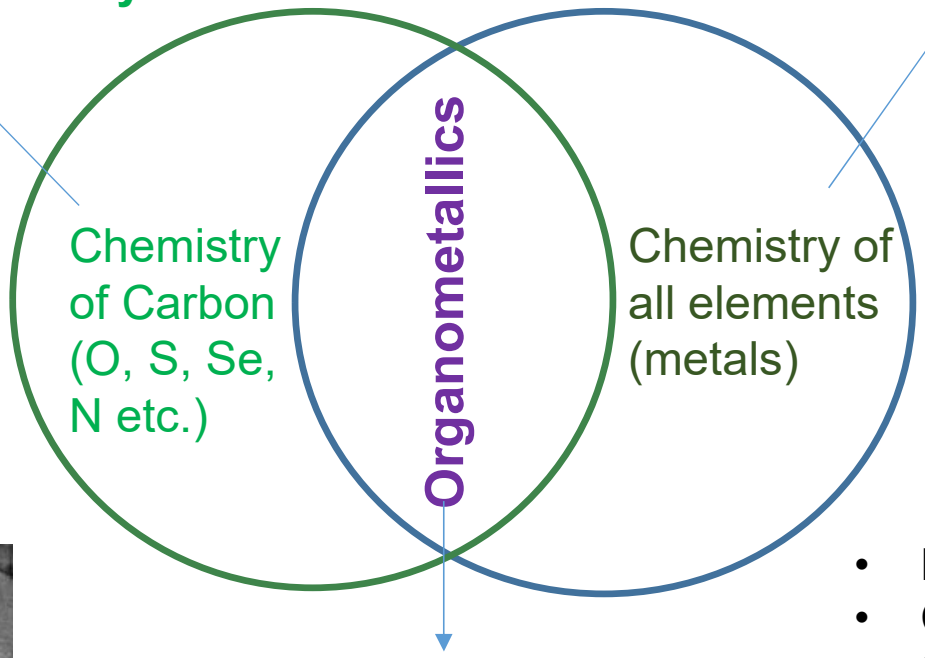
Organometallic Chemistry

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

Edward Frankland

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

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 whose oxidation state is not known, **Eg:** NO,

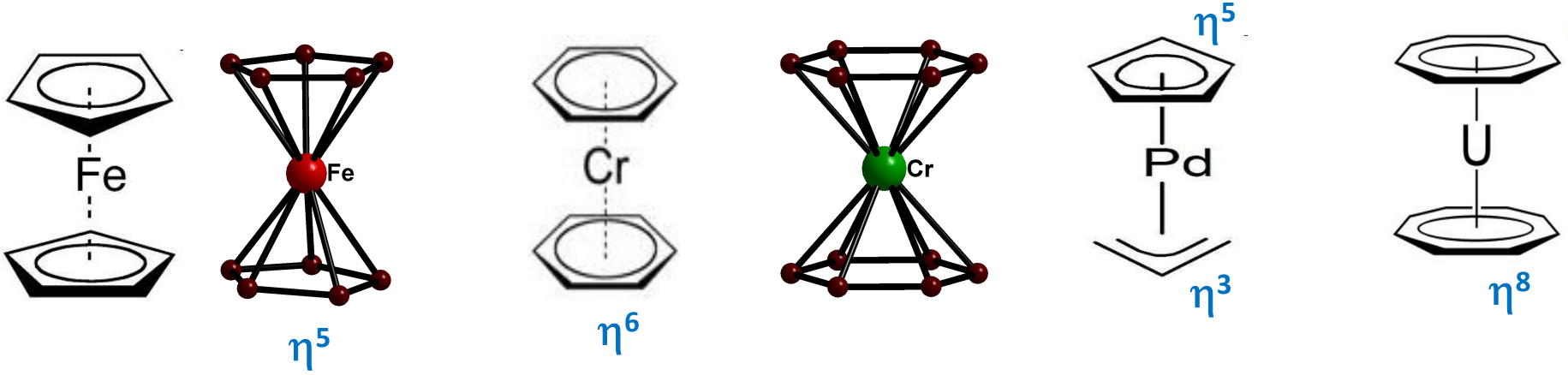
❑ The 18 Electron Rule

- 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***



Ligand contribution to Electron Count

	Neutral atom electron count
Terminal ligands	
Carbonyl (M—CO)	2
Thiocarbonyl (M—CS)	2
Phosphine ($M—PR_3$)	2
Amine ($M—NR_3$)	2
Dinitrogen ($M—N\equiv N$)	2
Dihydrogen M—H, H	2
Alkene M—(C=C)	2
Alkyne* M—(C≡C)	2
Isocyanide (M—CNR)	2
Nitrosyl, bent (M—N(:)=O)	1
Nitrosyl, linear ($M—N\equiv O$)	3
Halogen (M—X)	1
Hydrogen (M—H)	1
Alkyl (M—R)	1
Acyl (M—C(=O)—R)	1
Aryl (M—Ph)	1
Amide ($M—NR_2$)	1
Phosphide ($M—PR_2$)	1
Alkoxide (M—OR)	1
Thiolate (M—SR)	1
Carbene = alkylidene ($M=CR_2$)	2
Carbyne = alkylidyne ($M\equiv CR$)	3

