18 - ELECTRON RULE

This rule states that "*thermodynamically stable transition metal organometallic compounds are formed when the sum of the metal d-electrons and the electrons conventionally considered as being supplied by the surrounding ligands equals 18*".

•18 electron rule is only applicable for transition metal organometallic compound.

• The main group organometallic compound follows octet rule.

• Square planar complex follows 16- electron rule.

• The complex which follows 16- and 18- electron rule are stable.

• Complex which follows 17- electron rule and 19- electron rule are paramagnetic

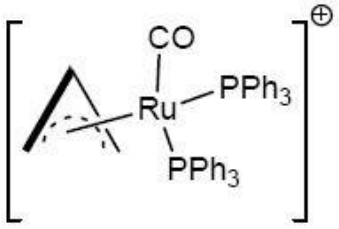
• Organometallic compound which follows this configuration $\rightarrow ns^2np^6 (n-1)d^{10}$ than complex is stable.

$$2+6+10 = 18\ e^-$$

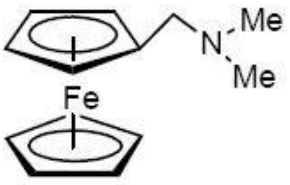
For complex, total no. of electron = the no. of valence electron donated by the metal + number of electron donated by the ligand $\pm$ charge.

Neutral atom method: In this method, metal is taken as in zero oxidation state for counting purpose.

Oxidation state method: First take the oxidation state of the metal. After it, the number of anionic ligands present and finally, overall charge of the complex.

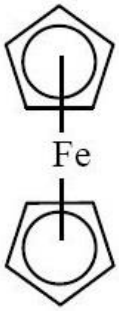


	neutral atom method	oxidation state method
Ru	8	6 (Ru^{++})
η^3- allyl	3	4
2 PPh_3	4	4
CO	2	2
charge	-1	not required
	16 e	16 e



Fe	8	6 (Fe^{++})
2 η^5-Cp	10	12
	18 e	18 e

Ferrocene



Neutral atom method		Oxidation state method	
Fe = 8	= 8	Fe = 6	(Fe^{++})
2Cp = 5	= 10	2Cp = 12	
	18 e^-		18 e^-

Ferrocene follows 18 electron rule

$Mn(CO)_5CH_3$

Neutral atomic method: 7 + 10 + 1 = 18 electron (Mn)

Oxidation state method: 6 + 2 + 10 = 18 electron (Mn^+)

$Ni(CO)_4$

Valence electrons of Ni = 10

Electrons donated by four CO ligands = 2 x 4 = 8

Thus, total outer electrons in $Ni(CO)_4$ = 10 + 8 = 18 electrons

Hence, $Ni(CO)_4$ exists as stable compound.

$Co(CO)_4$

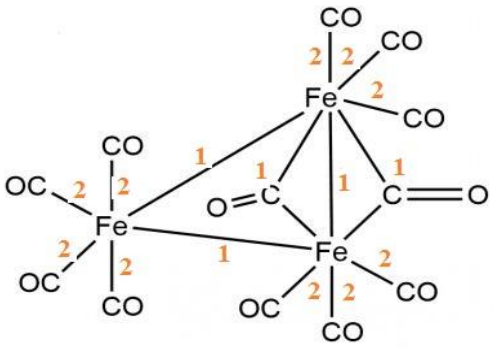
Valence electrons of Co = 9

Electrons donated by four CO ligands = 2 x 4 = 8

Thus, total outer electrons in $Co(CO)_4$ = 9 + 8 = 17 electrons

$Co(CO)_4$ doesn't obey 18- electron rule, and hence $Co(CO)_4$ is unstable compound.

$Fe_3(CO)_{12}$



For bridging, Fe: Fe^o + 3 terminal CO + 2μCO + 2 Fe-Fe bond

= $8e^-$ + (3 × 2) + (2 × 1) + (2 × 1)

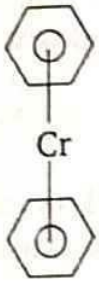
= 18 electrons

For Unique Fe: Fe^o + 4 terminal CO + 2 Fe-Fe bond

= $8e^-$ + (4 × 2) + (2 × 1) = 18 electrns

$HMn(CO)_5$

Neutral atom method		Oxidation state method	
Mn	7*e*	Mn^+	6*e*
H	1*e*	H^-	2*e*
5CO	10*e*	5CO	10*e*
	18*e*		18*e*

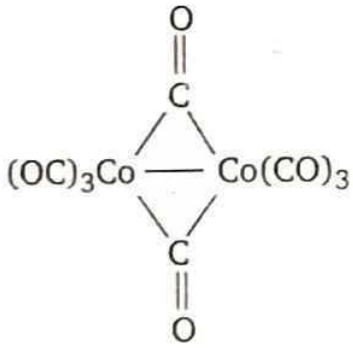


Cr	6*e*	Cr	6*e*
$2C_6H_6$	12*e*	$2C_6H_6$	12*e*
	18*e*		18*e*

$(OC)_5—Mn—Mn(CO)_5$

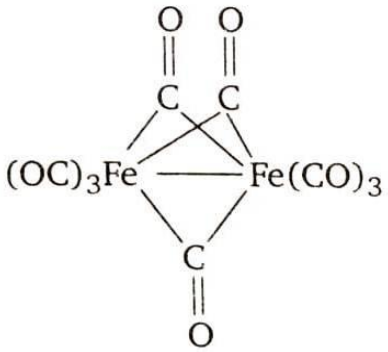
Mn	7*e*	Mn	7*e*
Mn—Mn	1*e*	Mn—Mn	1*e*
5CO	10*e*	5CO	10*e*
	18*e*		18*e*

