18 electrons Rules

18 electrons Rules

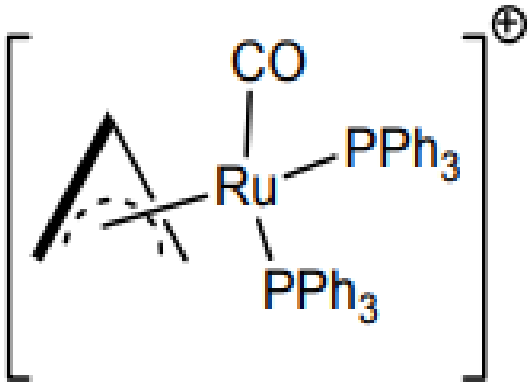
- The rule states that thermodynamically stable transition metal organometallic compounds are formed when the sum of the metal d electrons and the electrons conventionally considered as being supplied by the surrounding ligands equals 18.

- In general, the conditions favoring adherence to the 18-electron rule are, an electron rich metal (one that is in a low oxidation state) and ligands that are good π-acceptors

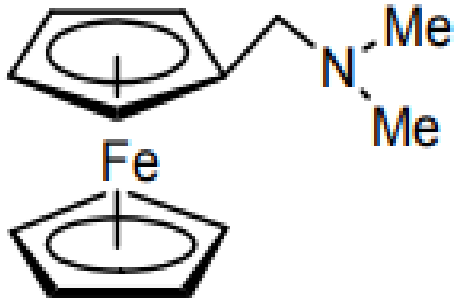
- The hapto symbol, η, with a numerical superscript, provides a topological description by indicating the connectivity between the ligand and the central atom. For example, if all the five carbon atoms of a cyclopentadienyl moiety are equidistant from a metal atom, we term it as η5-cyclopentadienyl

- Examples: η^1-R, η^1-Ar η^2-C_2R_4 η^1-allyl, η^3-allyl, η^4-Cb, η^5-Cp, η^6-C_6H_6, η^8-C_8H_8 η^2-C_{60}, η^5 -R_5C_{60}

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



	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

d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}	$d^{10}s^1$
21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper
39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver
57 La Lanthanum	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold

Early Transition Metals

16e- and sub-16e- configurations are common

Coordination geometries higher than 6 relatively common

Middle Transition Metals

18e- configurations are common

Coordination geometries of 6 are common

Late Transition Metals

16e- and sub-16e- configurations are common

Coordination geometries of 5 and lower are common:

d^8 = square planar

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

Easy way to remember ligand electron contribution for neutral atom counting method

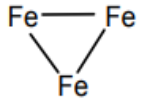
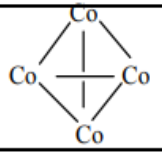
		Electron contribution
Neutral terminal :	**CO, PR_3, NR_3**	**2 electrons**
Anionic terminal :	**X-, H-, R-, Ar-, R_2N-, R_2P-, RO-**	**1 electron**
Hapto ligands	**: η^2-C_2R_4 η^2-C_2R_2, η^4-C_2R_2 ,η^1-allyl, η^3-allyl, η^4- Cb, η^5-Cp, η^6-C_6H_6 η^7-C_7H_7 η^8-C_8H_8 η^2-C_{60}, η^5-R_5C_{60}**	**same as hapticity**
bridging neutral	**μ_2-CO, μ_3-CO**	**2 electrons**
Bridging anionic	**μ_2-CH_3, μ_2-H (no lone pairs)**	**1 electron**
Bridging anionic (with 1 lone pair)	**μ_2-Cl, , μ_2-OR, μ_2-PR_2, μ_2-NR_2**	**3 electrons**
μ_3-Cl(2 l.p)		**5 electrons**
Bridging alkyne		**4 electrons**
NO linear		**3 electrons**
NO bent (l. p on nitrogen)		**1 electron**
Carbene M=C		**2 electron**
Carbyne M≡C		**3 electron**

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.

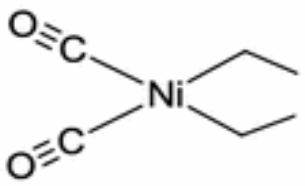
Subtract this number from n × 18 where n is the number of metals in the complex, that is, (n × 18) – A; say, it is B.

(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

Example 2: $[Ni(Et)_2(CO)_2]$



Ionic model:

Ni(II)	d^8	8 e^-
CO	2 e^- x 2	4 e^-
Et^-	2 e^- x 2	4 e^-
		16 e^-

Covalent model:

Ni(0)	d^{10}	10 e^-
CO	2 e^- x 2	4 e^-
Et·	1 e^- x 2	2 e^-
		16 e^-

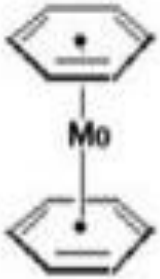
To obey the 18-electron rule, many carbonyl complexes are anions or cations, as in:

$[V(CO)_6]^-$	$[Mn(CO)_6]^+$	$[Fe(CO)_4]^{2-}$
V(0) = d^5	Mn(0) = d^7	Fe(0) = d^8
6 CO = 12*e*	6 CO = 12*e*	4 CO = 8*e*
1- = +1*e*	1+ = -1*e*	2- = 2*e*
= 18e	= 18 e	= 18e
Formal oxidation state = V(-I)	Formal oxidation state = Mn(I)	Formal oxidation state = Fe(-II)

