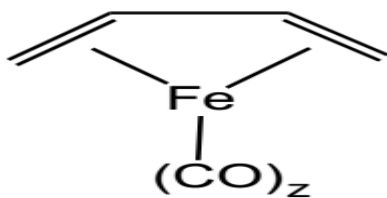
(g)



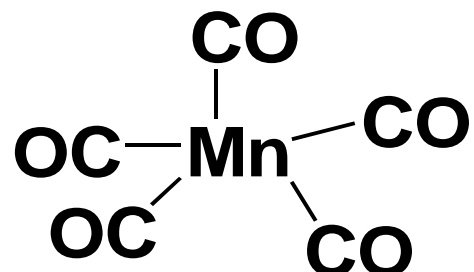
(h)

where M= one of second row metal

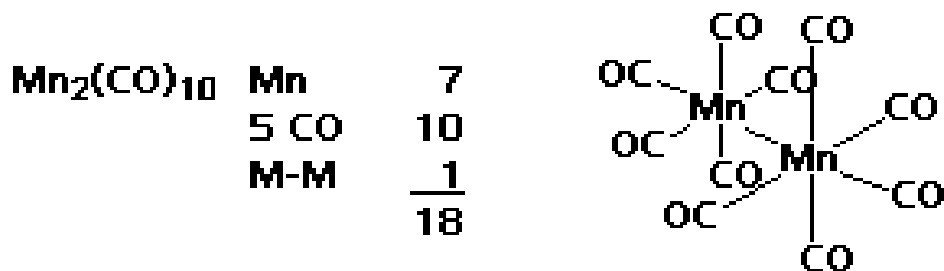
(i)



\*The 18-electron rule assist us to predict the structure of organometallic compound, Look at CO complexes of Mn. You may expect to have the following structure for a CO complex of Mn.



But in fact the structure as follows;



### \*\*Ligands in Organometallic Chemistry:-

Hundreds of ligands are known to bond to metal atoms through carbon. Carbon monoxide forms a very large number of metal complexes and deserves special mention, along with several similar diatomic ligands. Many organic molecules containing linear or cyclic pi systems also form numerous organometallic complexes. Special attention will be paid to two types of organometallic compounds that are especially important: carbene complexes, containing metal–carbon double bonds, and carbyne complexes, containing metal–carbon triple bonds.

\* Carbonyl (CO) Complexes

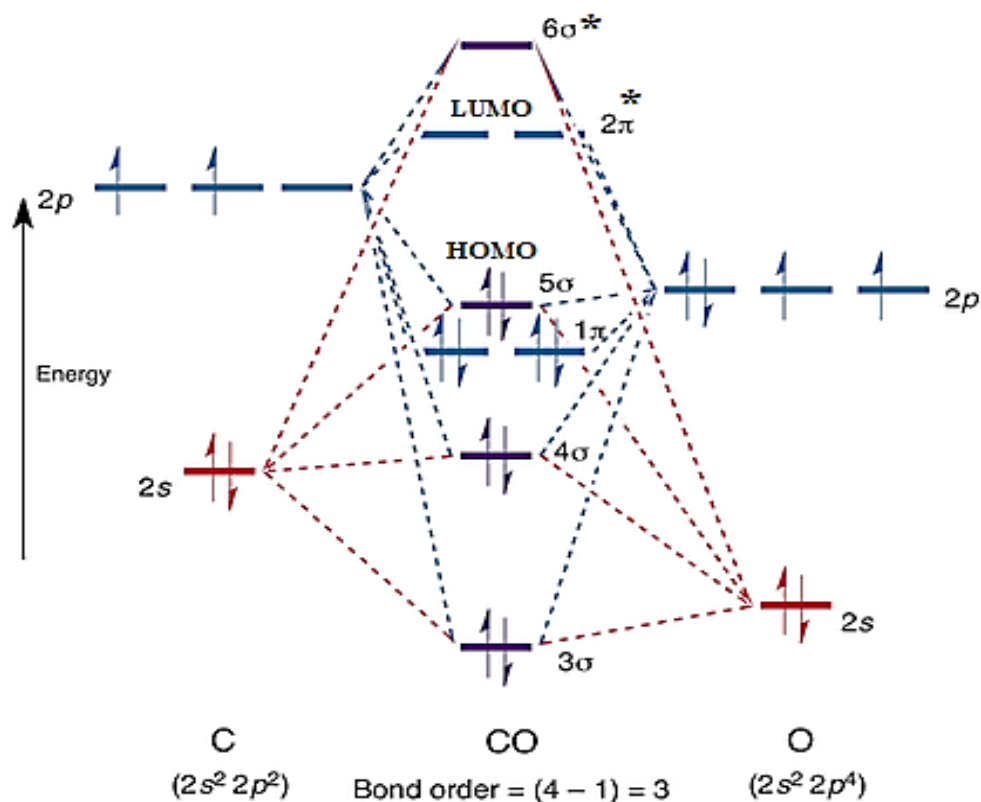
Carbon monoxide is the most common ligand in organometallic chemistry. It serves as the only ligand in binary carbonyls such as  $\text{Ni}(\text{CO})_4$ ,  $\text{W}(\text{CO})_6$ , and  $\text{Fe}_2(\text{CO})_9$  or, more commonly, in combination with other ligands, both organic and inorganic. CO may bond to a single metal, or it may serve as a bridge between two or more metals. We will consider the bonding between metals and CO, the synthesis and reactions of CO complexes, and examples of various types of CO complexes.

\*Table below lists many of the stable, neutral, d-block metal carbonyl compounds;

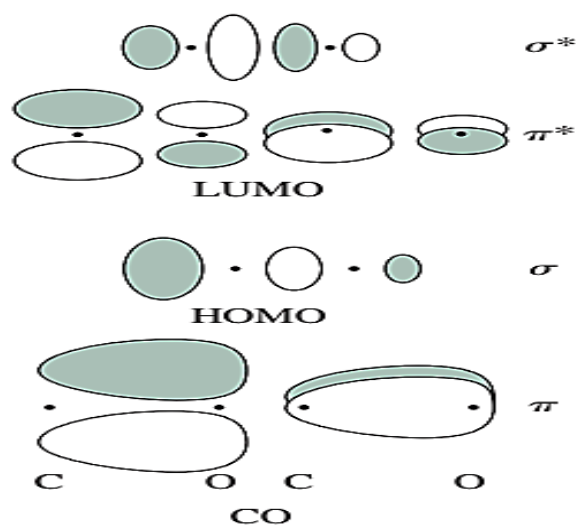
| Group number      | 5  | 6  | 7  | 8   | 9  | 10   |
|-------------------|--|--|--|---|--|--|
| First row metals  | $\text{V}(\text{CO})_6$<br>Dark blue solid; paramagnetic; dec. 343 K | $\text{Cr}(\text{CO})_6$<br>White solid; sublimes <i>in vacuo</i> ; dec. 403 K | $\text{Mn}_2(\text{CO})_{10}$<br>Yellow solid; mp 427 K                    | $\text{Fe}(\text{CO})_5$<br>Yellow liquid; mp 253 K; bp 376 K<br><br>$\text{Fe}_2(\text{CO})_9$<br>Golden crystals; mp 373 K (dec.)<br>$\text{Fe}_3(\text{CO})_{12}$<br>Dark green solid; dec. 413 K                | $\text{Co}_2(\text{CO})_8$<br>Air-sensitive, orange-red solid; mp 324 K<br><br>$\text{Co}_4(\text{CO})_{12}$<br>Air-sensitive, black solid<br>$\text{Co}_6(\text{CO})_{16}$<br>Black solid; slowly dec. in air | $\text{Ni}(\text{CO})_4$<br>Colourless, volatile liquid; highly toxic vapour; bp 316 K |
| Second row metals |  | $\text{Mo}(\text{CO})_6$<br>White solid; sublimes <i>in vacuo</i>              | $\text{Tc}_2(\text{CO})_{10}$<br>White solid; slowly dec. in air; mp 433 K | $\text{Ru}(\text{CO})_5$<br>Colourless liquid; mp 251 K; dec. in air at 298 K to $\text{Ru}_3(\text{CO})_{12} + \text{CO}$<br><br>$\text{Ru}_3(\text{CO})_{12}$<br>Orange solid; mp 427 K; sublimes <i>in vacuo</i> | $\text{Rh}_4(\text{CO})_{12}$<br>Red solid; >403 K dec. to $\text{Rh}_6(\text{CO})_{16}$<br><br>$\text{Rh}_6(\text{CO})_{16}$<br>Black solid; dec. >573 K  |  |
| Third row metals  |  | $\text{W}(\text{CO})_6$<br>White solid; sublimes <i>in vacuo</i>               | $\text{Re}_2(\text{CO})_{10}$<br>White solid; mp 450 K                     | $\text{Os}(\text{CO})_5$<br>Yellow liquid; mp 275 K<br><br>$\text{Os}_3(\text{CO})_{12}$<br>Yellow solid; mp 497 K  | $\text{Ir}_4(\text{CO})_{12}$<br>Slightly air-sensitive yellow solid; mp 443 K<br><br>$\text{Ir}_6(\text{CO})_{16}$<br>Red solid   |  |

**\*Bonding of CO ligand**

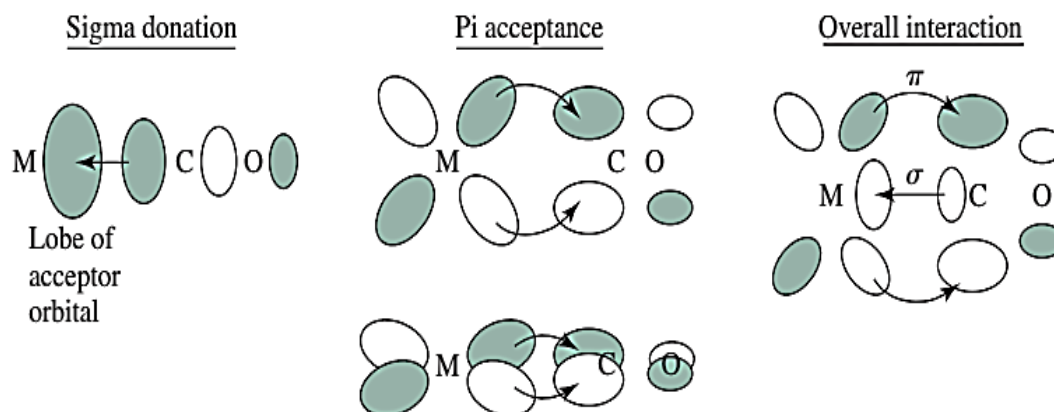
It is useful to review the bonding in CO. The molecular orbital picture of CO shown in Figure below;



\*The molecular orbitals derived primarily from the 2p atomic orbitals of these molecules are shown in Figure below;



The *highest energy occupied molecular orbital (HOMO)* has its largest lobe on carbon. It is through this orbital, occupied by an electron pair, that CO exerts its  $\sigma$ -donor function, donating electron density directly toward an appropriate metal orbital, such as an unfilled  $d$  or hybrid orbital. Carbon monoxide also has two empty  $p^*$  orbitals (the **lowest energy unoccupied molecular orbital**, (*LUMO*)); these also have larger lobes on carbon than on oxygen. A metal atom having electrons in a  $d$  orbital of suitable symmetry can donate electron density to these  $p^*$  orbitals. These  $\sigma$ -donor and  $\pi$ -acceptor interactions are illustrated in Figure below;



\*The  $\sigma$ -donor interaction increases the electron density on the metal and decreases the electron density on the CO ligand. The  $\pi$ -acceptor interaction decreases the electron density on the metal and increases the electron density on the CO ligand. Both effects 'reinforce' each other. Sometimes referred to as (*synergic bonding*).

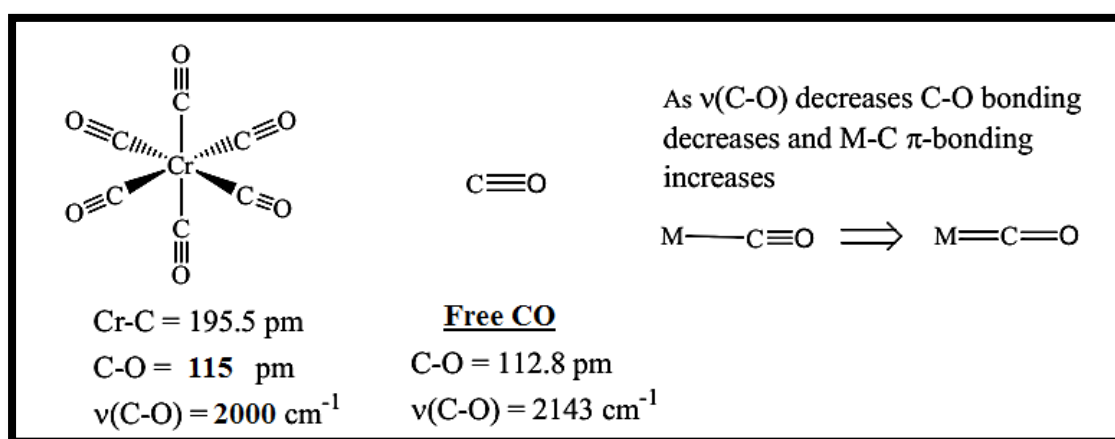
\* The strength of this bonding depends on several factors, including the *charge* on the complex and the *ligand environment* of the metal.

\* If this picture of bonding between CO and metal atoms is correct, it should be supported by **experimental evidence**. Two sources of such evidence are *infrared spectroscopy* and *X-ray crystallography*. First, any change in the bonding between carbon and oxygen should be reflected in the **C-O** stretching vibration as observed by IR. The **C-O** stretch in organometallic complexes is often very intense (stretching the C-O bond results in a substantial change in dipole moment), and its energy often provides valuable information about the molecular structure. **Free carbon monoxide** has a **C-O** stretch at ( $2143\text{ cm}^{-1}$ ).  $\text{Cr}(\text{CO})_6$ , on the other hand, has its **C-O** stretch at ( $2000\text{ cm}^{-1}$ ). The lower energy for the stretching mode means that the **C-O** bond is weaker in  $\text{Cr}(\text{CO})_6$ .

\* Both  $\sigma$  donation and  $\pi$  acceptance would be expected to weaken the **C-O** bond and to decrease the energy necessary to stretch that bond.



\*Additional evidence is provided by X-ray crystallography. In carbon monoxide, the C-O distance has been measured at **112.8 pm**. Weakening of the C-O bond would be expected to cause this distance to increase. Such an increase in bond length is found in complexes containing CO, with C-O distances approximately **115 pm** for many carbonyls.



\* The charge on a carbonyl complex is also reflected in its infrared spectrum. Five isoelectronic hexacarbonyls have the following C-O stretching bands (compare with  $\nu(\text{CO}) = 2143 \text{ cm}^{-1}$  for free CO):

| Complex                         | $\nu(\text{CO}), \text{cm}^{-1}$ |
|---------------------------------|----------------------------------|
| $[\text{Ti}(\text{CO})_6]^{2-}$ | 1748                             |
| $[\text{V}(\text{CO})_6]^{-}$   | 1859                             |
| $\text{Cr}(\text{CO})_6$        | 2000                             |
| $[\text{Mn}(\text{CO})_6]^{+}$  | 2100                             |
| $[\text{Fe}(\text{CO})_6]^{2+}$ | 2204                             |

**Note:-** The positions of the **C-O** stretching vibrations in previous ions may be affected by interactions with solvents or counter ions, and solid and solution spectra may differ slightly.

\* Of these **isoelectronic** five ions,  $[\text{Ti}(\text{CO})_6]^{2-}$  contains the most highly reduced metal, formally containing **Ti(2-)**; this means that titanium has the *weakest* ability *to attract* electrons and the *greatest* tendency *to back-donate* electron density to CO. The formal charges on the metals increase from **(-2)** for  $[\text{Ti}(\text{CO})_6]^{2-}$  to **(+2)** for  $[\text{Fe}(\text{CO})_6]^{2+}$ . The titanium in  $[\text{Ti}(\text{CO})_6]^{2-}$ , with the most negative formal charge, has the strongest tendency to donate to CO. The consequence is strong population of the  $\pi^*$  orbitals of CO in  $[\text{Ti}(\text{CO})_6]^{2-}$  and reduction of the strength of the **C-O** bond. In general, the *more negative* the charge on the organometallic species, the *greater the tendency* of the metal to donate electrons to the  $\pi^*$  orbitals of CO, and the lower the energy of the **C-O** stretching vibrations.

\* How is it possible for cationic carbonyl complexes such as  $[\text{Fe}(\text{CO})_6]^{2+}$  to have **C-O** stretching bands even higher in energy than those in free CO? It seems clear that the CO ligand does not engage in significant  $\pi$ -acceptor activity in these complexes, so weakening of the **C-O** bond via this interaction should be minimal, but how does the strength of the bond *increase*? Calculations have demonstrated that a polarization effect

caused by the metal cation plays a major role in these carbonyl cations. In free CO, the electrons are polarized toward the more electronegative oxygen. For example, the electrons in the p orbitals are concentrated nearer to the oxygen atom than to the carbon. The presence of a transition metal cation reduces the polarization in the C-O bond by attracting the bonding electrons:



The consequence is that the electrons in the positively charged complex are more equally shared by the carbon and the oxygen, giving rise to a stronger bond and a higher-energy C-O stretch.

\* The very high  $\nu(\text{CO})$  bands result from weak back donation. When the frequency of carbonyls appears at higher energy band of free CO, the complexes are sometimes called *nonclassical carbonyls*.