Ni^{++}	8*e*	Ni	10*e*
$2C_3H_5^-$	8*e*	$2C_3H_5$	6*e*
	16*e*		16*e*



Co	9*e*	Co	9*e*
Co—Co	1*e*	Co—Co	1*e*
3CO	6*e*	3CO	6*e*
2(μ-CO)	2*e*	2(μ-CO)	2*e*
	18*e*		18*e*

) $[PtCl_4]^{--}$	Pt^{++}	8e	Pt	10e
	$4Cl^-$	8e	4Cl	4e
			Charge	2e
		16e		16e
$[Cr(CO)_6]$	Cr	6e	Cr	6e
	6CO	12e	6CO	12e
		18e		18e
$[Fe(CO)_5]$	Fe	8e	Fe	8e
	5CO	10e	5CO	10e
		18e		18e



	Fe	8e	Fe	8e
	3CO	6e	3CO	6e
	Fe—Fe	1e	Fe—Fe	1e
	3(μ-CO)	3e	3(μ-CO)	3e
		18e		18e
$[Co(CO)_4]^{\ominus}$	Co	9e	Co	9e
	4CO	8e	4CO	8e
	Charge	1e	Charge	1e
		18e		18e
$[Co(NH_3)_6]^{+++}$	Co	9e	Co	9e
	$6NH_3$	12e	$6NH_3$	12e
	Charge	– 3e	Charge	– 3e
		18e		18e

Applications of 18 electron rule

- In the determination of the total number of metal-metal bonds
- Used to predict the stability of various organometallic compounds.
- To know the reactivity of transition elements.
- In the determination of the formula of organometallic compounds.

Limitations of 18 electron rule

- 16 electron compounds (both high spin octahedral and low spin square planar) fail to obey this rule.
- High spin compounds usually do not follow this rule as it lacks vacant orbitals in order to gain electrons in their valence shell.

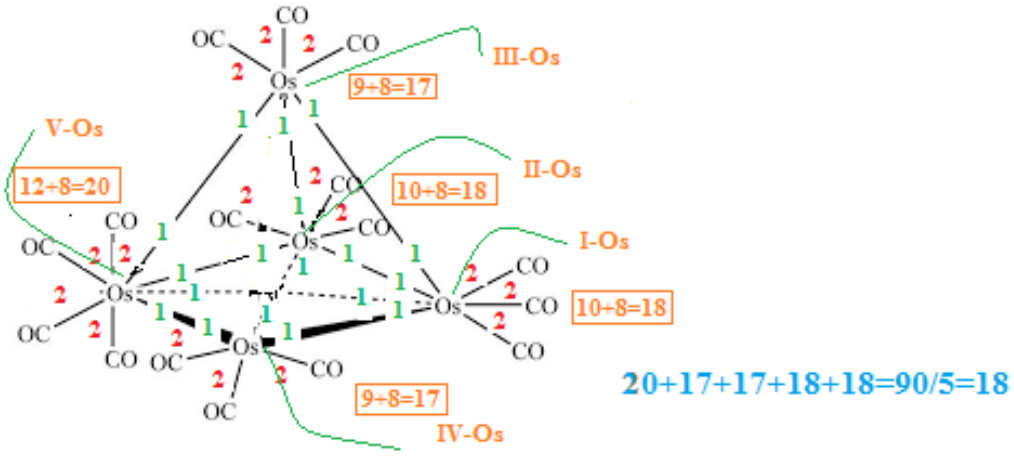
- The metal complexes containing bulky ligands violate the 18 electron rule by interfering with the ligands for bonding.
- **π**-donating ligands do not follow the 18 electron rule.
- When an organometallic compound consists of more than 6 metal atoms, the 18 electron rule does not apply.

WADE RULE: Ken Wade developed a method for the prediction of shapes of boranes clusters or carboranes or other clusters which is known as Polyhedral Skeletal Electron Pair Theory (PSEPT). In this rule, prediction of borane clusters done by *total electron count*. Example-

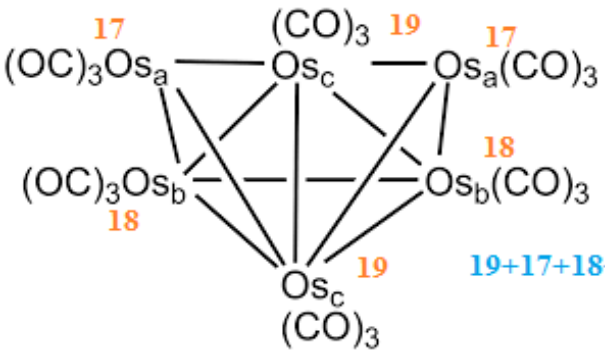
$Os_5(CO)_{16}$: The Os_5 skeleton is an irregular trigonal bipyramidal. The structure can not be explained on the basis of 18-electron rule and two electron Os−Os bond. But it can be explained on the basis of *Wade Rule*. In this case, two equatorial $Os(CO)_3$ metal atoms (I-Os & II-Os) would be assigned 18-electron configuration. The axial (III-Os & IV-Os) will represent 17-electrons while the Os_5 would have 20-electrons.

$Os \rightarrow d^6 s^2$ (8-electron)

20+17+17+18+18= 90/5 = 18



$Os_6(CO)_{18}$: The Os_6 skeleton has been found as a bicapped tetrahedral structure. All the CO-groups are terminal.



$Os_7(CO)_{21}$: It has a capped octahedral skeleton. Each Os has $(CO)_3$ terminal.