Organometallic Chemistry

Hapticity

* The ***hapticity*** of the ligand, defined as the number of C atoms in theligand 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 oct et 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 ***π -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, BCl_3 is electron-deficient while 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 π-acceptor ligands.

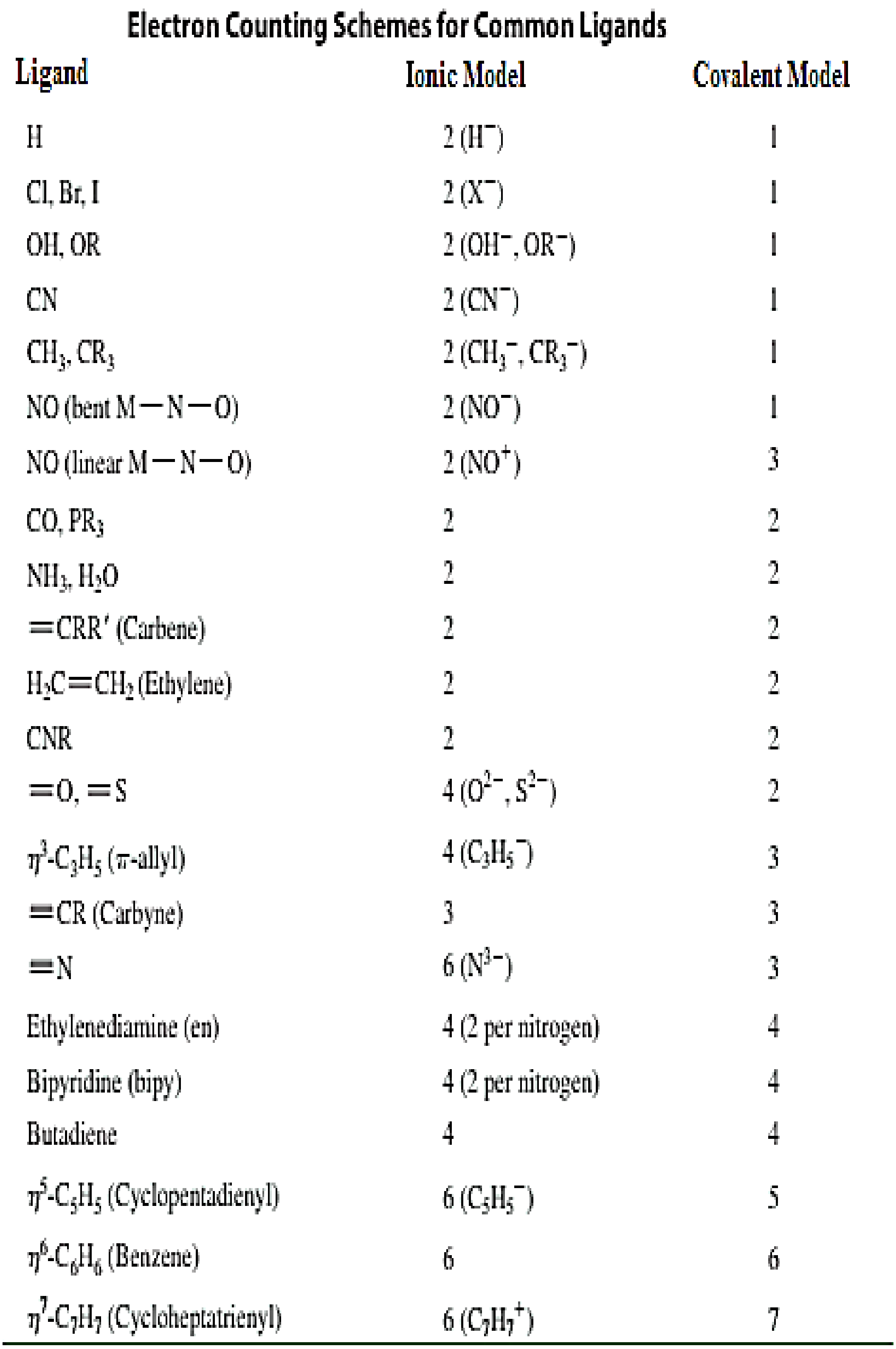
* This 18-electron rule often breaks down for ***early*** and ***late*** d-block metals. The majority of organometallic compounds with metals from the ***middle*** of the d-block obey the 18-electron rule.

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

***Counting Electrons**:-*

*The group number represents the number of valence electron.

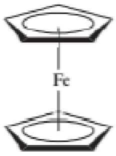
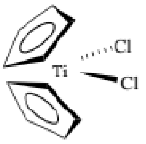
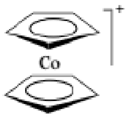
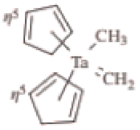
*The table below represents Electron Counting Schemes for CommonLigands:



Electron Counting Schemes for Common Ligands

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

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

Compound	Covalent Model	Ionic Model
	Fe(0)= 8 valence es. 2 $C\dot{p}$ = 10 electrons Total = 18 es.	Fe(II)= 6 valence es. 2 $C\bar{p}$ = 12 electrons Total = 18 es.
$MoH_4(PR_3)_4$	Mo(0)= 6 v. es. 4 $\dot{H}$= 4 es. 4 PR_3 = 8 es. Total = 18 es.	Mo(IV)= 2 v. es. 4 $\bar{H}$= 8 es. 4 PR_3 = 8 es. Total = 18 es.
	Ni(0)= 10 v. es. 2 $C_3\dot{H}_5$ = 6 es. Total = 16 es.	Ni(II)= 8 v. es. 2 $C_3\bar{H}_5$ = 8 es. Total = 16 es.
$Mo(C_6H_6)_2$	Mo(0)= 6 v. es. 2 $C_6\dot{H}_6$ = 12 es. Total = 18 es.	Mo(II)= 4 v. es. 2 $C_6\bar{H}_6$ = 14 es. Total = 16 es.
	Ti(0)= 4 v. es. 2 Cl = 2 es. 2 $C_5\dot{H}_5$ = 10 es. Total = 16 es.	Ti(V)= 0 v. es. 2 $C\bar{l}$ = 4 es. 2 $C_5\bar{H}_5$ = 12 es. Total = 16 es.
	Co(0)= 9 valence es. 2 $C\dot{p}$ = 10 es. positive charge = -1 e. Total = 18 es.	Co(III)= 6 valence es. 2 $C\bar{p}$ = 12 es. Total = 18 es.
(η^5-C_5H_5)$Fe(CO)_2$ Cl	Fe(0)= 8 valence es. $C\dot{p}$ = 5 es. 2 terminal CO = 4 es. Cl = 1 e. Total = 18 es.	Fe(II)= 6 valence es. $C\bar{p}$ = 6 es. 2 terminal CO = 4 es. $C\bar{l}$ = 2 es. Total = 18 es.
	Ta(0)= 5 valence es. 2 $C\dot{p}$ = 10 es. 1alkyl = 1 e. 1Carbene = 2 e. Total = 18 es.	Ta(III)= 2 valence es. 2 $C\bar{p}$ = 12 es. 1alkyl = 2 es. 1Carbene = 2 es. 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 [$MeTiCl_3$,(8e); [Me_2NbCl_3, (10e)]; [WMe_6, (12e)]; [$Pt(PCy_3)_2$, (14e)]; [$M(H_2O)_6$]$^{2+}$

(M = V, 15e; Cr, 16e; Mn, 17e; Fe, 18e)]. Much rarer are *d* blockexamples with >18e: CoCp2, 19e; and NiCp2, 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_2TiCl_2, WMe_6, Me_2NbCl_3, $CpWOCl_3$) [A possible reason for the sameis that some of the orbitals of these complexes are too high in energy for effective utilization in bonding or the ligands are mostly σ donors.

* Some high valent d^0 complexes have a lower electron count than 18.

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

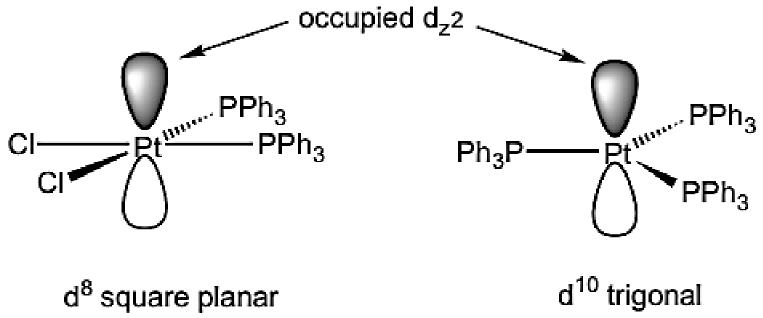
* The 18 electron rule fails when bonding of organometallic clusters ofmoderate to big sizes (6 Metal atoms and above) are considered.

* 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

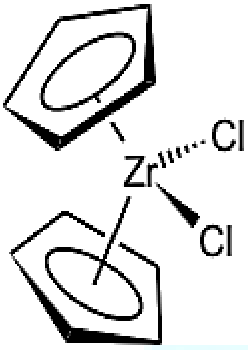
Late transition metals with d^8 electron configurations *e.g.* Rh(I), Ir(I), Pd(II), Pt(II) have a strong tendency to form square planar 16 VE complexes. Similarly, d^{10} complexes tend to form trigonal 16 VE complexes. As the atomic number Z increases, the d-shell is stabilized (lowers in energy). The occupied dz^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.

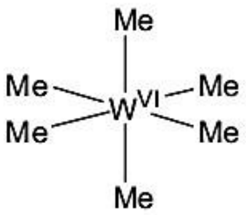


The 16e "Zirconocene dichloride."

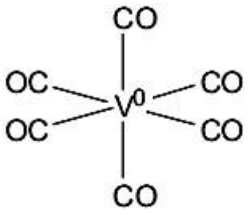
***** Steric effects can produce low-coordinate (not many ligands) complexes which often have <18 electrons.

* For early transition metals (*e.g.* with d0 metals) it is often not possible to fit the number of ligands necessary to reach 18 electrons around the metal.

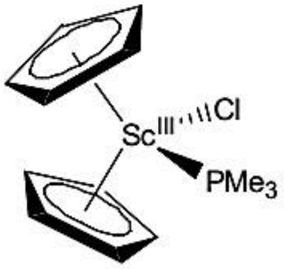
**** Linear complexes (d^{10}, 14 electrons)**



W^{6+} d^0 12 electrons



V^0 d^5 17 electrons



Sc^{3+} d^0 16 electrons

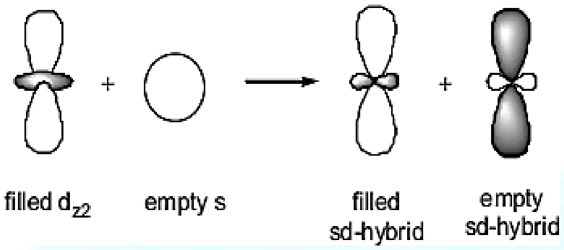
*****d^{10}-metals with 2 ligands, so 14-electron complexes.

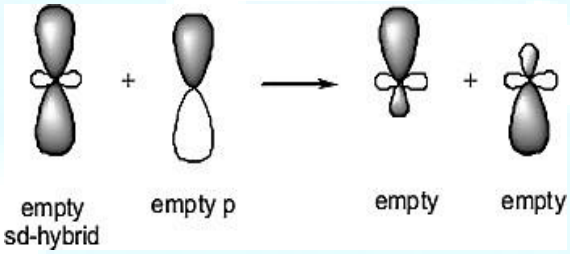
*Common for Ag(I), Au(I) and Hg(II), Less common for Cu(I), Zn(II) and Cd(II).

Explanation:

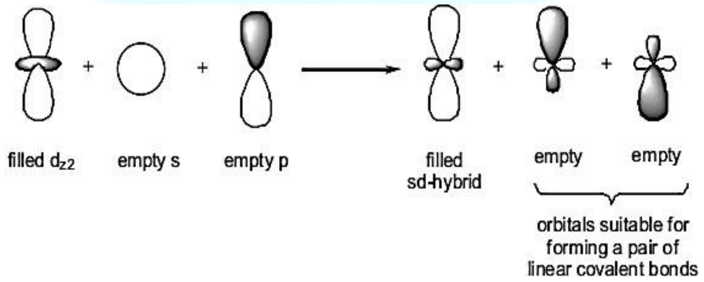
* For d^{10} compounds, there is a relatively small energy difference between the d, s and p orbitals (e.g. 5d, 6s and 6p for Au(I)).

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





Overall:

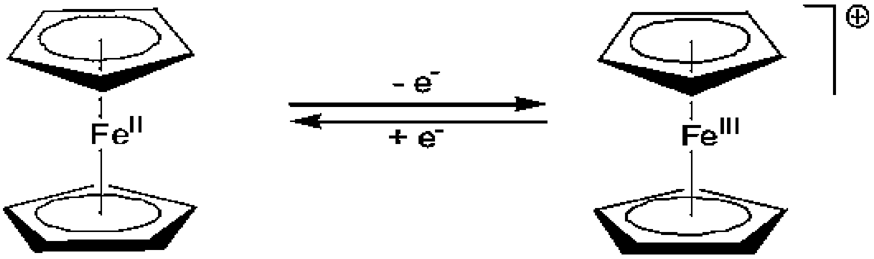


*More common for group 11 (Cu, Ag, Au) than group 12 (Zn, Cd, Hg) because the energy difference between the d, s and p-orbitals is smallerfor group 11.

*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 $[(R_3P)AuCl] + 2\ PR_3$ == 18 e-tetrahedral [$(R_3P)_3AuCl$]).