\* Non-classical carbonyls

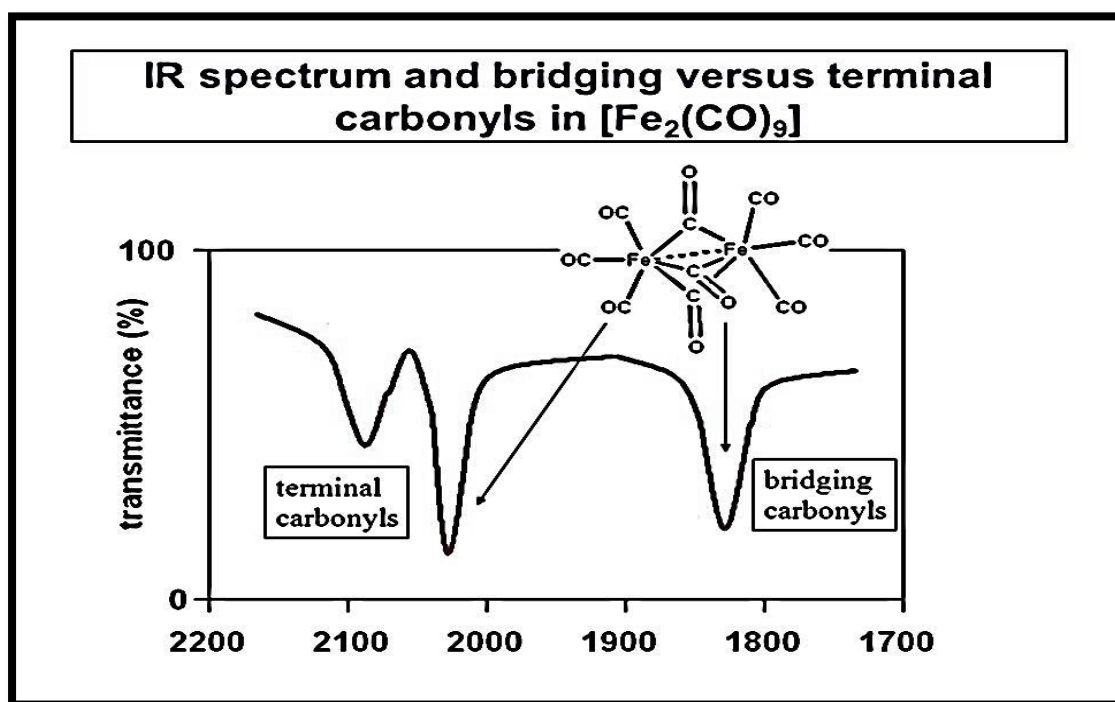
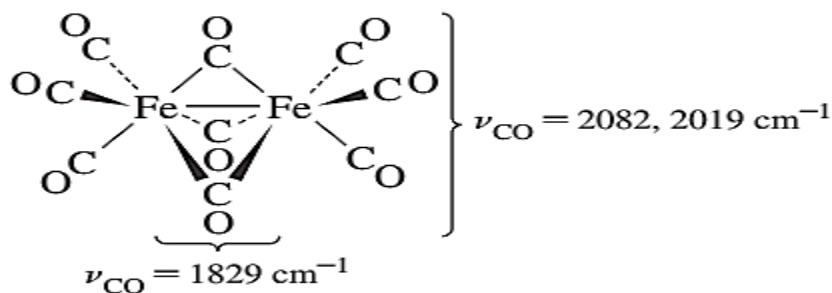
| The frequency of CO in each metal carbonyl is higher than that of free CO, where electron density is not transferred from the metal to the ligand $\pi$ -accepting orbitals. The major interaction is $\sigma$ -donation from the CO 5s (anti-bonding) orbital to the metal. Therefore the CO stretching frequency is > free CO. | Metal Carbonyl                | $\nu(\text{CO})/\text{cm}^{-1}$ |
|--|-------------------------------|---------------------------------|
|  | $\text{Pd}(\text{CO})_4^{2+}$ | 2248                            |
| $\text{Pt}(\text{CO})_4^{2+}$  | 2244                          |                                 |
| $\text{Ag}(\text{CO})_2^+$   | 2200                          |                                 |
| $\text{Au}(\text{CO})_2^+$   | 2217                          |                                 |
| $\text{Hg}(\text{CO})_2^{2+}$  | 2278                          |                                 |

\* **Exercise**:- Predict which of the complexes  $[\text{V}(\text{CO})_6]^+$ ,  $\text{Cr}(\text{CO})_6$ , or  $[\text{Mn}(\text{CO})_6]^+$  has the shortest C-O bond.

**\*\* Bridging Modes of CO**

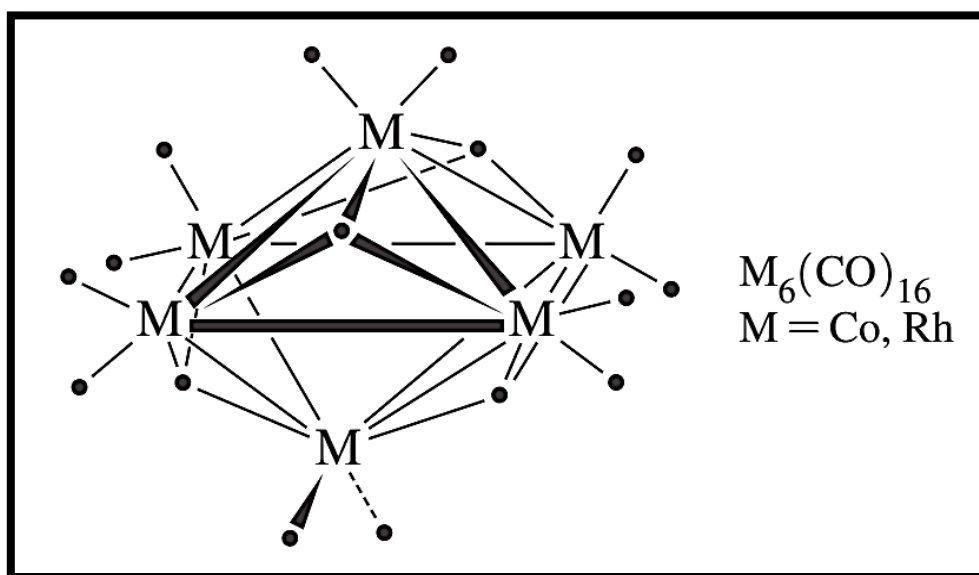
\* Many cases are known in which CO forms bridges between two or more metals. Many bridging modes are known **Table below**.

| Type of CO                               | Approximate Range for $\nu(\text{CO})$ in Neutral Complexes ( $\text{cm}^{-1}$ ) |
|--|--|
| Free CO                                  | 2143   |
| Terminal $\text{M}-\text{CO}$            | 1850–2120  |
| Symmetric <sup>a</sup> $\mu_2-\text{CO}$ | 1700–1860  |
| Symmetric <sup>a</sup> $\mu_3-\text{CO}$ | 1600–1700  |

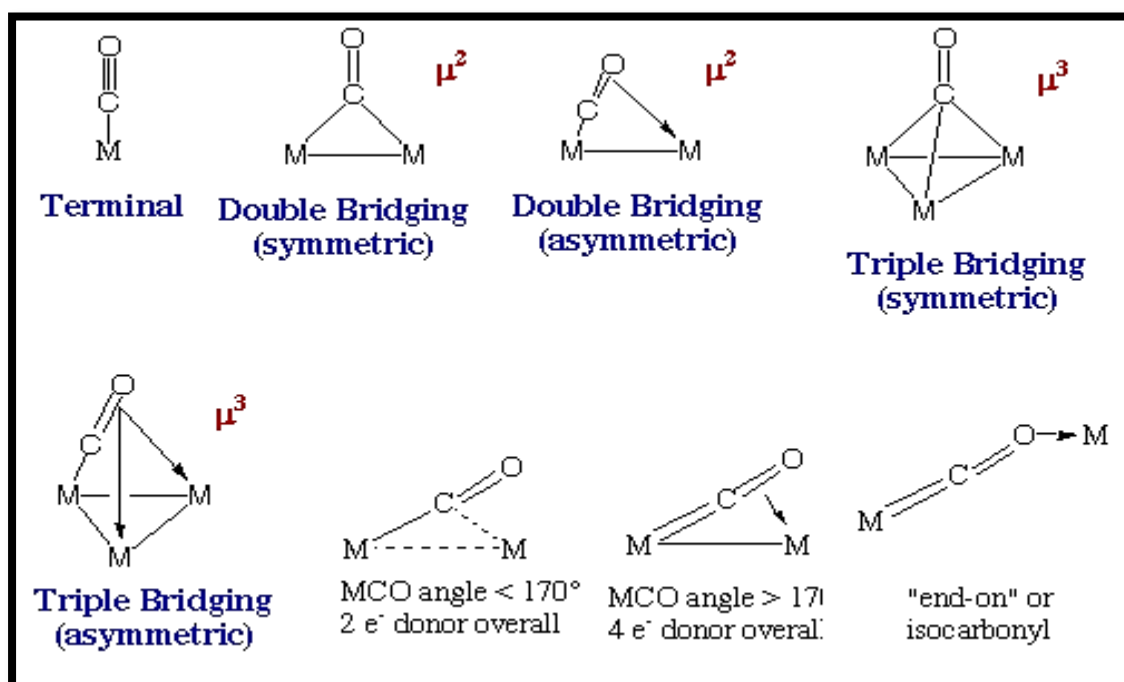
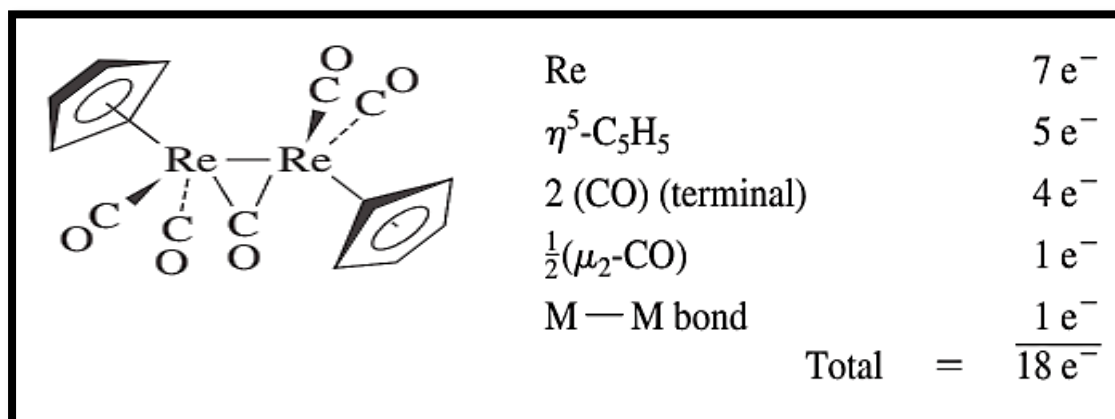


\*The bridging mode is strongly correlated with the position of the C-O stretching band. In cases in which CO bridges two metal atoms, both metals can contribute electron density into  $\pi^*$  orbitals of CO to weaken the C-O bond and lower the energy of the stretch. Consequently, the C-O stretch for doubly bridging CO is at a much lower energy than for terminal COs. An example is shown in **Figure above**.

\* Interaction of three metal atoms with a *triplly* bridging (as shown in figure below) CO further weakens the C-O bond; the infrared band for the C-O stretch is still lower than in the doubly bridging case.



\* Ordinarily, terminal and bridging carbonyl ligands can be considered 2 electron donors, with the donated electrons shared by the metal atoms in the bridging cases. For example, in the complex below, the bridging CO is a *2-electron* donor overall, with a single electron donated to each metal. The electron count for each Re atom according to covalent method



\*\*There are three points of interest with respect to metal carbonyls:-

- 1) CO is not ordinarily considered a very strong Lewis base, and yet it forms strong bonds to the metals in these compounds.
- 2) The metals are always in a low oxidation state, most often formally in an oxidation state of Zero, but also in low positive & negative oxidation states.

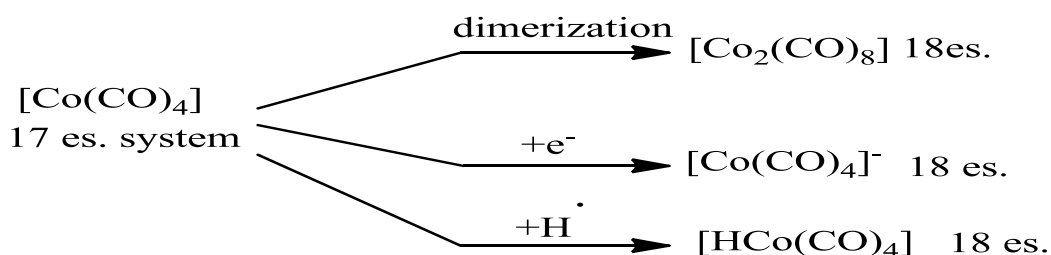
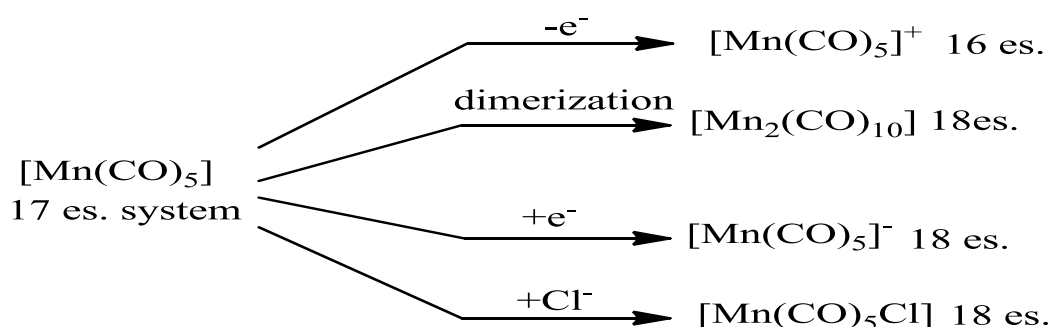
3) The 18-electrons rule is obeyed with remarkable frequency, perhaps 99% of the time.

\*\*Metals with odd atomic number cant satisfy the 18-es. By simple addition of CO ligand, since the resultant moiety will have an odd number of electrons. In such case there are several option open to these metals by which the 18-es. Rule can be satisfied:-

A. The addition of an electron by reducing agent to form an anion such as  $[\text{V}(\text{CO})_6]^-$ .

B. The electron deficient moiety can bond covalently with an atom or group that also has single unpaired electron available, example:- hydrogen or chlorine :  $\text{HM}(\text{CO})_n$  or  $\text{M}(\text{CO})_n\text{Cl}$  .

C. If no either species are available with which to react, two moieties each with an odd atom can dimerized with resultant pairing of the odd electrons, examples

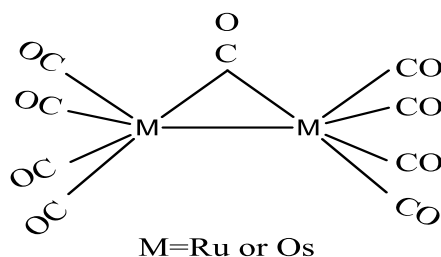


\* **Binary Carbonyl Complexes**

Binary carbonyls, containing only metal atoms and CO, are numerous. Most of these complexes obey the 18-electron rule. The cluster compounds  $\text{Co}_6(\text{CO})_{16}$  and  $\text{Rh}_6(\text{CO})_{16}$  do not obey the rule.

\* One other binary carbonyl does not obey the rule, the 17-electron  $\text{V}(\text{CO})_6$ . This complex is one of a few cases in which strong  $\pi$ -acceptor ligands do not afford an 18-electron configuration. In  $\text{V}(\text{CO})_6$ , the vanadium is apparently too small to permit a seventh coordination site; hence, no metal–metal bonded dimer, which would give an 18 electron configuration, is possible. However,  $\text{V}(\text{CO})_6$  is easily reduced to  $[\text{V}(\text{CO})_6]^-$ , an 18-electron complex.

\* An interesting feature of the structures of binary carbonyl complexes is that the tendency of CO to bridge transition metals *decreases* going *down* the periodic table. For example, in  $\text{Fe}_2(\text{CO})_9$  there are *three bridging* carbonyls; but in  $\text{Ru}_2(\text{CO})_9$  and  $\text{Os}_2(\text{CO})_9$ , there is a *single bridging* CO. A possible explanation is that the orbitals of bridging CO are less able to interact effectively with transition-metal atoms as the size of the metals increases, along with the metal–metal bond lengths.

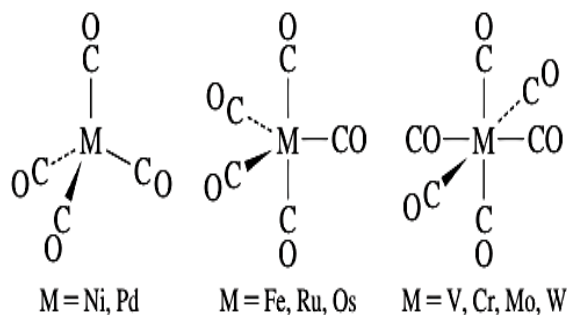




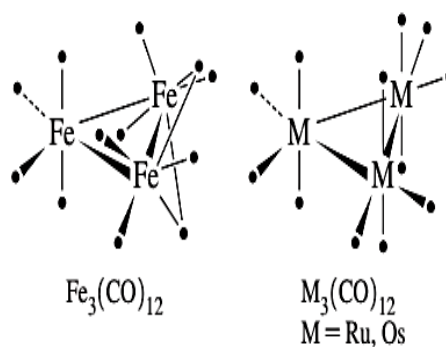
\* **Exercise**:- Verify the 18-electron rule for five of the binary carbonyls— other than  $V(CO)_6$ ,  $Co_6(CO)_{16}$ , and  $Rh_6(CO)_{16}$  shown in Figure below.

