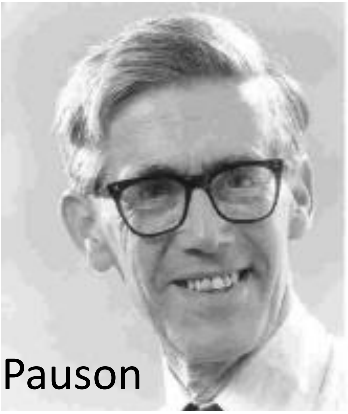
Lecture 6
Inorganic chemistry

Ferrocene: Path breaking discovery of a sandwich compound

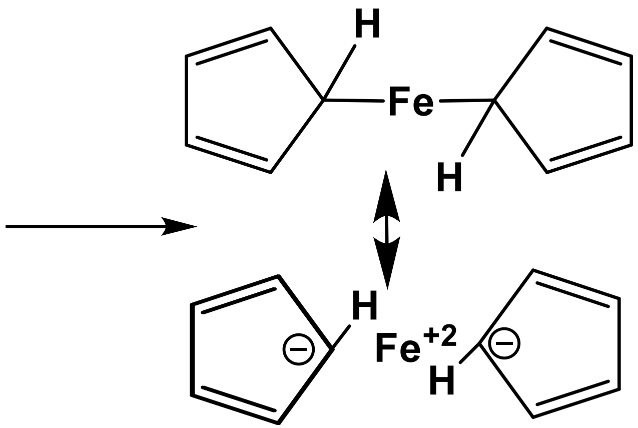


Pauson

$FeCl_3$ + CpMgBr

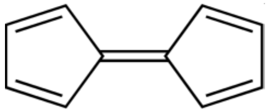
Kealy and Pauson

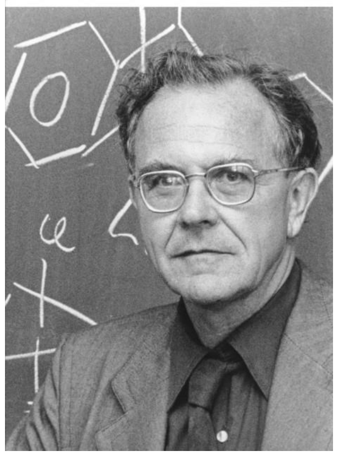
1951



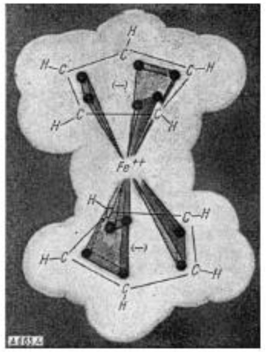
Kealy

However, instead of the expected fulvalene, they obtained a light orange powder of "remarkable stability", with the formula $C_{10}H_{10}Fe$



