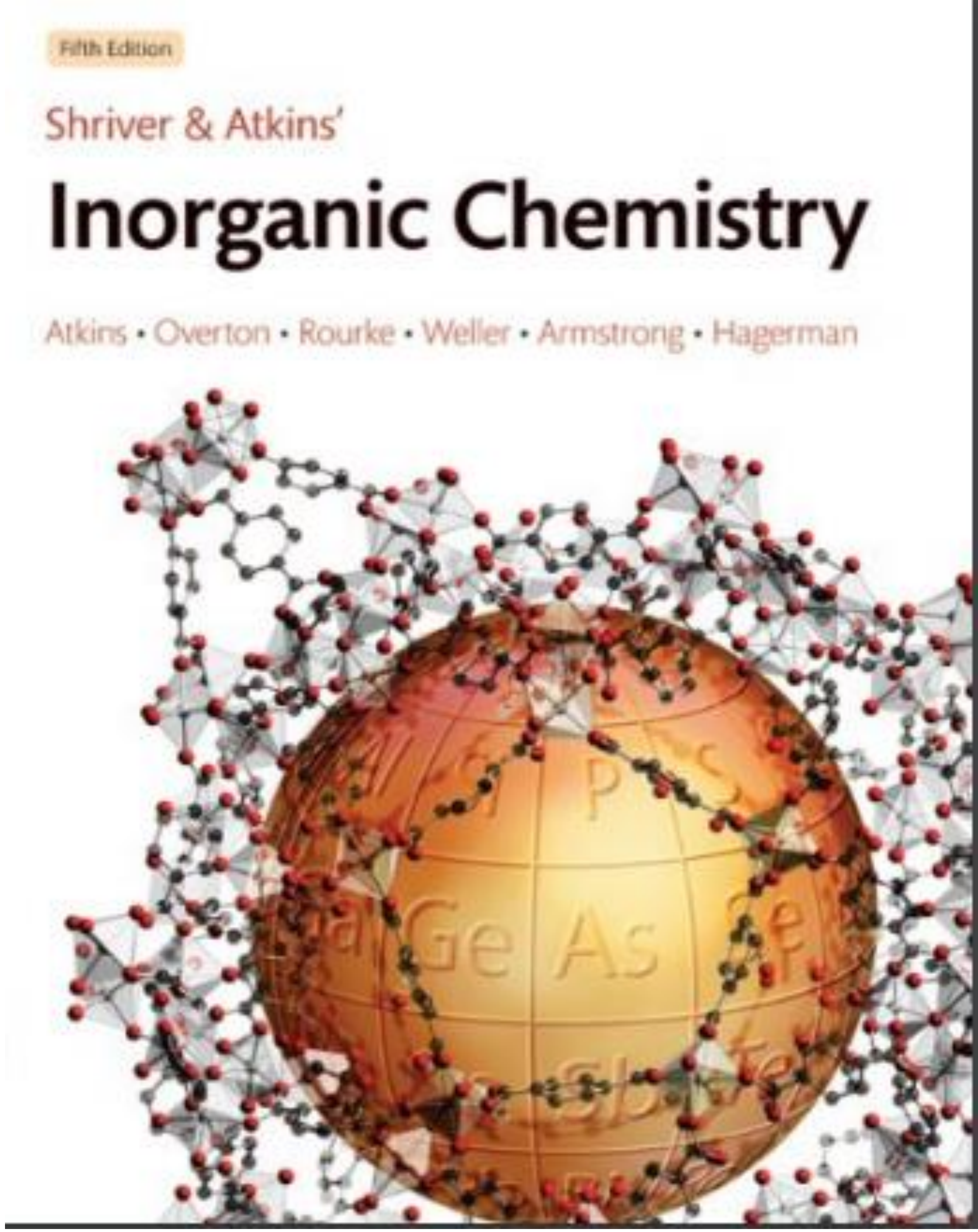
CY1001D: Chemistry: Module 3

Organometallic chemistry and Catalysis

18-electron rule



Inorganic Chemistry
Shriver and Atkins

Organometallic Chemistry

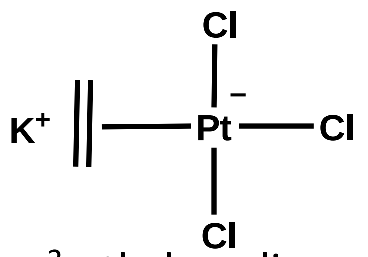
Chemistry of Metal-Carbon bonds

- Organometallic compounds: The compounds contain one or multiples **metal-carbon bond(s)**
- The metal center in such a compound is bonded to carbon of an organic molecule

R-Mg-X, R-Li, Cp-Fe-Cp

Zeise's salt

Potassium trichloro(ethene)platinate(II)



η^2-ethylene ligand

Zeise's salt was one of the first organometallic compounds reported in the **1827** by W. C. Zeise

Why Organometallic Chemistry ?