\*Figure below represents some of binary carbonyl complexes:-

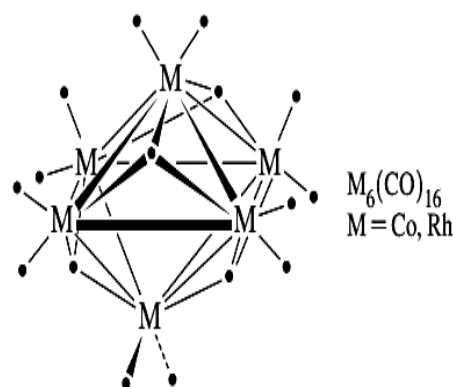
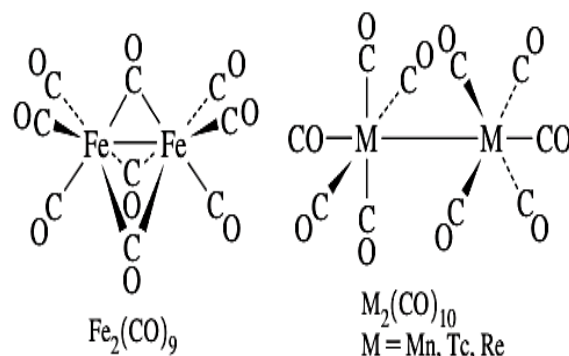
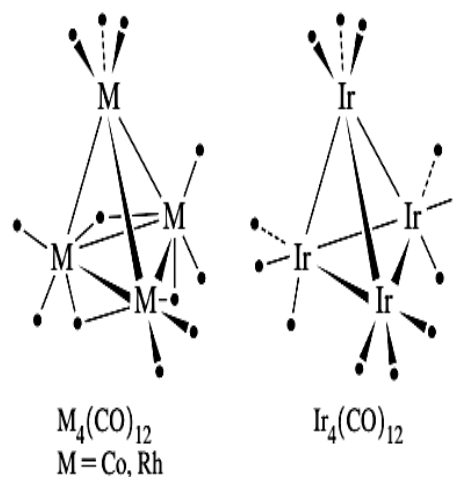
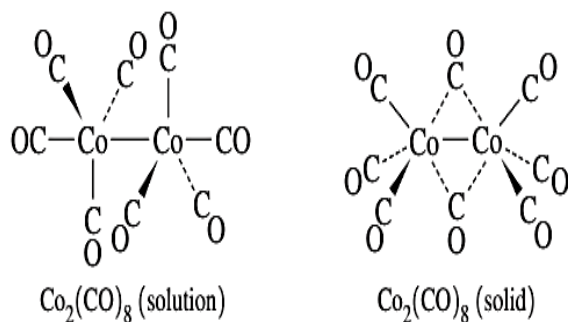
Mononuclear  $[M(CO)_x]$



Polynuclear (CO represented by • for clarity)



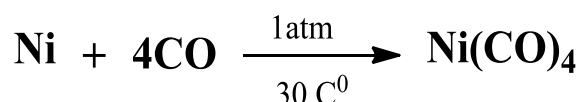
Binuclear  $[M_2(CO)_x]$



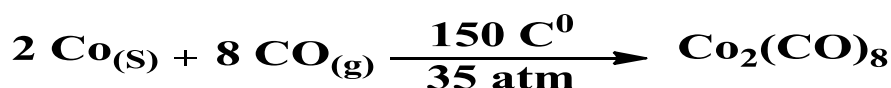
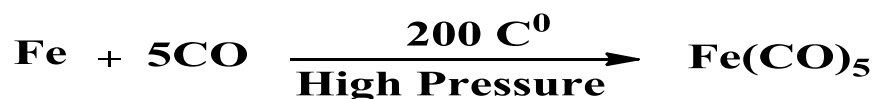
**\*\*Synthesis of Binary Carbonyl Complexes**

Binary carbonyl complexes can be synthesized in many ways. Several of the most common methods are as follows:

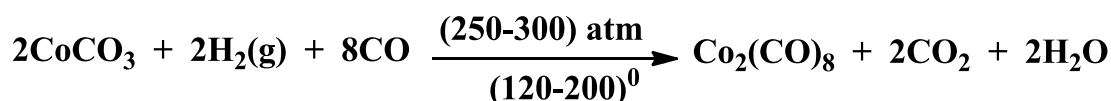
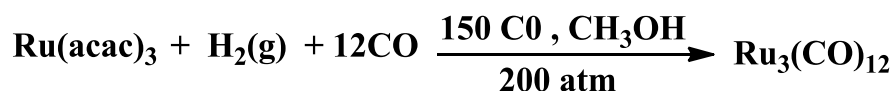
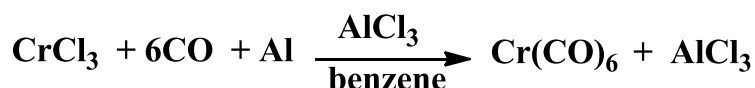
- 1) ***Direct reaction of a transition metal with CO***. The most facile of these reactions involves nickel, which reacts with CO at ambient temperature and 1 atm:



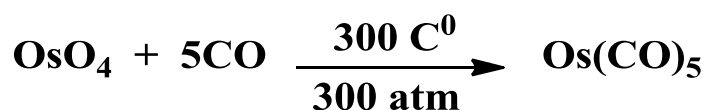
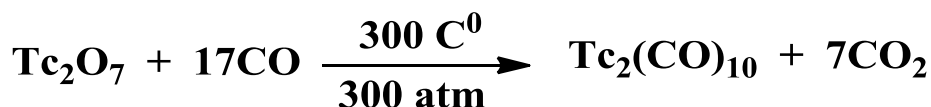
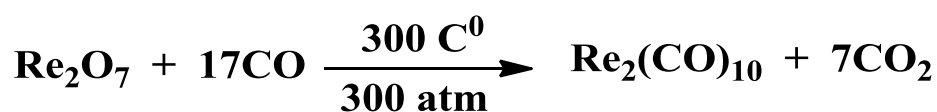
Ni(CO)<sub>4</sub> is a volatile, extremely toxic liquid that must be handled with great caution. Because the reaction can be reversed at high temperature, coupling of the forward and reverse reactions has been used commercially in the *Mond* process for obtaining purified nickel from ores. Other binary carbonyls can be obtained from direct reaction of metal powders with CO, but elevated temperatures and pressures are needed. For example



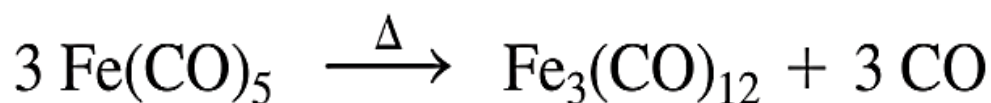
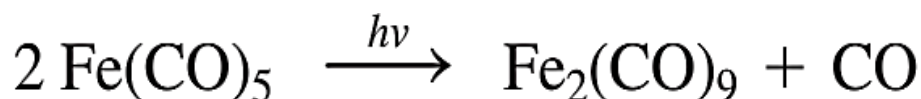
- 2) ***Reductive carbonylation***: reduction of a metal compound in the presence of CO and an appropriate reducing agent. Examples are shown below.



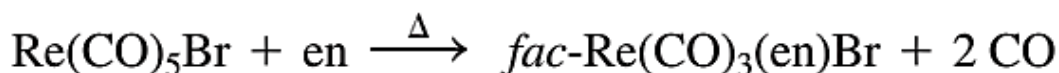
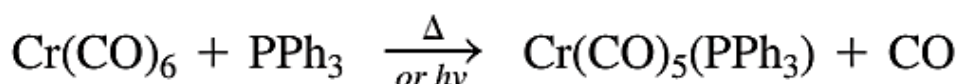
\*Some of metal carbonyls prepared from reducing their oxides at 300 C<sup>0</sup> and 300 atm.

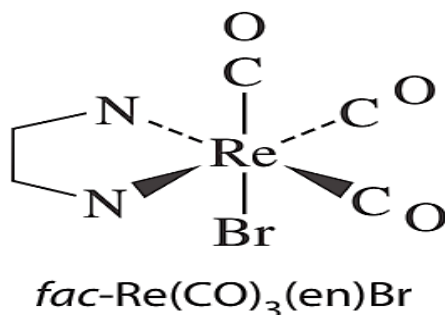


3) *Thermal or photochemical reaction of other binary carbonyls*. Examples are



\*The most common reaction of carbonyl complexes is CO dissociation. This reaction, which may be initiated **thermally** or by **absorption of ultraviolet light**, characteristically involves loss of CO from an 18-electron complex to give a 16-electron intermediate, which may react in a variety of ways, depending on the nature of the complex and its environment. A common reaction is replacement of the lost CO by another ligand to form a new 18-electron species as product. For example,



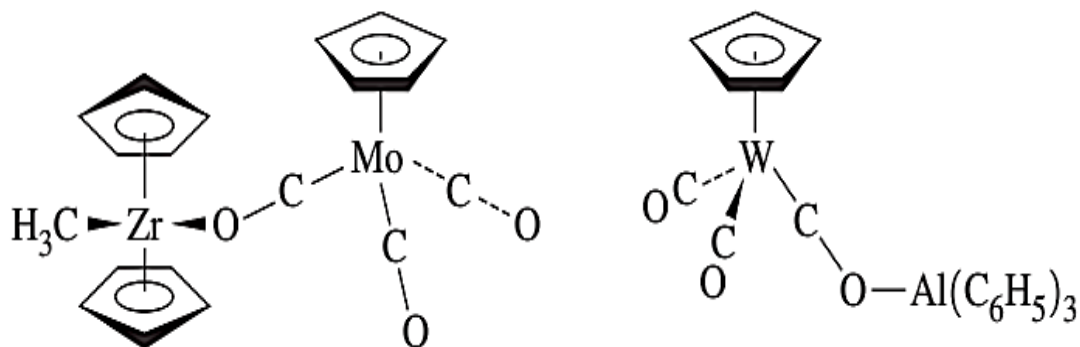


\*This type of reaction therefore provides a pathway in which CO complexes can be used as precursors for a variety of complexes of other ligands.

### \*\*Oxygen-Bonded Carbonyls

One additional aspect of CO as a ligand deserves mention: it can sometimes bond through oxygen as well as carbon. This phenomenon was first noted in the ability of the oxygen of a metal–carbonyl complex to act as a donor toward Lewis acids such as AlCl<sub>3</sub>, with the overall function of CO serving as a bridge between the two metals.

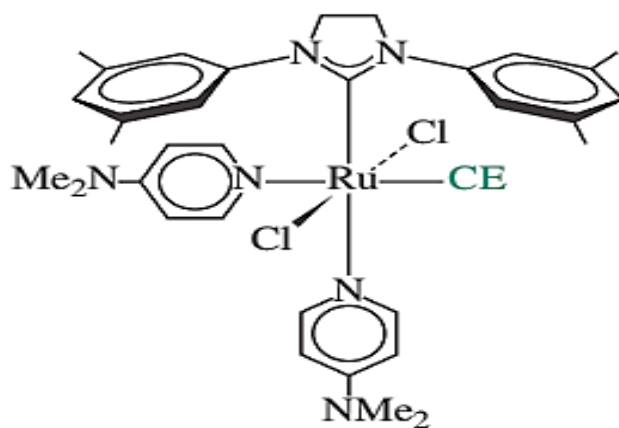
Many examples are known in which CO bonds through its oxygen to transition metal atoms, with the *C-O-metal* arrangement generally bent. Attachment of a Lewis acid to the oxygen results in significant weakening and lengthening of the *C-O* bond and a shift of the *C-O* stretching vibration to lower energy in the infrared. This shift is typically between *100* and *200 cm<sup>-1</sup>*. Examples of O-bonded carbonyls, sometimes called *isocarbonyls*, are in **Figure below**.



**\*\*Ligands Similar to CO**

\*CS (thiocarbonyl), CSe (selenocarbonyl), and CTe (tellurocarbonyl), are similar to CO in their bonding modes in that they behave as both  $\sigma$ -donors and  $\pi$ -acceptors and can bond to metals in terminal or bridging modes.

\* In several cases, isostructural complexes of the ligands CO through CTe have been prepared, providing opportunities for structural and spectroscopic comparisons. Data from a set of ruthenium complexes are provided in table below;

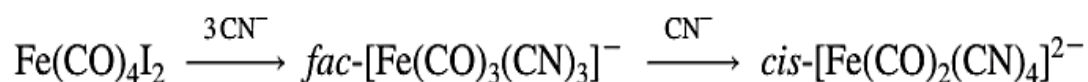


| CE  | $\nu(\text{C—E}), \text{cm}^{-1}$ | Ru—C Distance, nm |
|-----|-----------------------------------|-------------------|
| CO  | 1934                              | 1.829             |
| CS  | 1238                              | 1.793             |
| CSe | 1129                              | 1.766             |
| CTe | 1024                              | 1.748             |

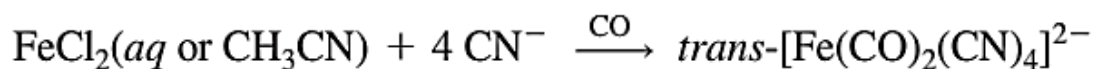
\* The decrease in ruthenium—carbon distance in going down this series is consistent with increasing  $\pi$ -acceptor activity of the ligands, populating orbitals that are bonding with respect to the Ru—C bond. Although increasing  $\pi$ -acceptor ability of the ligands accounts for some of the decrease in C—E stretching frequency.

\*Other ligands are *isoelectronic* with *CO* and, not surprisingly, exhibit structural and chemical parallels with CO. Two examples are  $\text{CN}^-$  and  $\text{N}_2$ . Complexes of  $\text{CN}^-$  have been known longer than carbonyl complexes. Blue complexes (*Prussian blue* and *Turnbull's blue*) containing the ion  $[\text{Fe}(\text{CN})_6]^{3-}$  have been used as pigments in paints and inks for approximately three centuries. Cyanide is a **stronger**  $\sigma$ -donor and a substantially **weaker**  $\pi$ -acceptor than CO; overall, it is close to CO in the spectrochemical series.

\* The discovery that hydrogenase enzymes contain both **CO** and **CN<sup>-</sup>** bound to iron has stimulated interest in complexes containing both ligands. Remarkably, only two iron complexes containing both CO and **CN<sup>-</sup>** and a single iron atom,  $[\text{Fe}(\text{CO})(\text{CN})_5]^{3-}$  (reported in 1887) and  $[\text{Fe}(\text{CO})_4(\text{CN})]^-$  (reported in 1974), were known before 2001. Both the *cis* and *trans* isomers of  $[\text{Fe}(\text{CO})_2(\text{CN})_4]^{2-}$  and *fac*- $[\text{Fe}(\text{CO})_3(\text{CN})_3]^-$  have been prepared. Two of the mixed ligand complexes can be made using  $\text{Fe}(\text{CO})_4\text{I}_2$ .



The complex *trans*- $[\text{Fe}(\text{CO})_2(\text{CN})_4]^{2-}$  can be made by the addition of cyanide to a solution of  $\text{FeCl}_2$  under an atmosphere of CO:

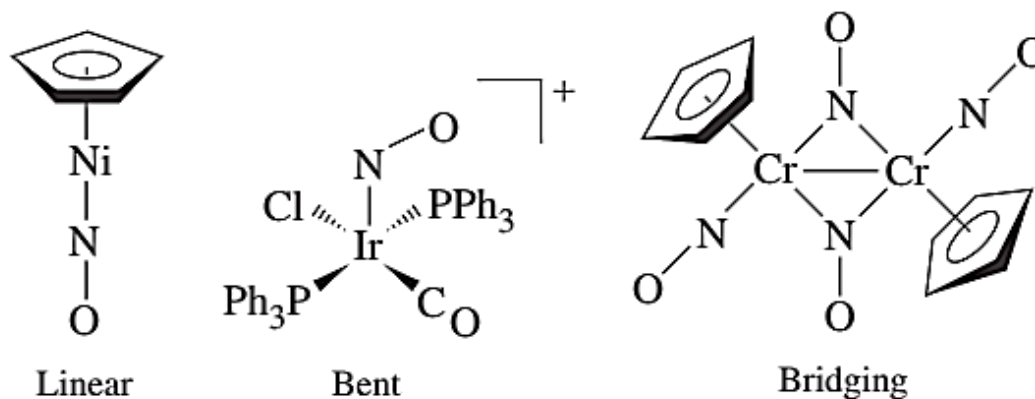


\* Dinitrogen is a weaker donor and acceptor than CO.

## \*\* NO Complexes

The NO (nitrosyl) ligand shares many similarities with CO. Like CO, it is a  **$\sigma$ -donor** and  **$\pi$ -acceptor** and can serve as a terminal or bridging ligand; useful information can be obtained about its compounds by analysis of its

infrared spectra. Unlike CO, however, terminal NO has two common coordination modes, linear (like CO) and bent. Examples of NO complexes are in figure below.



\*  $\text{NO}^+$  is isoelectronic with CO; therefore, in its bonding to metals, **linear NO** is considered by electron counting scheme (**ionic model**) as  $\text{NO}^+$ , a **2-electron** donor. By the (**covalent model**), linear NO is counted as a **3-electron** donor (it has one more electron than the **2-electron** donor CO).

\* The bent coordination mode of NO can be considered to arise formally from  $\text{NO}^-$ , with the bent geometry suggesting  $sp^2$  hybridization at the nitrogen. By electron-counting scheme (**ionic model**), therefore, bent NO is considered the **2-electron** donor  $\text{NO}^-$ , by the (**covalent model**), it is considered a **1-electron** donor.

\* Useful information about the linear and bent bonding modes of NO is summarized in **Figure below**. Many complexes containing each mode are known, and examples are also known in which both linear and bent NO occur in the same complex. Although linear coordination usually gives rise to **N-O** stretching vibrations at a higher energy than the bent mode, there is enough overlap in the ranges of these bands that infrared spectra alone may not be sufficient to distinguish between the two. Furthermore, the manner of packing in crystals may bend the **M-N-O** bond considerably from  $180^\circ$  in the linear coordination mode.