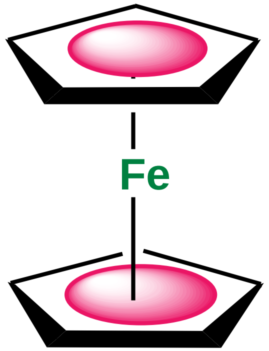


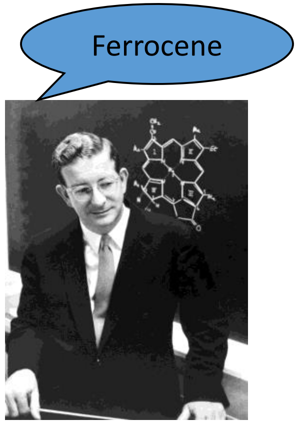
G. Wilkinson



1973 Nobel Prize
'sandwich compounds'

E. O. Fischer



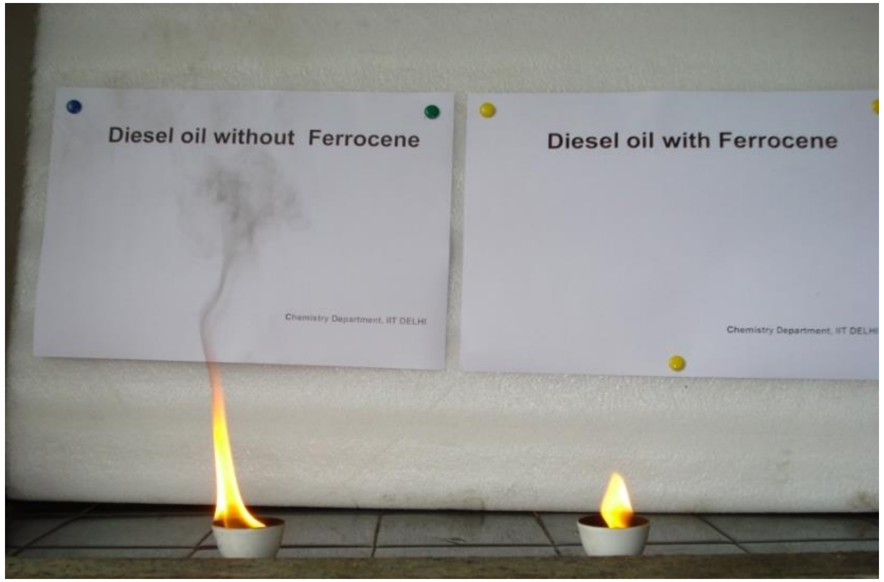


R. B. Woodward
1965 Nobel Prize
'art of organic synthesis'

Wilkinson, Rosenblum, Whitney, Woodward, *J. Am. Chem. Soc.*, 1952

Ferrocene: Fuel additive, smoke suppressant and chiral catalyst precursor

Ferrocene powder



Ferrocene crystals

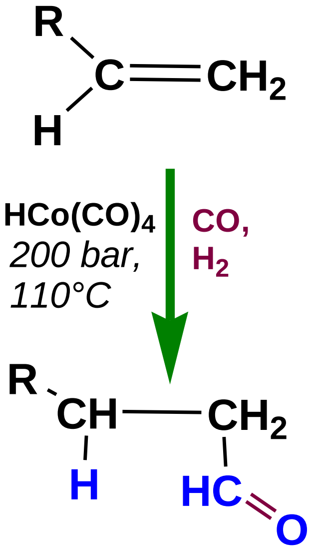
Ferox Gas & Diesel Fuel Additive is a catalyst that is an eco-friendly fuel additive and horsepower booster. It allegedly increases mileage from between 10 and 20% while also significantly reducing harmful emissions.

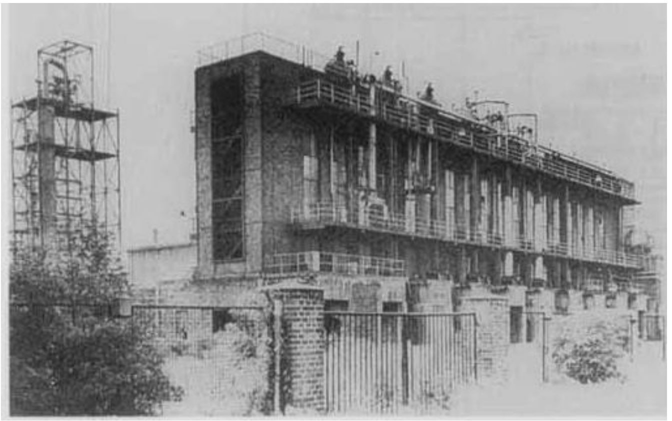
First organometallics in homogeneous catalysis-

The Hydroformylation (1938)

Otto Roelen

Pioneer in Industrial homogeneous catalysis (1897-1993)





First Industrial plant- hydroformylation

detergents

- Aldehydes are intermediates for a variety of chemicals: amines, acids, and especially alcohols.
- Aldehydes are normally reduced to alcohols that are used as solvents, as plasticizers, and in the synthesis of detergents.