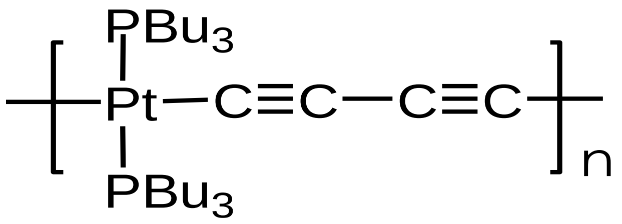
1. Useful for chemical synthesis, especially for catalytic processes

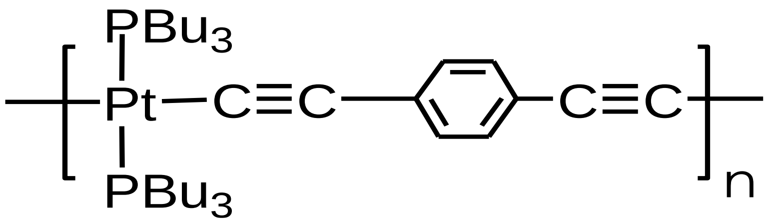
   e.g. production of fine chemicals

2. Application in material sciences

   e.g. organometallic polymers

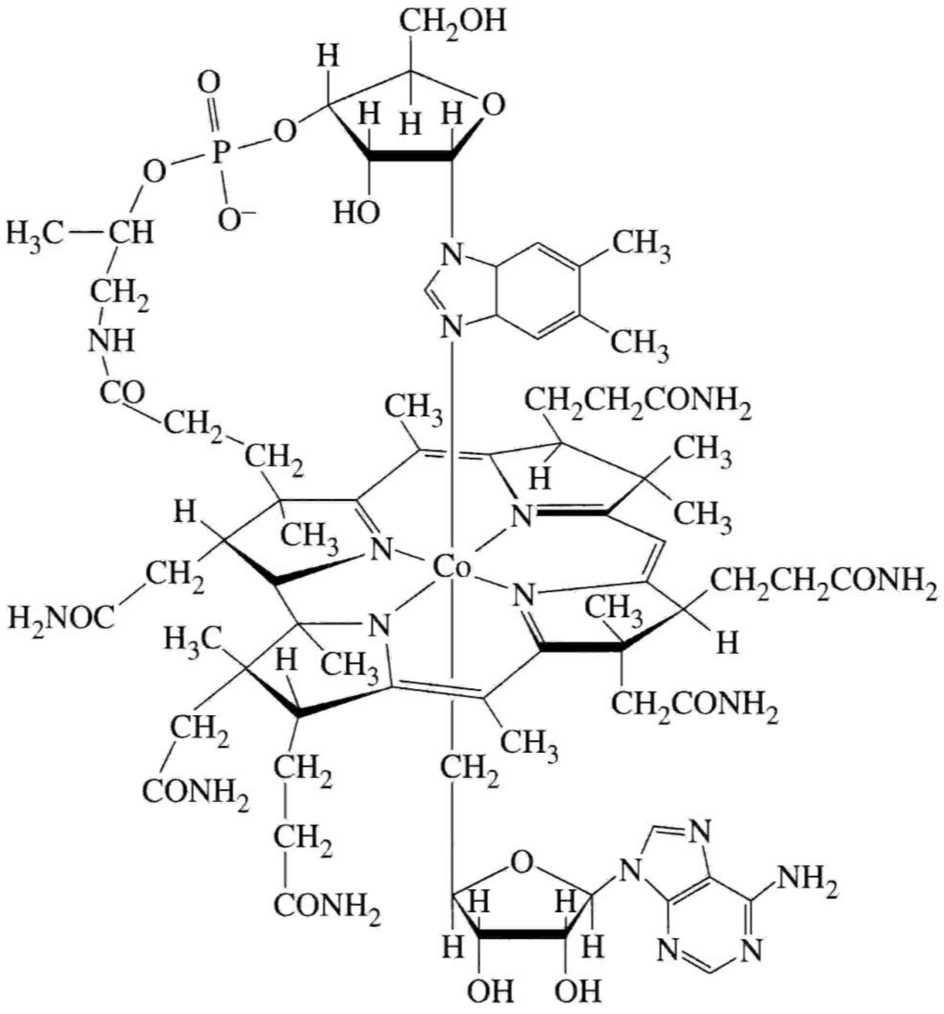
   Precursors to films for coating, Luminescent materials





3. Biological Science

Organometallic chemistry may help us to understand some enzyme-catalyzed reactions



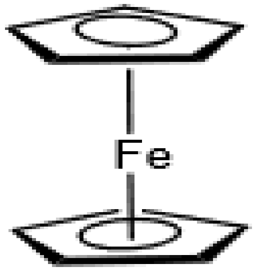
Vitamin B_{12}

Organometallic compounds:

Bond between Metal & Carbon

The 18-Electron rule:

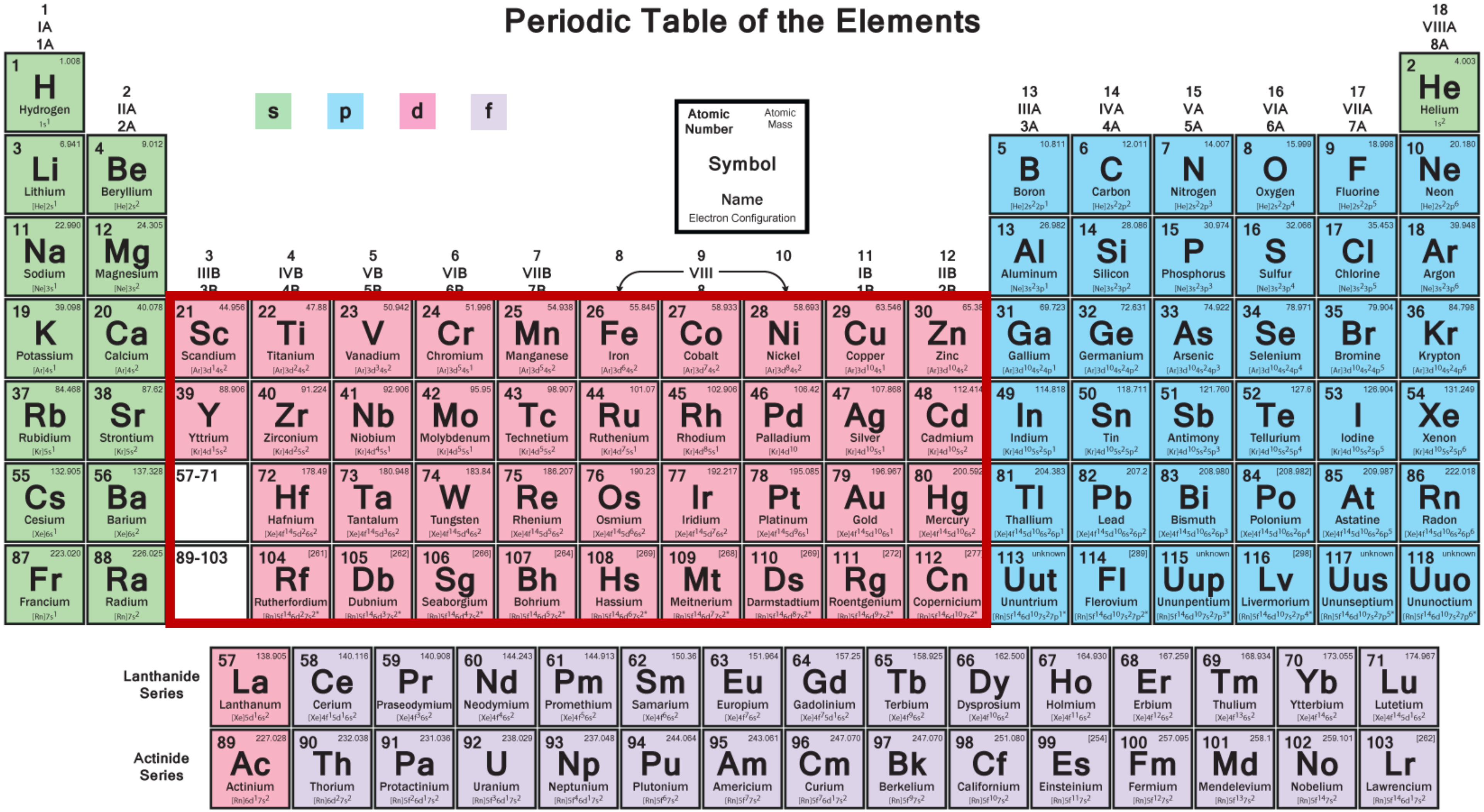
Thermodynamically stable transition metal organometallic compounds are formed when the **sum of the metal d electrons** and the electrons supplied by the **surrounding ligands equals to 18**



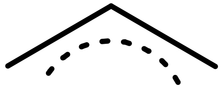
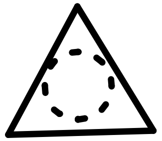
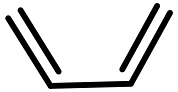
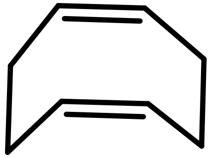
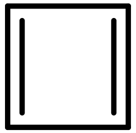
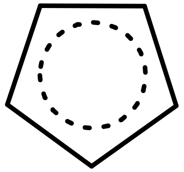
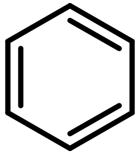
Fe	8
2 η^5-Cp	10
	18

Fe: [Ar]$3d^6$ $4s^2$

Periodic Table of the Elements



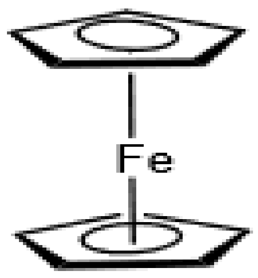
Electron counting for common ligands: Neutral ligand method

Ligand	Name	e^- count
CO	Carbonyl	2
$H_2C{=}CH_2$	Ethylene	2
η^3-C_3H_5 ≡ 	π-allyl	3
	Cyclopropenyl	3
	Butadiene	4
	1,3-cyclooctadiene(COD)	4
	Cyclobutadiene	4
η^5-C_5H_5 ≡ 	Cyclopentadienyl	5
η^6-C_6H_6 ≡ 	Benzene	6

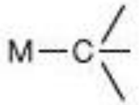
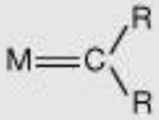
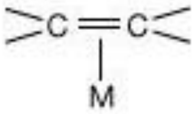
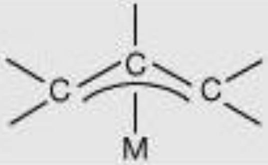
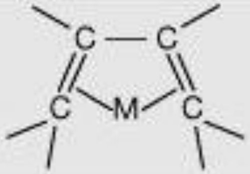
Hapticity (η):

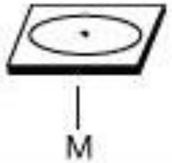
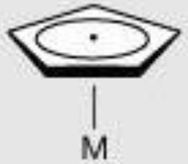
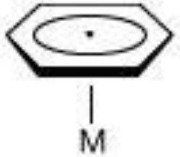
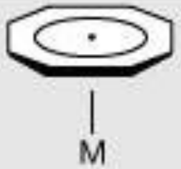
Hapticity is the coordination of a ligand to a metal center via an uninterrupted and contiguous series of atoms