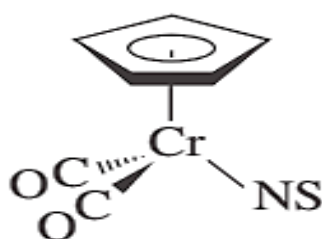
|                                  | <u>Linear</u>                                | <u>Bent</u>                                  |
|----------------------------------|--|--|
|                                  |  |  |
| M—N—O angle                      | 165°–180°                                    | 119°–140°                                    |
| $\nu$ (N-O) in neutral molecules | 1610–1830 cm <sup>-1</sup>                   | 1520–1720 cm <sup>-1</sup>                   |
| Electron donor count             | 2 (as NO <sup>+</sup> )<br>3 (as neutral NO) | 2 (as NO <sup>-</sup> )<br>1 (as neutral NO) |

|  |                |                              |
|--|----------------|------------------------------|
|  |                |                              |
| <b>Characterisation</b>                              |                |                              |
|  | M-N-O angle/ ° | $\nu$ (N-O)/cm <sup>-1</sup> |
| Fe(CN) <sub>5</sub> (NO) <sup>2-</sup>               | 178            | 1935                         |
| Mn(CN) <sub>5</sub> (NO) <sup>3-</sup>               | 174            | 1700                         |
| Co(NH <sub>3</sub> ) <sub>5</sub> (NO) <sup>2+</sup> | 119            | 1610                         |
| CoCl(en) <sub>2</sub> (NO) <sup>+</sup>              | 124            | 1611                         |

\* One compound containing only NO ligands is known, **Cr(NO)<sub>4</sub>**, a tetrahedral molecule that is isoelectronic with **Ni(CO)<sub>4</sub>**. Complexes containing bridging nitrosyl ligands are also known, with the neutral bridging ligand formally considered a 3-electron donor. One NO complex, the nitroprusside ion, **[Fe(CN)<sub>5</sub>(NO)]<sup>2-</sup>**, has been used as a vasodilator in the treatment of high blood pressure. Its therapeutic effect is a consequence of its ability to release its NO ligand; the NO acts as the vasodilating agent.



\* **NS (thionitrosyl)**. Like NO, NS can function in linear, bent, and bridging modes. In general, NS has been reported to act as a **stronger**  $\sigma$ -donor but **weaker**  $\pi$ -acceptor ligand than **NO**, a consequence of the greater concentration of negative charge on the nitrogen atom in NS. The difference in polarity of the NO and NS ligands also leads to significant differences in the electronic spectra of their complexes. The realm of **NSe (selenonitrosyl)** complex chemistry is limited; only a single complex of this ligand has been reported.



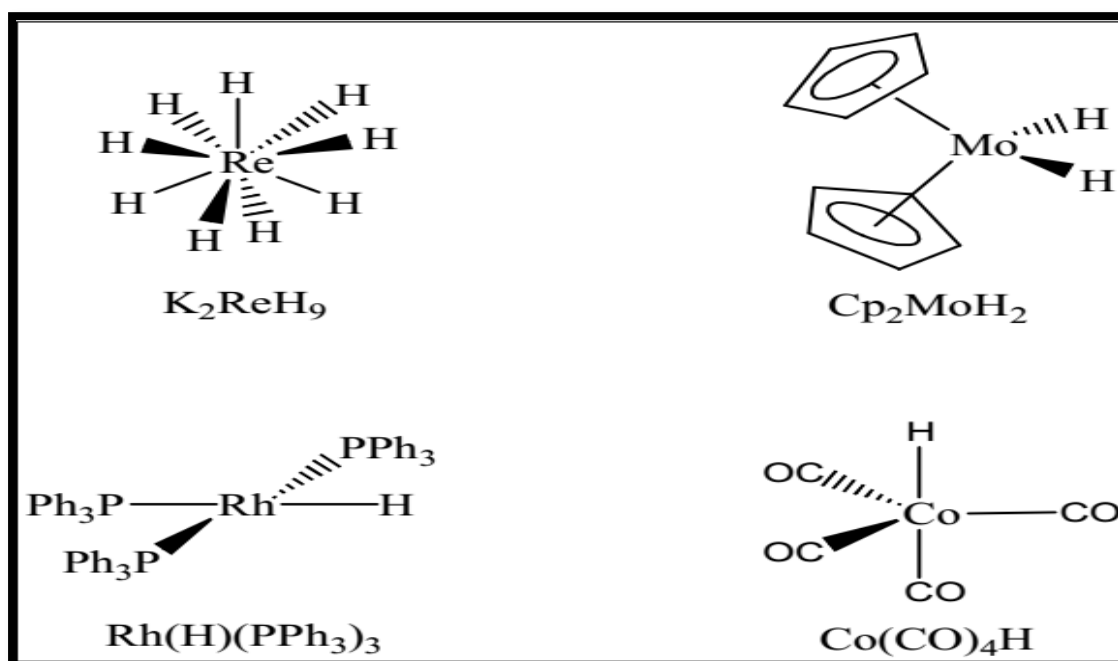
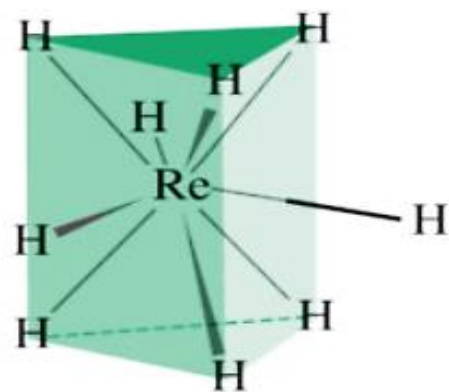
NS complex

## \*\* Hydride and Dihydrogen Complexes

### \* Hydride Complexes

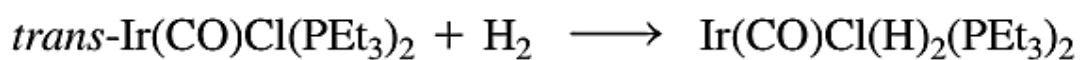
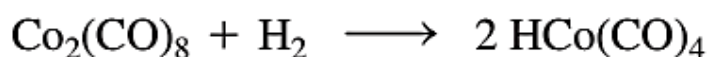
Although hydrogen atoms form bonds with nearly every element, we will specifically consider coordination compounds containing H bonded to transition metals. Because the hydrogen atom only has a **1s** orbital of suitable energy for bonding, the bond between H and a transition metal must be a  **$\sigma$ -interaction**, involving metal *s*, *p*, and/or *d* orbitals. As a ligand, H may be considered a **2-electron** donor as hydride (**H<sup>-</sup>**, ionic model) or a **1-electron** neutral donor (H atom, covalent model).

Although some transition-metal complexes containing only the hydride ligand are known—an example is the 9-coordinate **[ReH<sub>9</sub>]<sup>2-</sup>** ion ( Figure below), the classic example of a tricapped trigonal prism.

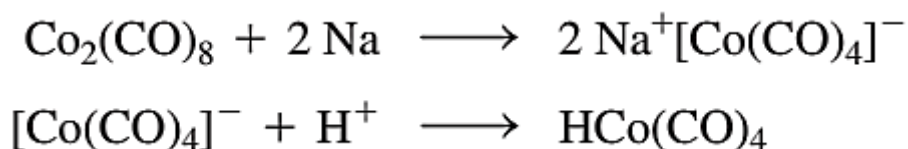


\* Compounds containing only a single ligand, such as NO in  $\text{Cr}(\text{NO})_4$  and CO in  $\text{Mo}(\text{CO})_6$ , are called **homoleptic** compounds.

\* We are principally concerned with complexes containing H in combination with other ligands. Such complexes may be made in a variety of ways. Probably the most common synthesis is by reaction of a transition metal complex with  $\text{H}_2$ . For example,



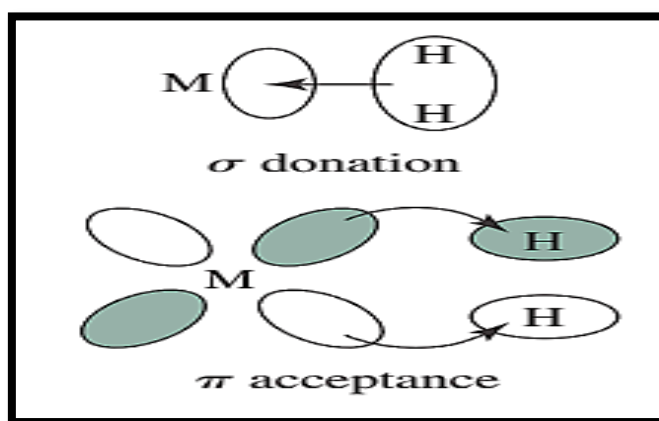
Carbonyl hydride complexes can also be formed by the reduction of carbonyl complexes, followed by the addition of acid. For example,

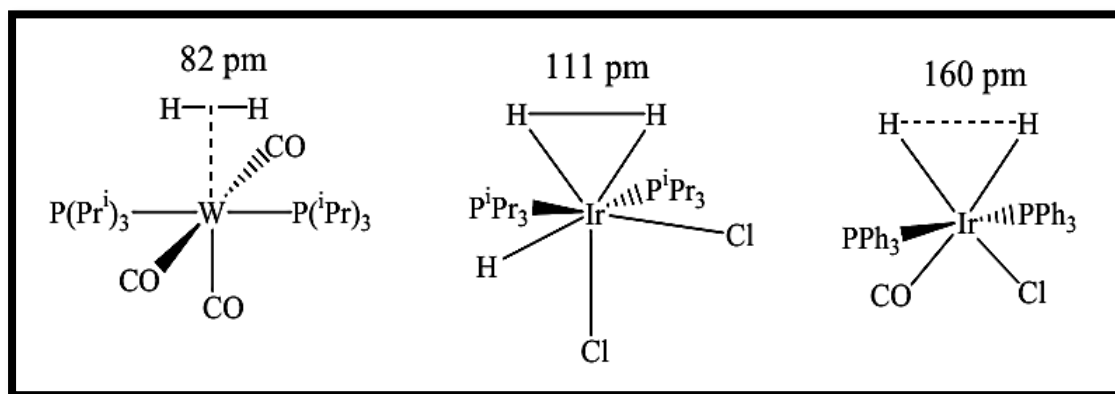


### \* Dihydrogen Complexes

The first structural characterization of a dihydrogen complex did not occur until 1984, when **Kubas** synthesized  $\text{M}(\text{CO})_3(\text{PR}_3)_2(\text{H}_2)$ , where  $\text{M} = \text{Mo}$  or  $\text{W}$  and  $\text{R} = \text{cyclohexyl}$  or  $\text{isopropyl}$ . Subsequently, many  $\text{H}_2$  complexes have been identified, and the chemistry of this ligand has developed rapidly.

\* The bonding between dihydrogen and a transition metal can be described as shown in **Figure below**. The  **$\sigma$ -electrons** in  $\text{H}_2$  can be donated to a suitable empty orbital on the metal (such as a  $d$  orbital or hybrid orbital), and the empty  **$\sigma^*$  orbital** of the ligand can accept electron density from an **occupied  $d$  orbital** of the metal. The result is an overall **weakening** and **lengthening** of the  $\text{H-H}$  bond in comparison with free  $\text{H}_2$ . Typical  **$\text{H-H}$  distances** in complexes containing coordinated dihydrogen are in the range of **82 to 90 pm**, in comparison with **74.14 pm** in free  $\text{H}_2$ .





\* If the metal is electron rich and donates strongly to the  $\sigma^*$  of  $\text{H}_2$  the **H-H** bond in the ligand can **rupture**, giving separate **H** atoms. Consequently, the search for stable  $\text{H}_2$  complexes has centered on metals likely to be relatively poor donors, such as those in high oxidation states or surrounded by ligands that function as strong electron acceptors. In particular, good  $\pi$ -acceptors, such as CO and NO, can be effective at stabilizing the dihydrogen ligand.

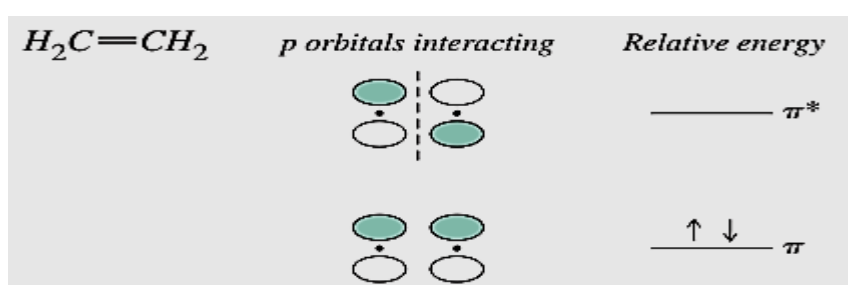
\* **E X E R C I S E:** *Explain why  $\text{Mo}(\text{PMe}_3)_5\text{H}_2$  is a di-hydride (contains two separate H ligands), but  $\text{Mo}(\text{CO})_3(\text{PR}_3)_2(\text{H}_2)$  contains the dihydrogen ligand (Me = methyl, R = isopropyl).*

Ans.  $\text{PMe}_3$  is a stronger  $\sigma$ -donor and weaker  $\pi$ -acceptor than CO. Therefore, the Mo in  $\text{Mo}(\text{PMe}_3)_5\text{H}_2$  has a greater concentration of electrons and a greater tendency to back-bond to the hydrogens by donating to the  $\sigma^*$  orbital of  $\text{H}_2$ . This donation is strong enough to rupture the **H-H** bond, converting  $\text{H}_2$  into two hydride ligands.

## \*\*Ligands Having Extended $\pi$ -Systems

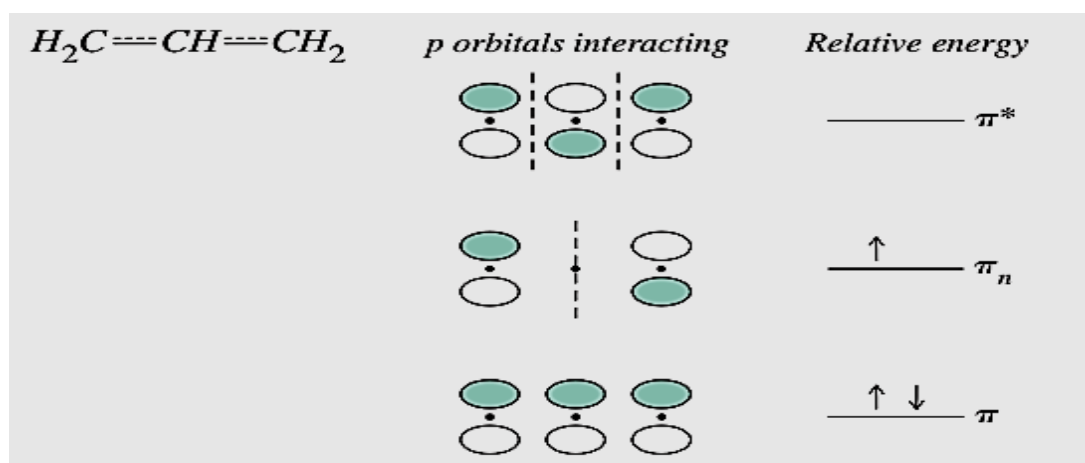
### \*Linear $\pi$ -Systems

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



\*The antibonding interaction has a nodal plane perpendicular to the internuclear axis, but the bonding interaction has no such nodal plane.

\*Next is the three-atom  $\pi$ -system, the  $\pi$ -allyl radical,  $C_3H_5$ . In this case, there are three  $2p$  orbitals to be considered, one from each of the carbon atoms participating in the  $\pi$ -system. The possible interactions are as follows:



\*The lowest energy  $\pi$ -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 ( $\pi_n$ ), 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  $\pi$ -orbital and thereby cancels it from participation. Highest in energy is the antibonding  $\pi^*$  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  $\pi$ -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.

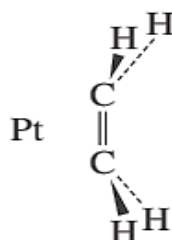
\*The term “linear” is used broadly to include not only ligands that have carbons in a straight line but acyclic ligands that are bent at inner  $sp^2$  carbons.

## \*\*Bonding between Metal Atoms and Organic Pi Systems

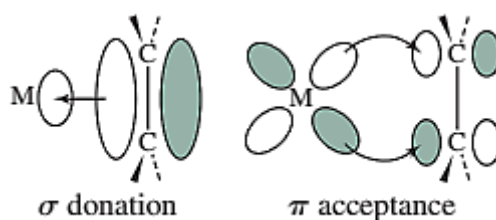
### \*Linear Pi Systems

#### \* $\pi$ -Ethylene Complexes

Many complexes involve ethylene,  $C_2H_4$ , as a ligand, including the anion of Zeise's salt,  $[Pt(\eta^2-C_2H_4)Cl_3]^-$ . In such complexes, ethylene commonly acts as a sidebound ligand with the following geometry with respect to the metal:



\*The 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  $\pi$ -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  $\pi^*$  orbital of the ligand. This is another example of the synergistic effect of  $\sigma$  donation and  $\pi$ -acceptance.

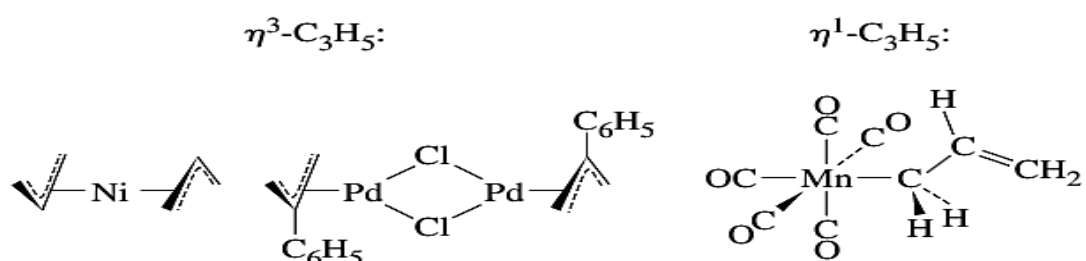


\*The C-C distance in Zeise's salt is **137.5 pm** in comparison with **133.7 pm** in free ethylene. The lengthening of this bond can be explained by a combination of the two factors involved in the synergistic  **$\sigma$ -donor,  $\pi$ -acceptor** nature of the ligand: donation of electron density to the metal in a sigma fashion reduces the  $\pi$ -bonding electron density within the ligand, weakening the **C-C bond**. The net effect weakens and lengthens the C-C bond in the C<sub>2</sub>H<sub>4</sub> ligand.

\*In addition, vibrational frequencies of coordinated ethylene are at lower energy than in free ethylene; for example, the C=C stretch in the anion of Zeise's salt is at **1516 cm<sup>-1</sup>**, compared to **1623 cm<sup>-1</sup>** in free ethylene.