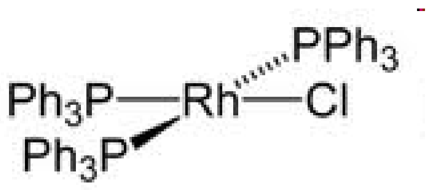
(1) 75% of all chemicals currently require catalysts at some stage in their manufacture

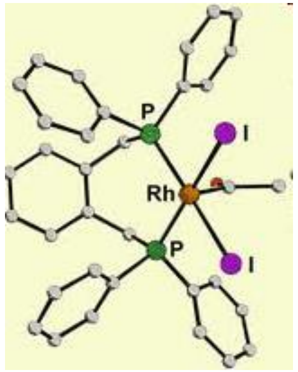
(2) In US, catalysis and catalytic processes account for ca. 20 % of GDP, with 30 of the 50 largest volume chemicals currently produced via catalytic routes

Organometallic catalysts in industrial synthesis : Three Nobel Prizes 2001, 2005 and 2010

Hydrogenation

$$RHC{=}CH_2 \; + \; H_2 \longrightarrow RCH_2CH_3$$

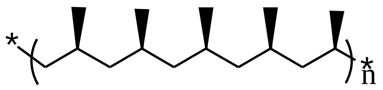




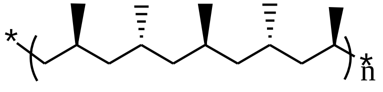
Methanol to acetic acid process

$$CH_3OH \; + CO \longrightarrow CH_3COOH$$

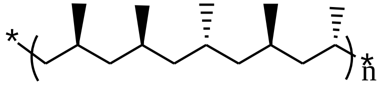
Olefin polymerization and oligomerization



Isotactic polypropylene

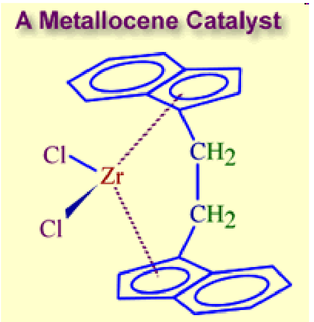


Syndiotactic polypropylene



Atactic polypropylene

C_4-C_8	40%
C_{10}- C_{18}	40 %
C_{20} & >	20 %



On practical side, nearly 25 billion dollars was realized from industrial processes utilizing homogeneous catalysis based on organometallic chemistry in 1985. It was predicted that the role of organometallic chemistry in the production of pharmaceceuticals, agrichemicals, flavours, fragrances and semiconductors will continue to expand in the next decades.

18 electron rule : How to count electrons

Nevil Vincent Sidgwick
(1873–1952)
British Chemist

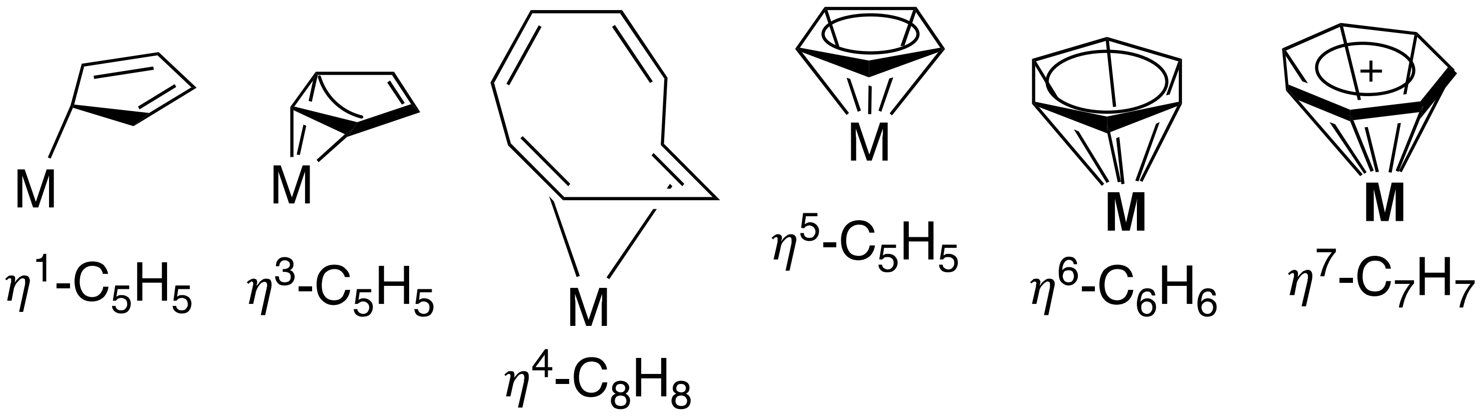
The rule states that thermodynamically stable transition metal organometallic compounds are formed when the sum of the electrons on the metal plus the electrons donated from the ligands is equal to 36(Kr), 54 (Xe), 86 (Rn), the EAN rule was said to be obeyed.