The hapticity of a ligand is described with the Greek letter η ('eta').
η^5 describes a ligand that coordinates through 5 neighboring atoms



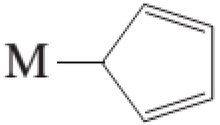
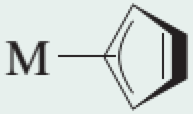
Common organic ligands and their heptacity

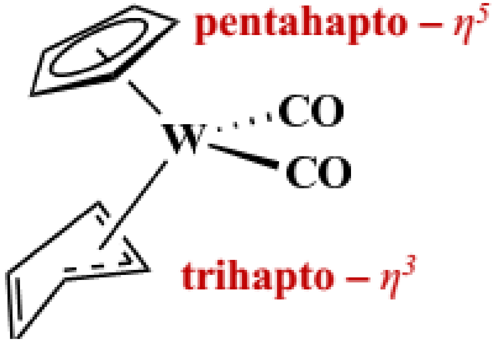
available electrons*	hapticity†	ligand	metal-ligand‡, § structure
1	η^1	methyl, alkyl CH_3, CH_2R	
2	η^1	alkylidene (carbene)	
2	η^2	alkene $H_2C=CH_2$	
3	η^3	π-allyl C_3H_5	
3	η^1	alkylidyne (carbyne) $C-R$	$M\equiv C-R$
4	η^4	1,3-butadiene C_4H_6	

available electrons*	hapticity†	ligand	metal-ligand‡, § structure
4	η^4	cyclobutadiene C_4H_4	
5 (3) (1)	η^5 η^3 η^1	cyclopentadienyl C_5H_5 (Cp)	
6	η^6	benzene C_6H_6	
8 (6) (4)	η^8 η^6 η^4	cyclooctatetraene C_8H_8 (cot)	

*For neutral ligands. †The number of carbon atoms attached to a metal. ‡For the first six entries hydrogen atoms are indicated by —, R is an organic group such as CH_3. §For the cyclic ligands (the last four entries) each vertex represents a C — H.

Variable Hapticity

1	η^1-C_5H_5	Monohaptocyclopentadienyl	
3	η^3-C_5H_5	Trihaptocyclopentadienyl	
5	η^5-C_5H_5	Pentahaptocyclopentadienyl	

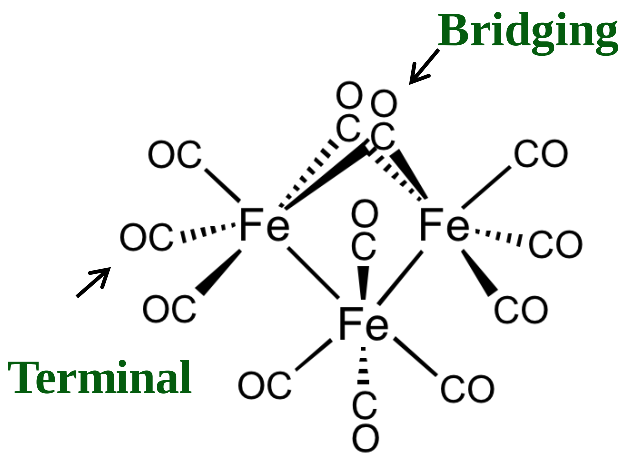


W:	**6**
2CO:	**4**
η^5-Cp :	**5**
η^3-Cp :	**3**
Total :	**18**

W: [Xe] $4f^{14}$ $5d^4$ $6s^2$

Bridging ligands:

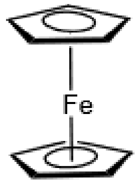
A ligand that connects two or more atoms, usually metal ions is conseder as bridging ligand and described with the Greek letter (‘μ').



$Fe_3(CO)_{12}$

Carbonyl group can also bridge between two metals
Where they can be seen as one electron each to the two metals

18 electron counting: neutral-ligand method



Fe	8
2 η^5-Cp	10
	18

Fe: $3d^6\ 5s^2$

Each metal atom and ligand is treated as neutral

Count all valence electrons of the metal atom and all the electrons donated by the ligands

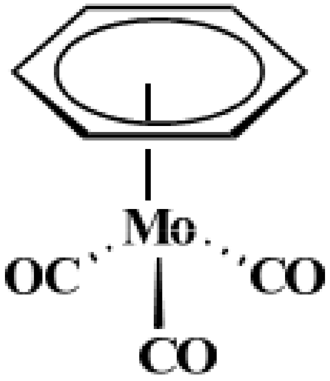
If the complex is charged, simply add or subtract the appropriate number of electrons to the total.

Key point: All ligands are treated as neutral and are categorized according to how many electrons they are considered to donate.