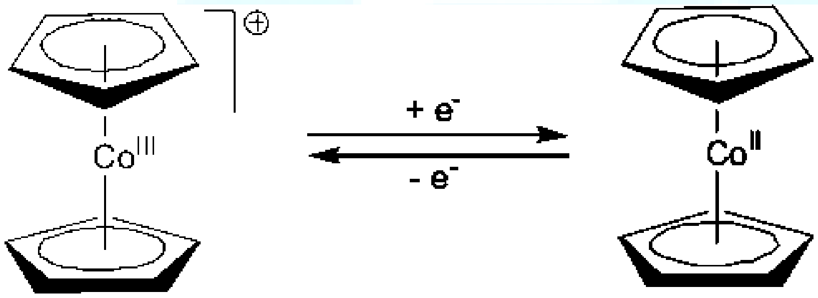
**<u>Strong oxidants or reductants</u>

*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).



Ferrocene
Fe^{II}, d^6, 18 electrons
Orange, diamagnetic

Ferrocenium cation
Fe^{III}, d^5, 17 electrons
Dark blue, paramagnetic
Oxidant



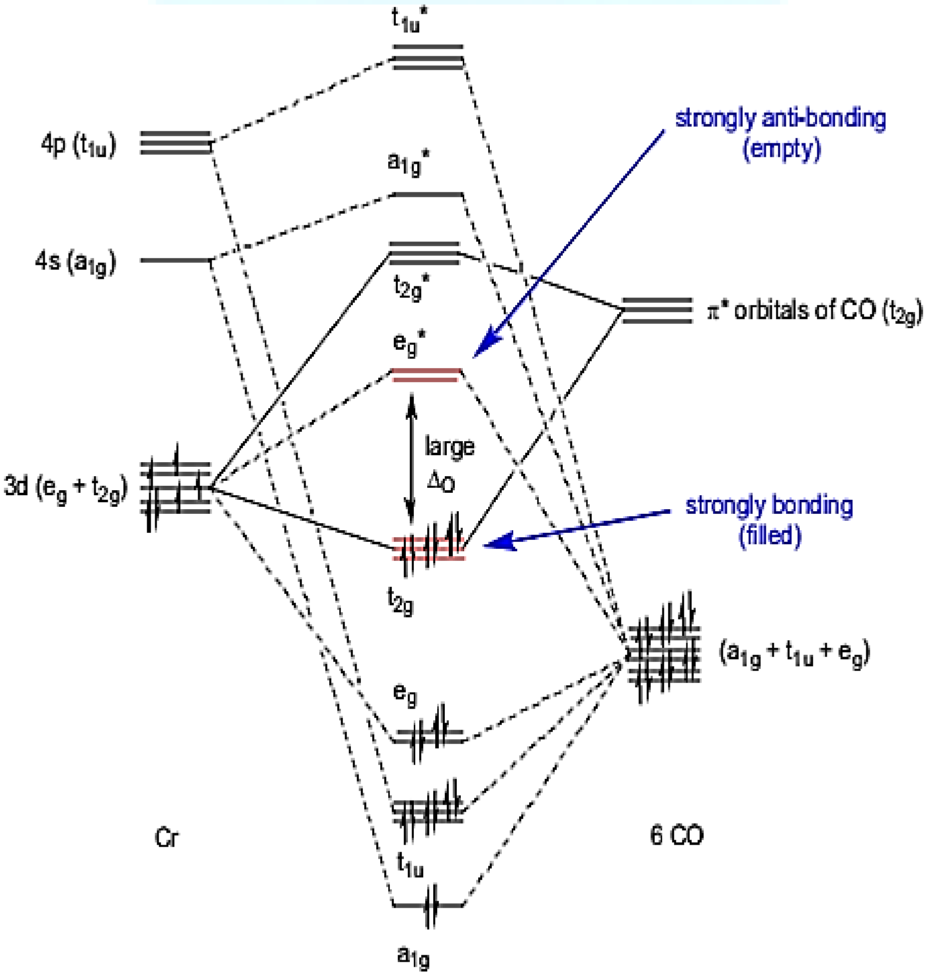
Cobaltocenium cation
Co^{III}, d^6, 18 electrons
Yellow, diamagnetic
Perfectly Happy !

Cobaltocene
Co^{II}, d^7, 19 electrons
Dark purple, paramagnetic
Strong Reductant

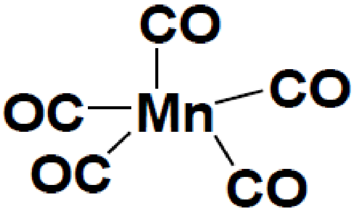
*Why 18 Electrons?

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

Chromium(0) has **6 electrons** outside its noble gas core. Each CO contributes a pair of electrons to give a total electron count of **18es.**. In the molecular orbital diagram, these 18 electrons appear as the (**12 σ**) electrons—the **σ** electrons of the CO ligands, stabilized by their interaction with the metal orbitals—and the (**6 *t2g***) electrons. Addition of one or more electrons to $Cr(CO)_6$ would populate the ***eg*** orbitals, which are antibonding; the consequence would be destabilization of the molecule. Removal of electrons from Cr(CO)6 would depopulate the ***t***$_2$***g*** orbitals, which are bonding as a consequence of the strong π-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.



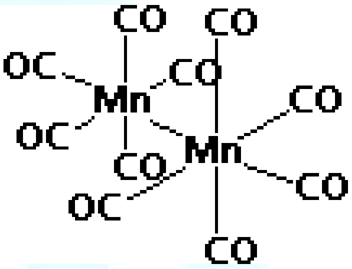
*The 18-electron rule assist us to predict the structure of organometallic compound, Look at CO complexes of Mn. You may expect to have the following structure for a CO complex of Mn.



But in fact the structure as follows;

$Mn_2(CO)_{10}$

Mn	7
5 CO	10
M-M	1
	18

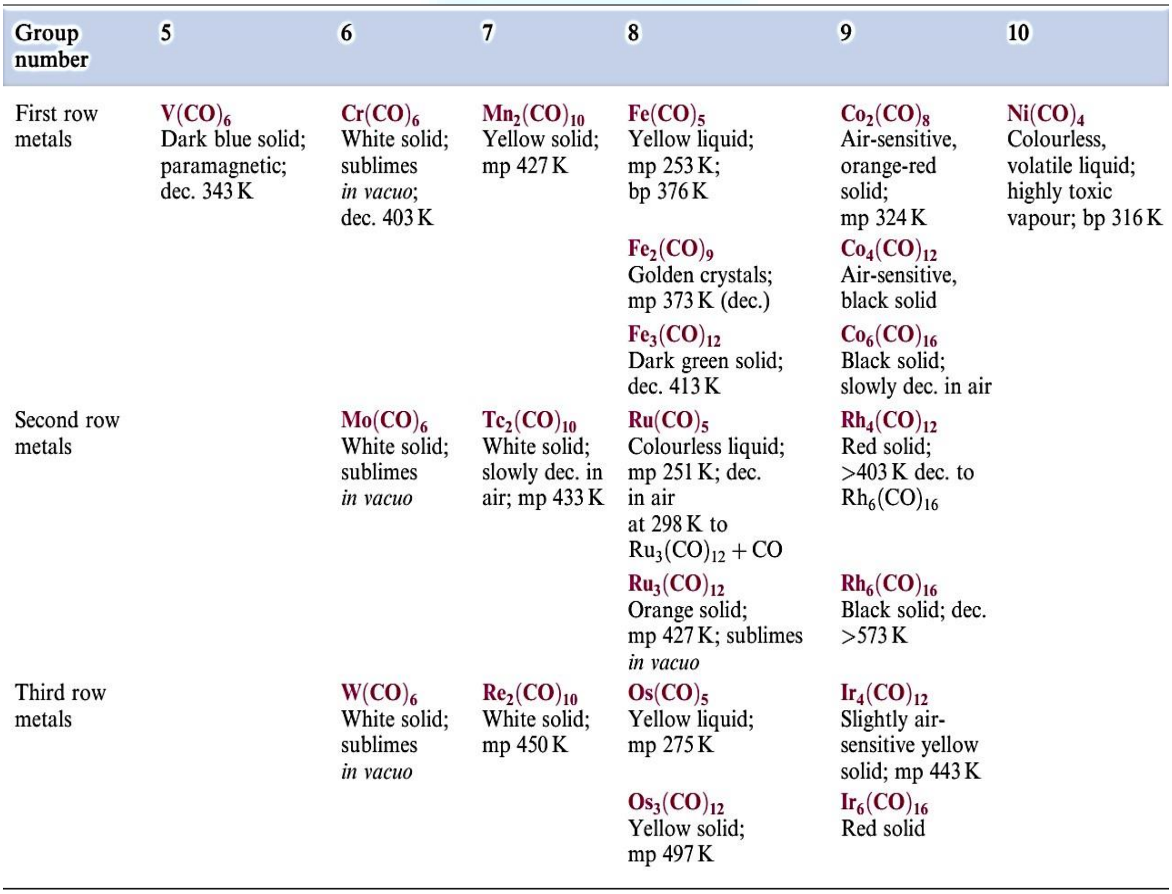


Ligands in Organometallic Chemistry:-

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 twotypes of organometallic compounds that are especially important: carbenecomplexes, containing metal–carbon double bonds, and carbyne complexes, containing metal–carbon triple bonds.

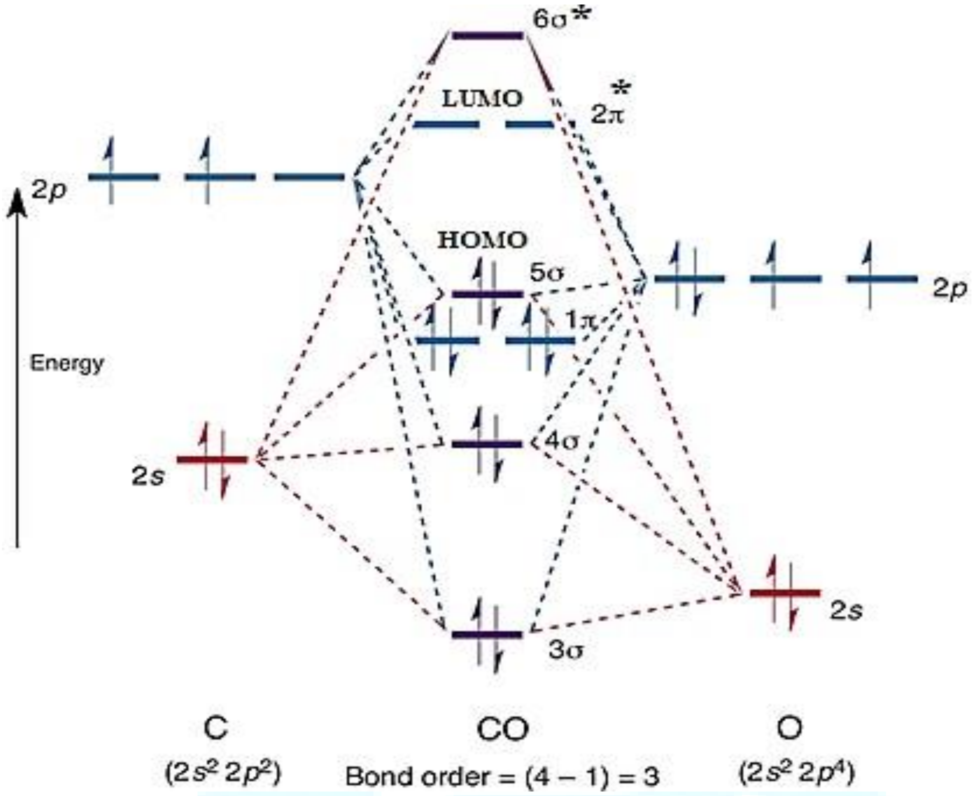
* Carbonyl (CO) Complexes

Carbon monoxide is the most common ligand in organometallicchemistry. It serves as the only ligand in binary carbonyls such as $Ni(CO)_4$, $W(CO)_6$, and $Fe_2(CO)_9$ or, more commonly, in combinationwith other ligands, both organic and inorganic. CO may bond toa 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.

