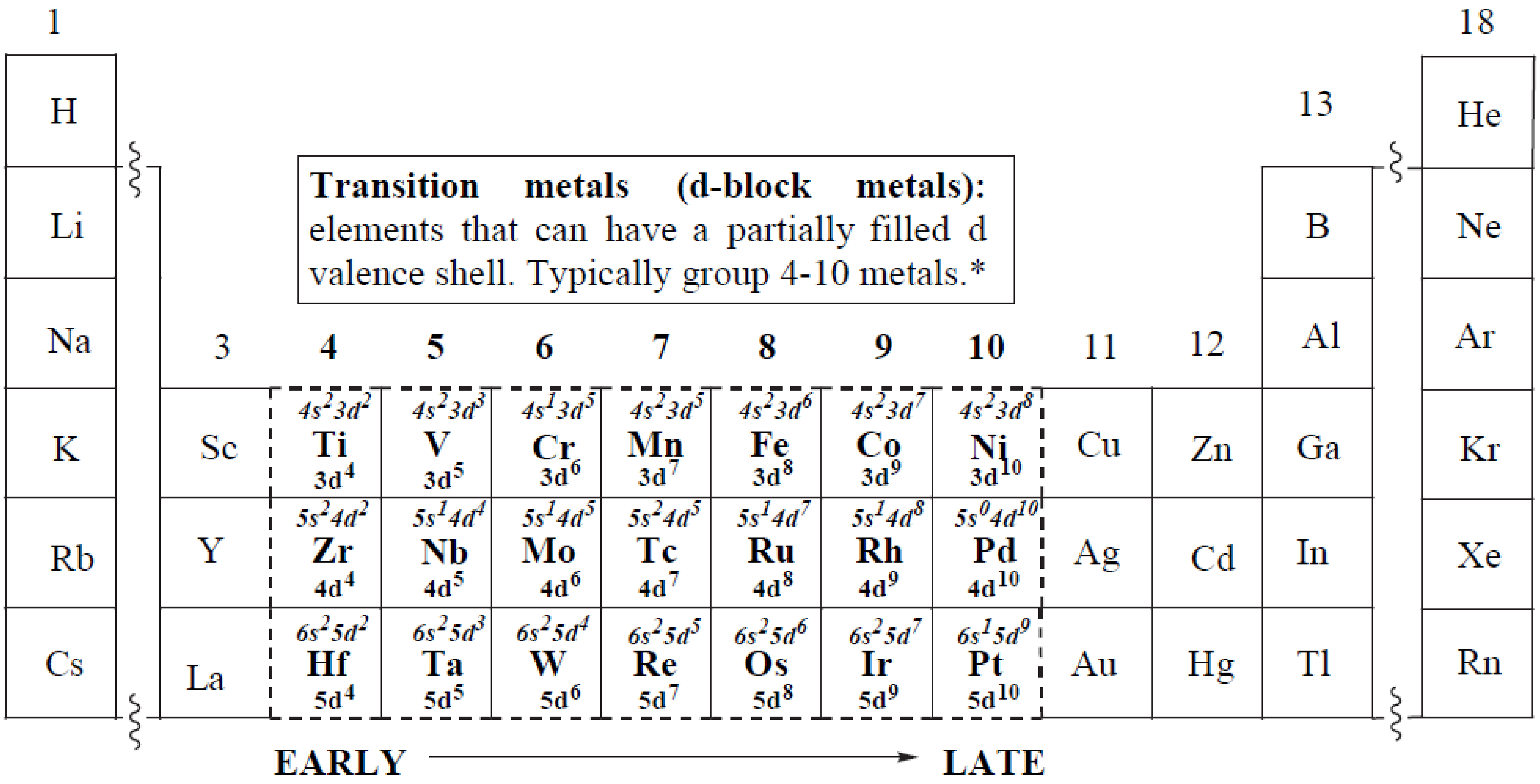
The Transition Metals



Transition metals (d-block metals): elements that can have a partially filled d valence shell. Typically group 4-10 metals.*

1	3	4	5	6	7	8	9	10	11	12	13	18
H												He
Li											B	Ne
Na											Al	Ar
K	Sc	$4s^2 3d^2$ **Ti** $3d^4$	$4s^2 3d^3$ **V** $3d^5$	$4s^1 3d^5$ **Cr** $3d^6$	$4s^2 3d^5$ **Mn** $3d^7$	$4s^2 3d^6$ **Fe** $3d^8$	$4s^2 3d^7$ **Co** $3d^9$	$4s^2 3d^8$ **Ni** $3d^{10}$	Cu	Zn	Ga	Kr
Rb	Y	$5s^2 4d^2$ **Zr** $4d^4$	$5s^1 4d^4$ **Nb** $4d^5$	$5s^1 4d^5$ **Mo** $4d^6$	$5s^2 4d^5$ **Tc** $4d^7$	$5s^1 4d^7$ **Ru** $4d^8$	$5s^1 4d^8$ **Rh** $4d^9$	$5s^0 4d^{10}$ **Pd** $4d^{10}$	Ag	Cd	In	Xe
Cs	La	$6s^2 5d^2$ **Hf** $5d^4$	$6s^2 5d^3$ **Ta** $5d^5$	$6s^2 5d^4$ **W** $5d^6$	$6s^2 5d^5$ **Re** $5d^7$	$6s^2 5d^6$ **Os** $5d^8$	$6s^2 5d^7$ **Ir** $5d^9$	$6s^1 5d^9$ **Pt** $5d^{10}$	Au	Hg	Tl	Rn