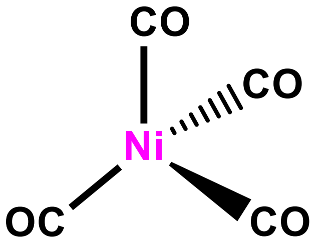
18 electron counting for common ligands: neutral ligand method

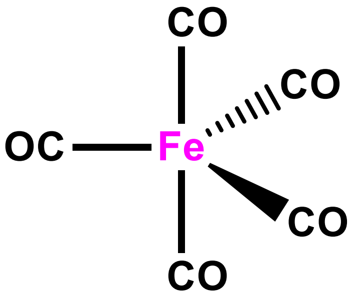
-H, -Cl, -Br, -I, -OH, -OR, -CN, $-CH_3$, $-CR_3$	1
CO, PR_3, NH_3, H_2O	2
=O, =S,	2
=CRR' (carbene), $H_2C{=}CH_2$	2
≡CR (carbyne)	3
η^3-C_3H_5 (π-allyl)	3
Ethylenediamine(en)	4
Bipyridine(bipy)	4
Butadiene, cyclobutadiene, 1,3-cyclooctadiene(COD)	4
η^5-C_5H_5 (Cyclopentadienyl)	5
η^6-C_6H_6 (Benzene)	6
η^7-C_7H_7 (cycloheptatrienyl)	7

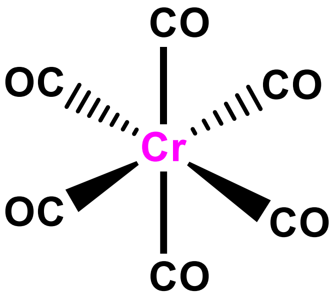
Mo: [Kr]$4d^5$ $5s^1$



Mo :	6
3CO:	6
1(C_6H_6):	6
Total :	18







Ni: [Ar]$3d^8$ $5s^2$

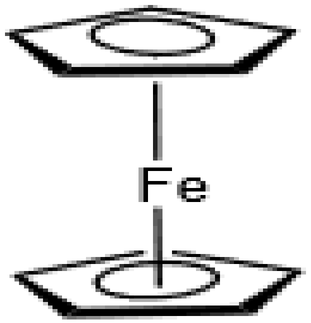
Fe: [Ar]$3d^6$ $4s^2$

Cr: [Ar]$3d^5$ $4s^1$

Ni :	10
4CO:	8
Total :	18

Fe :	8
5CO:	10
Total :	18

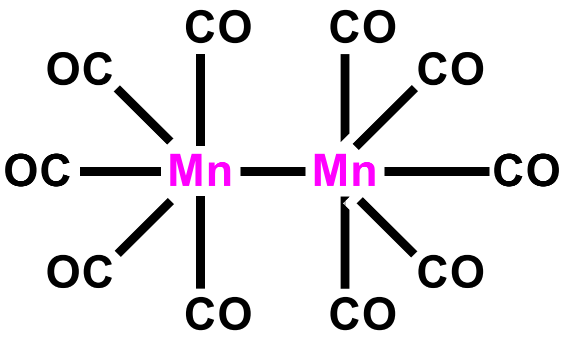
Cr :	6
6CO:	12
Total :	18



Fe :	8
2x η^5Cp:	10
Total :	**18**

Fe: [Ar]$3d^6\ 4s^2$

Ferrocene: Iron is sandwich between two η^5cyclopentadienyl ligand



Mn: $3d^5\ 4s^2$

Mn :	7
5CO:	10
1M-M:	1
Total :	**18**

2x Mn :	14
2x5 CO:	20
2x M-M:	2
Total :	**36**

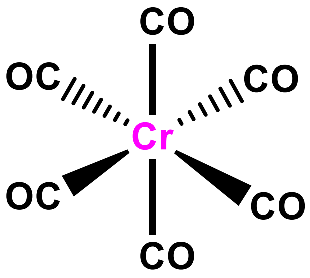
e count for each metal = $\frac{36}{2} = 18$

18-electrons rule: Stability of metal complex

Cr: [Ar]$3d^5\ 4s^1$

$Cr(CO)_6$

A Cr atom has 6 electrons outside its Noble gas core. Each CO is considered to act as a donar of 2 electrons. The total electrons count is therefore:



Cr :	6
6CO:	12
Total :	18

$Cr(CO)_6$ is therefore considered an 18 electron complex thermally stable and can be sublimed without decomposition

On the other hand, $Cr(CO)_5$, a 16-electron species and $Cr(CO)_7$ a 20-electron species, are much less stable and are known only as transient species.

Similarly, $Cr(CO)_6^+$ having 17 electrons and $Cr(CO)_6^-$ having 19-electrons are far less stable than the 18-electron $Cr(CO)_6$.

Scope of 18 electron rule for d-block organometallic compounds

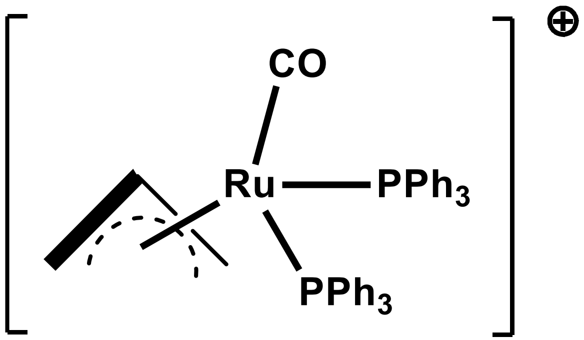
Usually less than 18 electrons			Usually 18 electrons			16 or 18	
Sc	Ti	V	Cr	Mn	Fe	Co	Ni
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
La	Hf	Ta	W	Re	Os	Ir	Pt