### \* $\pi$ -Allyl Complexes

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

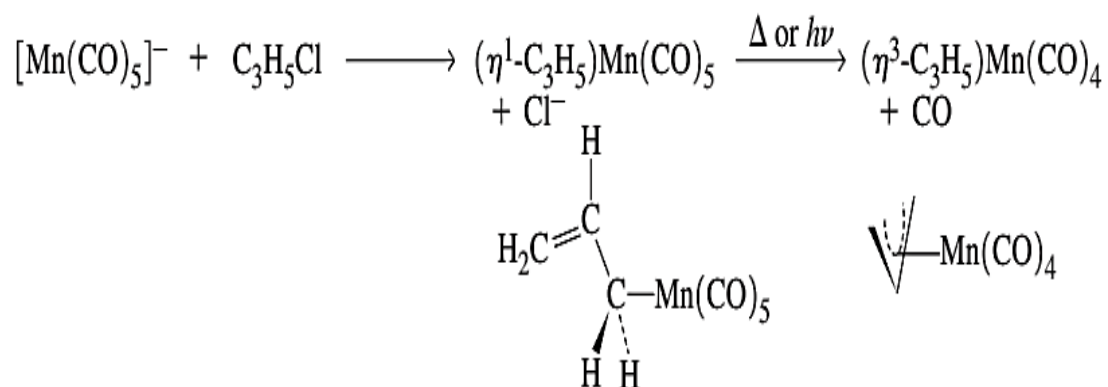


\*The lowest energy  $\pi$ -orbital can donate electron density in a sigma fashion to a suitable orbital on the metal. The next orbital, nonbonding in free allyl, can act as a donor or acceptor, depending on the electron



distribution between the metal and the ligand. The highest energy  $\pi$ -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  $120^\circ$ , 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  $\eta^3$  and  $\eta^1$  fashion. Loss of CO from carbonyl complexes containing  $\eta^1$ -allyl ligands often results in conversion of  $\eta^1$ -allyl to  $\eta^3$ -allyl. For example,

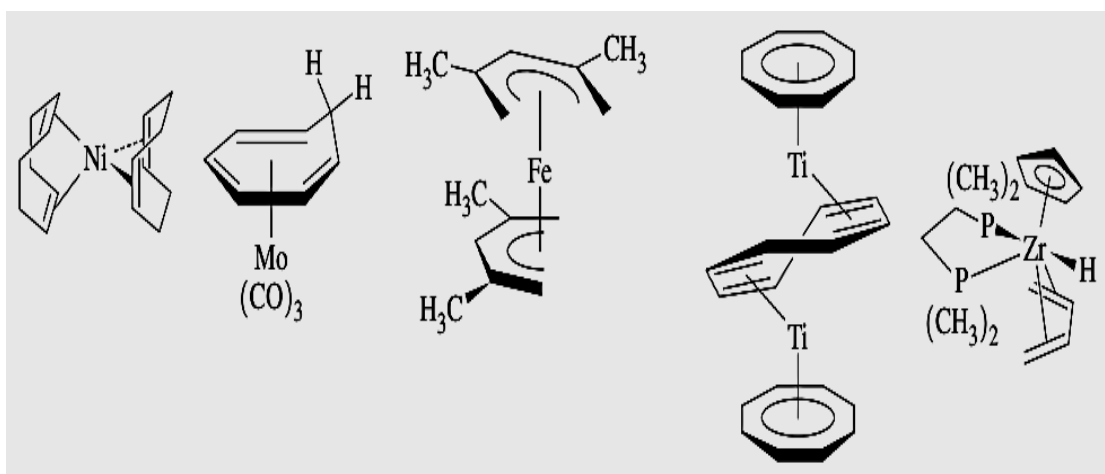


The  $[\text{Mn}(\text{CO})_5]^-$  ion displaces  $\text{Cl}^-$  from allyl chloride to give an 18-electron product containing  $\eta^1\text{-C}_3\text{H}_5$ . The allyl ligand switches to trihapto when a CO is lost, preserving the 18-electron count.

### \*Other Linear Pi Systems

Many other such systems are known; several examples of organic ligands having longer  $\pi$ -systems are in Figure below. **Butadiene** and longer conjugated  $\pi$ -systems have the possibility of isomeric ligand forms (*cis*

and *trans* for butadiene). Larger cyclic ligands may have a  $\pi$ -system extending through part of the ring. An example is **cyclooctadiene (COD)**; the 1,3-isomer has a 4-atom  $\pi$ -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.



\***Exercise:** Identify the transition metal in the following 18-electron complexes: **a.**  $(\eta^5\text{-C}_5\text{H}_5)(\text{cis-}\eta^4\text{C}_4\text{H}_6)\text{M}(\text{PMe}_3)_2(\text{H})$  (M)=second row transition metal) **b.**  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{C}_2\text{H}_4)_2$  (M = first-row transition metal).

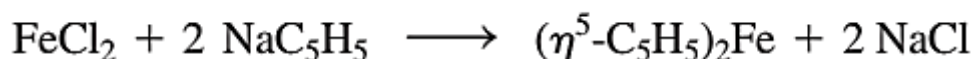
### \*\*Cyclic $\pi$ -Systems

#### \*Cyclopentadienyl (Cp) Complexes

The cyclopentadienyl group,  $\text{C}_5\text{H}_5$ , may bond to metals in a variety of ways, with many examples known of the  $\eta^1$ -,  $\eta^3$ -, and  $\eta^5$ -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  $\pi$ -bonded organic

ligands. Substituted cyclopentadienyl ligands are also known, such as  $C_5(CH_3)_5$ , often abbreviated Cp\*, and  $C_5(\text{benzyl})_5$ .

\* Ferrocene and other cyclopentadienyl complexes can be prepared by reacting metal salts with  $NaC_5H_5$ .



\* **Ferrocene,  $(\eta^5-C^5H^5)_2Fe$**

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.

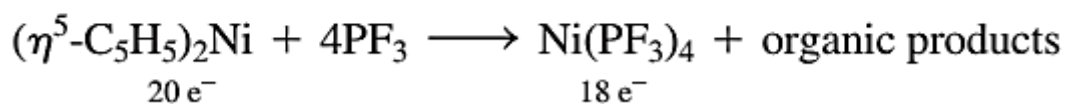
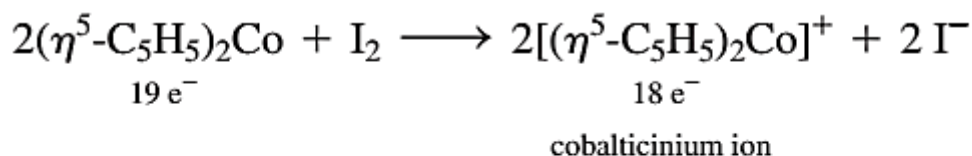
\* **Other Metallocenes and Related Complexes**

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.

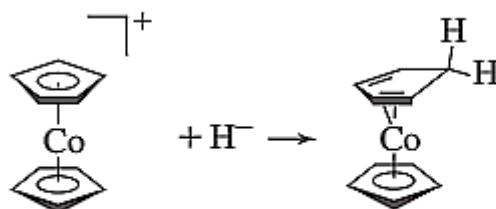
| Complex               | Electron Count | M—C Distance (pm) | $\Delta H$ for $M^{2+} - C_5H_5^-$ Dissociation (kJ/mol) |
|-----------------------|----------------|-------------------|--|
| $(\eta^5-C_5H_5)_2Fe$ | 18             | 206.4             | 1470   |
| $(\eta^5-C_5H_5)_2Co$ | 19             | 211.9             | 1400   |
| $(\eta^5-C_5H_5)_2Ni$ | 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  $\Delta H$  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:

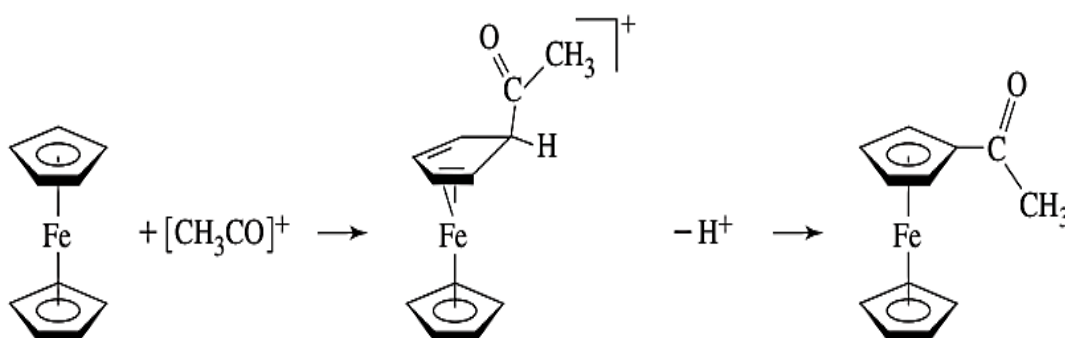


\* Cobalticinium reacts with hydride to give a neutral, 18-electron sandwich compound in which one cyclopentadienyl ligand has been modified into  $\eta^4\text{-C}_5\text{H}_6$  (**Figure below**)

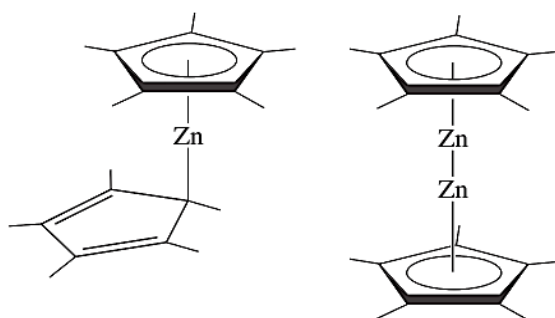


Reaction of Cobalticinium with Hydride.

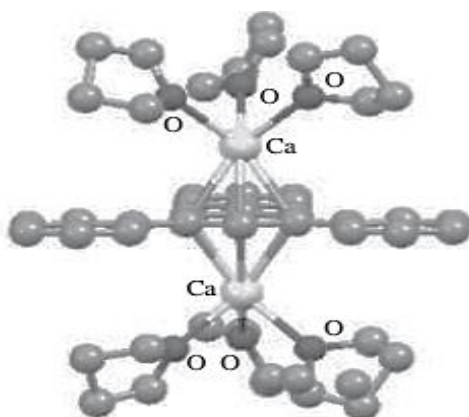
Ferrocene,. It undergoes a variety of reactions, including many on the cyclopentadienyl rings. A good example is that of electrophilic acyl substitution (**Figure below**), a reaction paralleling that of benzene and its derivatives. In general, electrophilic aromatic substitution reactions are much more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



\*Binuclear metallocenes with two atoms, rather than one in the center of a sandwich structure are also known. Perhaps the best known of these metallocenes is decamethyldizincocene,  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zn}_2$  (**Figure below**), which was prepared from decamethylzincocene,  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zn}$ , and diethylzinc. Particularly notable is  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zn}_2$ , the first example of a stable molecule with a **zinc–zinc** bond; moreover, its zinc atoms are in the exceptionally rare **+1** oxidation state.

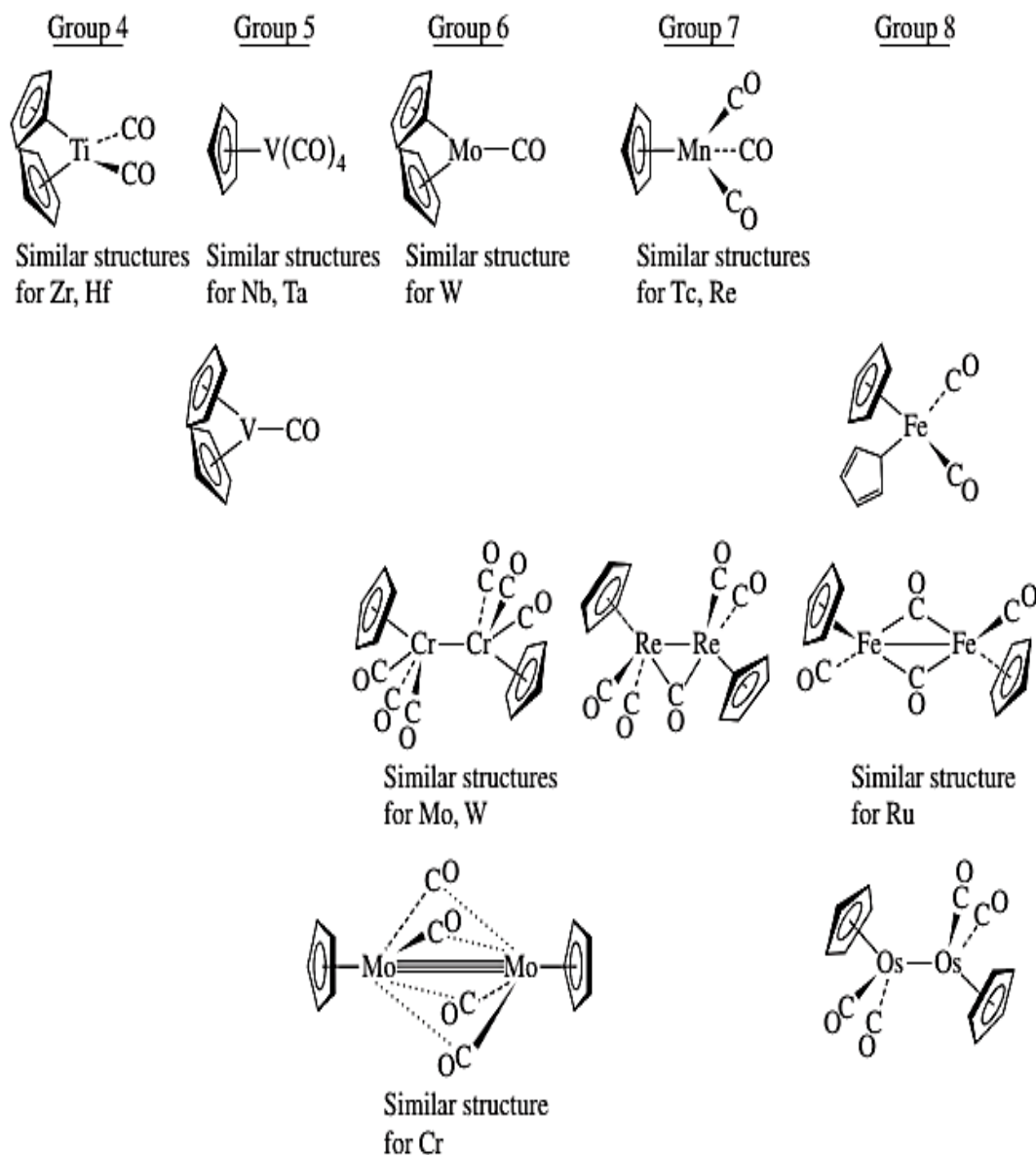


\*A variation on the theme of metallocenes and related sandwich compounds is provided by the “**inverse**” sandwich in **Figure below**, with calcium(I) ions on the outside and the cyclic pi ligand 1,3,5-triphenylbenzene in between. This compound was most efficiently prepared by reacting 1,3,5-triphenylbenzene with activated calcium in THF solvent using catalytic amounts of 1-bromo-2,4,6-triphenylbenzene. Although the product of this reaction is highly sensitive to moisture and air and it represents a rare example of a **+1** oxidation state among the alkaline earths.



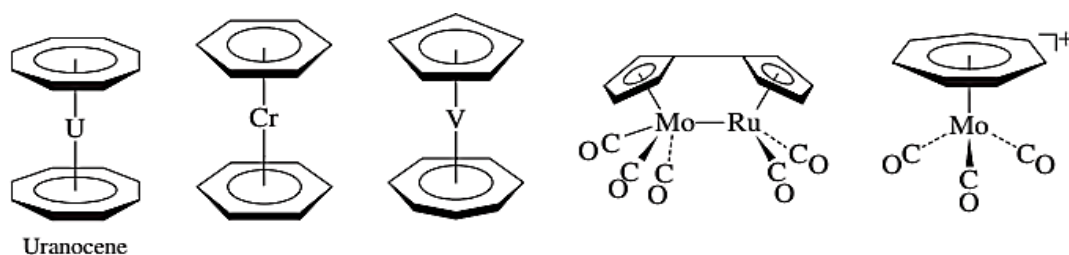
## **\*\*Complexes Containing Cyclopentadienyl and CO Ligands**

Many complexes are known containing both Cp and CO ligands. These include “**half-sandwich**” compounds such as  $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$  and dimeric and larger cluster molecules. Examples are in **Figure below**. As for the binary CO complexes, complexes of the second- and third-row transition metals show a decreasing tendency of CO to act as a bridging ligand.



\*Many other linear and cyclic pi ligands are known. Examples of complexes containing some of these ligands are in **Figure below**.

Depending on the ligand and the electron requirements of the metal (or metals), these ligands may be capable of bonding in a mono-hapto or polyhapto fashion, and they may bridge two or more metals.



**\*\* Complexes containing M—C, M=C and M≡C bonds**

Complexes containing direct metal–carbon single, double, and triple bonds have been studied extensively. **Table below** gives examples of the most important types of ligands in these complexes.