EARLY → **LATE**

- **d electrons in group 3 are readily removed *via ionization*.**
- **d electrons in group 11 are stable and generally form part of the core electron configuration.**

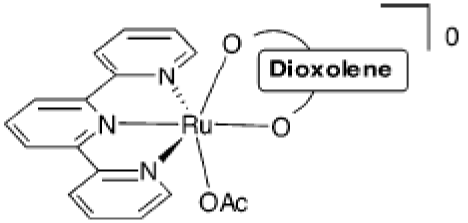
Group electronegativity

- $\chi(M)$ only useful for purely M-L σ-bonding complexes.
- Characteristic bonding in transition metal complexes has exceptionally strong effect on $\chi(L_nM)$.
- Thus reactivity determined by **influence of σ and π interaction on $\chi(M)$ orbitals.**
- Group electronegativity e.g. $\chi(L_5M)$ will vary depending on the ligand set

➢ ***EN(L_5M) increases with π acceptor (and decreasing π donor) strength of L.***

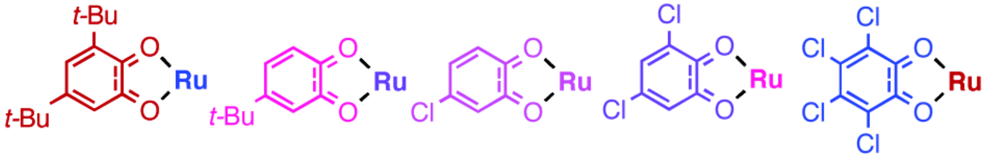
- Must consider $\chi(L_nM)$ as trends deviate from that predicted by $\chi(M)$ alone.
- Mulliken electronegativity – mean of ionization potential and electron affinity (Volts)

$$\chi_M = (IP + EA)/2$$

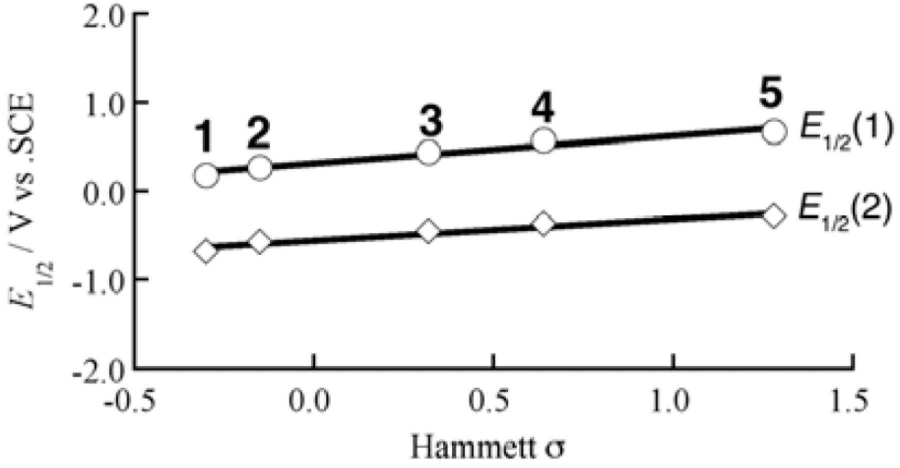


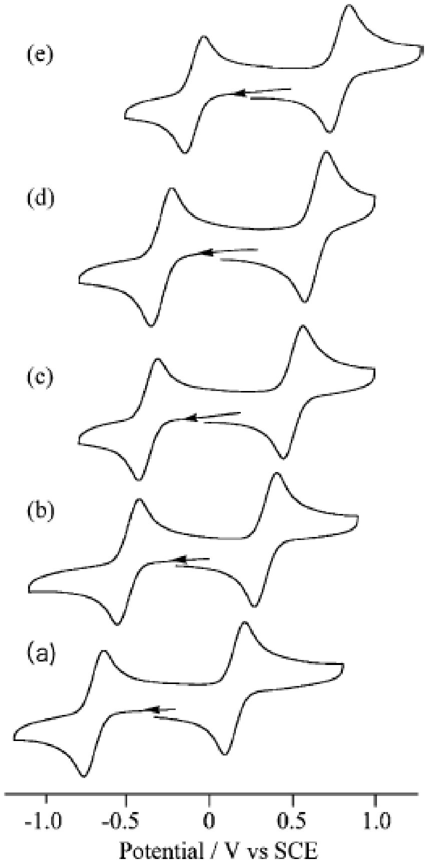
Influence of ligand effects on $Ru^{III/II}$ redox potential

– can be associated with $\chi(L_nM)$



Ru^{II}-sq ← **1** **2** **3** **4** **5** → Ru^{III}-cat

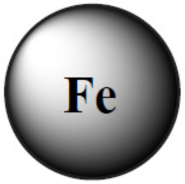




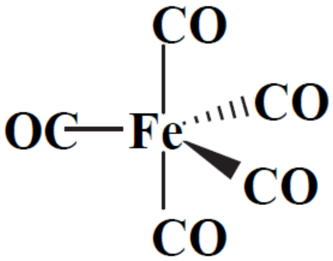
Wada, Tanaka et. al Inorg. Chem. 2006, 45, 8887

- for free (gas phase) transition metals: (n+1)s is below (n)d in energy (recall: n = principal quantum #).