[NOTE: In applying the 18-electron rule, metal ions are always considered to be zero-valent, not the formal oxidn. state]

Covalent Counting Rules

5e
8e
5e
18e

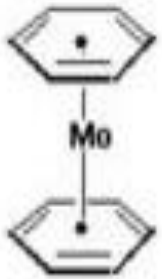


6e
6e
6e
18e

16e

Ionic Counting Rules

6e ($Cp^{\ominus}$)
6e (Fe^{2+})
6e ($Cp^{\ominus}$)
18e

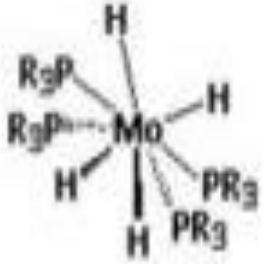


6e
6e
6e
18e

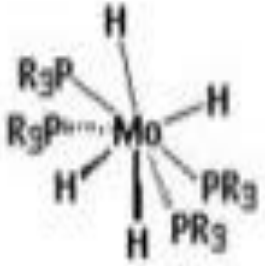
16e

-1e
5e
9e
5e
18e

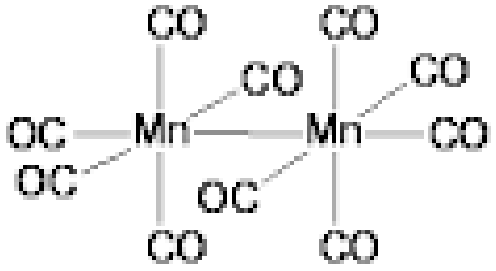
6e ($Cp^{\ominus}$)
6e (Co^{3+})
6e ($Cp^{\ominus}$)
18e



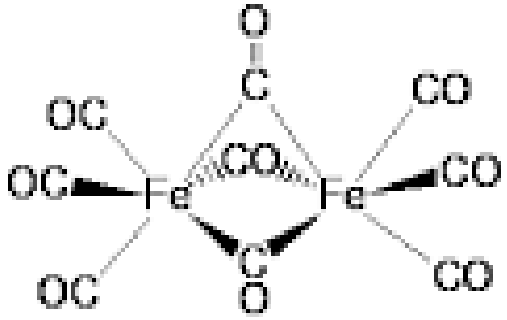
Mo 6e
4 H 4e
4 PR_3 8e
18



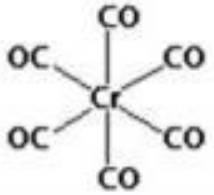
Mo^{4+} 2e
4 H - 8e
4 PR_3 8e
18



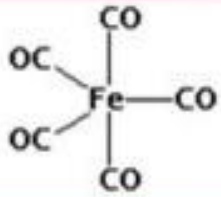
for each Mn:	
5 CO	10e
Mn	7e
1 Mn-Mn	1e
Total	18e



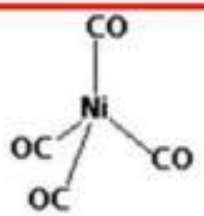
for each Fe:	
3 term CO	6e
3 bridging CO	3e
1 Fe	8e
1 Fe-Fe	1e
Total	18e

d Group	Formula	Valence electrons		Structure
6	$Cr(CO)_6$	Cr	6	
		6 CO	12	
			18	

7	Mn

8	$Fe(CO)_5$	Fe	8	
		5 CO	10	
			18	

9	Co

10	$Ni(CO)_4$	Ni	10	
		4 CO	8	
			18	

Example 1: $[Pd(\eta^3\text{-allyl})Br]_2$

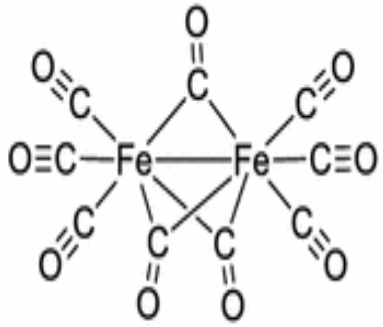
Ionic model:

Pd(II)	d^8	8 e^-
allyl$^-$	4 e^- x 1	4 e^-
Br^-	2 e^- x 1	2 e^-
μ-Br	2 e^- x 1	2 e^-
		16 e^-

Covalent model:

Pd(0)	d^{10}	10 e^-
allyl·	3 e^- x 1	3 e^-
Br·	1 e^- x 1	1 e^-
μ-Br	2 e^- x 1	2 e^-
		16 e^-

Example 2: $[Fe_2(CO)_9]$



Ionic & Covalent model:

Fe(0)	d^8	8 e^-
CO	2 e^- x 3	6 e^-
μ-CO	1 e^- x 3	3 e^-
M–M	1 e^-	1 e^-
		18 e^-

Example 3: $[Ti(\eta^5\text{-Cp})H]_2(Cp\text{-}Cp)$

Ionic model:

Ti(III)	d^1	1 e^-
Cp^-	6 e^- x 2	12 e^-
H^-	2 e^- x 1	2 e^-
μ-H	2 e^- x 1	2 e^-
M–M	1 e^-	1 e^-
		18 e^-

Covalent model:

Ti(0)	d^4	4 e^-
Cp·	5 e^- x 2	10 e^-
H·	1 e^- x 1	1 e^-
μ-H	2 e^- x 1	2 e^-
M–M	1 e^-	1 e^-
		18 e^-