An alternative and more general statement is that when a metal achieves an outer shell configuration of $ns^2\,(n\text{-}1)d^{10}\,np^6$, there will be 18 electrons in the valence orbitals and a closed, stable configuration. This rule of thumb, which is referred to as the 18-electron rule

It has the advantage of being the same for all rows of the periodic chart, eliminating the need to remember a EAN for each nobel gas. Furthure more, the number is an easy one to recall since it is merely the total capacity of nine orbitals, one set each of s, p, and d orbitals

Terminology of Ligands

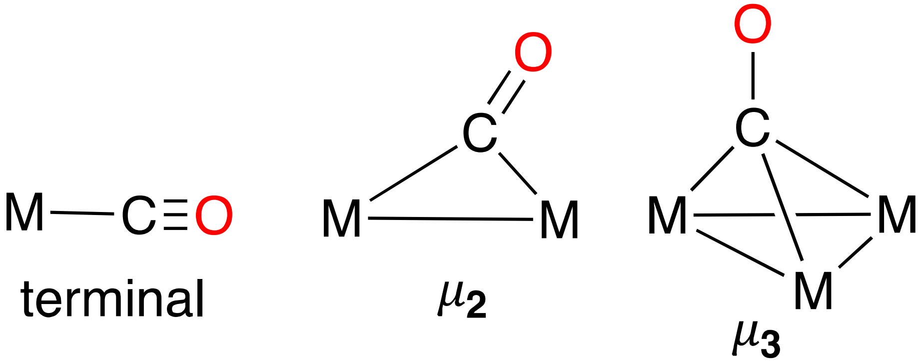
Hapticity of a ligand



The hapto symbol, **η,** with a numerical superscript, indicates the total number of donor atoms of a ligand attached to a metal centre.

For example, if all the five carbon atoms of a cyclopentadienyl moiety are equidistant from a metal atom, we term it as η^5-cyclopentadienyl

Bridging modes of CO: The symbol ***μ*** indicates bridging normally we have μ_2 and rarely μ_3 bridging



μ_2-H, μ_2-Cl, , μ_3-Cl, μ_2-OR, μ_2-PR_2, μ_2-NR_2

Covalent Electron Counting Model

- This method uses the number of electrons that would be donated by ligands *if they were neutral*. For example chlorine ($Cl^{\cdot}$)considers as radical and it is 1e donor in this method.
- Formal oxidation state of metal considers as 0, in this method.

Ionic Electron Counting Model

- In the ionic model, each M–X is considered as arising from M^+ and X^- ions. For example, Cl^- considers as a 2e donor in this method . **Neutral ligands pose no problem because they are always 2e donors on either model.**
- To determine the total electron count, one must take into account the charge on each ligand and determine the formal oxidation state of the metal.

$[Fe(CO)_2(Cl)_4]^{2-}$

Fe atom	8 electrons
2(CO)	4 electrons
4 (Cl)	4 electron
2 −Charge	2 electron
Total	**18 electrons**

$[Re(CO)_5(PF_3)]^+$

Re atom	7 electrons
5(CO)	10 electrons
1(PF_3)	2 electron
1 +Charge	−1 electron
Total	**18 electrons**

$[Fe(CO)_2(Cl)_4]^{2-}$

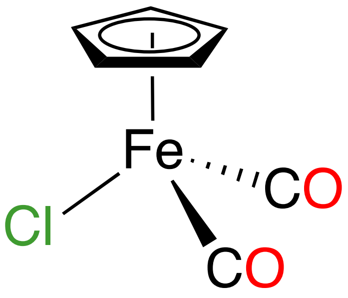
Fe(II) ion	6 electrons
2(CO)	4 electrons
4 (Cl^-)	8 electron
Total	**18 electrons**

$[Re(CO)_5(PF_3)]^+$

Re(I) ion	6 electrons
5(CO)	10 electrons
1(PF_3)	2 electron
Total	**18 electrons**

Covalent Model

Fe atom	8 electrons
η^5-C_5H_5	5 electrons
2(CO)	4 electrons
Cl	1 electron
Total	**18 electrons**