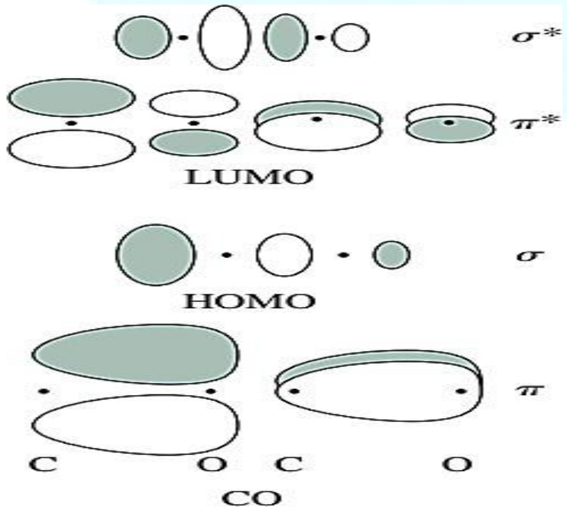


Group number	5	6	7	8	9	10
First row metals	**$V(CO)_6$** Dark blue solid; paramagnetic; dec. 343 K	**$Cr(CO)_6$** White solid; sublimes *in vacuo*; dec. 403 K	**$Mn_2(CO)_{10}$** Yellow solid; mp 427 K	**$Fe(CO)_5$** Yellow liquid; mp 253 K; bp 376 K	**$Co_2(CO)_8$** Air-sensitive, orange-red solid; mp 324 K	**$Ni(CO)_4$** Colourless, volatile liquid; highly toxic vapour; bp 316 K
				$Fe_2(CO)_9$ Golden crystals; mp 373 K (dec.)	**$Co_4(CO)_{12}$** Air-sensitive, black solid	
				$Fe_3(CO)_{12}$ Dark green solid; dec. 413 K	**$Co_6(CO)_{16}$** Black solid; slowly dec. in air	
Second row metals		**$Mo(CO)_6$** White solid; sublimes *in vacuo*	**$Tc_2(CO)_{10}$** White solid; slowly dec. in air; mp 433 K	**$Ru(CO)_5$** Colourless liquid; mp 251 K; dec. in air at 298 K to $Ru_3(CO)_{12} + CO$	**$Rh_4(CO)_{12}$** Red solid; >403 K dec. to $Rh_6(CO)_{16}$	
				$Ru_3(CO)_{12}$ Orange solid; mp 427 K; sublimes *in vacuo*	**$Rh_6(CO)_{16}$** Black solid; dec. >573 K	
Third row metals		**$W(CO)_6$** White solid; sublimes *in vacuo*	**$Re_2(CO)_{10}$** White solid; mp 450 K	**$Os(CO)_5$** Yellow liquid; mp 275 K	**$Ir_4(CO)_{12}$** Slightly air-sensitive yellow solid; mp 443 K	
				$Os_3(CO)_{12}$ Yellow solid; mp 497 K	**$Ir_6(CO)_{16}$** Red solid	

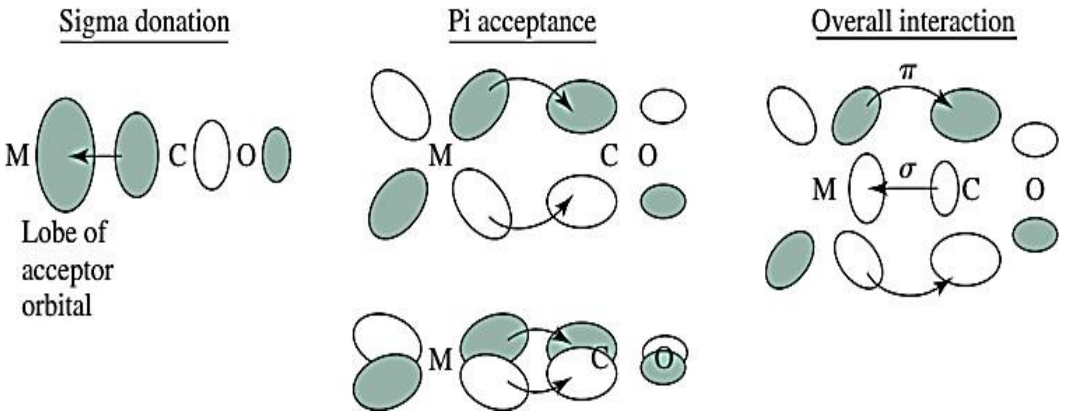
Bonding of CO ligand It is useful to review the bonding in CO. The molecular orbital picture of CO shown in Figure below;



*The molecular orbitals derived primarily from the 2*p* atomic orbitals ofthese 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 σ-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 σ-donor and π-acceptor interactions are illustrated in Figure below;



*The □-donor interaction increases the electron density on the metal and decreases the electron density on the CO ligand. The □-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***).

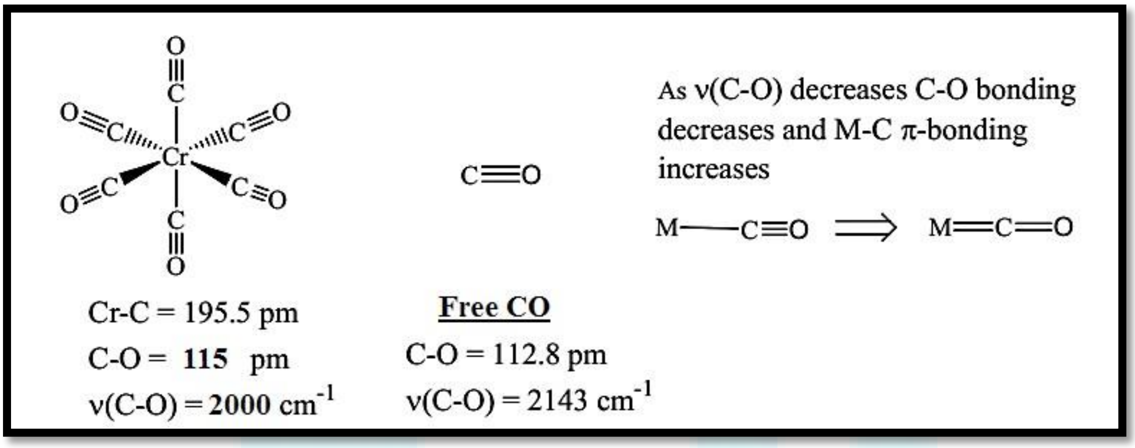
* The strength of this bonding depends on several factors, includingthe ***charge*** on the complex and the ***ligand environment*** of the metal.

*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*** cm^{-1}). $Cr(CO)_6$, on the other hand, has its **C-O** stretch at (***2000*** cm^{-1}). The lower energy for the stretching mode means that the **C-O** bond is weaker in $Cr(CO)_6$.

* Both σ donation and π 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.



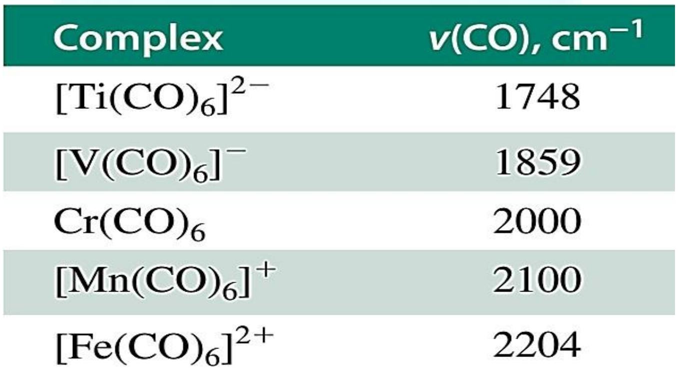
Cr-C = 195.5 pm
C-O = **115** pm
ν(C-O) = 2000 cm^{-1}

Free CO
C-O = 112.8 pm
ν(C-O) = 2143 cm^{-1}

As ν(C-O) decreases C-O bonding decreases and M-C π-bonding increases

$$M{-}C{\equiv}O \Longrightarrow M{=}C{=}O$$

* 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 n(CO) = ***2143 cm^{-1}*** for free CO):



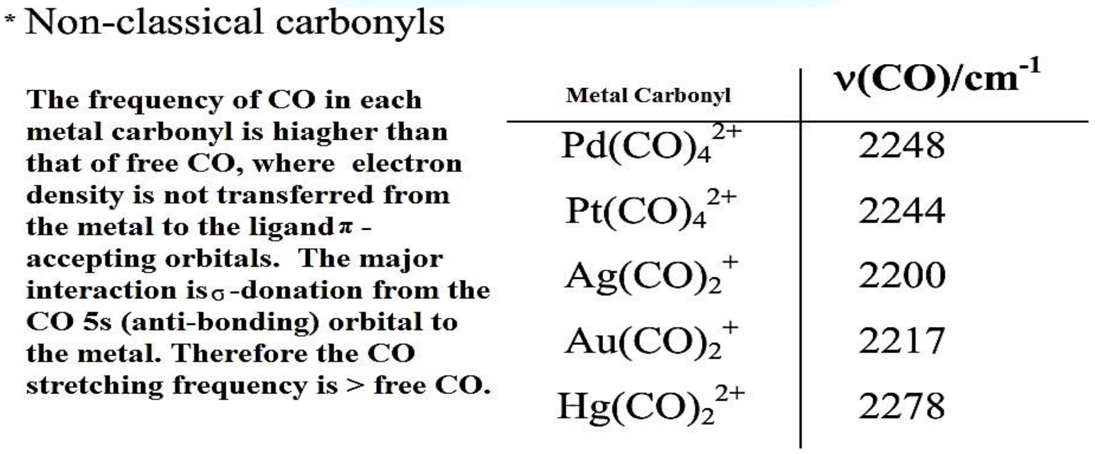
Complex	ν(CO), cm^{-1}
$[Ti(CO)_6]^{2-}$	1748
$[V(CO)_6]^{-}$	1859
$Cr(CO)_6$	2000
$[Mn(CO)_6]^{+}$	2100
$[Fe(CO)_6]^{2+}$	2204

*Of these **isoelectronic** five ions, $[Ti(CO)_6]^{2-}$ 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 $[Ti(CO)_6]^{2-}$ to (**+2**) for $[Fe(CO)_6]^{2+}$. The titanium in $[Ti(CO)_6]^{2-}$, with the most negative formal charge, has the strongest tendency to donate to CO. The consequence is strong population of the **π***orbitals of CO in $[Ti(CO)_6]^{2-}$ 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**π*** orbitals of CO, and the lower the energy of the **C-O** stretching vibrations.

Calculations have demonstrated that a polarization effect caused by the metal cation plays a major role in these carbonyl cations. Infree CO, the electrons are polarized toward the more electronegativeoxygen. For example, the electrons in the p orbitals are concentrated nearer to the oxygen atom than to the carbon. The presence of a transitionmetal 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 ν(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

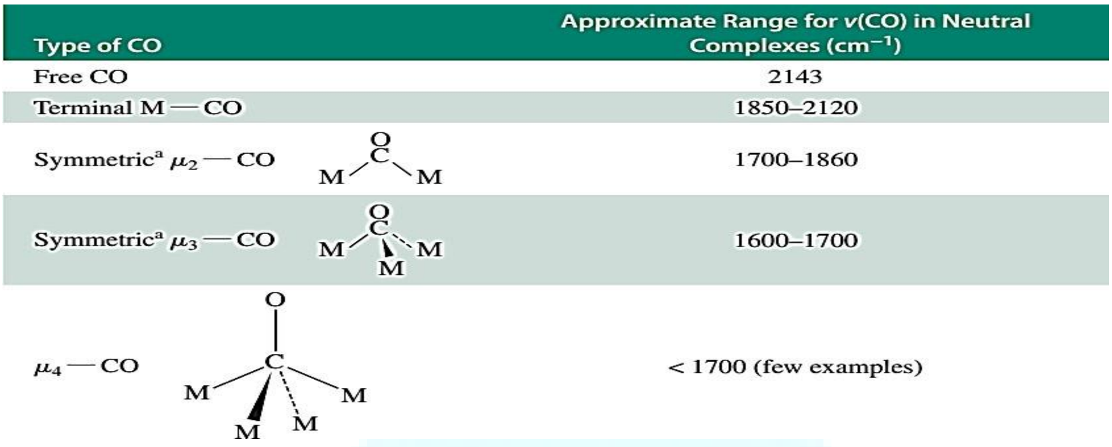
The frequency of CO in each metal carbonyl is hiagher than that of free CO, where electron density is not transferred from the metal to the ligand π -accepting orbitals. The major interaction is σ -donation from the CO 5s (anti-bonding) orbital to the metal. Therefore the CO stretching frequency is > free CO.

Metal Carbonyl	$\nu(CO)/cm^{-1}$
$Pd(CO)_4^{2+}$	2248
$Pt(CO)_4^{2+}$	2244
$Ag(CO)_2^{+}$	2200
$Au(CO)_2^{+}$	2217
$Hg(CO)_2^{2+}$	2278

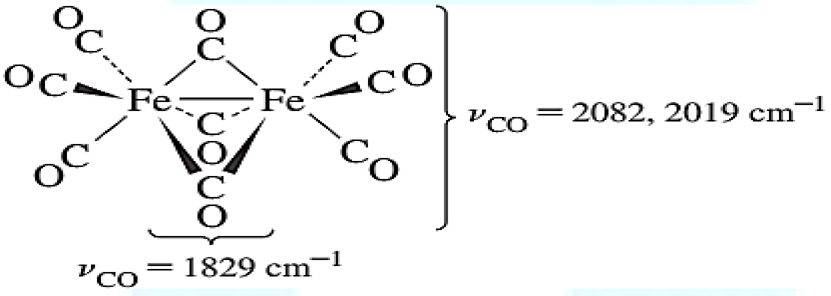
** ***<u>Bridging Modes of CO</u>***

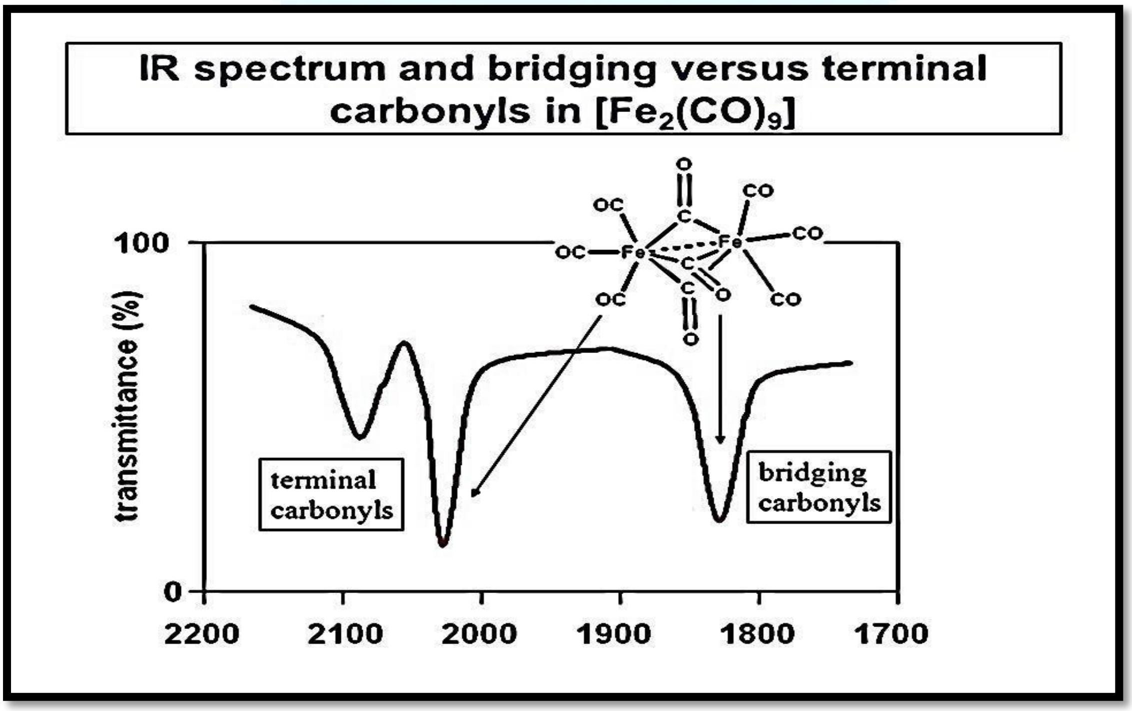
* Many cases are known in which CO forms bridges between two ormore metals.