- for complexed transition metals: the (n)d levels are below the (n+1)s and thus get filled first. (note that group # = d electron count)

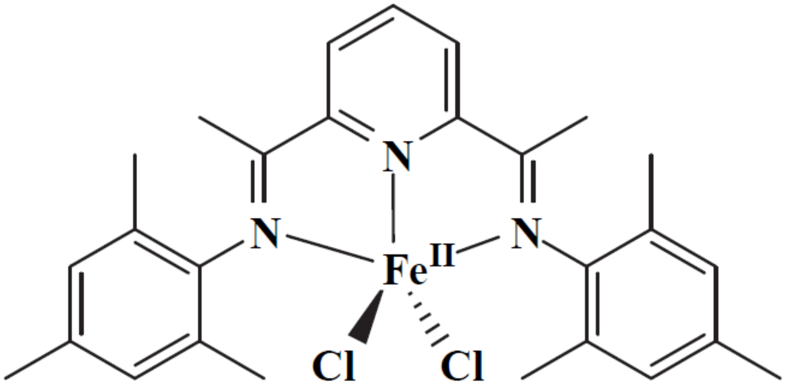


$4s^2 3d^6$

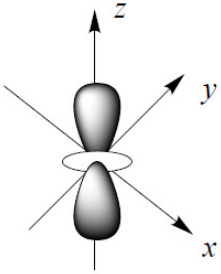


$3d^8$

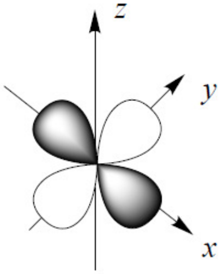
- for oxidized metals, subtract the oxidation state from the group #.



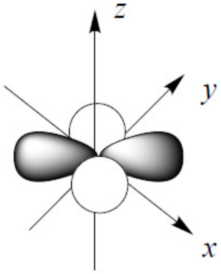
$3d^6$



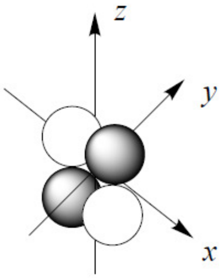
dz^2



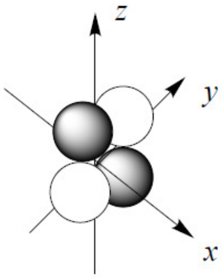
dx^2-y^2



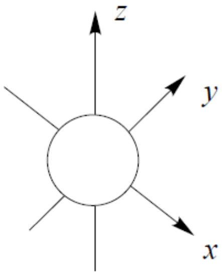
dxy



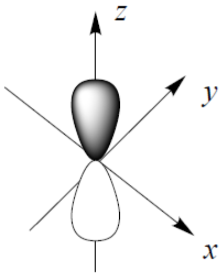
dxz



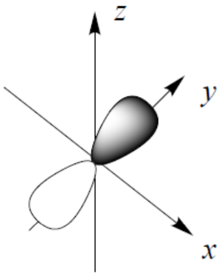
dyz



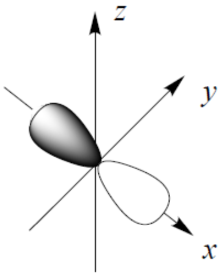
s



pz



py



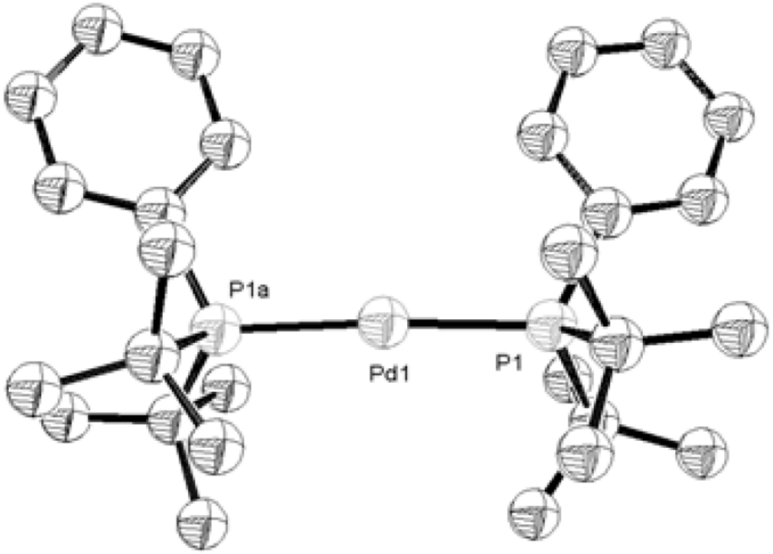
px

- orbitals oriented orthogonal wrt each other creating unique possibilities for ligand overlap.
- Total of ***9 valence orbitals available*** for bonding (2 x 9 = 18 valence electrons!)
- For an σ bonding only O_h complex, ***6 σ bonds*** are formed and the remaining d orbitals are *non-bonding*.
- It's these non-bonding d orbitals that give TM complexes many of their unique properties

