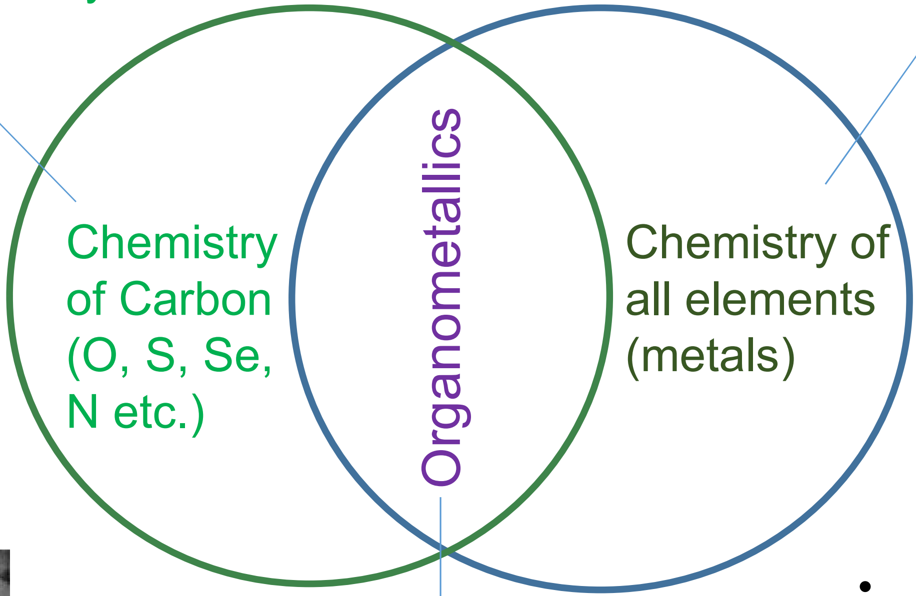
Organometallic Chemistry

Organic Chemistry

- more or less covalent bonds
- rigid element environments
- fixed oxidation states



Inorganic Chemistry

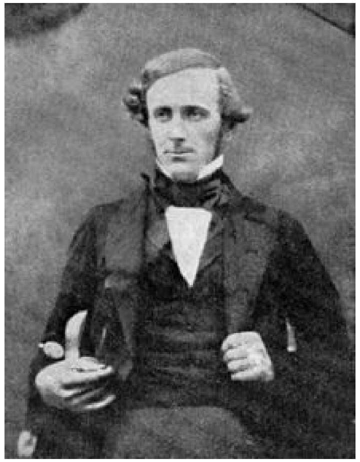
- primarily ionic M-X bonds,
  dative M-L bonds
- variable and often fluxional environments
- variable oxidation states

Direct M-C bond

- more covalent (less ionic)
- often less symmetric than coordination compounds

Importance

- Easy access to C-C bond
- Catalysis
- Small molecule activation
- New industry
- Around 2000 research article
- Six Nobel Prizes



Edward Frankland

Innocent Ligands: In a metal complex, if the ligands whose oxidation state is clearly known, **Eg:** O^{2-}, Cl^-