Many bridging modes are known **Table below**.



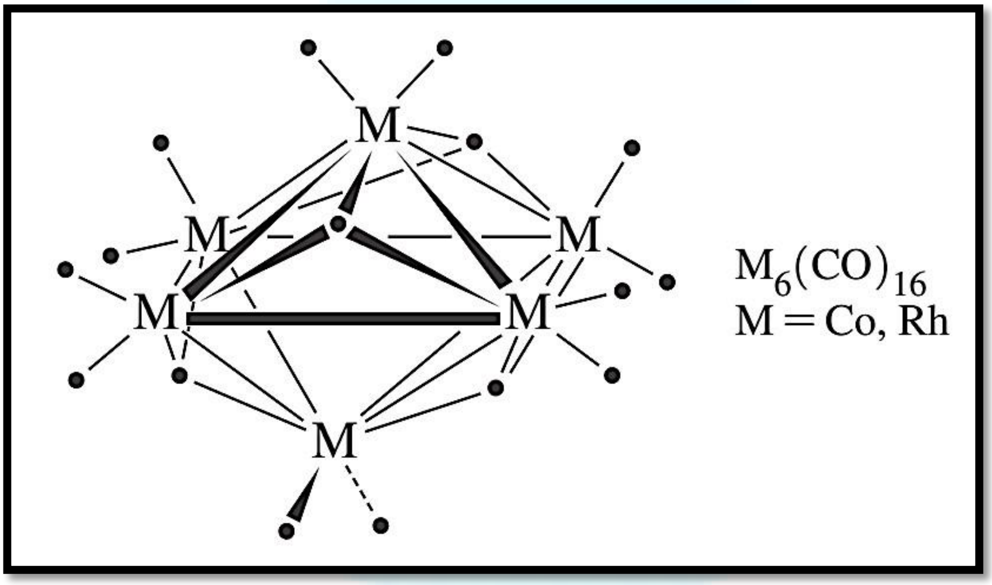
Type of CO	Approximate Range for ν(CO) in Neutral Complexes (cm^{-1})
Free CO	2143
Terminal M—CO	1850–2120
Symmetric[a] μ_2—CO	1700–1860
Symmetric[a] μ_3—CO	1600–1700
μ_4—CO	< 1700 (few examples)



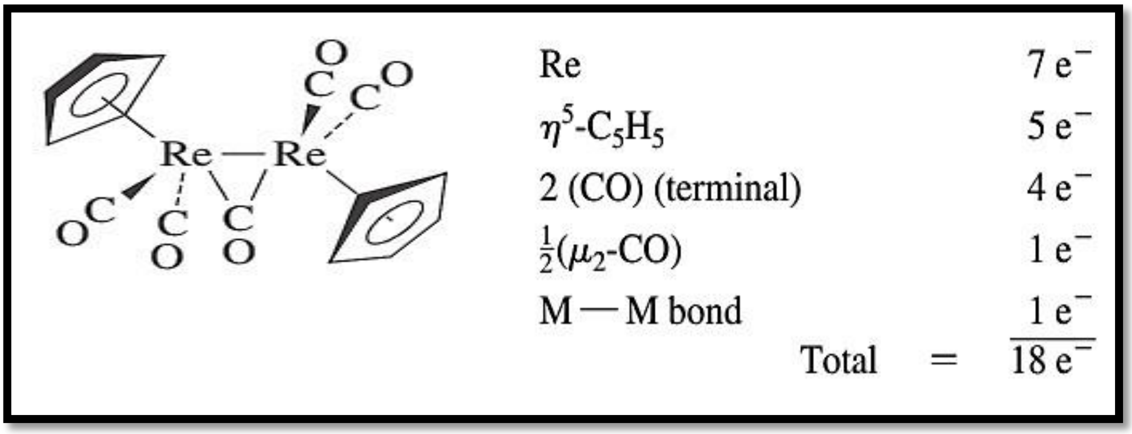


*The bridging mode is strongly correlated with the position of the **C-O** stretching band. In cases in which CO bridges two metal atoms, both metals can contribute electron density into ***π**** orbitals of CO to weaken the **C-O** bond and lower the energy of the stretch. Consequently, the **C-O**stretch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

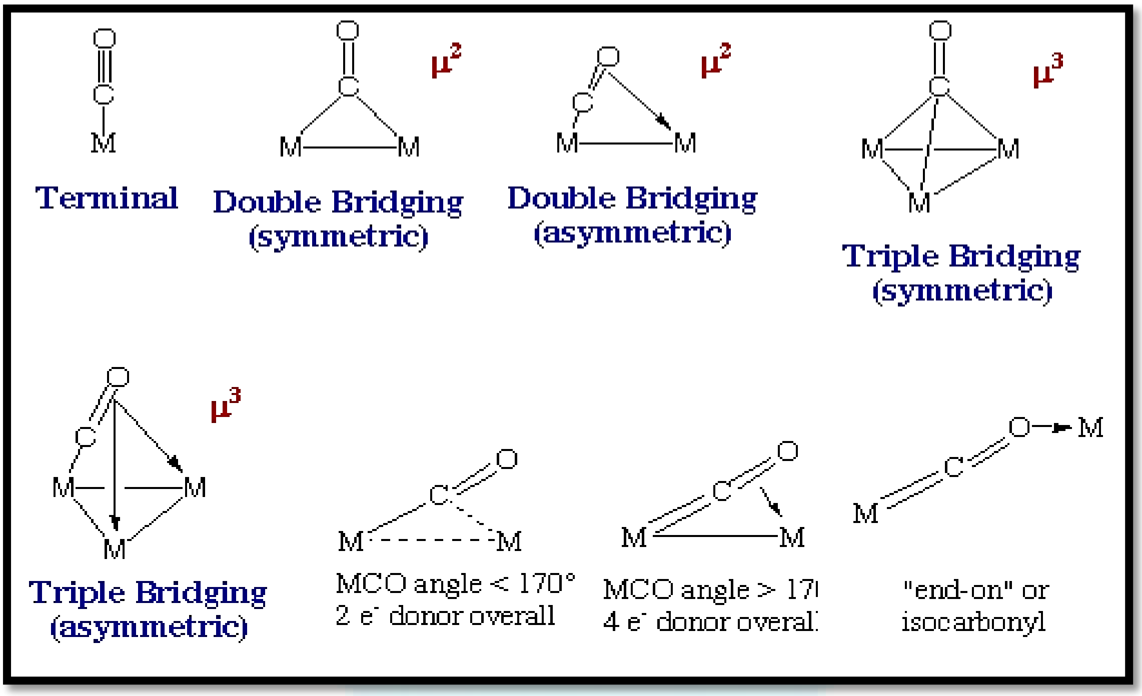
* Interaction of three metal atoms with a ***triply*** bridging (as shown in figure below) CO further weakens the **C-O** bond; the infrared band for the **C-O** stretch is still lower than in the doubly bridging case.



* 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 COis a ***2-electron*** donor overall, with a single electron donated to each metal. The electron count for each Re atom according to covalent method



Re	7 e^-
η^5-C_5H_5	5 e^-
2 (CO) (terminal)	4 e^-
$\frac{1}{2}(\mu_2$-CO)	1 e^-
M—M bond	1 e^-
Total =	18 e^-



**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.

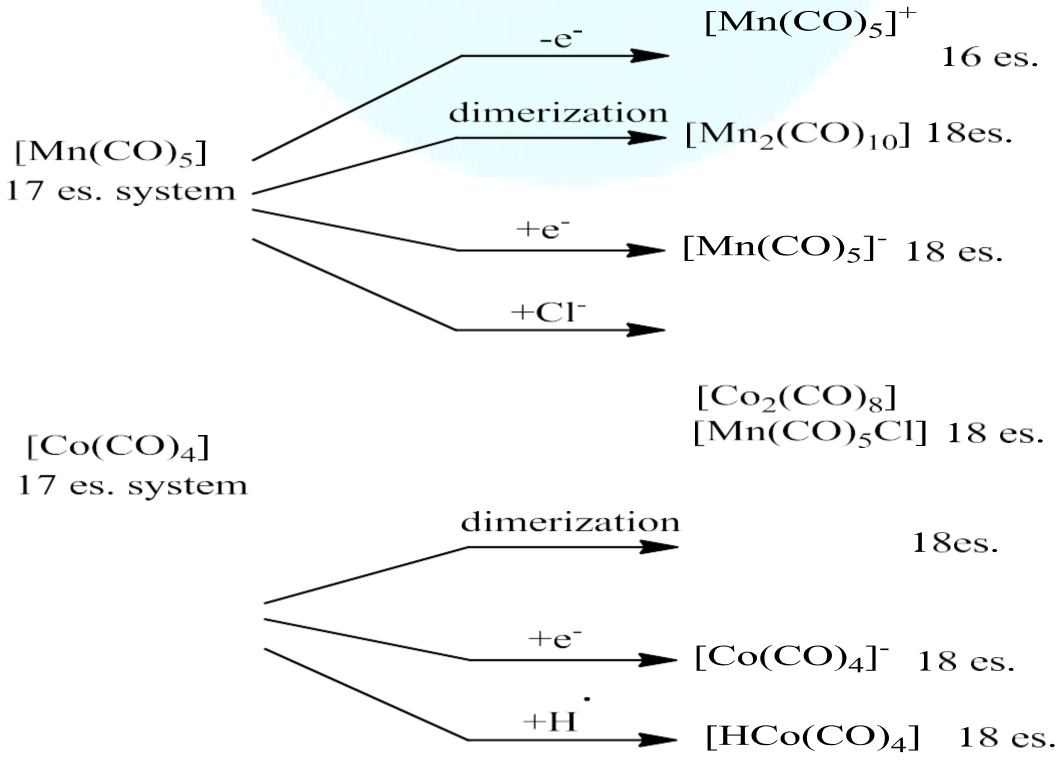
3) The 18-electrons rule is obeyed with remarkable frequency, perhaps 99% of the time.

**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 tothese metals by which the 18-es. Rule can be satisfied:-

A. The addition of an electron by reducing agent to form an anionsuch as $[V(CO)_6]^-$.

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

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

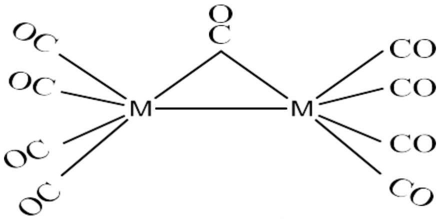


* ***Binary Carbonyl Complexes***

Binary carbonyls, containing only metal atoms and CO, are numerous. Most of these complexes obey the 18-electron rule. The cluster compounds $Co_6(CO)_{16}$ and $Rh_6(CO)_{16}$ do not obey the rule.

* One other binary carbonyl does not obey the rule, the 17-electron $V(CO)_6$. This complex is one of a few cases in which strong π-acceptor ligands do not afford an 18-electron configuration. In $V(CO)_6$, 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, $V(CO)_6$ is easily reduced to $[V(CO)_6]^-$, 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 $Fe_2(CO)_9$ there are ***three bridging*** carbonyls; but in $Ru_2(CO)_9$ and $Os_2(CO)_9$, 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.