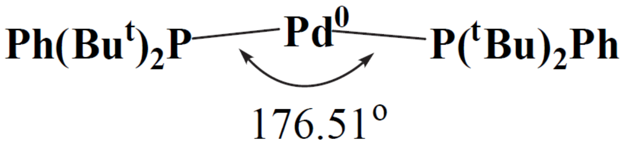
- ***Coordination Number*** **(CN) – the number of bonding groups at metal centre**
  - ***Low CN favored by:***

    1. Low oxidation state (e^- rich) metals.

    2. Large, bulky ligands.



Although $Pd(P(^tBu)_2Ph)_2$ is *coordinatively unsaturated electronically*, the steric bulk of both $P(^tBu)_2Ph$ ligands prevents additional ligands from coordinating to the metal.



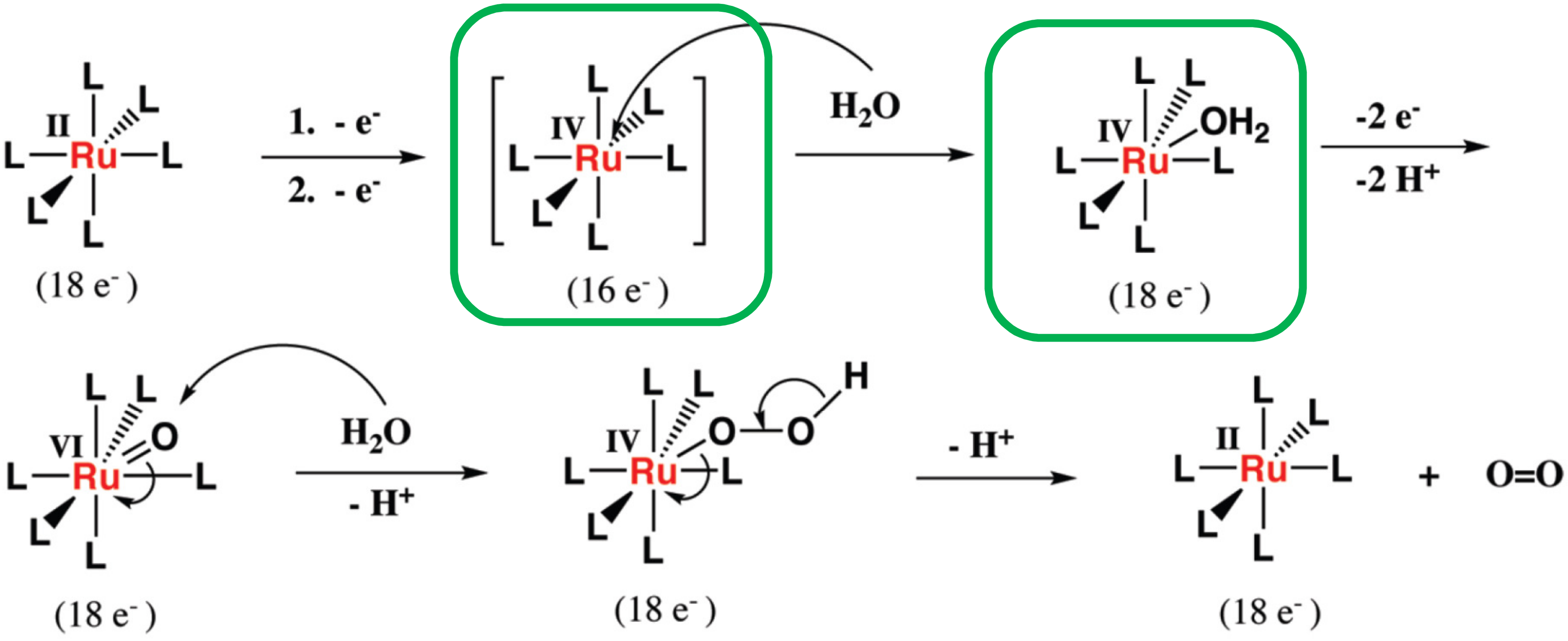
What is the d electron count for Pd?

Otsuka *JACS*, 1976 (98)5850.

- ***Coordination Number*** **(CN) – the number of bonding groups at metal centre**
  - ***High CN favored by:***

    1. High oxidation state (e^- poor) metals.

    2. Small ligands.

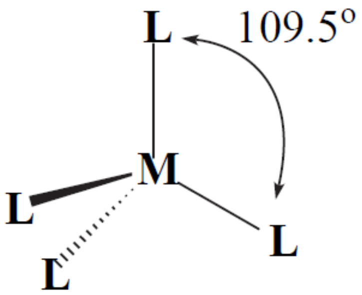


Water oxidation by mononuclear Ru complex involving a 7 coordinate Ru(IV) species.