	Neutral atom electron count
η^1-Allyl M—CH_2	1
η^3-Allyl M	3
η^3-Enyl M	3
η^1-Cyclopentadienyl M	1
η^5-Cyclopentadienyl M	5
η^6-Benzene M	6
η^7-Cycloheptatrienyl M	7
η^8-Cyclooctatetraenyl M	8
Bridging ligands	
Carbonyl [M—(CO)—M]	2
Halogen (M—X—M)	3
Alkyne M—(C≡C)—M	4
Hydrogen (M—H—M)	1
Alkyl [M—(CR_3)—M]	2
Amide [M—(NR_2)—M]	3
Phosphide [M—(PR_2)—M]	3
Alkoxide [M—(OR)—M]	3

Methods of counting:
Neutral atom method & Oxidation state method

Ligand	Neutral atom	Oxidation state		Ligand	Neutral atom	Oxidation state	
		Electron contribution	Formal charge			Electron contribution	Formal charge
Carbonyl (M–CO)	2	2	0	Halogen (M–X)	1	2	–1
Phosphine (M–PR_3)	2	2	0	Alkyl (M–R)	1	2	–1
Amine (M–NR_3)	2	2	0	Aryl (M–Ar)	1	2	–1
Amide (M–NR_2)	1	2	–1	acyl (M–C(O)–R	1	2	–1
Hydrogen (M–H)	1	2	–1	η^1-cyclopentadienyl	1	2	–1
Alkene (sidewise) η^2-	2	2	0	η^1-allyl	1	2	–1
Alkyne (sidewise) η^2-	2	2	0	η^3-allyl	3	4	–1
η^2-C_{60}	2	2	0	η^5-cyclopentadienyl	5	6	–1
Nitrosyl bent	1	2	–1	η^6-benzene	6	6	0
Nitrosyl linear	3	2	+1	η^7-cycloheptatrienyl	7	6	+1
Carbene (M=CR_2)	2	4	–2	Carbyne (M≡CR)	3	6	–3
Alkoxide (M–OR)	1	2	–1	Thiolate (M–SR)	1	2	–1
μ-CO (M–(CO)–M)	2	2	0	μ-H	1	2	–1
μ-alkyne	4	4	0	μ-X (M–X–M) X = halogen	3	4	–1
μ-alkyl	1	2	–1	μ-amido (M–(NR_2)–M	3	4	–1
μ-phosphido (M–(PR_2)–M	3	4	–1	μ-alkoxide (M–(OR)–M	3	4	–1

Counting electrons in complexes

Example 1:

$[Cr(CO)_6]$

Cr	_____	6 e^-
6.CO	_____	6×2 e^- = 12 e^-
		Total= 18 e^-

Example 2:

$[Fe(CO)_5]$

Fe	_____	8 e^-
5.CO	_____	5×2 e^- = 10 e^-
		Total= 18 e^-

Example 3:

$[ClMn(CO)_5]$

Mn	_____	7 e^-
Cl	_____	1 e^-
5.CO	_____	5×2 e^- = 10 e^-
		Total= 18 e^-

Example 4:

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

Re	_____	7 e^-
PF_3	_____	2 e^-
5.CO	_____	5×2 e^- = 10 e^-
+ Charge	_____	-1 e^-
		Total= 18 e^-

Example 5:

$[Mn(CO)_5]^-$

Mn	_____	7 e^-
- Charge	_____	1 e^-
5.CO	_____	5×2 e^- = 10 e^-
		Total= 18 e^-

Example 6:

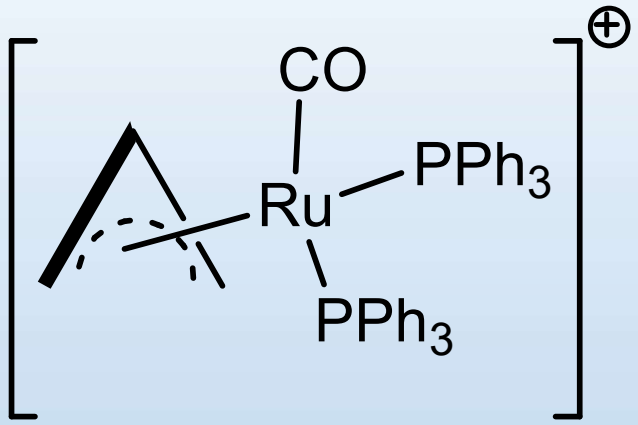
$[Co(CO)_4]^-$

Re	_____	9 e^-
- Charge	_____	1 e^-
4.CO	_____	4×2 e^- = 8 e^-
		Total= 18 e^-

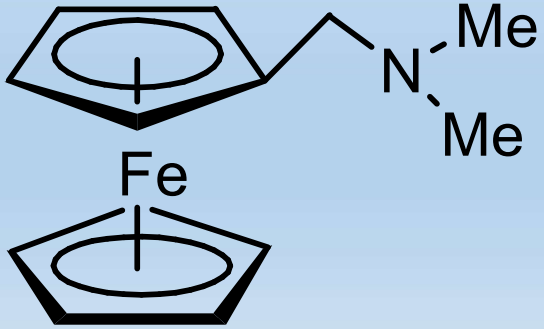
Example 7:

$[Rh_2(CO)_4Cl_2]$

2.Rh	_____	18 e^-
2.Cl (bridging)	_____	2×3 e^- = 6 e^-
4.CO	_____	4×2 e^- = 8 e^-
		Total= 32 e^- Or
		16 e^-/ Rh



	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



Fe	8	6 (Fe +2)
2 η^5-Cp	10	12
	18	18