M=Ru or Os

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:

$$\mathrm{Ni} + 4\mathrm{CO} \xrightarrow[30\ \mathrm{C}^{0}]{1\mathrm{atm}} \mathrm{Ni(CO)_4}$$

Ni(CO)4 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 hasbeen used commercially in the ***Mond*** process for obtaining purifiednickel 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

$$\mathrm{Fe} + 5\mathrm{CO} \xrightarrow[\text{High Pressure}]{200\ \mathrm{C}^{0}} \mathrm{Fe(CO)_5}$$

$$2\ \mathrm{Co_{(S)}} + 8\ \mathrm{CO_{(g)}} \xrightarrow[35\ \mathrm{atm}]{150\ \mathrm{C}^{0}} \mathrm{Co_2(CO)_8}$$

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

$$\mathrm{CrCl_3} + 6\mathrm{CO} + \mathrm{Al} \xrightarrow[\text{benzene}]{\mathrm{AlCl_3}} \mathrm{Cr(CO)_6} + \mathrm{AlCl_3}$$

$$\mathrm{Ru(acac)_3} + \mathrm{H_2(g)} + 12\mathrm{CO} \xrightarrow[200\ \mathrm{atm}]{150\ \mathrm{C0},\ \mathrm{CH_3OH}} \mathrm{Ru_3(CO)_{12}}$$

$$2\mathrm{CoCO_3} + 2\mathrm{H_2(g)} + 8\mathrm{CO} \xrightarrow[(120\text{-}200)^{0}]{(250\text{-}300)\ \mathrm{atm}} \mathrm{Co_2(CO)_8} + 2\mathrm{CO_2} + 2\mathrm{H_2O}$$

Some of metal carbonyls prepared from reducing their oxides at 300 C^{0} and 300 atm.

$$\mathrm{Re_2O_7} + 17\mathrm{CO} \xrightarrow[300\ \mathrm{atm}]{300\ \mathrm{C}^{0}} \mathrm{Re_2(CO)_{10}} + 7\mathrm{CO_2}$$

$$Tc_2O_7 + 17CO \xrightarrow[300\ atm]{300\ C^0} Tc_2(CO)_{10} + 7CO_2$$

$$OsO_4 + 5CO \xrightarrow[300\ atm]{300\ C^0} Os(CO)_5$$

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

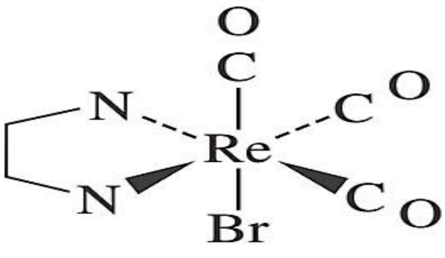
$$2\,Fe(CO)_5 \xrightarrow{h\nu} Fe_2(CO)_9 + CO$$

$$3\,Fe(CO)_5 \xrightarrow{\Delta} Fe_3(CO)_{12} + 3\,CO$$

*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 byanother ligand to form a new 18-electron species as product. For example,

$$Cr(CO)_6 + PPh_3 \xrightarrow[or\ h\nu]{\Delta} Cr(CO)_5(PPh_3) + CO$$

$$Re(CO)_5Br + en \xrightarrow{\Delta} \textit{fac}\text{-}Re(CO)_3(en)Br + 2\,CO$$



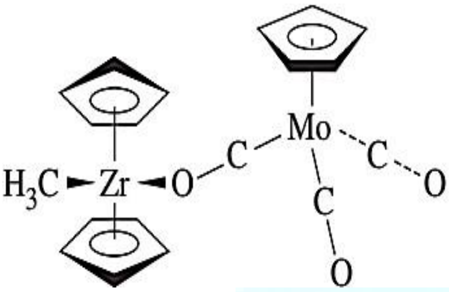
fac-Re(CO)$_3$(en)Br

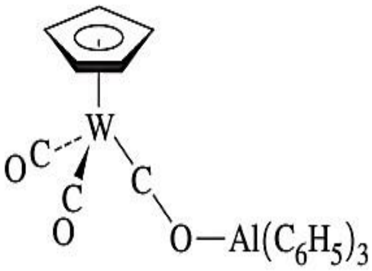
*This type of reaction therefore provides a pathway in which CO complexes can be used as precursors for a variety of complexes of other ligands.

****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 $AlCl_3$, 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 generallybent. 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*** $\boldsymbol{cm^{-1}}$. Examples of O-bonded carbonyls, sometimes called ***isocarbonyls***.





<u>Ligands Similar to CO</u>

*CS (thiocarbonyl), CSe (selenocarbonyl), and CTe (tellurocarbonyl), aresimilar to CO in their bonding modes in that they behave as both σ- donors and π-acceptors and can bond to metals in terminal or bridging modes.

* In several cases, isostructural complexes of the ligands CO through CTehave been prepared, providing opportunities for structural and spectroscopic comparisons.

*Other ligands are ***isoelectronic*** with ***CO*** and, not surprisingly, exhibit structural and chemical parallels with CO. Two examples are $\mathbf{CN^-}$ and $\mathbf{N_2}$.Complexes of $\mathbf{CN^-}$ have been known longer than carbonyl complexes. Blue complexes (***Prussian blue*** and ***Turnbull's blue***) containing the ion $\mathbf{[Fe(CN)_6]^{3-}}$ have been used as pigments in paints and inks for approximately three centuries. Cyanide is a **stronger** σ-donor and a substantially **weaker** π-acceptor than CO; overall, it is close to CO in the spectrochemical series.

*The discovery that hydrogenase enzymes contain both **CO** and $\mathbf{CN^-}$ bound to iron has stimulated interest in complexes containing both ligands. Remarkably, only two iron complexes containing both CO and $\mathbf{CN^-}$ and a single iron atom, $\mathbf{[Fe(CO)(CN)_5]^{3-}}$ (reported in 1887) and $\mathbf{[Fe(CO)_4(CN)]^-}$ (reported in 1974), were known before 2001. Both the*cis* and *trans* isomers of $\mathbf{[Fe(CO)_2(CN)_4]^{2-}}$ and ***fac***-$\mathbf{[Fe(CO)_3(CN)_3]^-}$ have been prepared. Two of the mixed ligand complexes can be made using $\mathbf{Fe(CO)_4I_2}$.

$$\mathrm{Fe(CO)_4I_2} \xrightarrow{3\,\mathrm{CN^-}} fac\text{-}[\mathrm{Fe(CO)_3(CN)_3}]^- \xrightarrow{\mathrm{CN^-}} cis\text{-}[\mathrm{Fe(CO)_2(CN)_4}]^{2-}$$

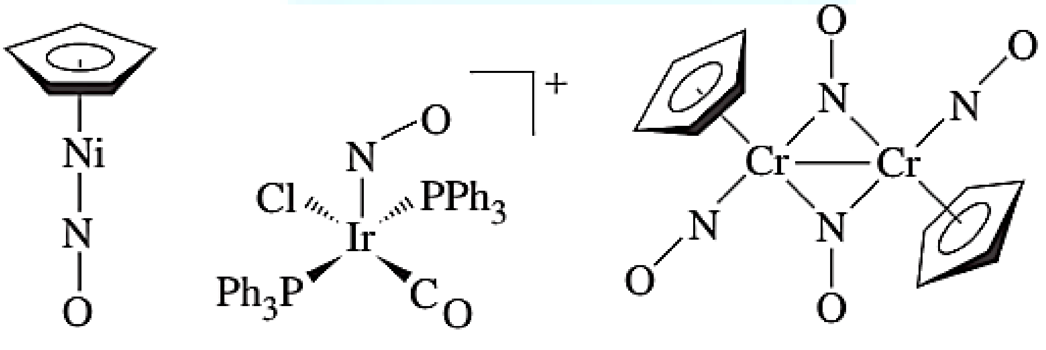
The complex ***trans*-[Fe(CO)$_2$(CN)$_4$]$^{2-}$** can be made by the addition of cyanide to a solution of $FeCl_2$ under an atmosphere of CO:

$$\mathrm{FeCl_2}(aq \text{ or } \mathrm{CH_3CN}) + 4\,\mathrm{CN^-} \xrightarrow{\mathrm{CO}} trans\text{-}[\mathrm{Fe(CO)_2(CN)_4}]^{2-}$$

* Dinitrogen is a weaker donor and acceptor than CO.

** **NO Complexes**

The NO (nitrosyl) ligand shares many similarities with CO. Like CO, it isa **σ-donor** and **π-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.

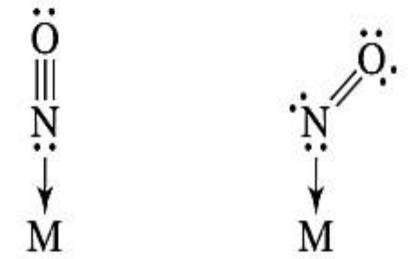


Linear Bent Bridging

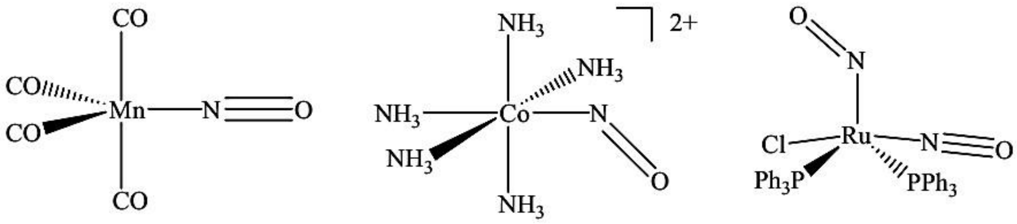
* **NO$^+$** is isoelectronic with CO; therefore, in its bonding to metals, **linearNO** is considered by electron counting scheme (**ionic model**) as **NO$^+$**, a **2-electron** donor. By the (**covalent model**), linear NO is counted as a **3- electron** donor (it has one more electron than the **2-electron**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

* The bent coordination mode of NO can be considered to arise formally from **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 **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 areknown, 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** bondconsiderably from 180° in the linear coordination mode.



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



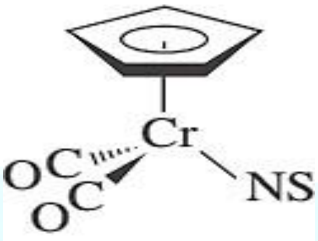
Characterisation

	M-N-O angle/ °	ν(N-O)/cm^{-1}
$Fe(CN)_5(NO)^{2-}$	178	1935
$Mn(CN)_5(NO)^{3-}$	174	1700
$Co(NH_3)_5(NO)^{2+}$	119	1610
$CoCl(en)_2(NO)^+$	124	1611

* One compound containing only NO ligands is known, **$Cr(NO)_4$**, a tetrahedral molecule that is isoelectronic with **$Ni(CO)_4$**. 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, **$[Fe(CN)_5(NO)]^{2-}$**, has been used as avasodilator in the treatment of high blood pressure. Its therapeutic effectis 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** σ- donor but **weaker** π-acceptor ligand than **NO**, a consequence of thegreater 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.



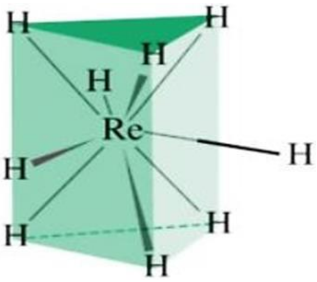
NS complex

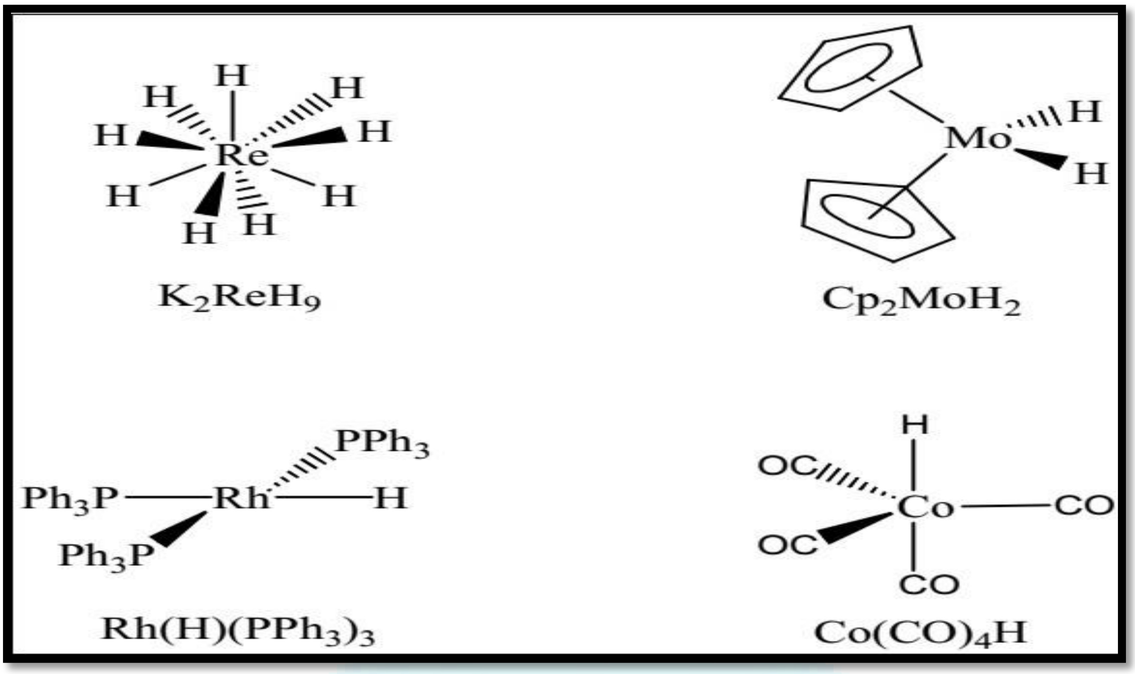
** **Hydride and Dihydrogen Complexes**

* **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 **1*s*** orbital of suitable energy for bonding, the bond between H and a transition metal must be a **σ-interaction**, involving metal *s*, *p*, and/or *d* orbitals. As a ligand, H may be considered a **2-electron** donor as hydride (**H^-**, 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 **$[ReH_9]^{2-}$** ion (Figure below), the classic example of a tricapped trigonal prism.