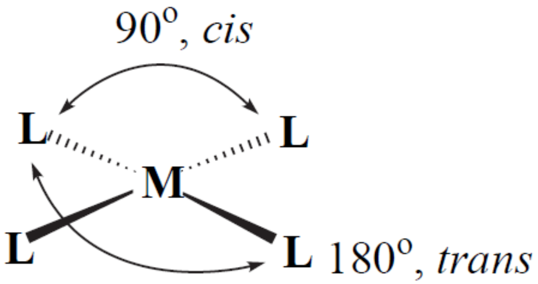
Muckerman & Thummel *Inorg. Chem.* 2008

- **CN # 4**

  - **Tetrahedral or square planar geometries**
  - Commonly found for electron rich transition metals



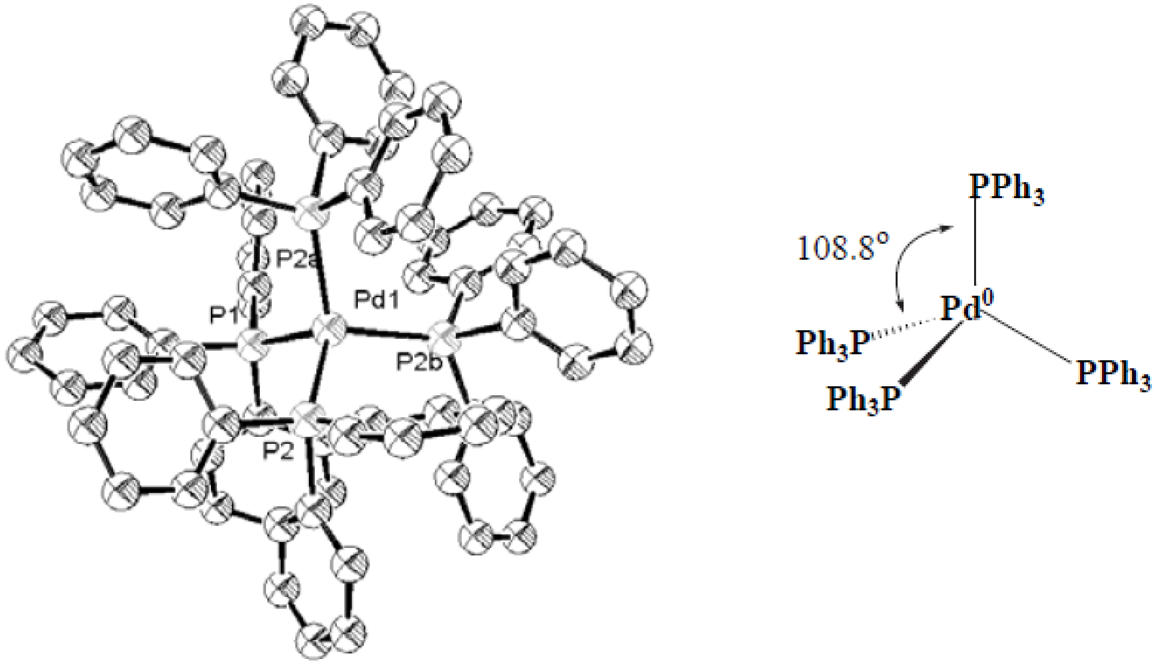
tetrahedral

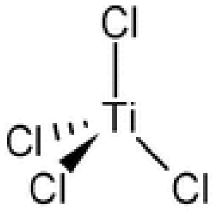


square planar

e.g. $AlCl_4^-$ $Ni(CO)_4$ Ni^{2+},Pd^{2+},Pt^{2+},Rh^+

- **CN # 4 contd.**
  - tetrahedral geometry is preferred for d^0 or d^{10}

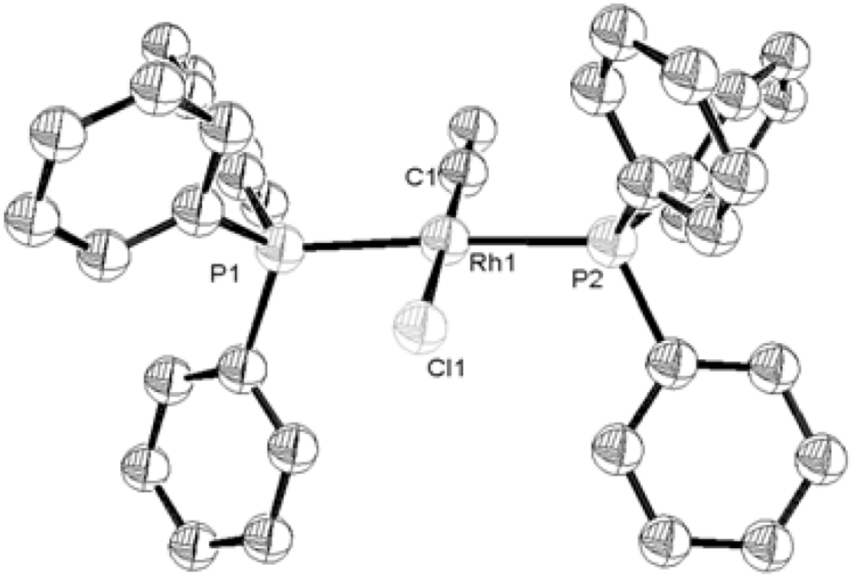


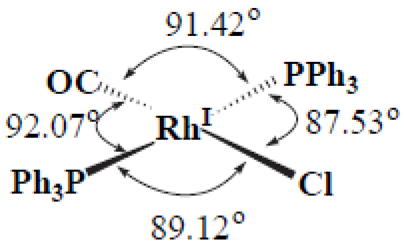


Oxidation state of Ti?