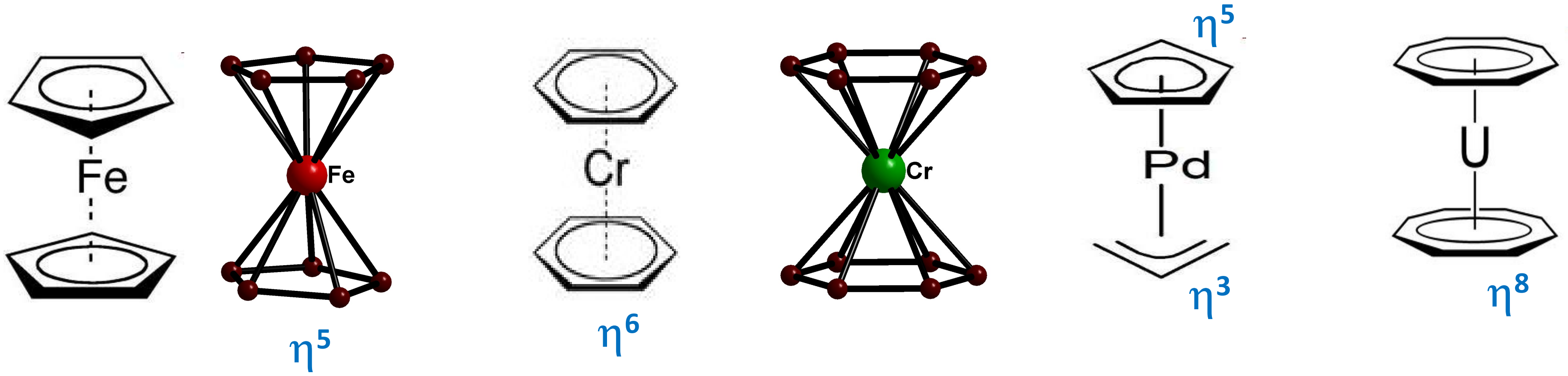
Non-innocent ligands: In a metal complex, if the ligands igands whose oxidation state is not known, **Eg:** NO

The 18 Electron Rule

- 18 electrons in the outer shell (s, p and d orbitals) is an indication of stability.
- Compounds that can attain 18 electrons within the bonding orbitals show increased stability.
- **Statement:** *Thermodynamically stable transition metal organometallic compounds are formed when total valence electrons (that is the number of valance electrons of the metal plus the number of electrons from each ligand) equals to 18*.

Hapticity (η^x)?

- **It is the number of ligand atoms simultaneously bound to a metal center.**
- Examples: η^1 – Monohapto; η^3 – trihapto; η^5 – pentahapto etc.
- **Example:** If all the five carbon atoms of a cyclopentadienyl moiety are equidistant from a metal atom, we term it as ***η^5-cyclopentadienyl***



M-M bond calculation:

1. **Determine the total valence electrons (TVE) in the entire molecule = number of valence electrons of the metal + number of electrons from each ligand and the charge; say, it is A.**

2. **Subtract this number from n×18 where n is the number of metal in complex, that is, (n×18)-A; say, it is B.**

3. **(a) B divided by 2 gives the total number of M-M bonds in the complex.**

   (b) A divided by n gives the number of electrons per metal. If the number of electrons is 18, it indicates that there is no M-M bond; if it is 17 electrons, it indicates that there is 1 M-M bond; if it is 16 electrons, it indicates that there are 2 M-M bonds and so on.

$$\boxed{\text{M-M bonds} = \frac{(n\times 18)-TVE}{2}}$$

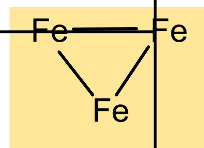
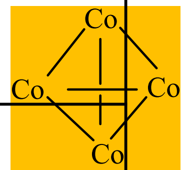
How to determine the total number of metal - metal bonds

Determine the total valence electrons (TVE) in the entire molecule (that is, the number of valence electrons of the metal plus the number of electrons from each ligand and the charge); say, it is *A*.

Subtract this number from $n \times 18$ where n is the number of metals in the complex, that is, $(n \times 18) - A$; say, it is *B*.

(a) *B* divided by 2 gives the total number of M–M bonds in the complex.

(b) *A* divided by n gives the number of electrons per metal. If the number of electrons is 18, it indicates that there is no M–M bond; if it is 17 electrons, it indicates that there is 1 M–M bond; if it is 16 electrons, it indicates that there are 2 M–M bonds and so on.