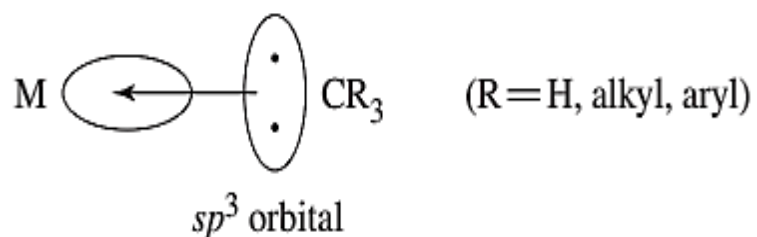
**Complexes Containing M—C, M=C, and M≡C Bonds**

| Ligand               | Formula                 | Example                                       |
|----------------------|-------------------------|---|
| Alkyl                | —CR <sub>3</sub>        | W(CH <sub>3</sub> ) <sub>6</sub>              |
| Carbene (alkylidene) | =CR <sub>2</sub>        | (OC) <sub>5</sub> Cr=C(OCH <sub>3</sub> )<br> |
| Carbyne (alkylidyne) | ≡CR                     |   |
| Carbide (carbon)     | ≡C                      |   |
| Cumulene             | =C(=C) <sub>n</sub> RR' |   |



### **\*Alkyl and Related Complexes**

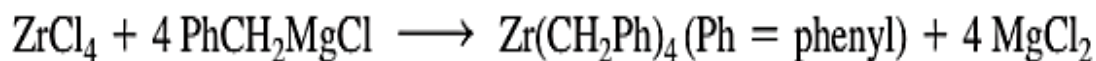
Some of the earliest known organometallic complexes were those having  **$\sigma$ -bonds** between main group metal atoms and alkyl groups. Examples include Grignard reagents, having magnesium–alkyl bonds, and alkyl complexes with alkali metals, such as methyllithium. Stable transition metal alkyls were 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  **$\cdot CR_3$**  (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

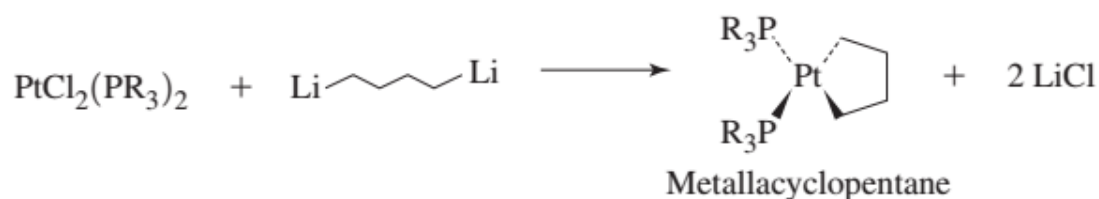


2- Reaction of a metal carbonyl anion with an alkyl halide

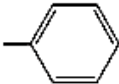
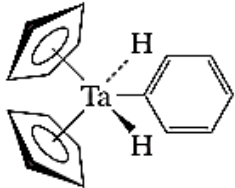
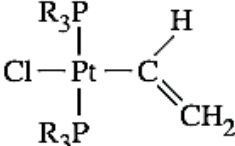
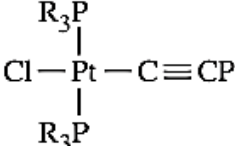


Although many complexes contain alkyl ligands, transition-metal complexes that contain alkyl groups as the only ligands, are relatively rare. Examples include  $\text{Ti}(\text{CH}_3)_4$ ,  $\text{W}(\text{CH}_3)_6$ , and  $\text{Cr}[\text{CH}_2\text{Si}(\text{CH}_3)_3]_4$ . Alkyl complexes have a tendency to be kinetically unstable; their stability is enhanced by structural crowding, which protects the coordination sites of the metal. The 6-coordinate  $\text{W}(\text{CH}_3)_6$  can be melted at  $30\text{ }^\circ\text{C}$  without decomposition, whereas the 4-coordinate  $\text{Ti}(\text{CH}_3)_4$  is subject to decomposition at approximately  $-40\text{ }^\circ\text{C}$ .

\*Other ligands have direct metal–carbon  $\sigma$ -bonds (**Table below**). In addition, there are many examples of **metallacycles**, complexes in which organic ligands attach to metals at two positions, thereby incorporating the metals into organic rings. The reaction below is an example of a metallacycle synthesis. Metallacycles are important intermediates in catalytic processes.



### Other Ligands Forming Sigma Bonds to Metals

| Ligand          | Formula   | Example  |
|-----------------|---|--|
| Aryl            |  |   |
| Alkenyl (vinyl) | $\text{C}=\text{C}$   |   |
| Alkynyl         | $\text{C}\equiv\text{C}$  |  |

### \*Carbene Complexes

Carbene complexes contain metal–carbon double bonds. First synthesized in 1964 by **Fischer**, carbene complexes are known for the majority of transition metals and for a wide range of carbene ligands, including the simple carbene,  $:\text{CH}_2$ . The majority of such complexes contain one or two highly electronegative heteroatoms—such as O, N, or S—directly attached to the carbene carbon. These are designated as ***Fischer-type carbene complexes***. Other carbene complexes contain only carbon and/or hydrogen attached to the carbene carbon. First synthesized several years after the initial Fischer carbene complexes, these have been studied

extensively by **Schrock** and several others. They are sometimes designated as *Schrock-type carbene complexes*, commonly referred to as *alkylidenes*. Distinctions between Fischer- and Schrock-type carbene complexes are summarized in **Table below**. We will focus primarily on Fischer-type carbene complexes.

**Fischer- and Schrock-Type Carbene Complexes**

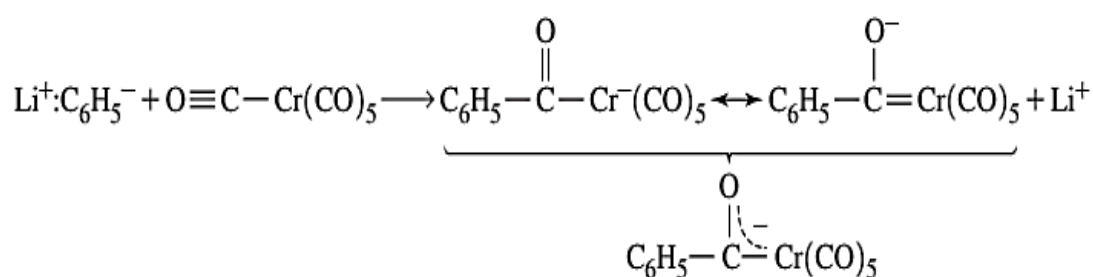
| Characteristic                                | Fischer-Type Carbene Complex  | Schrock-Type Carbene Complex           |
|---|---|--|
| Typical metal [oxidation state]               | Middle to late transition metal [Fe(0), Mo(0), Cr(0)]               | Early transition metal [Ti(IV), Ta(V)] |
| Substituents attached to C <sub>carbene</sub> | At least one highly electronegative heteroatom (such as O, N, or S) | H or alkyl                             |
| Typical other ligands in complex              | Good $\pi$ acceptors  | Good $\sigma$ or $\pi$ donors          |
| Electron count                                | 18  | 10–18                                  |

\*The formal double bond in carbene complexes may be compared with the double bond in alkenes. In the case of a carbene complex, the metal must use a *d* orbital to form the  $\pi$ - bond with carbon.

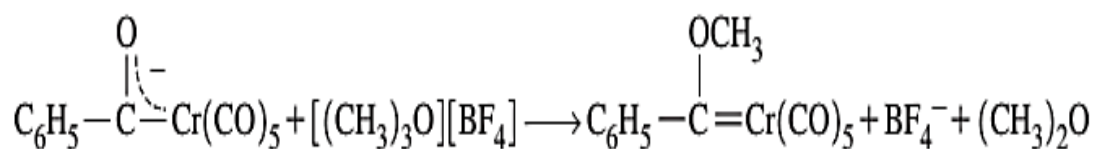
\*Carbene complexes having a highly electronegative atom such as **O**, **N**, or **S** attached to the carbene carbon tend to be more stable than complexes lacking such an atom. For example,  $\text{Cr}(\text{CO})_5[\text{C}(\text{OCH}_3)\text{C}_6\text{H}_5]$ , with an oxygen on the carbene carbon, is much more stable than  $\text{Cr}(\text{CO})_5[\text{C}(\text{H})\text{C}_6\text{H}_5]$ . The stability of the complex is enhanced if the highly electronegative atom can participate in the  $\pi$ - bonding, with the result a delocalized, 3-atom  $\pi$  system involving a

$d$  orbital on the metal and  $p$  orbitals on the carbon and on the electronegative atom. Such a delocalized 3-atom system provides more stability to the bonding  $\pi$  electron pair than would a simple metal-to-carbon  $\pi$  bond.

\*The methoxycarbene complex  $\text{Cr}(\text{CO})_5[\text{C}(\text{OCH}_3)\text{C}_6\text{H}_5]$  synthesized via reacting **phenyllithium** with  $\text{Cr}(\text{CO})_6$  to give the anion  $[\text{C}_6\text{H}_5\text{C}(\text{O})\text{Cr}(\text{CO})_5]^-$ , which has two important resonance structures:



Alkylation by a source of  $\text{CH}_3^+$ , such as  $[(\text{CH}_3)_3\text{O}][\text{BF}_4]$  or  $\text{CH}_3\text{I}$ , gives the methoxycarbene complex:



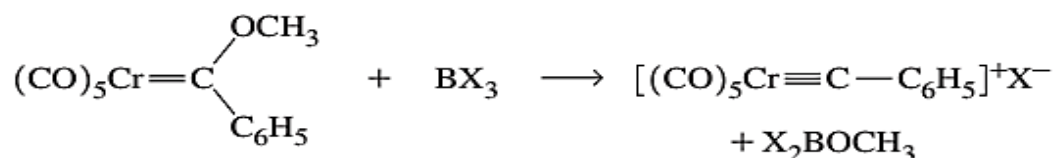
Evidence for double bonding between chromium and carbon is provided by X-ray crystallography, which measures this distance at **204 pm**, compared with a typical **Cr-C** single-bond distance of approximately **220 pm**.

\***Carbyne (Alkylidyne) Complexes**

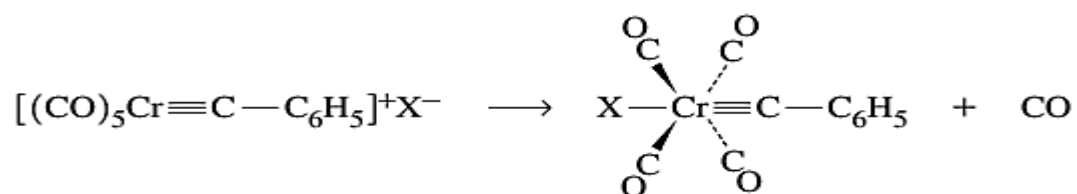
Carbyne complexes have metal–carbon triple bonds; they are formally analogous to alkynes. Many carbyne complexes are now known; examples of carbyne ligands include the following:



where R = aryl, alkyl, H, SiMe<sub>3</sub>, NEt<sub>2</sub>, PMe<sub>2</sub>, SPh, or Cl. Carbyne complexes were first synthesized by chance as products of the reactions of carbene complexes with Lewis acids. The methoxycarbene complex  $\text{Cr}(\text{CO})_5[\text{C}(\text{OCH}_3)\text{C}_6\text{H}_5]$  was found to react with the Lewis acids  $\text{BX}_3$  (X = Cl, Br, or I). First, the Lewis acid attacks the oxygen, the basic site on the carbene:

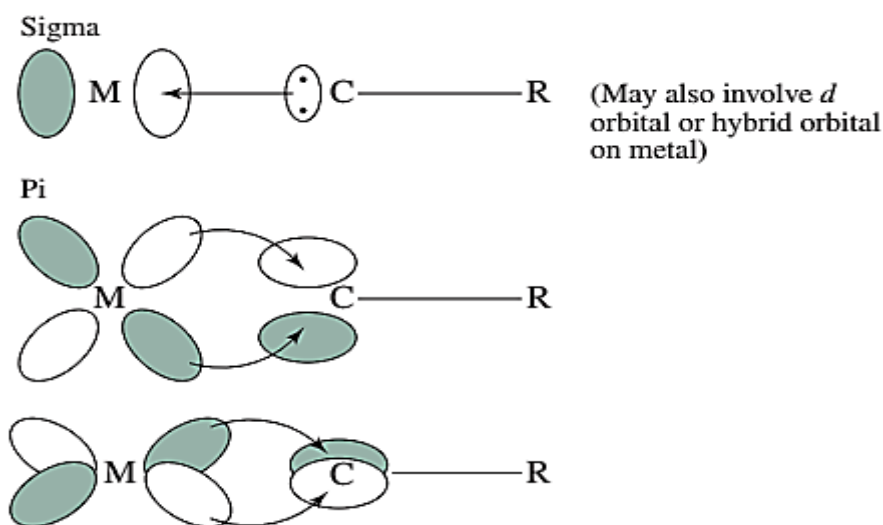


The intermediate loses CO, with the halide coordinating *trans* to the carbyne:

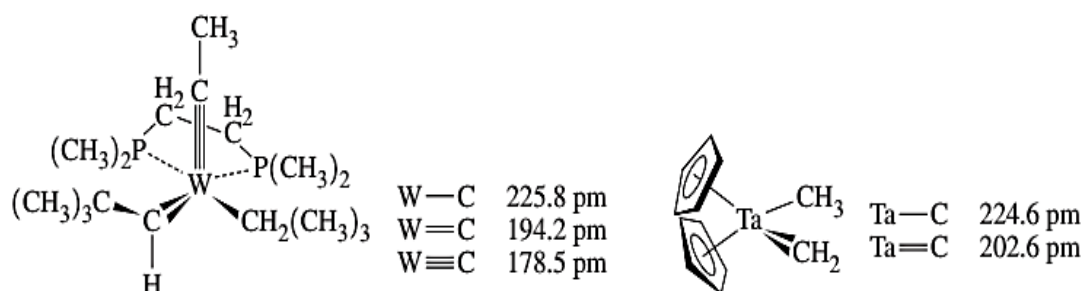


The best evidence for the carbyne nature of the complex is provided by X-ray crystallography, which gives a Cr–C bond distance of **168 pm** (for X = Cl), considerably shorter than the **204 pm** for the parent carbene complex. The  $\text{Cr}\equiv\text{C}-\text{C}$  angle is, as expected, 180° for this complex; however, slight deviations from linearity are observed for many complexes in crystalline form, in part a consequence of crystal packing effects.

\*Bonding in carbyne complexes may be viewed as a combination of a  $\sigma$ -bond plus two  $\pi$ -bonds (**Figure below**). The carbyne ligand has a lone pair of electrons in an  $sp$  hybrid on carbon; this lone pair can donate to a suitable orbital on Cr to form a  $\sigma$ -bond. In addition, the carbon has two  $p$  orbitals that can accept electron density from  $d$  orbitals on Cr to form  $\pi$  bonds. Thus, the overall function of the carbyne ligand is as both a  $\sigma$  donor and  $\pi$  acceptor. (For electron counting purposes, a  $:\text{CR}^+$  ligand can be considered a 2-electron donor; it is usually more convenient to count neutral CR as a 3-electron donor).

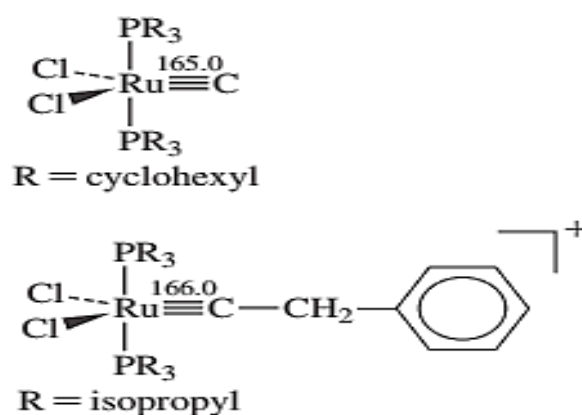


In some cases, molecules have been synthesized containing two or three of the types of ligands discussed in this section (alkyl, carbene, and carbyne).



**\*Carbide and Cumulene Complexes**

The first neutral carbide complex was a *trigonal-bipyramidal* ruthenium complex (**Figure below**). The *Ru-C* distance in this complex is perhaps longer than might be expected, **165.0 pm**, only slightly shorter than the comparable distance in the structurally similar ruthenium carbyne complex, also shown.



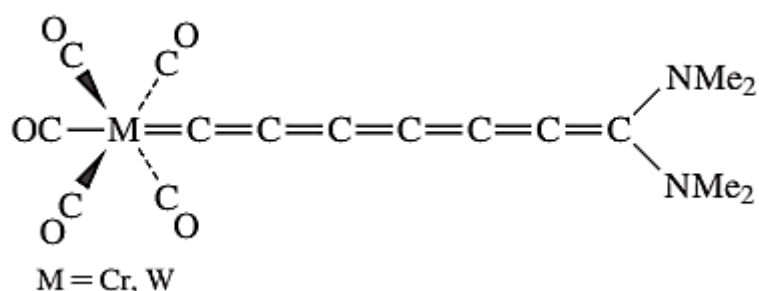
\*Calculations have indicated that bonds between transition metals and terminal carbon atoms are quite strong, with bond dissociation enthalpies comparable to those of transition-metal complexes with  $\text{M}\equiv\text{N}$  and  $\text{M}=\text{O}$  bonds. In addition, the frontier orbitals of the carbide complex in Figure above (where  $\text{R} = \text{methyl}$ ) have many similarities to those of  $\text{CO}$ , suggesting that such complexes may potentially show similar coordination chemistry to the carbonyl ligand.

\*Ligands with chains of carbon atoms that have cumulated (consecutive) double bonds, designated *cumulenyliene* ligands, are also known. Such **metallacumulene** complexes have drawn interest because of possible



applications as *1-dimensional molecular wires* and for use in *nanoscale optical devices*. In recent years, complexes with 2- and 3-carbon chains have also been developed as effective catalysts.

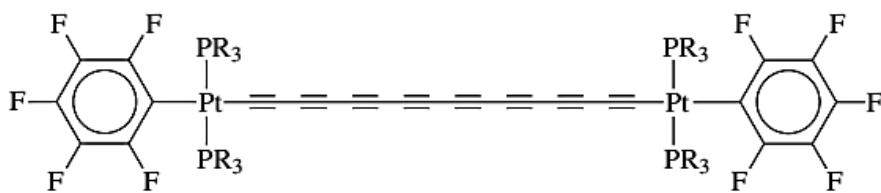
The longest cumulenylidene ligand reported to date is the heptahexaenylidene complex shown in **Figure below**. As in the case of extended organic pi systems, the difference in energy between the HOMO and the LUMO decreases as the length of the cumulene ligand increases.



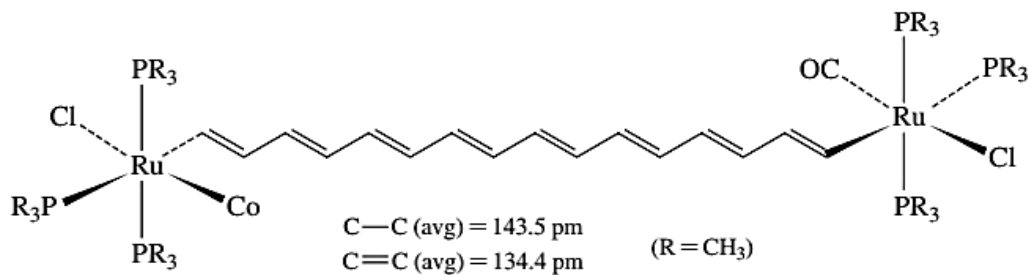
### \*Carbon Wires: Polyene and Polyene Bridges

The most widely studied types of these bridges have been the **polyynediyl** bridges with alternating single and triple bonds and **polyenediyl** bridges with alternating single and double bonds.