- **CN # 4 contd.**

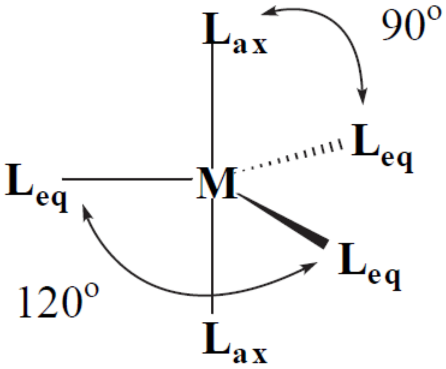
  - d^8 electron configuration usually leads to square planar geometries (as only one d-orbital required for forming the 4 metal ligand s-bonds)



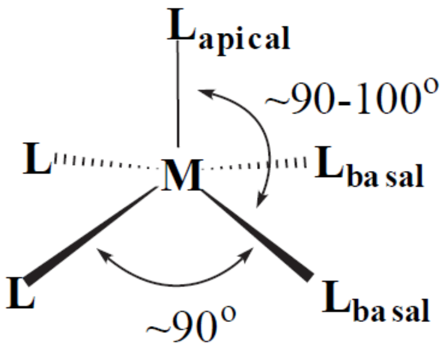


- **CN # 5**

  - Trigonal bipyramidal and square pyramidal exist



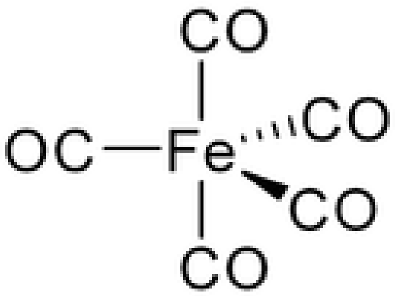
trigonal bipyramidal



square pyramidal

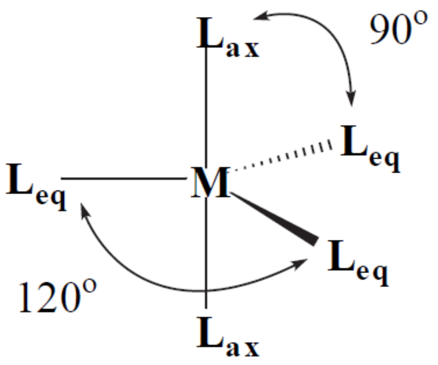
  - This geometry is less common than 4 and 6.

- **CN # 5 contd.**

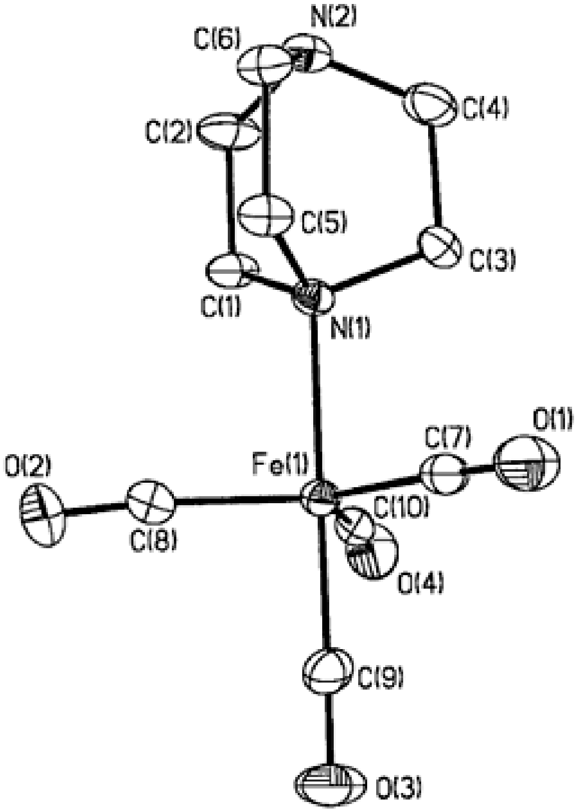


Iron pentacarbonyl

very toxic !!!



trigonal bipyramidal

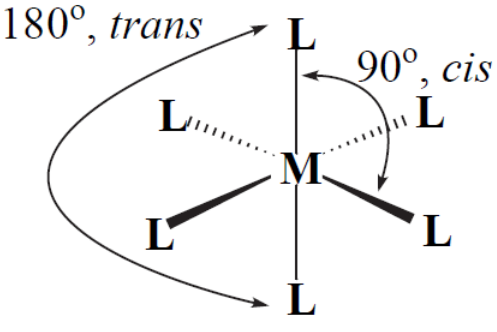


$(DABCO)Fe(CO)_4$

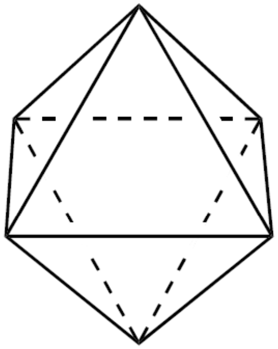
[DABCO = 1,4-diazabicyclo[2.2.2]octane]