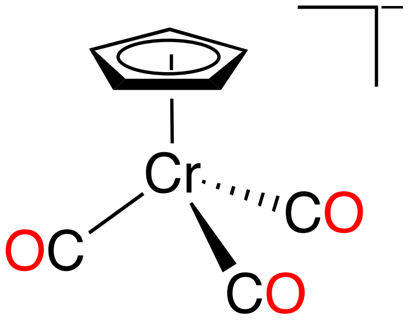


Ionic Model

Fe(II) ion	6 electrons
η^5-$C_5H_5^-$	6 electrons
2(CO)	4 electrons
Cl^-	2 electron
Total	**18 electrons**

Covalent Model

Cr atom	6 electrons
η^5-C_5H_5	5 electrons
3(CO)	6 electrons
1 −Charge	1 electron
Total	**18 electrons**



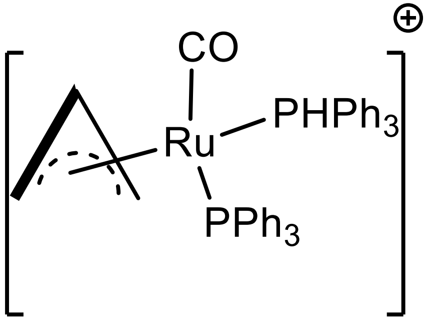
Ionic Model

Cr(0) ion	6 electrons
η^5-$C_5H_5^-$	6 electrons
3(CO)	6 electrons
Total	**18 electrons**

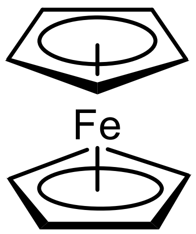
Neutral atom method: Metal is taken as in zero oxidation state for counting purpose

Oxidation state method: We first arrive at the oxidation state of the metal by considering the number of anionic ligands present and overall charge of the complex

Suggestion: Focus on one counting method till you are confident



	neutral atom method	oxidation state method
Ru	8	6 (Ru +2)
η^3- allyl	3	4
2 PPh_3	4	4
CO	2	2
charge	-1	not required
	16	16



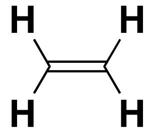
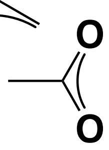
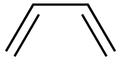
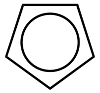
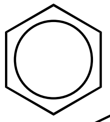
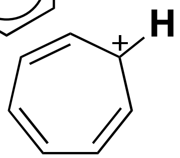
	neutral atom method	oxidation state method
Fe	8	6 (Fe +2)
2 η^5-Cp	10	12
	18	18

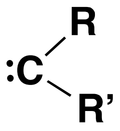
Neutral atom method: Metal is taken as in zero oxidation state for counting purpose

Oxidation state method: We first arrive at the oxidation state of the metal by considering the number of anionic ligands present and overall charge of the complex

Suggestion: Focus on one counting method till you are confident

Electron Counting Schemes for Common Ligands

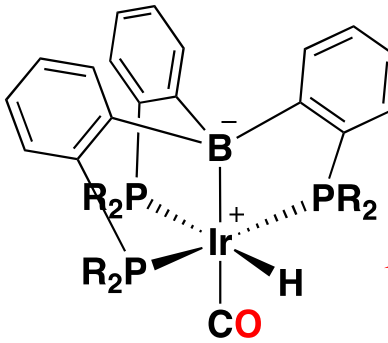
Ligands	Covalent Model	Ionic Model
X = H, F, Cl, Br, I, OH, CN, CH_3	1 (as X•)	2 (as X⁻)
Lone-pair donors		
CO, PR_3, NH_3, H_2O	2	2
π-bond donors		
	2	2
σ-bond donors		
H–H	2	2
η^3-allyl, 	3	4
η^2-acetate, 	3	4
η^4-butadiene, 	4	4
η^5-cyclopentadienyl, 	5	6
η^6-benzene, 	6	6
η^7-tropylium ion, 	6	6

Ligands	Covalent Model	Ionic Model
Carbene, 	2	2
Nitride, ≡N	3	6 (N^{3-})
=O, =S	2	4 (O^{2-})

Zero electron ligands

$$L_nM \rightarrow BR_3 \longleftrightarrow L_n\overset{+}{M}-\overset{-}{B}R_3$$

BR_3, having a 6e boron, completes its octet by accepting lone pairs, as in $H_3N \rightarrow BR_3$ to become an 8e boron.