* Compounds containing only a single ligand, such as NO in **$Cr(NO)_4$** and CO in **$Mo(CO)_6$**, 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 **H_2**. For example,

$$Co_2(CO)_8 + H_2 \longrightarrow 2\,HCo(CO)_4$$

$$\textit{trans}\text{-}Ir(CO)Cl(PEt_3)_2 + H_2 \longrightarrow Ir(CO)Cl(H)_2(PEt_3)_2$$

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

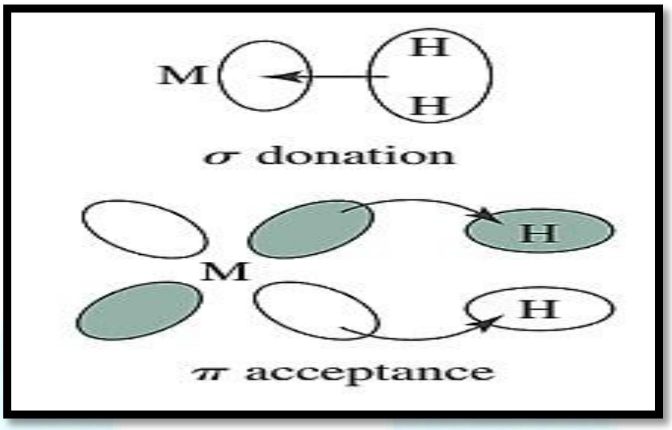
$$Co_2(CO)_8 + 2\,Na \longrightarrow 2\,Na^+[Co(CO)_4]^-$$

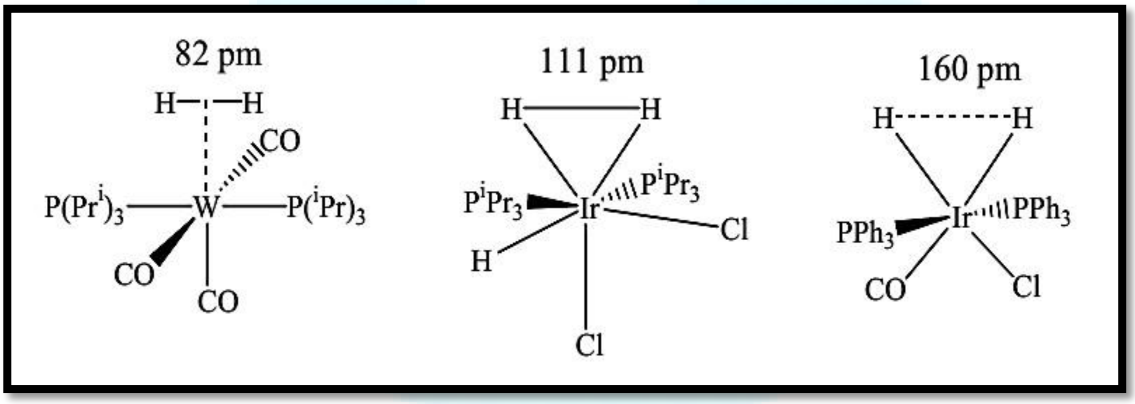
$$[Co(CO)_4]^- + H^+ \longrightarrow HCo(CO)_4$$

* **Dihydrogen Complexes**

The first structural characterization of a dihydrogen complex did not occur until 1984, when **Kubas** synthesized $M(CO)_3(PR_3)_2(H_2)$, where M = Mo or W and R = cyclohexyl or isopropyl. Subsequently, many 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 **σ-electrons** in H_2 can bedonated to a suitable empty orbital on the metal (such as a *d* orbital or hybrid orbital), and the empty **σ* orbital** of the ligand can accept electrondensity from an **occupied *d* orbital** of the metal. The result is an overall **weakening** and **lengthening** of the H-H bond in comparison with free **H_2**. Typical **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 H_2.



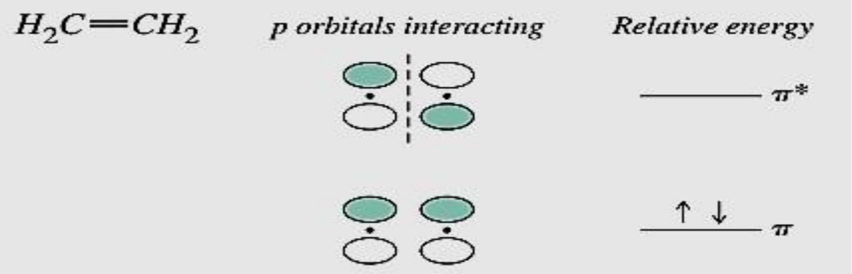


* If the metal is electron rich and donates strongly to the **σ*** of H_2 the **H- H** bond in the ligand can **rupture**, giving separate **H** atoms. Consequently, the search for stable **H_2** complexes has centered on metals likely to be relatively poor donors, such as those in high oxidation states or surrounded by ligands that function as strong electron acceptors. In particular, good π-acceptors, such as CO and NO, can be effective at stabilizing the dihydrogen ligand.

**<u>Ligands Having Extended π-Systems</u>

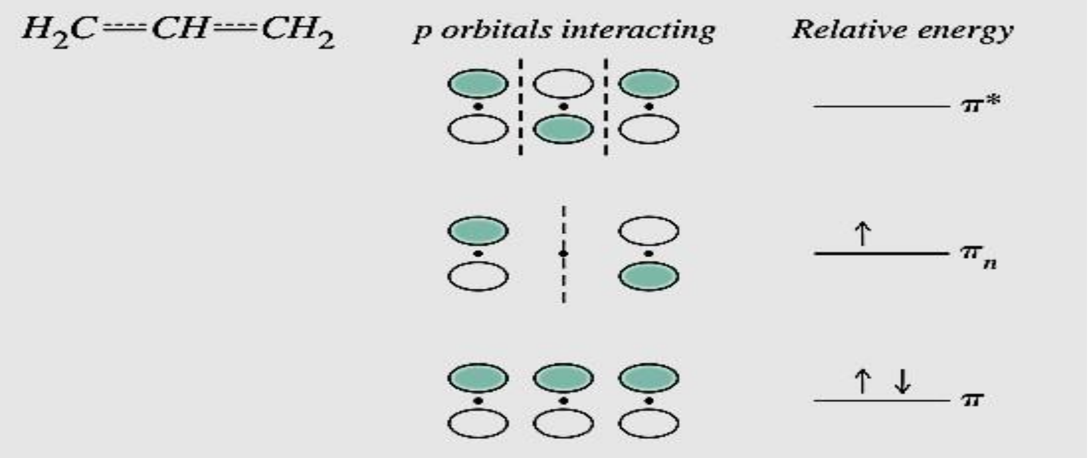
*<u>Linear π-Systems</u>

The simplest case of an organic molecule having a linear π-system is ethylene, which has a single π-bond resulting from the interactions of two2*p* orbitals on its carbon atoms. Interactions of these *p* orbitals result in one bonding and one antibonding π-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 π-system, the π-allyl radical, C_3H_5. In this case, there are three 2*p* orbitals to be considered, one from each of the carbon atoms participating in the π-system. The possible interactions are as follows:



*The lowest energy π-molecular orbital for this system has all three *p* orbitals interacting constructively, to give a bonding molecular orbital. Higher in energy is the nonbonding orbital (**π_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 themolecular orbital; a nodal plane passes through the center of this π-orbitaland thereby cancels it from participation. Highest in energy is the antibonding π* orbital, in which there is an antibonding interaction between each neighboring pair of carbon *p* orbitals.

*The number of nodes perpendicular to the carbon chain increases in going from lower energy to higher energy orbitals; for example, in the π- allyl system, the number of nodes increases from zero to one to two from the lowest to the highest energy orbital. This is a trend that will also appear in the following examples.

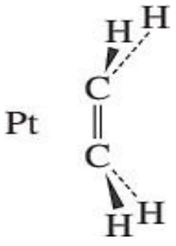
*The term "linear" is used broadly to include not only ligands that have carbons in a straight line but acyclic ligands that are bent at inner *sp*2 carbons.

Bonding between Metal Atoms and Organic Pi Systems

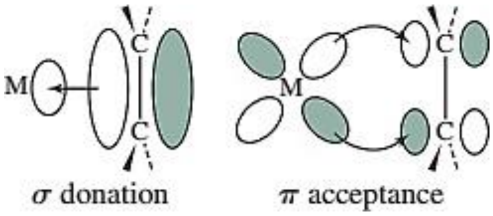
*Linear Pi Systems

*π–Ethylene Complexes

Many complexes involve ethylene, C_2H_4, as a ligand, including the anion of Zeise's salt, **$[Pt(\eta^2\text{-}C2H4)Cl_3]^-$**. 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 π-bonding electron pair, as shown in **Figure below**. At the same time, electron density can be donated back to the ligand in a pi fashion from a metal *d* orbital to the empty π* orbital of the ligand. This is another example of the synergistic effect of s donation and π-acceptance.

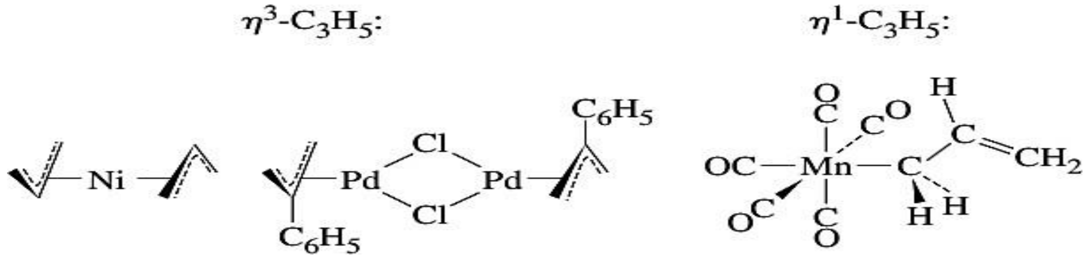


*The **C-C** distance in Zeise's salt is **137.5 pm** in comparison with **133.7 pm** in free ethylene. The lengthening of this bond can be explained bya combination of the two factors involved in the synergistic **σ-donor**, **π- acceptor** nature of the ligand: donation of electron density to the metal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

*In addition, vibrational frequencies of coordinated ethylene are at lower energy than in free ethylene; for example, the **C=C** stretch in the anion ofZeise's salt is at **1516 cm^{-1}**, compared to **1623 cm^{-1}** in free ethylene.

*<u>**π–Allyl Complexes**</u>

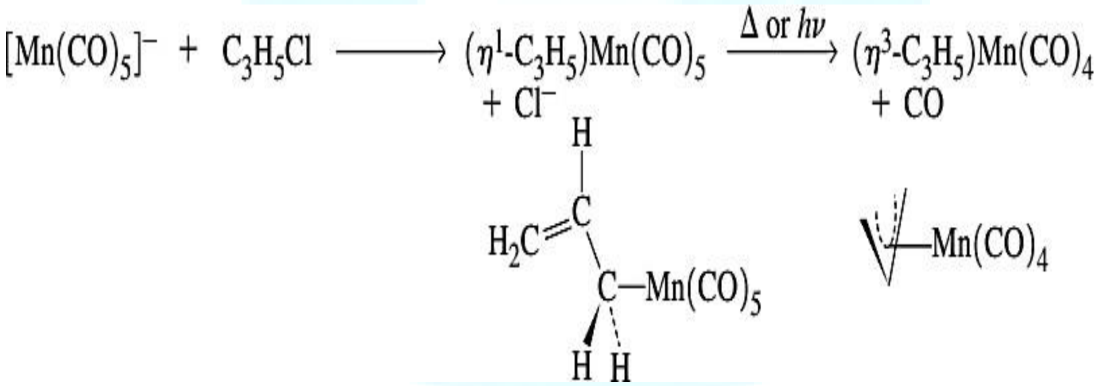
*The allyl group most commonly functions as a trihapto ligand, using delocalized π-orbitals as described previously, or as a monohapto ligand, primarily σ-bonded to a metal.



*The lowest energy π-orbital can donate electron density in a sigma fashion to a suitable orbital on the metal. The next orbital, nonbonding in free allyl, can act as a donor or acceptor, depending on the electron distribution between the metal and the ligand. The highest energy π- orbital acts as an acceptor; thus, there can be synergistic **sigma** and **pi** interactions between allyl and the metal. The **C-C-C** angle within the ligand is generally near 120°, consistent with *sp*2 hybridization.

*Allyl complexes (or complexes of substituted allyls) are intermediates in many reactions, some of which take advantage of the capability of this ligand to function in both a **η^3 and η^1** fashion. Loss of CO from carbonyl complexes containing **η^1-allyl** ligands often results in conversion of **η^1**- allyl to **η^3-allyl**. For example,

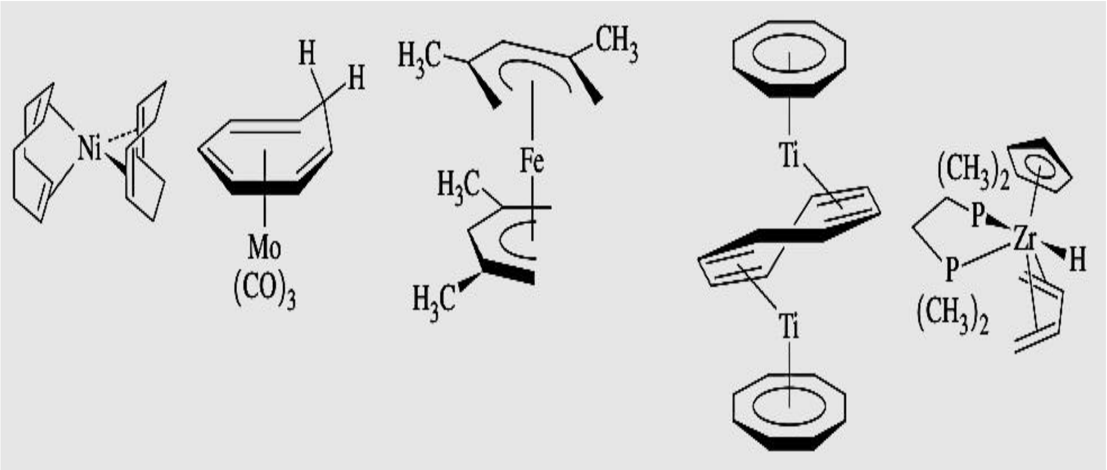
The **$[Mn(CO)_5]^-$** ion displaces **Cl^-** from allyl chloride to give an 18- electron product



containing **η^1-C_3H_5**. The allyl ligand switches to trihaptowhen a CO is lost, preserving the 18-electron count.

*<u>**Other Linear Pi Systems**</u>

Many other such systems are known; several examples of organic ligands having longer π-systems are in Figure below. **Butadiene** and longer conjugated π-systems have the possibility of isomeric ligand forms (*cis* and *trans* for butadiene). Larger cyclic ligands may have a π-systemextending through part of the ring. An example is **cyclooctadiene (COD)**; the 1,3-isomer has a 4-atom π-system comparable to butadiene; 1,5-cyclooctadiene has two isolated double bonds, one or both of which may interact with a metal in a manner similar to ethylene.