- **CN # 6**

  - Octahedral….by far the most common geometry for transition metal complexes



octahedral

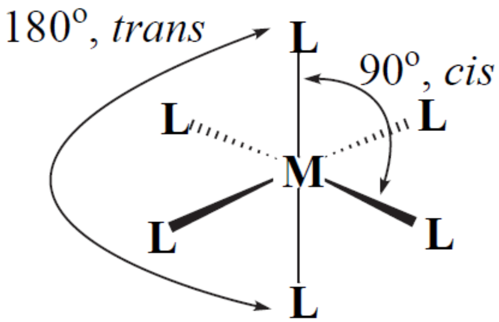


Octahedron

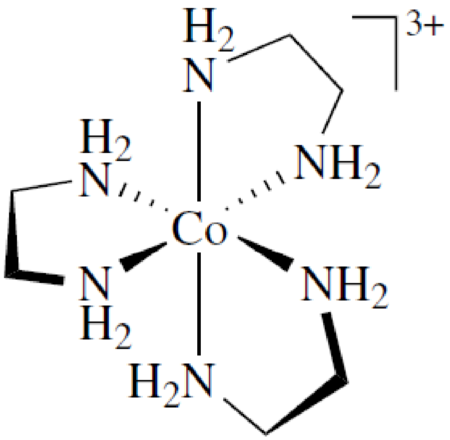
The 6 ligands occupy the 6 vertices of an octahedron, which allows them to minimize their M−L bonding distances, while maximizing their L· · ·L nonbonding distances.

- **CN # 6**

  - Octahedral



octahedral



[chelate effect: multidentate ligands increase formation constant and increase stability of complex]

The 18-valence electron rule

“thermodynamically stable transition-metal complexes are formed when the sum of the metal *d* electrons plus the electrons conventionally regarded as being supplied by the ligand equals 18.”

- The 18 valence electron (18VE) rule introduced in 1927 by *Sidgwick* is based on the valence bond (VB) formalism of localized metal-ligand bonds.
- The transition metal formally attains the electron configuration of the subsequent noble gas in the periodic table.
- **18VE rule *aka***
  - ➢ *inert-gas rule*
  - ➢ *effective atomic number (EAN) rule*

Common oxidation states

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
+8								
+7				○				
+6			○	○	○			
+5		○	○	○	○	○		
+4	●	●	○	○	○	○	○	
+3	○	○	●	○	●	○	○	○
+2	○	○	○	●	○	●	●	●
+1		○	○	○	○	○	○	○

	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
+8					○			
+7				○	○			
+6			●	●	○	○		
+5		●	○	○	○	○		
+4	●	○	○	○	○	○	○	
+3	○	○	○	○	●	●	○	○
+2	○	○	○	○	○	○	●	○
+1		○	○	○	○	○	○	●

	Hf	Ta	W	Re	Os	Ir	Pt	Au
+8					○			
+7				●	○			
+6			●	○	○	○		
+5		●	○	○	○	○		
+4	●	○	○	○	●	●	●	
+3	○		○	○	○	○	○	●
+2		○	○	○	○	○	○	○
+1		○	○	○	○	○	○	○

○ - Observed positive oxidation state

● - Most stable oxidation state (aqueous solution)

Mingos *Essential Trends in Inorganic Chemistry*;
Oxford University Press, 1998.

Electron Counting

- Organic compounds obey the octet (or 8 electron) rule:

$$\mathbf{C + 4H = CH_4}$$

$$\mathbf{(4\ valence\ e^{-}) + [4\ x(1\ valence\ e^{-})] = 8e^{-}}$$

- An octet is appropriate for carbon, where one 2s and three 2p orbitals make up the valence shell; $8e^{-}$ fill four orbitals.
- Transition metal complexes follow the 18 electron rule, appropriate for an atom having 9 valence orbitals,

  e.g. a first row transition metal has one 4s, three 4p and five 3d valence orbitals:

$$\mathbf{Cr^{0} + 6CO = Cr(CO)_6}$$

$$\mathbf{(6\ valence\ e^{-}) + [6\ x(2\ valence\ e^{-})] = 18e^{-}}$$

Ionic *vs.* covalent model

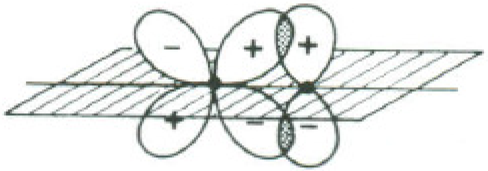
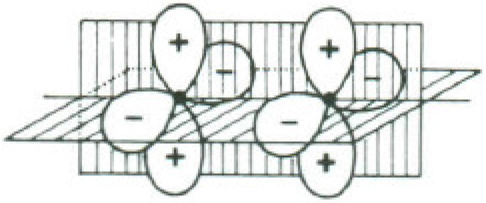
- Both the *covalent model* and the *ionic model* differ only in the way the electrons are considered as coming from the metal or from the ligands

  - emphasize model…not a true representation of metal charge!!!

- Each model is often invoked without any warning in the literature therefore it is important to be able to identify their use.
- The ***ionic model is most commonly used for traditional M–L inorganic coordination compounds*** therefore coordinating ligands are treated equally in both models.
- The *ionic model* is more appropriate for *high-valent metals* with N, O or Cl ligands.
- In the ionic model the M–X bond is considered as arising from a cationic M^+ and an anionic X^- (heterolytic)
- The ***covalent model is sometimes preferred for organometallic species*** with *low-valent metals* where the metal and ligand oxidation states cannot be unambiguously defined.
- In the covalent model the M–X bond is considered as arising from a neutral metal and ligand radical $X^\bullet$ (homolytic).