Donation of electron From Ir filled *d* orbitals to B *p* orbitals

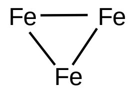
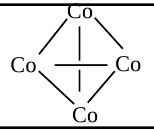
How to determine the total number of metal - metal bonds

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*.

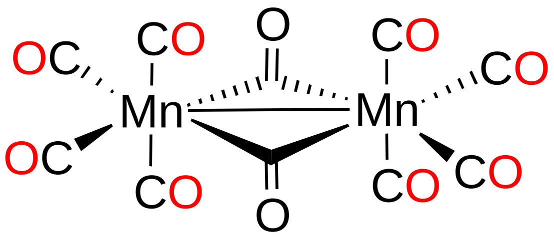
Subtract this number from $n \times 18$ where n is the number of metals in the complex, that is, $(n \times 18) - A$; say, it is *B*.

(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 × *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**

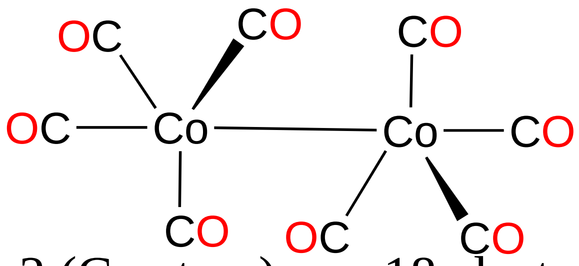
$Mn_2(CO)_{10}$



2 (Mn atom) 14 electrons
10(CO) 20 electrons
1 M−M 2 electron
Total 36 electrons

$18e^-$/Mn atom

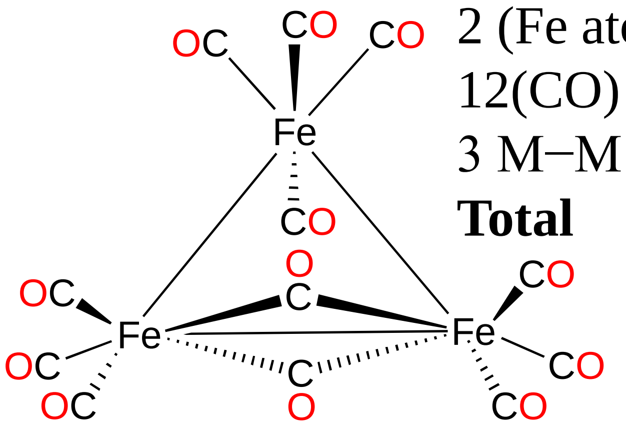
$Co_2(CO)_8$



2 (Co atom) 18 electrons
10(CO) 16 electrons
1 M−M 2 electron
Total 36 electrons

$18e^-$/Co atom

$Fe_3(CO)_{12}$



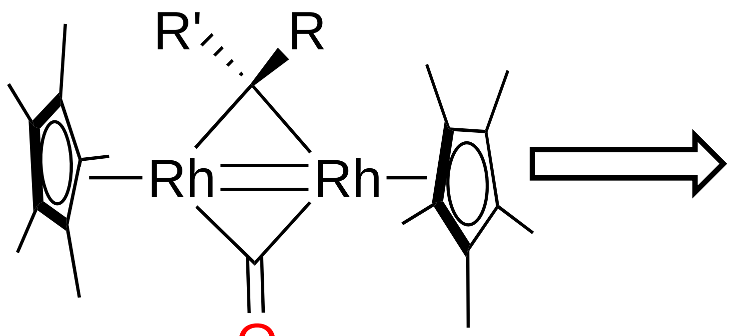
2 (Fe atom) 24 electrons
12(CO) 24 electrons
3 M−M 6 electron
Total 36 electrons