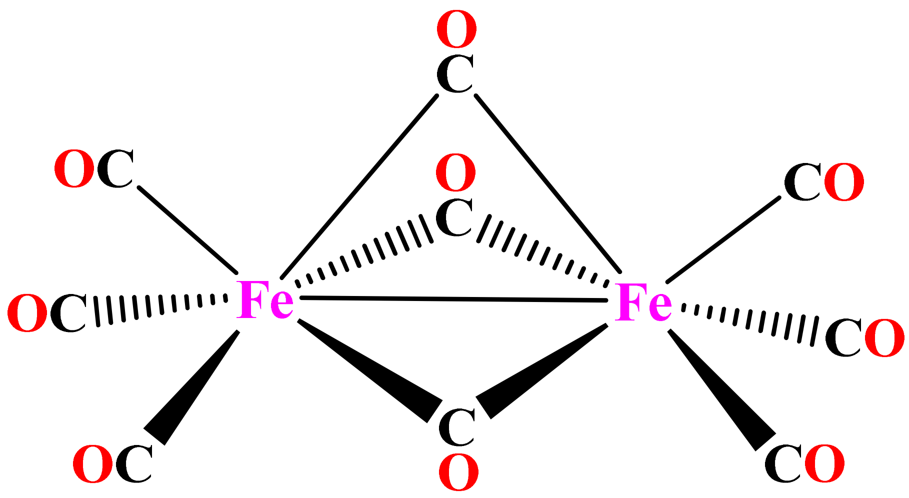
Molecule	TVE (A)	$(18 \times n) - A$ (B)	Total M–M bonds ($B/2$)	Bonds per metal	Basic geometry of metal atoms
$Fe_3(CO)_{12}$	48	54 – 48 = 6	6/2 = 3	48/3 = 16; 2	
$Co_4(CO)_{12}$	60	72 – 60 = 12	12/2 = 6	60/4 = 15; 3	
$[\eta^5\text{-}CpMo(CO)_2]_2$	30	36 – 30 = 6	6/2 = 3	30/2 = 15; 3	Mo≡Mo
$(\eta^4\text{-}C_4H_4)_2Fe_2(CO)_3$	30	36 – 30 = 6	6/2 = 3	30/2 = 15; 3	Fe≡Fe
$Fe_2(CO)_9$	34	36 – 34 = 2	2/2 = 1	34/2 = 16; 1	Fe–Fe

$Fe_2(CO)_9$

2.Fe___________2×8 e^- = 16 e^-
9.CO___________9×2 e^- = 18 e^-
Total= 34 e^- (TVE)

No of M-M bonds $= \frac{(2\times18)-34}{2}$
$= \frac{36-34}{2}$
$= 1$

Proposed structure:

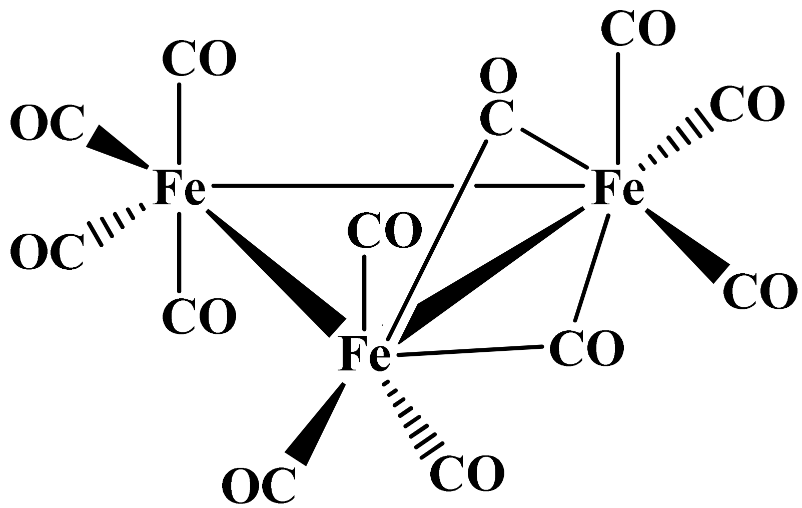


$Fe_3(CO)_{12}$

3.Fe___________3×8 e^- = 24e^-
12.CO___________12×2 e^- = 24e^-
Total= 48e^- ....(TVE)

No of M-M bonds $= \frac{(3\times18)-48}{2}$
$= \frac{54-48}{2}$
$= 3$

Proposed structure:



$Co_4(CO)_{12}$

4.Co___________$4 \times 9\ e^- = 36\ e^-$

12.CO___________$12 \times 2\ e^- = 24\ e^-$

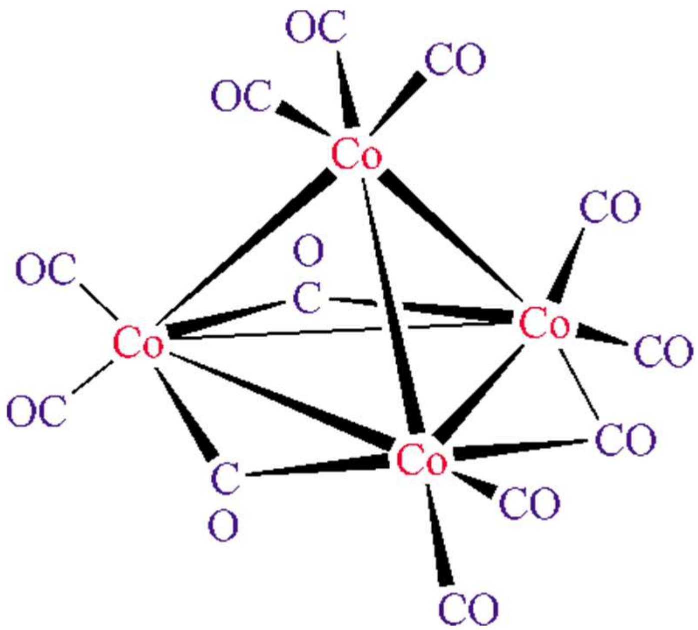
Total= $60\ e^-$ (TVE)

No of M-M bonds = $\frac{(4 \times 18) - 60}{2}$

$= \frac{72 - 60}{2}$

$= 6$

Proposed structure:



$Ir_4(CO)_{12}$

4.Ir___________$4 \times 9\ e^- = 36\ e^-$

12.CO___________$12 \times 2\ e^- = 24\ e^-$

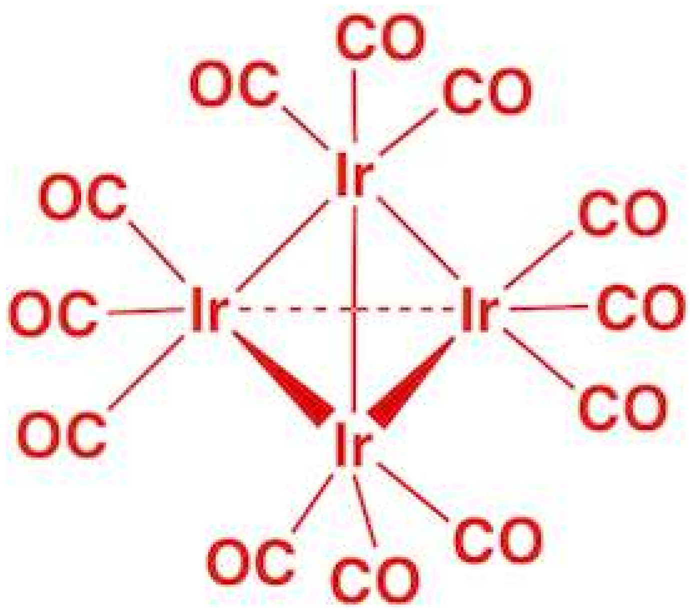
Total= $60\ e^-$ (TVE)

No of M-M bonds = $\frac{(4 \times 18) - 60}{2}$

$= \frac{72 - 60}{2}$

$= 6$

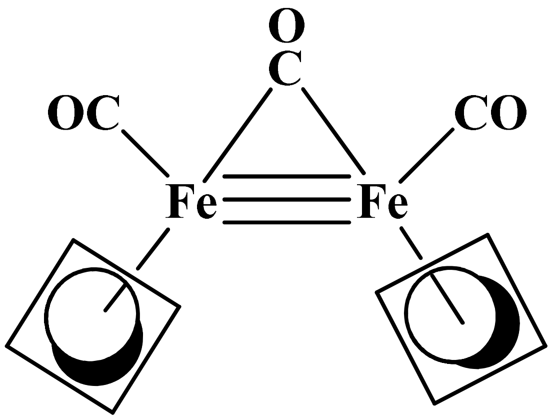
Proposed structure:



$(\mu\text{-}CO)\text{-}[\eta^4\text{-}(C_4H_4)Fe(CO)]_2$

$2+2\times[4+8+2]=30$

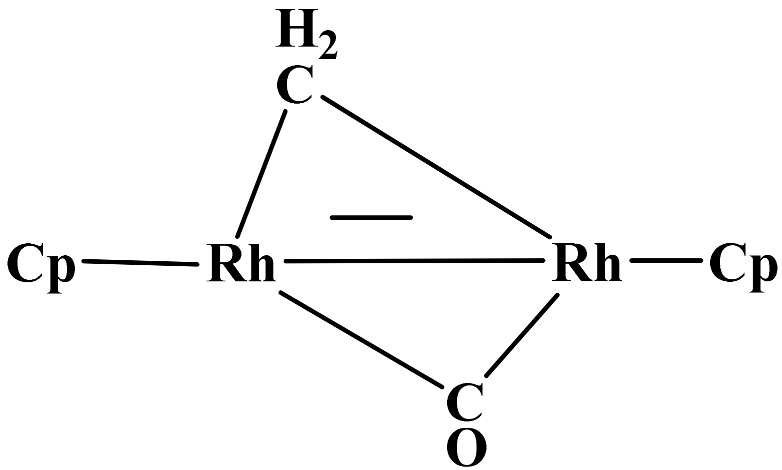
$(18\times2)-30=6/2=3$



1) $\mu\text{-}CO\text{-}\mu\text{-}CH_2\text{-}[\eta^5\text{-}CpRh]_2$

$2+2+5\times2+9\times2=32$

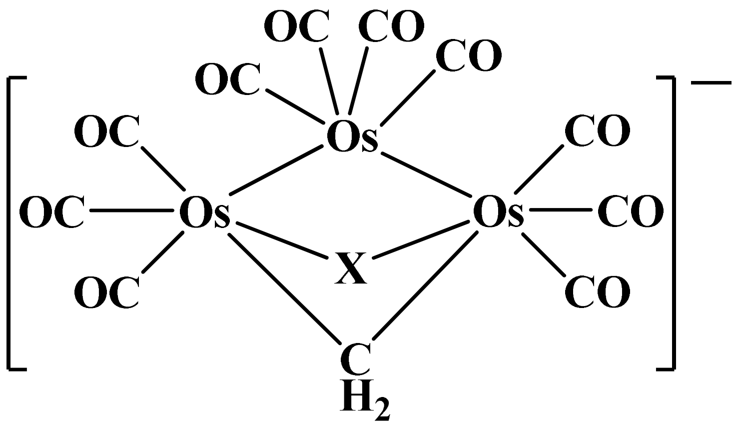
$(18\times2)-32=4/2=2$



2) $[\mu\text{-}X\text{-}\mu\text{-}CH_2(Os_3(CO)_{10})]^-$

$3+2+8\times3+10\times2+1(\text{charge})=50$

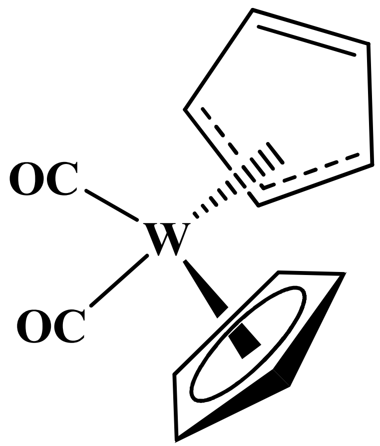
$(18\times3)-50=4/2=2$



$[\eta^5\text{-}CpMo(CO)_2]_2$???

Q1. Predict the structure of the complex $[W(CO)_2(C_5H_5)_2]$.