Exceptions to the 18 electron rule

$ZrCl_2(C_5H_5)_2$	: Zr (4) + [2 x Cl(1) =2] + [2 x C_5H_5(5)=10] =16
$TaCl_2Me_3$	: Ta(5) + [2+ x Cl(1) =2] + [3 x M(1)=3] =10
WMe_6	: W(6) + [6 x Me(1)=6] =12
$Pt(PPh_3)_3$	: Pt(10) + [3 x PPh_3(2)=6] =16
$IrCl(CO)(PPh_3)_2$	: Ir(9) + Cl(1) + CO(2) + [2 x PPh_3(2)=4] =16
$Rh(Cl)(PPh_3)_3$	: Rh(9) + Cl(1) + [3 x PPh3(2)= 6] = 16

Zr: [Kr]$4d^2\,5s^2$ Ta: $4f^{14}5d^3\,6s^2$ W: [Xe] $4f^{14}\,5d^4\,6s^2$ Pt: [Xe] $4f^{14}\,5d^9\,6s^1$ Ir: $4f^{14}\,5d^7\,6s^2$ Rh: [Kr]$4d^8\,5s^1$

Electron counting for ionic complex



Ru: [Kr]$4d^7\ 5s^1$

Ru:	8
η^3-allyl :	3
2x PPh_3:	4
CO:	2
Charge:	-1
Total :	16

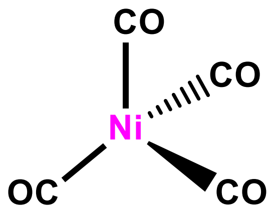
Exception to 18 electron rule

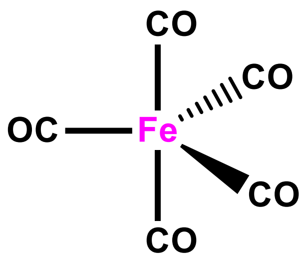
- Square planar organometallic complexes of the late transition metals (16e)

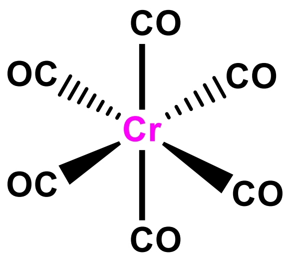
- Some organometallic complexes of early transition metals (e.g. Cp_2TiCl_2, WMe_6, Me_2NbCl_3, $CpW(=O)Cl_3$

- Sterically demanding bulky ligands force complexes to have less than 18 e

Structure of metal carbonyl







Ni: [Ar]$3d^8$ $4s^2$

Fe: [Ar]$3d^6$ $4s^2$

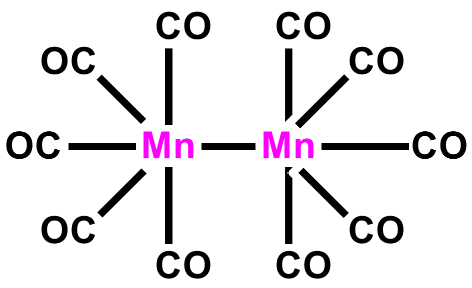
Cr: [Ar]$3d^5$ $4s^1$

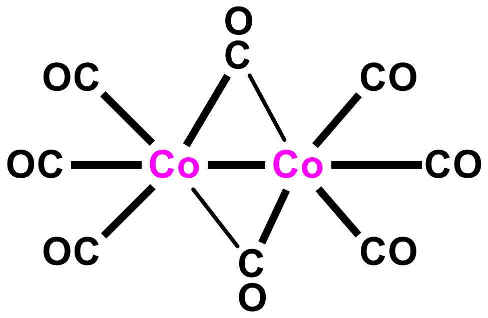
Ni :	10
4CO:	8
Total :	18

Fe :	8
5CO:	10
Total :	18

Cr :	6
6CO:	12
Total :	18

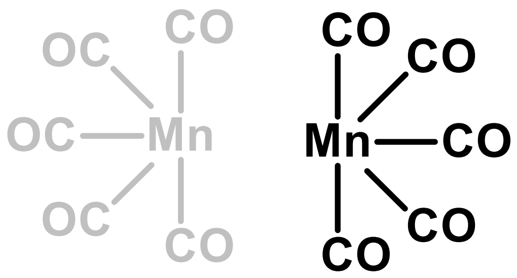
Q. $Ni(CO)_4$, $Fe(CO)_5$ and $Cr(CO)_6$ exist as monomeric form. However $Mn(CO)_5$, $Co(CO)_4$ exist as dimer, why?