$18e^-$/Fe atom

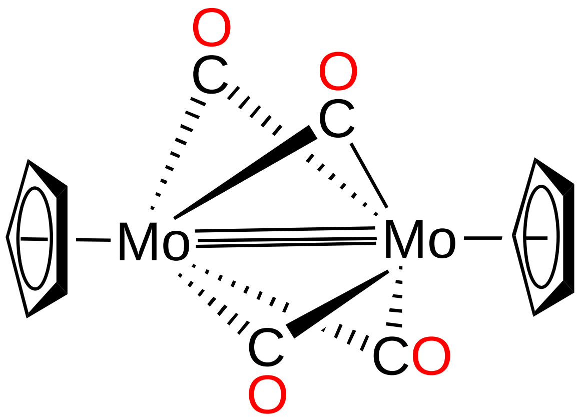
Compound Name	Total valence electrons	e necessary to follow 18e rule	Number of M−M bond
$Ru_3(CO)_{12}$	$(3\times8) + (2\times12) = 48$	$(3\times18) - 48 = 6$	3
$Ir_4(CO)_{12}$	$(4\times9) + (12\times2) = 60$	$(4\times18) - 60 = 12$	6
$Os_4(CO)_{16}$	$(4\times8) + (16\times2) = 64$	$(4\times18) - 64 = 8$	4
$Rh_6(CO)_{16}$	$(6\times9) + (16\times2) = 86$	$(6\times18) - 86 = 22$	11

➢ **18-electron rule is very much useful to predict the number of M−M bond in a complex. However, it does not assist us to predict a terminal and bridging ligand.**

Find out the metal-metal bond in the following compounds?

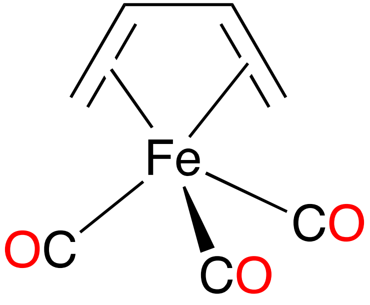


2 Rh atoms	18 electrons
2 (Cp*)	10 electrons
1(CO)	2 electrons
1C(RR')	2 electrons
2 M−M Bond	4 electron
Total	**36 electrons**



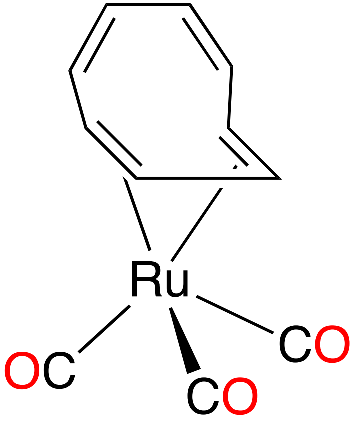
2 Mo	12 electrons
2 (Cp)	10 electrons
4(CO)	8 electrons
3 M−M	6 electron
Total	**36 electrons**

➢ Calculate the total number of valence electrons for each of the complexes.



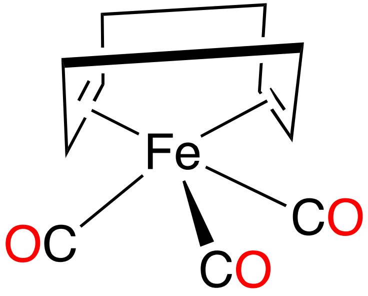
[Fe(CO)$_3$(butadiene)]

Fe atom	8 electrons
η^4-C_4H_6	4 electrons
3(CO)	6 electrons
Total	**18 electrons**



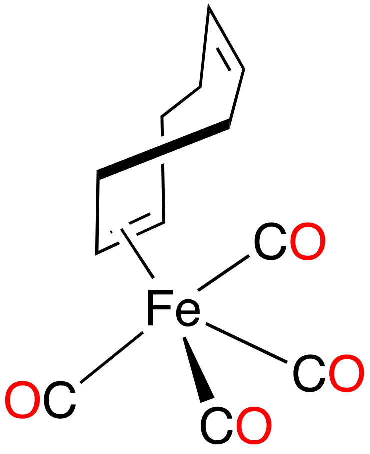
[Ru(CO)$_3$(η^4-COT)]

Ru atom	8 electrons
η^4-COT	4 electrons
3(CO)	6 electrons
Total	**18 electrons**



[Fe(CO)$_3$(η^4-COD)]

Fe atom	8 electrons
η^4-COD	4 electrons
3(CO)	6 electrons
Total	**18 electrons**



[Fe(CO)$_3$(η^2-COD)]

Fe atom	8 electrons
η^2-COD	2 electrons
3(CO)	6 electrons
Total	**18 electrons**