W	6e-
2×CO	4e-
1×η^3	3e-
1×η^5	5e-
Total	18e-



Q2. Consider the 18 electron rule as a guide and determine the value of n in the following complexes.

a) $[Na_2Fe(CO)_n]$ — Fe(8)+n×2+charge(2)=18; n=4

b) $[MnBr(CO)_n]$ — Mn(7)+Br(1)+n×2 =18; n=5

c) $[W(\eta^6\text{-}C_6H_6)(CO)_n]$ — W(6)+η^6-C_6H_6(6)+n×2=18; n=3

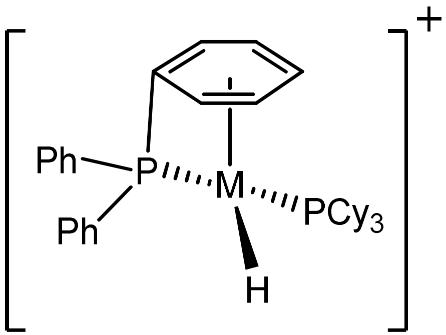
d) $[Rh(\eta^5\text{-}C_5H_5)(CO)_n]$ — Rh(9)+η^5-C_5H_5(5)+n×2=18; n=2

e) $[Cr(\eta^3\text{-}C_5H_5)(CO)_n(CH_3)]$ — Cr(6)+η^3-C_5H_5(3)+CH_3(1)+ n×2=18; n=4

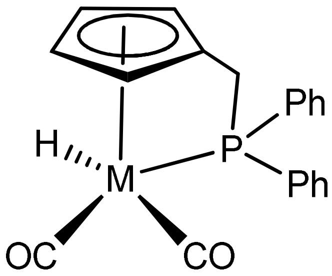
f) $[IrBr_2(CO)_n(PPh_3)_2(CH_3)]$ — Ir(9)+2×Br (2)+2×PPh_3(4)+CH_3(1)+ n×2=18; n=1

Exercises

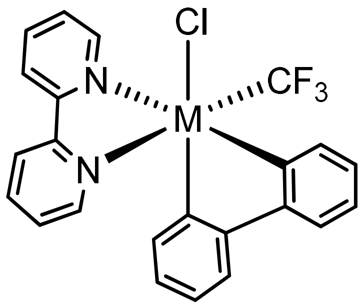
The following organometallic compounds are stable and have a 2nd row transition metal at its centre. Find out the metal and its oxidation state



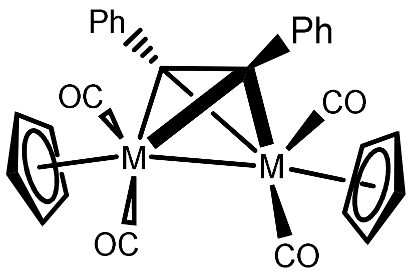
A



B

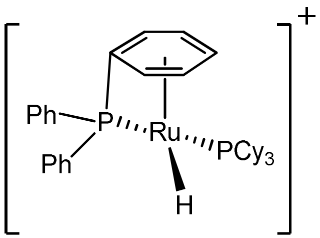


C

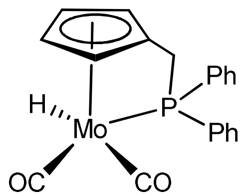


D

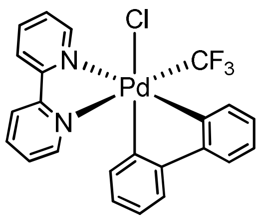
yttrium	zirconium	niobium	molybdenum	technetium	ruthenium	rhodium	palladium	silver	cadmium
39	40	41	42	43	44	45	46	47	48
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
88.906	91.224	92.906	95.94	[98]	101.07	102.91	106.42	107.87	112.41



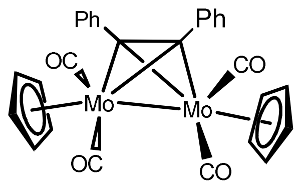
A



B



C



D

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, $CpWOCl_3$) [Possible reason: 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 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.