The bond conjugation (extended  $\pi$  system) is needed to enable electronic communication between the metal atoms at the ends of the bridges; saturated bridges or sections of bridges inhibit such communication. Examples of structures containing polyene and polyene bridges are in **Figure below**.



C—C (avg) = 135.1 pm  
 C≡C (avg) = 121.6 pm (R = *p*-Tol)



C—C (avg) = 143.5 pm  
 C=C (avg) = 134.4 pm (R = CH<sub>3</sub>)

# Organometallic Reactions

## **\*\*Reactions Involving Gain or Loss of Ligands**

Many reactions of organometallic compounds involve a change in metal coordination number by a gain or loss of ligands. If the oxidation state of the metal is retained, these reactions are considered addition or dissociation reactions; if the metal oxidation state is changed, they are termed oxidative additions or reductive eliminations. In classifying these reactions, it is often necessary to determine oxidation states of the metals.

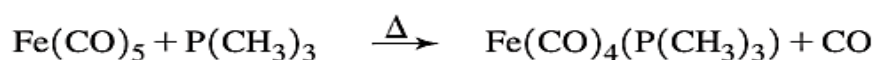
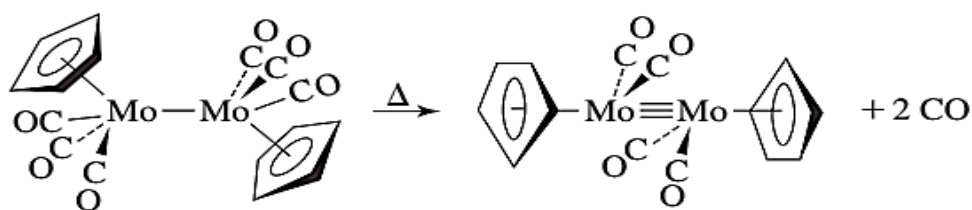
| Type of Reaction      | Change in Coordination Number | Change in Formal Oxidation State of Metal |
|-----------------------|-------------------------------|---|
| Addition              | Increase                      | None                                      |
| Dissociation          | Decrease                      | None                                      |
| Oxidative addition    | Increase                      | Increase                                  |
| Reductive elimination | Decrease                      | Decrease                                  |

### **1- Ligand Dissociation and Substitution reaction**

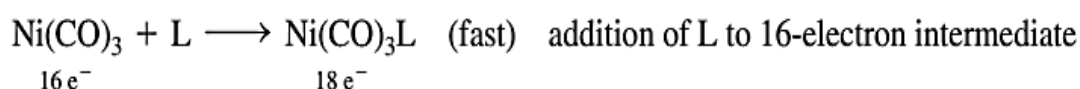
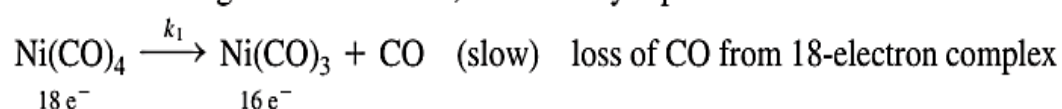
These reactions involved replace ligands such as *carbon monoxide* and *phosphines*.

#### **a- CO Dissociation**

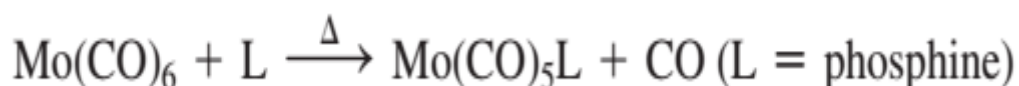
We previously mentioned carbonyl dissociation reactions, in which CO may be lost thermally or photo chemically. Such a reaction may result in rearrangement of the remaining molecule or replacement of CO by another ligand:



The second type of reaction shown above, involving ligand replacement, is an important way to introduce new ligands into complexes. Most thermal reactions involving replacement of CO by another ligand, L, have rates that are independent of the concentration of L; they are first order with respect to the metal complex. This behavior is consistent with a *dissociative* mechanism involving slow loss of CO, followed by rapid reaction with L:



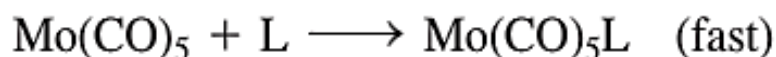
The first step is rate limiting, and has the rate law  $\text{Rate} = k_1[\text{Ni(CO)}_4]$ . Some ligand replacement reactions show more complicated kinetics. Study of the following reaction



has shown that, for some phosphines, the rate law is:

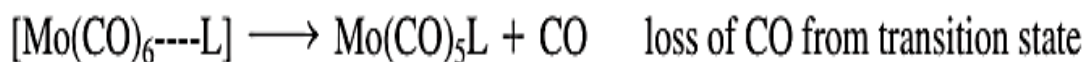
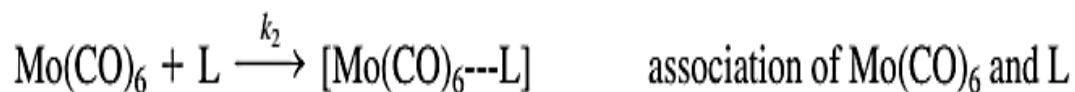
$$\text{Rate} = k_1[\text{Mo(CO)}_6] + k_2[\text{Mo(CO)}_6][\text{L}]$$

The two terms in the rate law imply parallel pathways for the formation of  $\text{Mo(CO)}_5\text{L}$ . The first term is consistent with a dissociative mechanism:



$$\text{Rate}_1 = k_1[\text{Mo(CO)}_6]$$

There is strong evidence that solvent is involved in the first-order mechanism for the replacement of CO; however, because the solvent is in great excess, it does not appear in the above rate law; this pathway exhibits pseudo–first order kinetics. The second term is consistent with an **associative** process, involving a bimolecular reaction of  $\text{Mo(CO)}_6$  and L to form a transition state that loses CO:



Formation of the transition state is the rate-limiting step in this mechanism; the rate law for this pathway is

$$\text{Rate}_2 = k_2[\text{Mo(CO)}_6][\text{L}]$$

The overall rate of formation of  $\text{Mo(CO)}_5\text{L}$  is the sum of the rates of the unimolecular and bimolecular mechanisms,  $\text{Rate}_1 + \text{Rate}_2$ .

\* Most CO substitution reactions proceed by dissociative mechanisms.

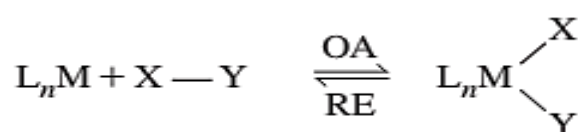
### b- Dissociation of Phosphine

Ligands other than carbon monoxide can dissociate, with the ease of dissociation a function of the strength of metal–ligand bonding. The metal–ligand bond strength depends on an interplay of electronic effects (for example, the match of energies of the metal and ligand orbitals) and steric effects (for example, the degree to which crowding of ligands around the metal can reduce the strength of metal-ligand orbital overlap). These steric effects have been investigated for many ligands but especially for neutral donor ligands such as phosphines.

\*The presence of bulky ligands results in crowding around the metal. This can lead to more rapid ligand dissociation as a consequence of slight elongation of metal–ligand bonds to relieve steric hindrance at the metal center.

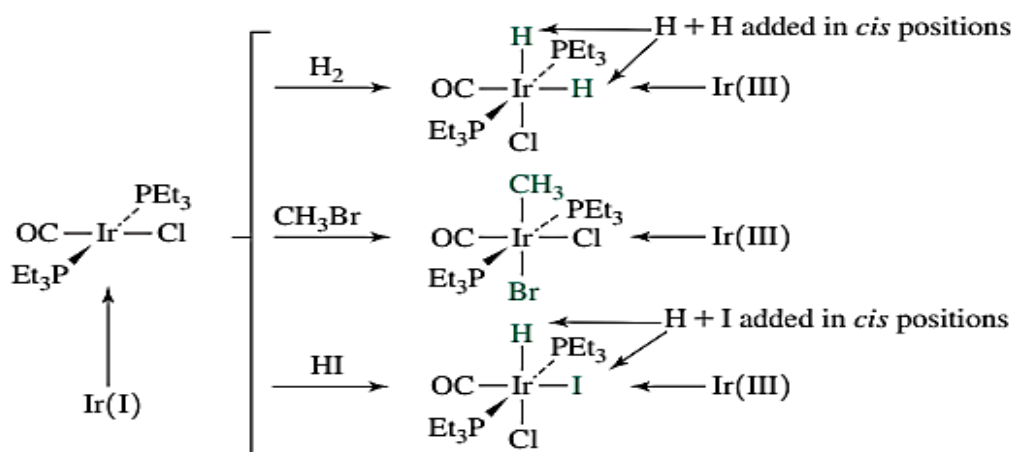
### 2- Oxidative Addition and C—H Bond Activation

These reactions involve an increase in both the oxidation state and the coordination number of the metal. *Oxidative addition (OA)* reactions are essential steps in many catalytic processes. The reverse reaction, designated *reductive elimination (RE)*, is also very important. These reactions are described schematically by the following:



| Type of Reaction      | Change in Coordination Number | Change in Formal Oxidation State of Metal | Change in Electron Count |
|-----------------------|-------------------------------|---|--------------------------|
| Oxidative addition    | Increase by 2                 | Increase by 2                             | Increase by 2            |
| Reductive elimination | Decrease by 2                 | Decrease by 2                             | Decrease by 2            |

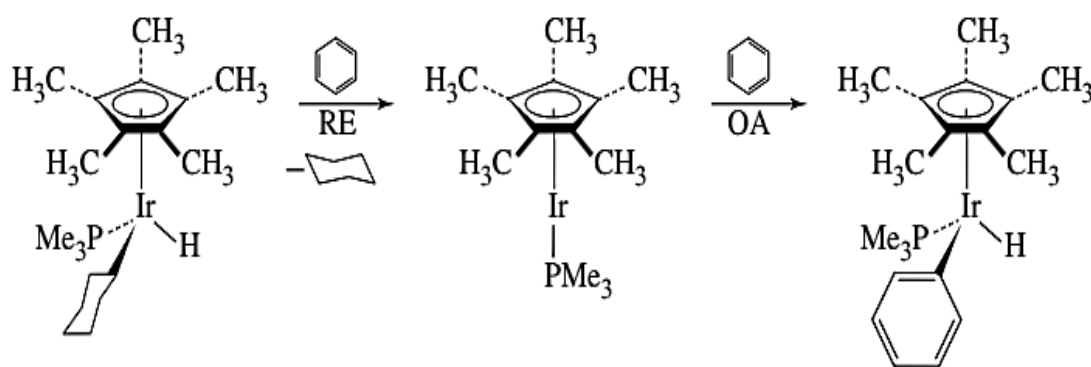
\*Oxidative addition reactions of square-planar  $d^8$  complexes are ubiquitous; we will use one such complex, **trans-Ir(CO)Cl(PEt<sub>3</sub>)<sub>2</sub>**, to illustrate these reactions.



\*In next Figure , the iridium oxidation state increases from **(I) to (III)**, and the coordination number increases from **4 to 6**. The new ligands add in a *cis* or *trans* fashion, with their orientation a function of the mechanistic pathway.

\*The expansion of the coordination number of the metal brings the newly added ligands into close proximity to the original ligands; this can enable reactions to occur between them. Such reactions are encountered frequently in the mechanisms of catalytic cycles.

\*Oxidative addition and reductive elimination reactions play key roles in C—H activation reactions, where a strong C—H bond is cleaved by a transition-metal complex. These are important reactions because they permit unfunctionalized hydrocarbons to be transformed into complex molecules. *Bergman* reported the following classic C—H reductive elimination/oxidative addition sequence.



The first step involves reductive elimination of cyclohexane from a six-coordinate Ir(III) complex ( $ML_3X_3$ ) to afford a four-coordinate Ir(I) intermediate ( $ML_3X$ ). Like most reductive eliminations, this first step involves a decrease by two in both the oxidation state and coordination number of the metal. The second step results in oxidation from Ir(I) to Ir(III) as benzene oxidatively adds to the iridium center. Like most oxidative additions, this second step involves an increase by two in both the oxidation state and the coordination number of the metal.

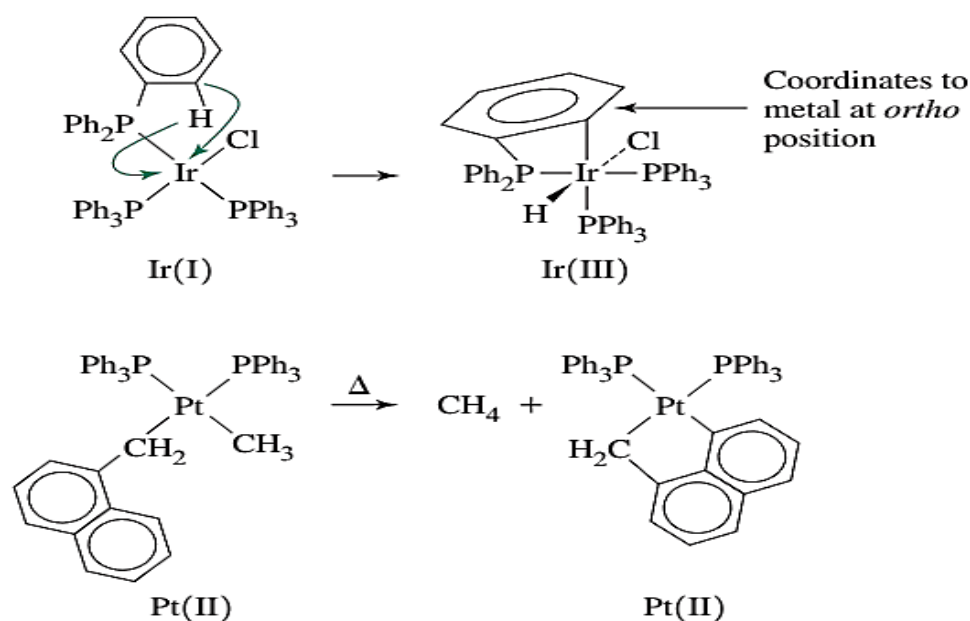
### \*\*Cyclometallations

These are reactions that incorporate metals into organic rings.

*Orthometallations*, oxidative additions in which an *ortho* position of an

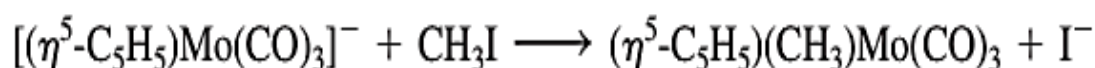


aromatic ring becomes attached to the metal, are quite common. The first (**Figure below**) example features oxidative addition in which the *ortho* carbon to the phosphorus of a triphenylphosphine ligand and the hydrogen originally in the *ortho* position add to iridium, resulting in a four-membered ring involving the iridium center. Orthometallation is not the favored pathway in the second reaction even though the platinum reactant also has triphenylphosphine ligands. A five-membered ring is formed instead by oxidative addition of a C—H bond of the naphthalene substituent, concurrently with reductive elimination of methane. In these reactions, the reactants are kinetic products that are converted to cyclometallated thermodynamic products. These reactions are also classified as C—H bond activations. The metal facilitates the cleavage of C—H bonds.



**\* Nucleophilic Displacement**

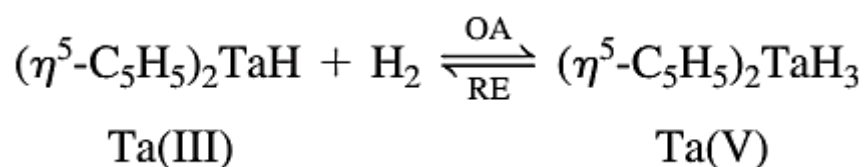
Another class of reaction that can be classified as oxidative addition, is nucleophilic displacement. Negatively charged organometallic complexes often behave as nucleophiles in displacement reactions. For example,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]^-$  can displace iodide from methyl iodide:



This reaction results in formal oxidation of the metal (from Mo(0) to Mo(II)) and the coordination number increases by 1 .

**3-Reductive Elimination and Pd-Catalyzed Cross-Coupling**

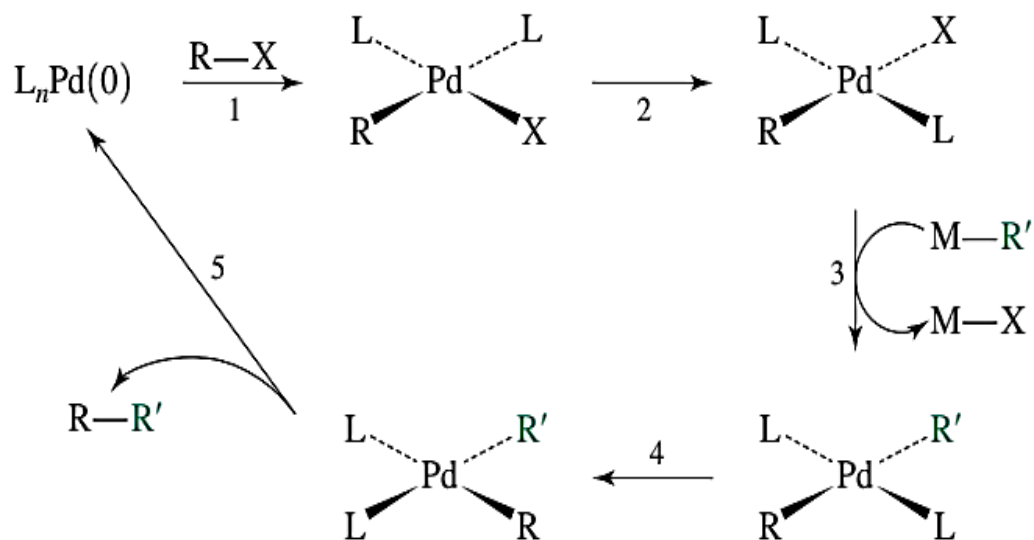
Reductive elimination is the reverse of oxidative addition. To illustrate this distinction, consider the following equilibrium:



The forward reaction involves formal oxidation of the metal, accompanied by an increase in coordination number; it is an OA. The reverse reaction is an example of RE, which involves a decrease in both oxidation number and coordination number.