**Cyclic π-Systems

*Cyclopentadienyl (Cp) Complexes

The cyclopentadienyl group, C_5H_5, may bond to metals in a variety of ways, with many examples known of the η^1-, η^3-, and η^5-bonding modes. The discovery of the first cyclopentadienyl complex, ferrocene, was a landmark in the development of organometallic chemistry and stimulated the search for other compounds containing π-bonded organic ligands. Substituted cyclopentadienyl ligands are also known, such as $C_5(CH_3)_5$, often abbreviated Cp*, and C_5(benzyl)$_5$.

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

$$FeCl_2 + 2\ NaC_5H_5 \longrightarrow (\eta^5\text{-}C_5H_5)_2Fe + 2\ NaCl$$

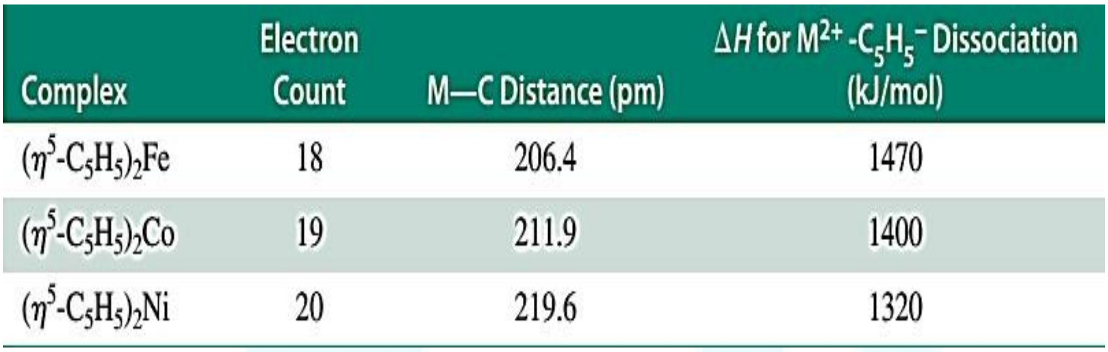
* Ferrocene, $(\eta^5\text{-}C^5H^5)_2Fe$

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 C5H5 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.

* **<u>Other Metallocenes and Related Complexes</u>**

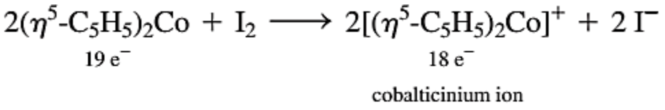
Other metallocenes have similar structures but do not necessarily obey the rule. For example, cobaltocene and nickelocene are structurally similar 19- and 20-electron species.



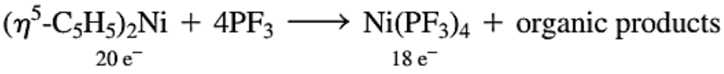
Complex	Electron Count	M—C Distance (pm)	ΔH for M^{2+}-$C_5H_5^-$ Dissociation (kJ/mol)
$(\eta^5\text{-}C_5H_5)_2Fe$	18	206.4	1470
$(\eta^5\text{-}C_5H_5)_2Co$	19	211.9	1400
$(\eta^5\text{-}C_5H_5)_2Ni$	20	219.6	1320

* The extra electrons have chemical and physical consequences, as can beseen 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 ΔH 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:

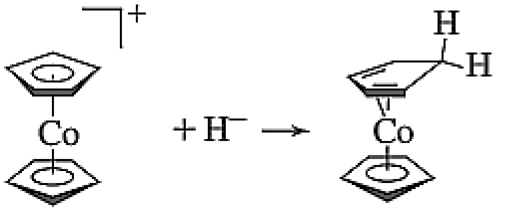


$$2\underset{19\,e^-}{(\eta^5\text{-}C_5H_5)_2Co} + I_2 \longrightarrow 2\underset{\substack{18\,e^-\\ \text{cobalticinium ion}}}{[(\eta^5\text{-}C_5H_5)_2Co]^+} + 2\,I^-$$



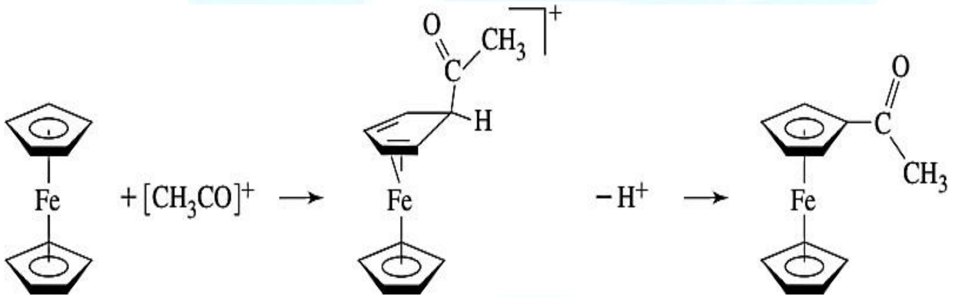
$$\underset{20\,e^-}{(\eta^5\text{-}C_5H_5)_2Ni} + 4PF_3 \longrightarrow \underset{18\,e^-}{Ni(PF_3)_4} + \text{organic products}$$

* Cobalticinium reacts with hydride to give a neutral, 18 -electron sandwich compound in which one cyclopentadienyl ligand has been modified into η4-C_5H_6

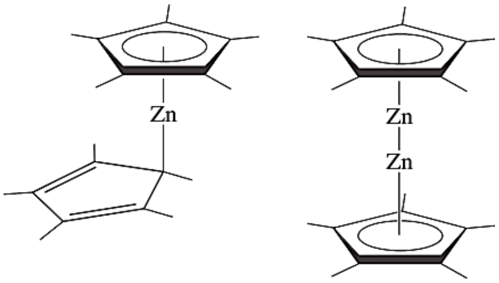


Reaction of Cobalticinium with Hydride.

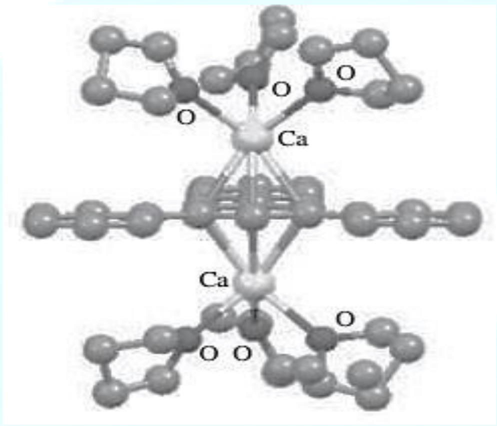
Ferrocene,. It undergoes a variety of reactions, including many on the cyclopentadienyl rings. A good example is that of electrophilic acyl substitution (**Figure below**), a reaction paralleling that of benzene and its derivatives. In general, electrophilic aromatic substitutionreactions are much more 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 ofa sandwich structure are also known. Perhaps the best known of these metallocenes is decamethyldizincocene, **(η5-$C_5Me_5)_2Zn_2$**, which was prepared from decamethylzincocene, **(η5-$C_5Me_5)_2$**Zn, and diethylzinc. Particularly notable is **(η5-$C_5Me_5)_2Zn_2$**, the first exampleof a stable molecule with a **zinc–zinc** bond; moreover, its zinc atoms are in the exceptionally rare **+1** oxidation state.

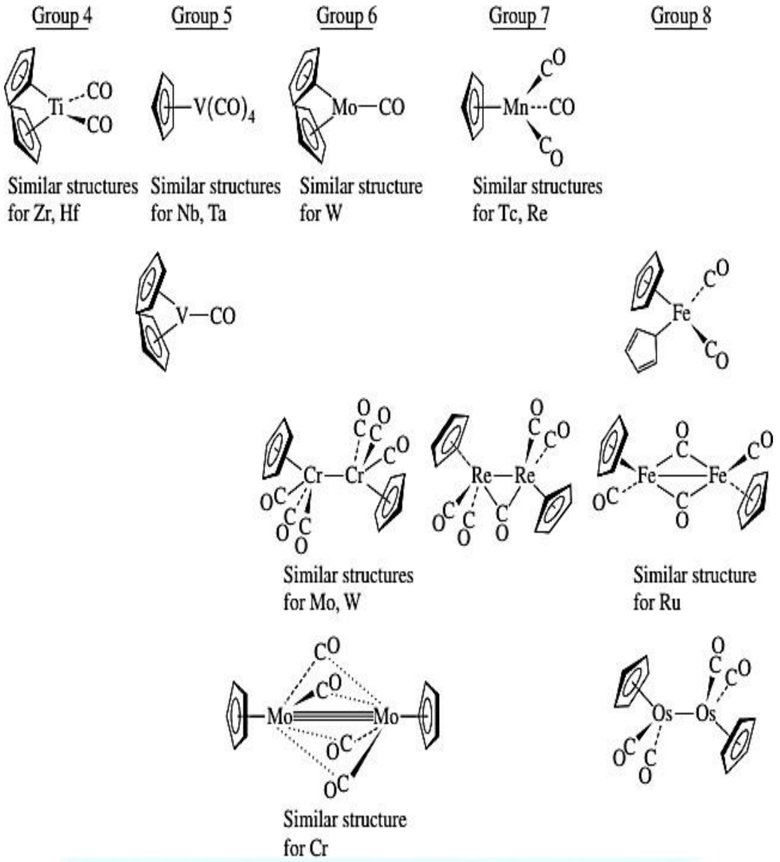


*A variation on the theme of metallocenes and related sandwich compounds is provided by the “**inverse**” sandwich in **Figure below**, with calcium(I) ions on the outside and the cyclic pi ligand 1,3,5- triphenylbenzene in between. This compound was most efficiently prepared by reacting 1,3,5-triphenylbenzene 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.



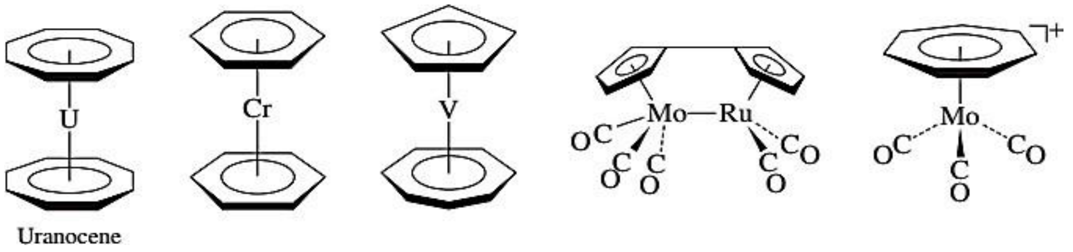
****<u>Complexes Containing Cyclopentadienyl and CO Ligands</u>**

Many complexes are known containing both Cp and CO ligands. These include “**half-sandwich**” compounds such as **$(\eta5\text{-}C_5H_5)Mn(CO)_3$** and dimeric and larger cluster molecules.



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.

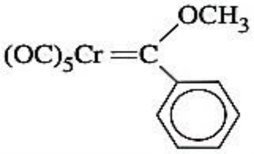
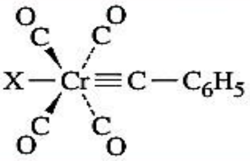
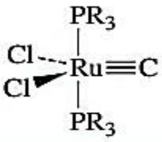
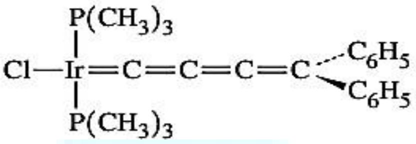
*Many other linear and cyclic pi ligands are known. Examples of complexes containing some of these ligands are in **Figure below**. Depending on the ligand and the electron requirements of the metal (or metals), these ligands may be capable of bonding in a mono-hapto or polyhapto fashion, and they may bridge two or more metals.



** Complexes containning $M\text{-}C$, $M{=}C$ and $M{\equiv}C$ bonds

Complexes containing direct metal–carbon single, double, and triple bonds have been studied extensively.

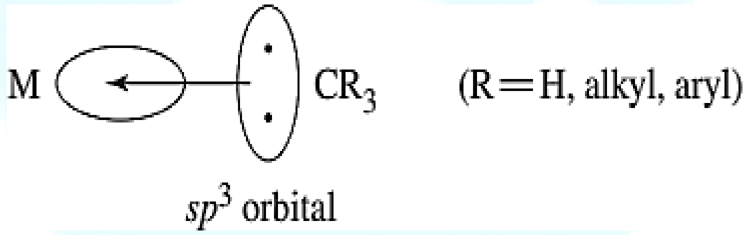
Complexes Containing $M{-}C$, $M{=}C$, and $M{\equiv}C$ Bonds

Ligand	Formula	Example
Alkyl	$-CR_3$	$W(CH_3)_6$
Carbene (alkylidene)	$=CR_2$	
Carbyne (alkylidyne)	$\equiv CR$	
Carbide (carbon)	$\equiv C$	
Cumulene	$=C(=C)_nRR'$	

*<u>**Alkyl and Related Complexes**</u>

Some of the earliest known organometallic complexes were those having **σ-bonds** between main group metal atoms and alkyl groups. Examples include Grignard reagents, having magnesium–alkyl bonds, and alkylcomplexes 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 sigmafashion:

In terms of electron counting, the alkyl ligand may be considered a **2**- electron donor **:CR$_3$-** (Ionic model) or a **1**-electron donor **.**CR3 (covalentmodel). 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 beendeveloped.