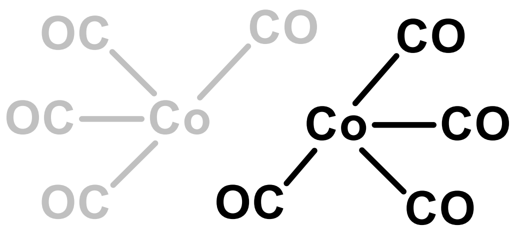


$Mn(CO)_5$, $Co(CO)_4$ dimerize to form stable 18 electrons complex

Monomer

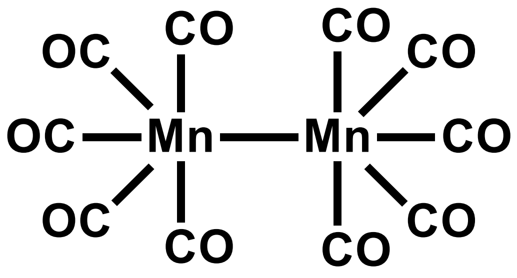


Mn :	7
5CO:	10
Total :	17

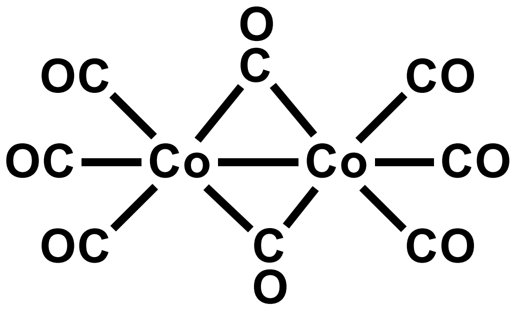


Co :	9
4CO:	8
Total :	17

Dimer



Mn :	7
5CO:	10
1M-M :	1
Total :	18



Co :	9
3CO:	6
2μ2-CO:	2
1M-M :	1
Total :	18

Mn: [Ar]$3d^5$ $4s^2$

Co: [Ar]$3d^7$ $4s^2$

18-electrons rule: Stability of metal complex

Cr: [Ar]$3d^5\ 4s^1$

$Cr(CO)_6$

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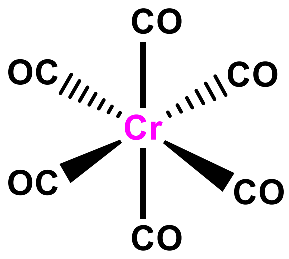

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Calculation for number of metal-metal bond

$Mn_2(CO)_{10}$ ⟶ $[Mn(CO)_5]_2$

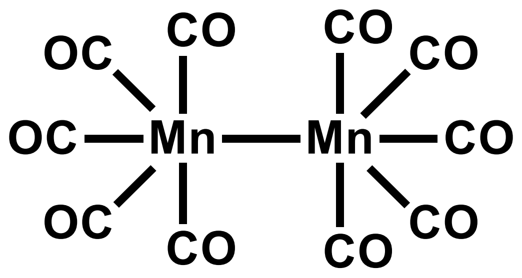
Mn :	7
5CO:	10
M-M :	X
Total :	17+X = 18

X = 1

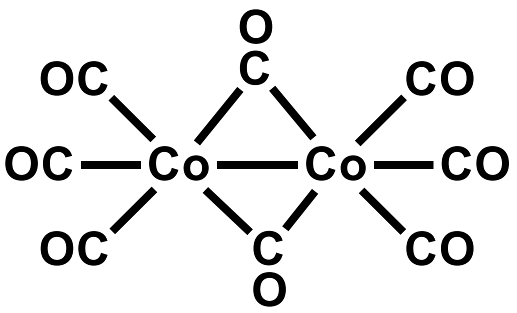
$Co_2(CO)_8$ ⟶ $[Co(CO)_4]_2$

Co :	9
4CO:	8
M-M :	X
Total :	17+X = 18

X = 1



Mn: [Ar]$3d^5\ 4s^2$



Co: [Ar]$3d^7\ 5s^2$

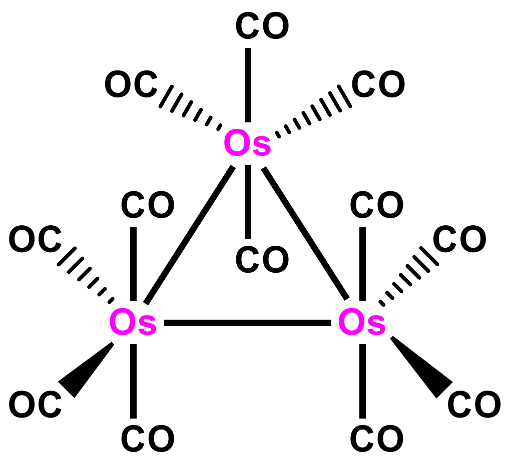
Calculation for number of metal-metal bond

$Os_3(CO)_{12}$ ➡ $[Os(CO)_4]_3$

Os = [Xe]$4f^{14}5d^6\ 6s^2$

Os :	8
4CO:	8
M-M :	X
Total :	16+X = 18

X = 2

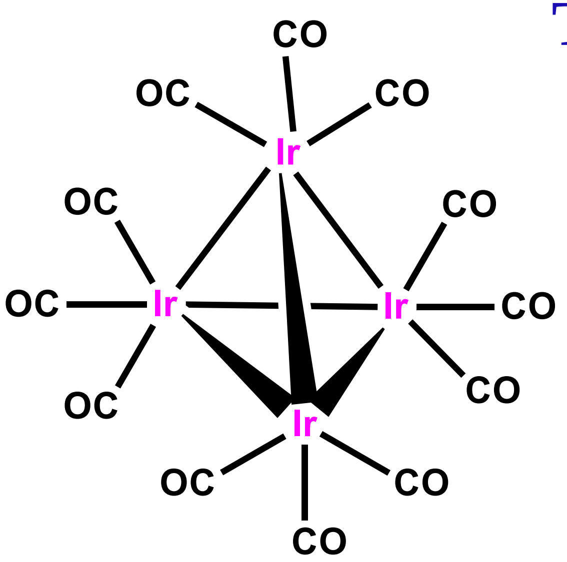


$Ir_4(CO)_{12}$ ➡ $[Ir(CO)_3]_4$

Ir= [Xe] $4f^{14}\ 5d^7\ 6s^2$

Ir :	9
3CO:	6
M-M :	X
Total :	15+X = 18

X = 3



18 electron counting: donor pair method

Account the **charge on each ligand** and determine the formal **oxidation state of the metal**.

Common organometallic ligands are assigned an electron count and charge.

The charge on ligands helps determine d-electron count of metal.