Reductive elimination can result in the formation of a wide range of bonds including H—H, C—H, C—C, and C—X (X = halide, amide, alkoxide, thiolate, and phosphide).

Reductive eliminations from palladium are of great interest because they comprise an important step in Pd-catalyzed cross-coupling; **Figure below**, (A generic Pd-catalyzed cross-coupling cycle.) provides a generic catalytic cycle. **Step 1** is oxidative addition of RX (R = alkyl, aryl) to a Pd(0) reactant, resulting in a square planar Pd(II) complex. If this product is *cis* (as shown), rapid *cis–trans* isomerization (**step 2**) is likely to avoid having a strong donor R *trans* to another good  $\sigma$  donor (L). **Step 3** is *transmetallation*, a ligand substitution reaction, that introduces  $R'$  ( $R' =$  alkyl, aryl) to the Pd(II) center. Reductive elimination of a C—C bond (**step 5**) requires the *cis* orientation of R and  $R'$ , so a *cis–trans* isomerization is necessary (**step 4**) if the transmetallation product is *trans* (as shown).

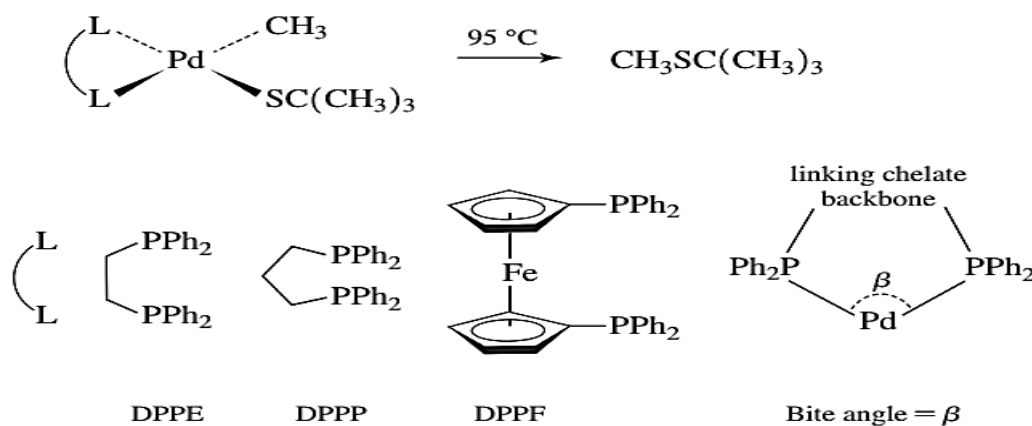


The reductive elimination reaction (**step 5**) generally proceeds faster as the steric bulk imposed by L increases.

\*A series of C—S bond-forming reductive elimination reactions with bidentate ligands (**Figure below**) with different **bite angles** illustrates this trend. Bite angles are steric parameters specific to bidentate ligands. As the bite angle increases, the bidentate ligand imposes increasing steric hindrance when coordinated. The rate of dialkylsulfide reductive elimination increases with the bite angle (**Table below**).

**Rates of Reductive Elimination with  $(L_2)Pd(CH_3)(SC(CH_3)_3)$**

| Phosphine ( $L_2$ ) | Rate Constant ( $k_{obs}$ ) at 95 °C ( $h^{-1}$ ) | Bite Angle (°) |
|---------------------|---|----------------|
| DPPE                | 0.069   | 85.8           |
| DPPP                | 0.35  | 90.6           |
| DPPF                | 1.4   | 99.1           |



\*The electronic properties of the ligands also have a large impact on the rates of reductive elimination from Pd(II) complexes for the formation of carbon–carbon and carbon–heteroatom bonds.

\*Palladium-catalyzed cross-coupling reactions to form carbon–carbon bonds have become extremely important tools in organic synthesis during

the past several decades. In recognition of their work as pioneers in this field, R. F. Heck, E.-I. Negishi, and A. Suzuki were awarded the Nobel Prize in Chemistry in 2010.

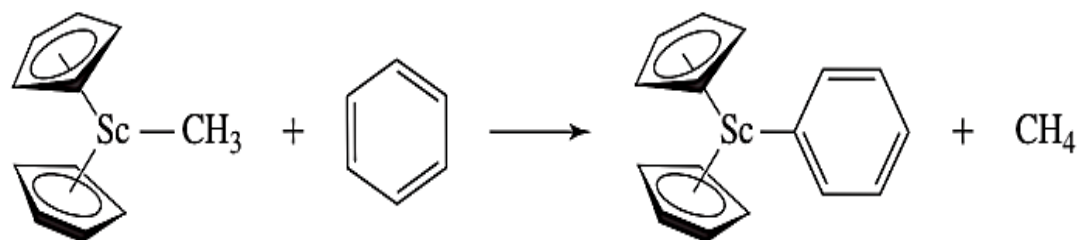
\***Table below** provides representative examples of the types of Pd-catalyzed cross-coupling reactions associated with these Nobel recipients and two other major chemists in this field, K. Sonogashira and J. K. Stille.

**Types of Palladium-Catalyzed Cross-Coupling Reactions**

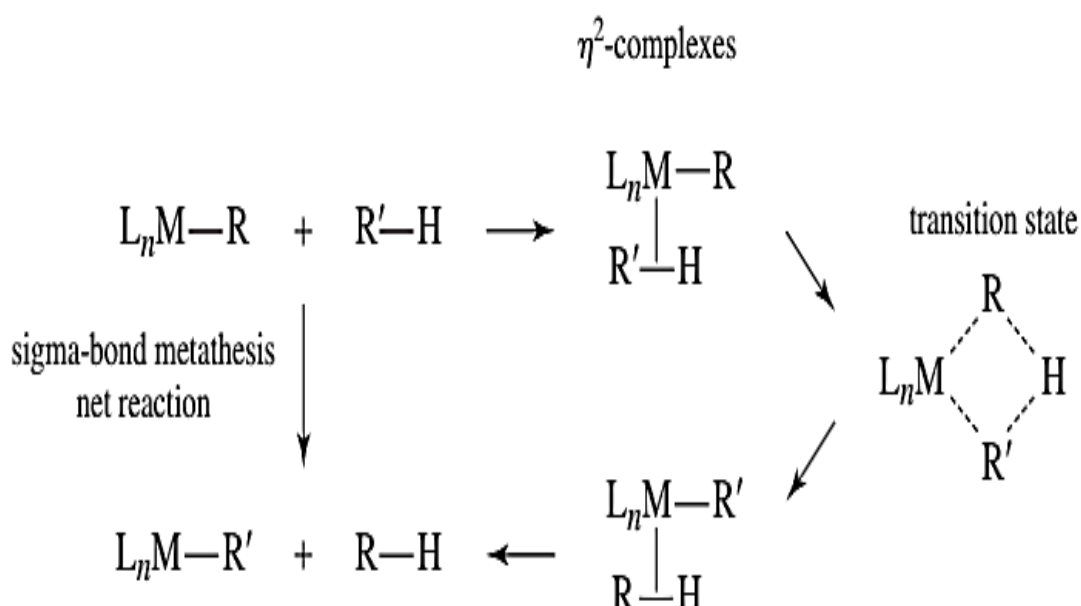
| Name                | First Reported | M  | Example of Catalyst Precursor                     |
|---------------------|----------------|----|---|
| Heck                | 1968           | Hg | $\text{Li}_2\text{PdCl}_4$                        |
| Sonogashira         | 1975           | Cu | $\text{PdCl}_2(\text{PPh}_3)_2$                   |
| Negishi             | 1977           | Zn | $\text{PdCl}_2(\text{PPh}_3)_2$                   |
| Stille              | 1978           | Sn | $\text{PhCH}_2\text{Pd}(\text{PPh}_3)_2\text{Cl}$ |
| Suzuki <sup>a</sup> | 1979           | B  | $\text{Pd}(\text{PPh}_3)_4$                       |

#### **4-Sigma Bond Metathesis**

All previously mentioned C—H bond activation examples exhibit the classic characteristics of oxidative addition and involve metal centers with eight valence electrons (Ir(I), Pd(II), Fe(0)). These metals have relatively low oxidation states and are predisposed toward being able to oxidize C—H bonds. Does this mean that complexes with metals in their formally highest oxidation states are inherently unable to effect C—H bond activation? It is fascinating that some  $d^0$  transition-metal complexes are able to activate C—H bonds without any change in -oxidation state. For example, consider the following classic reaction:



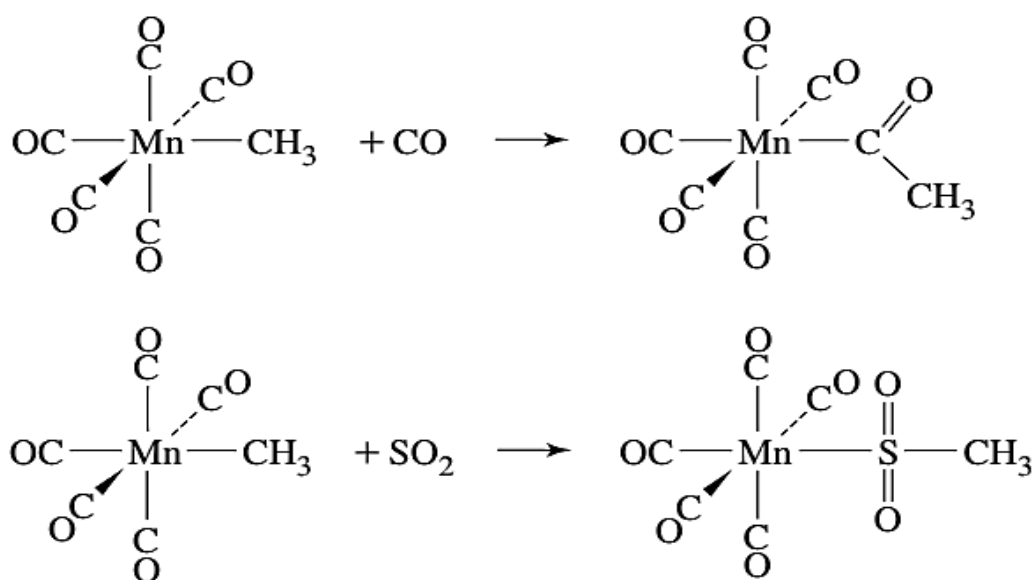
In this reaction, a C—H bond in methane is made, and a C—H bond of benzene is cleaved, but the oxidation state of the scandium center remains (+3). This class of reaction, which is not limited to early transition metals, is called **sigma-bond metathesis**. In this mechanism, the metal is first postulated to coordinate the bond to be activated in an  $\eta^2$  fashion, followed by formation of a four-centered transition state that leads to an exchange of ligands at the metal (**Figure below**).



### General Sigma-Bond Metathesis Mechanism

**\*\*Reactions Involving Modification of Ligands****1-Insertion Reactions**

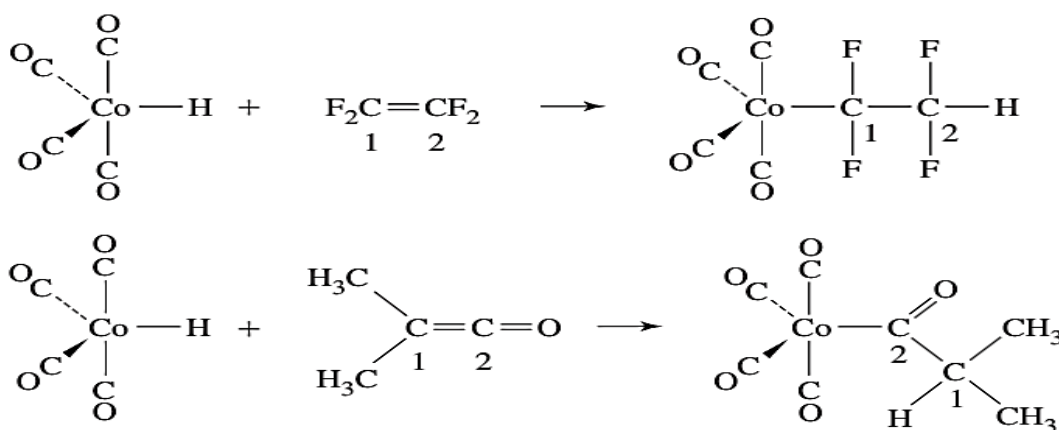
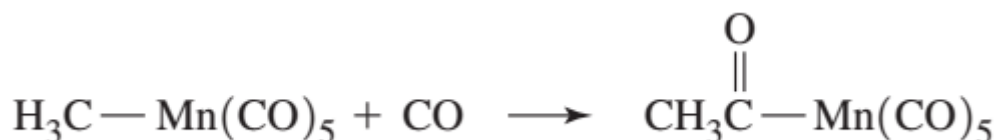
The reactions in **Figure below** may be designated as 1,1 insertions, indicating that both bonds to the inserted molecule are made to the same atom in that molecule. For example, in the second reaction, both the Mn and CH<sub>3</sub> are bonded to the sulfur of the inserted SO<sub>2</sub>.

**Examples of 1,1 Insertion Reactions**

\*In 1,2 insertions, bonds to the inserted molecule are made to adjacent atoms. For example, in the reaction of HCo(CO)<sub>4</sub> with tetrafluoroethylene (next Figure), the product has the Co(CO)<sub>4</sub> group attached to one carbon and the H attached to the neighboring carbon.

**2-Carbonyl Insertion (Alkyl Migration)**

Carbonyl insertion, the reaction of CO with an alkyl complex to give an acyl  $[-C(=O)R]$  product, has been well-studied. The reaction of  $\text{CH}_3\text{Mn}(\text{CO})_5$  with CO is an excellent example:



\*The insertion of CO into a metal–carbon bond in alkyl complexes is of particular interest for its potential applications to organic synthesis and catalysis, and its mechanism deserves careful consideration.

\*From the net equation, we might expect that the CO inserts directly into the Mn-CH<sub>3</sub> bond. However, other mechanisms are possible that would give the overall reaction stoichiometry and involve steps other than the insertion of an incoming CO. Three plausible mechanisms have been suggested:



\* The stoichiometry of a reaction, can be used to predict how much reactant is needed to create a certain amount of product or to predict how much of the product will be formed from a certain amount of reactant.

**Mechanism 1: CO Insertion**

Direct insertion of CO into a metal–carbon bond.

**Mechanism 2: CO Migration**

Migration of a CO ligand to give intramolecular CO insertion. This would yield a 5-coordinate intermediate, with a vacant site available for attachment of an incoming CO.

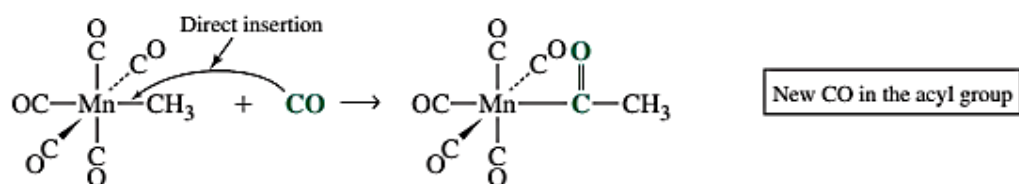
**Mechanism 3: Alkyl Migration**

In this case, the alkyl group would migrate, rather than the CO, and attach itself to a CO *cis* to the alkyl. This would also give a 5-coordinate intermediate with a vacant site available for an incoming CO.

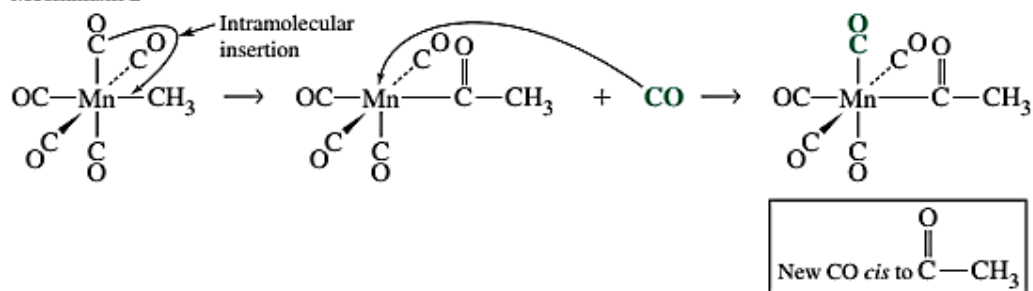
\* These mechanisms are described schematically in **Figure below**. In both mechanisms 2 and 3, the intramolecular migration is considered to occur to one of the migrating group's nearest neighbors, located in *cis* positions.

**CO Insertion Reactions**

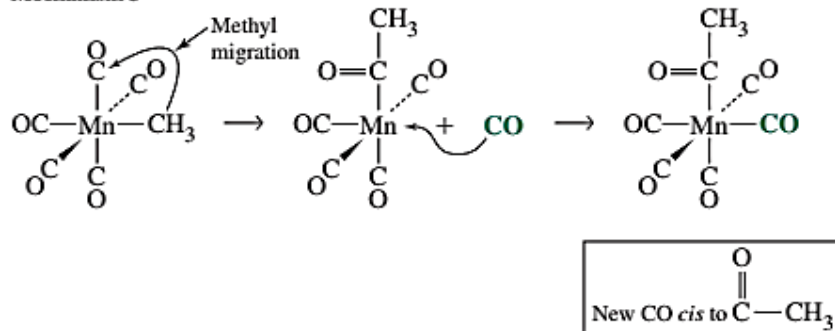
**Mechanism 1**



**Mechanism 2**



**Mechanism 3**



**Possible Mechanisms for CO Insertion Reactions**