Two of the most important of these methods are:

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

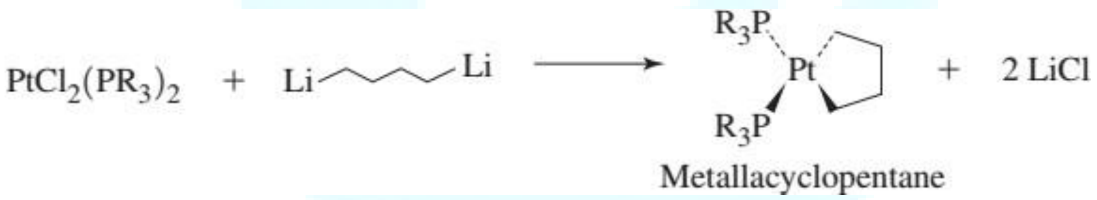
$$ZrCl_4 + 4\,PhCH_2MgCl \longrightarrow Zr(CH_2Ph)_4\,(Ph = \text{phenyl}) + 4\,MgCl_2$$

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

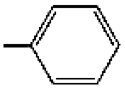
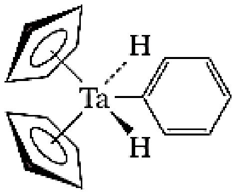
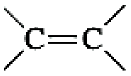
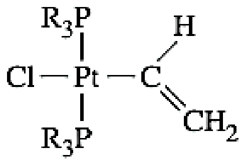
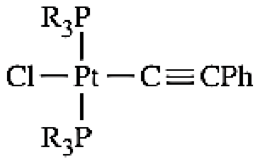
$$Na[Mn(CO)_5]^- + CH_3I \longrightarrow CH_3Mn(CO)_5 + NaI$$

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

*Other ligands have direct metal–carbon σ-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.



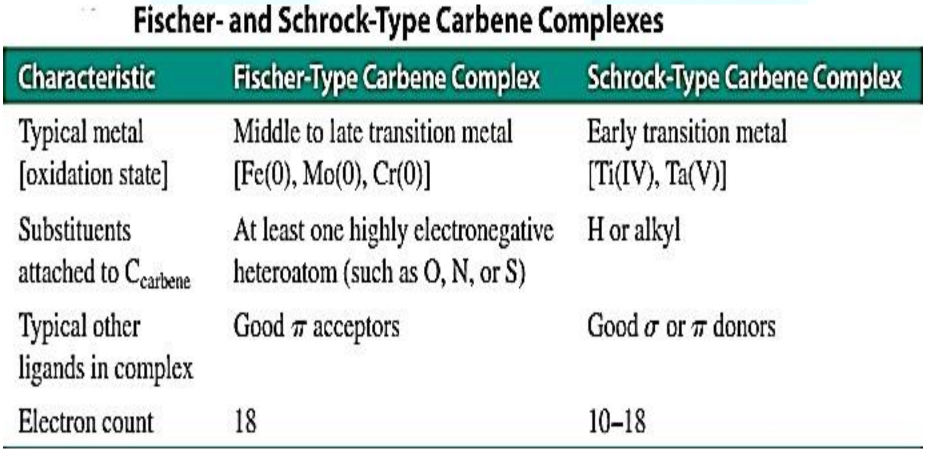
Other Ligands Forming Sigma Bonds to Metals

Ligand	Formula	Example
Aryl		
Alkenyl (vinyl)		
Alkynyl	$-C\equiv C-$	

*<u>**Carbene Complexes**</u>

Carbene complexes contain metal–carbon double bonds. First synthesizedin 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, **$:CH_2$**. 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/orhydrogen 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***. We will focus primarily on Fischer-type carbene complexes.

*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 π- bond with carbon.

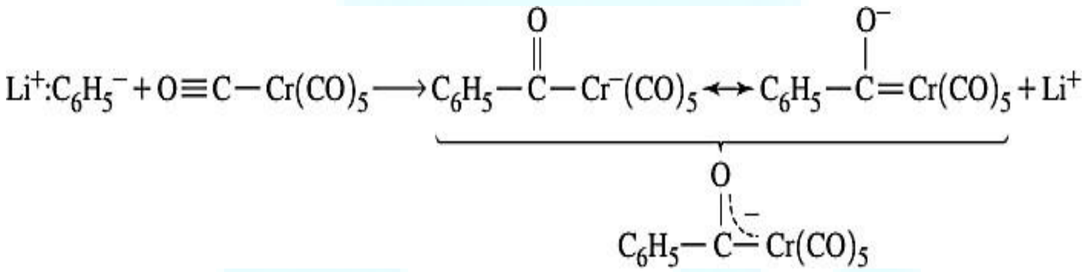


Fischer- and Schrock-Type Carbene Complexes

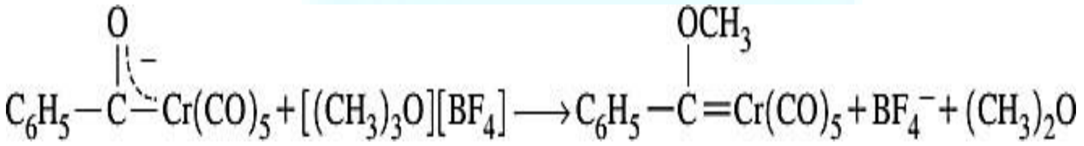
Characteristic	Fischer-Type Carbene Complex	Schrock-Type Carbene Complex
Typical metal [oxidation state]	Middle to late transition metal [Fe(0), Mo(0), Cr(0)]	Early transition metal [Ti(IV), Ta(V)]
Substituents attached to $C_{carbene}$	At least one highly electronegative heteroatom (such as O, N, or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

*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, **$Cr(CO)_5[C(OCH_3)C_6H_5]$**, with an oxygen on the carbene carbon, is much more stable than **$Cr(CO)_5[C(H)C_6H_5]$**. The stability of the complex is enhanced if the highly electronegative atom can participate in the π- bonding, with the result a delocalized, 3-atom π 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 π electron pair than would a simple metal-to- carbon π bond.

*The methoxycarbene complex **$Cr(CO)_5[C(OCH_3)C_6H_5]$** synthesized via reacting **phenyllithium** with **$Cr(CO)_6$** to give the anion **$[C_6H_5C(O)Cr(CO)_5]^-$**, which has two important resonance structures:



Alkylation by a source of **CH_3^+**, such as **$[(CH_3)_3O][BF_4]$** or **CH_3I**, 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 **220pm**.

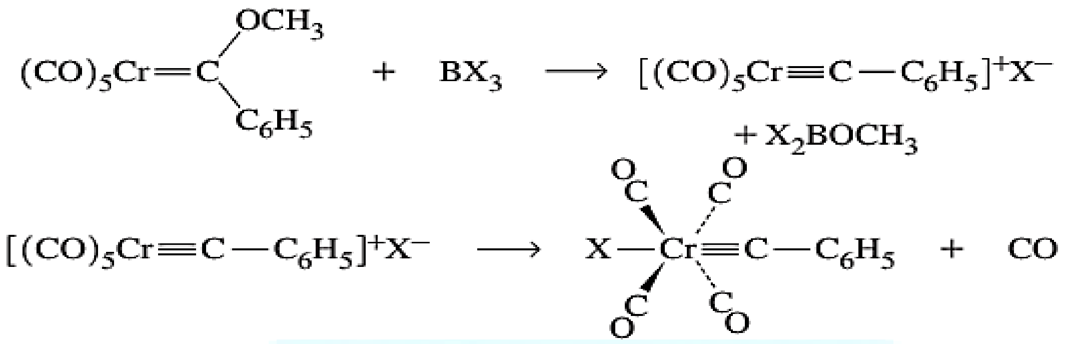
*<u>**Carbyne (Alkylidyne) Complexes**</u>

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:

$$\mathbf{M\equiv C-R}$$

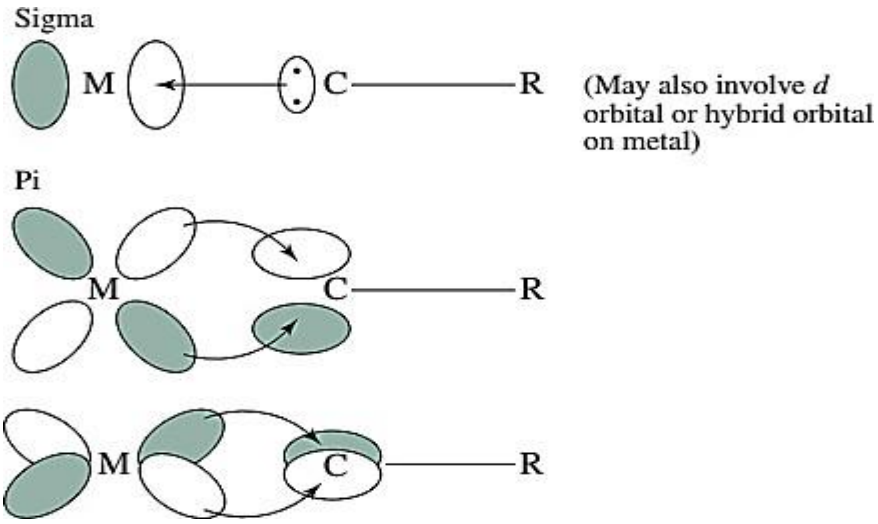
where R = aryl, alkyl, H, $SiMe_3$, NEt_2, PMe_2, SPh, or Cl. Carbyne complexes were first synthesized by chance as products of the reactions of carbene complexes with Lewis acids. The methoxycarbene complex **$Cr(CO)_5[C(OCH_3)C_6H_5]$** was found to react with the Lewis acids **BX_3** (X = Cl, Br, 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:

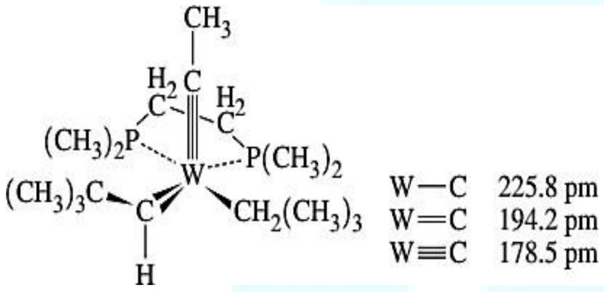


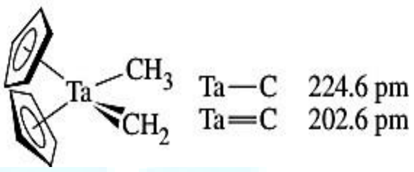
The best evidence for the carbyne nature of the complex is provided by X-ray crystallography, which gives a Cr-C bond distance of **168 pm** (for X = Cl), considerably shorter than the **204 pm for** the parent carbene complex. The angle is, as expected, 180° for thiscomplex; however, slight deviations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

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



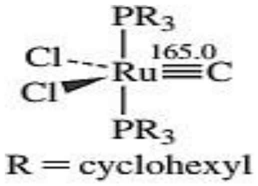
In some cases, molecules have been synthesized containing two or three of the types of ligands discussed in this section (alkyl, carbene, andcarbyne).

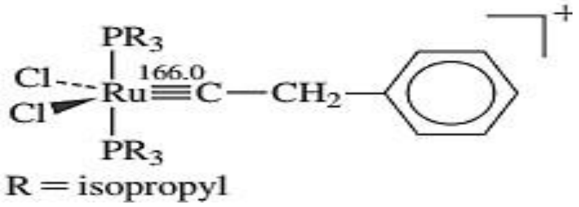




*Carbide and Cumulene Complexes

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.

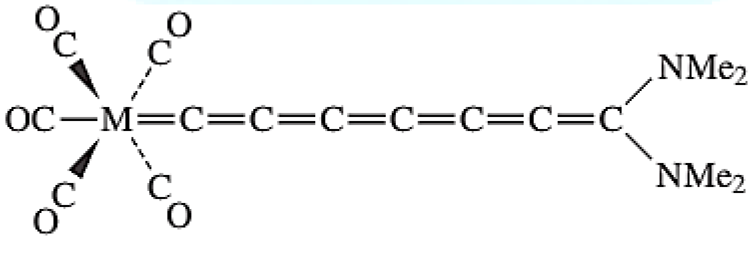




*Calculations have indicated that bonds between transition metals and terminal carbon atoms are quite strong, with bond dissociation enthalpies comparable to those of transition-metal complexes with **M≡N** and **M=O** bonds. In addition, the frontier orbitals of the carbide complex in Figure above (where R = methyl) have many similarities to those of 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 ***cumulenylidene*** 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.

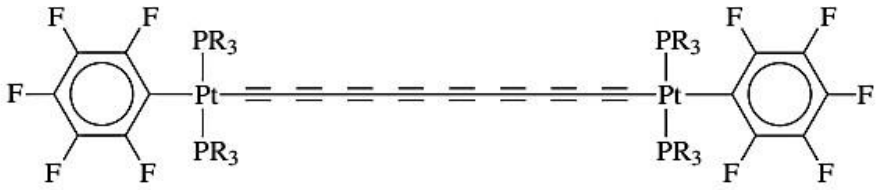


M = Cr, W

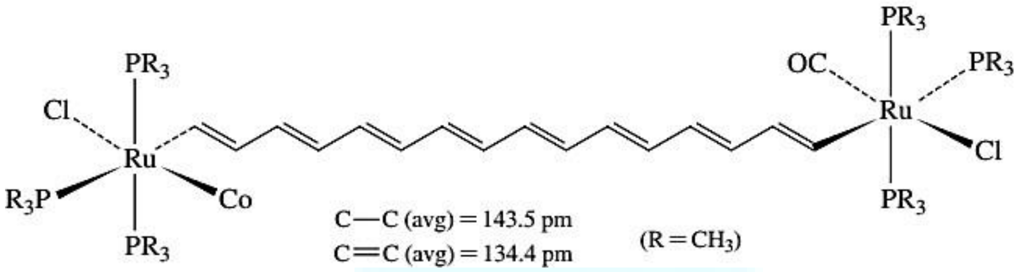
*Carbon Wires: Polyyne and Polyene Bridges

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 π 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.



$C-C$ (avg) = 135.1 pm
$C\equiv C$ (avg) = 121.6 pm
(R = *p*-Tol)



$C-C$ (avg) = 143.5 pm
$C=C$ (avg) = 134.4 pm
(R = CH_3)