Add up all electrons from Metal d orbitals and ligands to find total e- count.
The donor-pair method requires a calculation of the oxidation number

Key point: Ligands are considered to donate electrons in pairs (eg.Lewis base), resulting in the need to treat some ligands as neutral and others as charged.

The **oxidation number** of the metal atom is the total charge of the complex minus the charges of any ligands

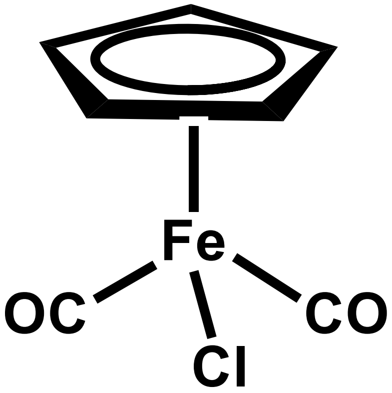
The **number of d electrons** the metal provides is its **group number minus its oxidation number**

The total electron count is the sum of the number of electrons on the metal atom and the number of electrons provided by the ligands

Electron counting for common ligands

Name of the Ligand	Neutral ligand	Donor pair
-H, -Cl, -Br, -I, -OH, -OR, -CN, $-CH_3$, $-CR_3$	1	2
CO, PR_3, NH_3, H_2O, $H_2C{=}CH_2$	2	2
=O, =S,	2	4
≡CR (carbyne)	3	3
η^3-C_3H_5 (p-allyl)	3	4
Ethylenediamine(en)	4	4
Bipyridine(bipy)	4	4
Butadiene, cyclobutadiene, 1,3-cyclooctadiene(COD)	4	4
η^5-C_5H_5 (Cyclopentadienyl)$^-$	5	6
η^6-C_6H_6 (Benzene)	6	6
η^7-C_7H_7 (cycloheptatrienyl)$^+$	7	6

$(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$



Fe: $[Ar]3d^6\ 4s^2$

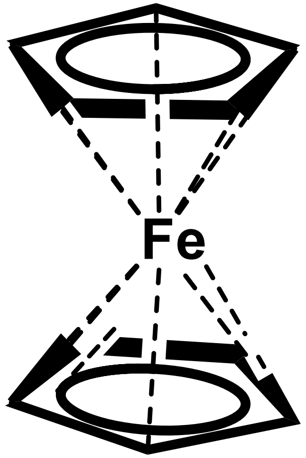
Neutral –ligand method

Fe :	8
η^5-Cp :	5
2x CO :	4
Cl :	1
Total :	18

Donor Pair method

Fe(+2) :	6
η^5-Cp :	6
2x CO :	4
Cl :	2
Total :	18

$(\eta^5\text{-}C_5H_5)_2Fe$



Fe: $[Ar]3d^6\ 4s^2$

Neutral –ligand method

Fe :	**8**
2x η^5-Cp :	**10**
Total :	**18**

Donor Pair method

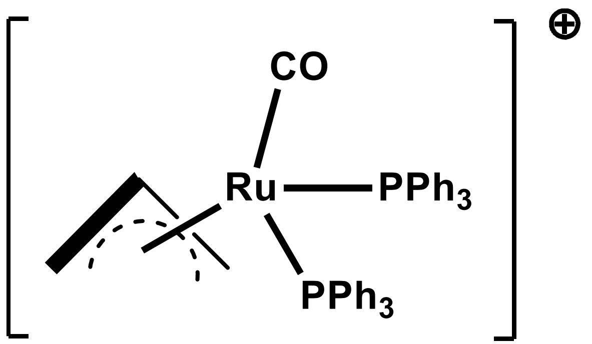
Fe(+2) :	**6**
2x η^5-Cp :	**12**
Total :	**18**

	Neutral ligand method		Donor pair method	
$ClMn(CO)_5$	Mn :	7	Mn(+1) :	6
Mn: [Ar]$3d^5$ $4s^2$	5x CO :	10	5x CO :	10
	Cl :	1	Cl :	2
	Total :	**18**	**Total :**	**18**

	Neutral ligand method		Donor pair method	
$Co(\eta^4\text{-}C_4H_6)(\eta^3\text{-}C_3H_5)$	Co :	9	Co(+1) :	8
Co: [Ar]$3d^7$ $4s^2$	$\eta^4\text{-}C_4H_6$:	4	$\eta^4\text{-}C_4H_6$:	4
	$\eta^3\text{-}C_3H_5$:	3	$\eta^3\text{-}C_3H_5$:	4
	Total :	**16**	**Total :**	**16**

	Neutral ligand method	Donor pair method
$Ta(Me)_5$	Ta : 5 5x Me : 5 Total : 10	Ta(+5) : 0 5x Me : 10 Total : 10

Ta: [Xe]$4f^{14}$ $5d^3$ $6s^2$



Ru: [Kr]$4d^7\ 5s^1$

	Neutral ligand method		Donor pair method
Ru :	8	Ru (+2) :	6
CO :	2	CO :	2
2x PPh_3 :	4	2x PPh_3 :	4
η^3-allyl:	3	η^3-allyl:	4
Charge :	-1		
Total :	16	Total :	16

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

Re: [Xe]$4f^{14}\ 5d^5\ 6s^2$

	Neutral ligand method		Donor pair method
Re :	7	Re(+1) :	6
5x CO :	10	5x CO :	10
PF_3 :	2	PF_3 :	2
Charge :	-1		
Total :	18	Total :	18