Types of bonding

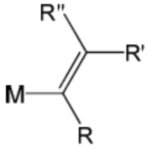
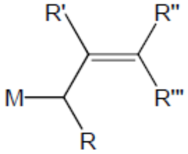
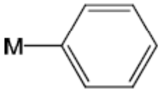
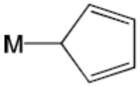
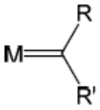
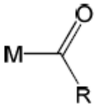
σ π δ

Overlap	Number of nodal planes including the bond axis	Bond type	Example
	0	σ	$>B-CH_3$
	1	π	$(CO)_5Cr=CR_2$
	2	δ	$[R_4Re\equiv ReR_4]^{2-}$

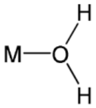
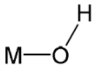
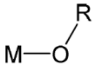
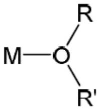
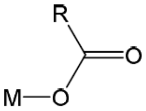
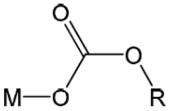
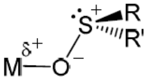
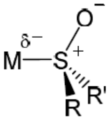
- Bond polarity is evaluated by the difference in electronegativities of neighboring atoms

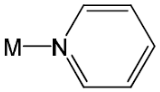
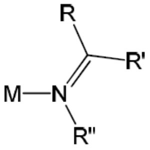
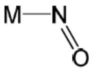
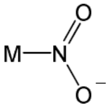
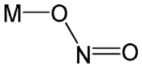
(n/a = not applicable)

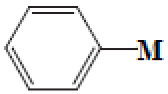
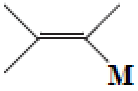
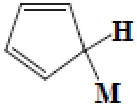
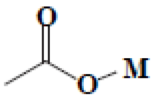
η^1 contd.

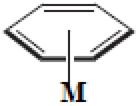
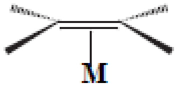
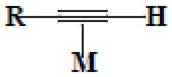
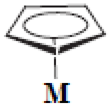
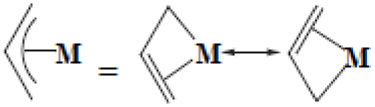
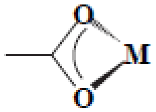
		ionic model		covalent model	
		formal charge	# of e− donated	formal charge	# of e− donated
Hydride	$M{-}H$	-1	2	0	1
Alkyl (e.g. methyl)	$M{-}CH_3$	-1	2	0	1
Alkenyl		-1	2	0	1
Alkynyl	$M{-}{\equiv}{-}R$	-1	2	0	1
Allyl		-1	2	0	1
Aryl		-1	2	0	1
Cyclopentadienyl		-1	2	0	1
Carbene		0	2	n/a	n/a
Carbyne	$M{\equiv}{-}R$	0	4	n/a	n/a
Acyl		-1	2	0	1
Carbon monoxide	$M{-}C{\equiv}O$	0	2	n/a	n/a
Nitrile	$M{-}C{\equiv}N$	-1	2	0	1
Fulminate	$M{-}C{\equiv}\overset{+}{N}{-}O^{-}$	-1	2	0	1

η^1 contd.

		ionic model		covalent model	
		formal charge	# of e^- donated	formal charge	# of e^- donated
Aqua		0	2	n/a	n/a
Hydroxyl		-1	2	0	1
Oxo	$M{=}O$	-2	4	n/a	n/a
Alkoxide **(Thiolate O = S)**		-1	2	0	1
Ether **(Sulfide/Thioether O = S)**		0	2	n/a	n/a
Carboxylate		-1	2	0	1
Carbonate		-1	2	0	1
Cyanate **(Thiocyanate O = S)**	$M-O-C\equiv N$	-1	2	0	1
Sulfoxide		0	2	n/a	n/a
		0	2	n/a	n/a

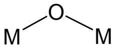
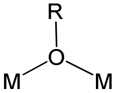
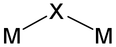
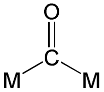
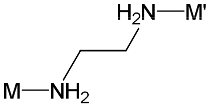
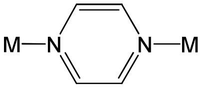
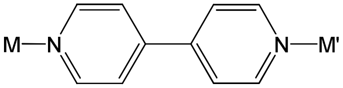
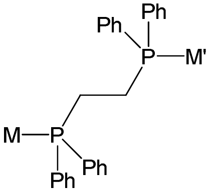
		ionic model		**covalent model**	
η^1		**formal charge**	**# of e⁻ donated**	**formal charge**	**# of e⁻ donated**
Isocyanate (Isothiocyanate O = S)	$M-N=C=O$	**-1**	**2**	**0**	**1**
Nitrogen	$M-N\equiv N$	**0**	**2**	**n/a**	**n/a**
Amine	$M-NR_3$	**0**	**2**	**n/a**	**n/a**
Pyridyl		**0**	**2**	**n/a**	**n/a**
Imine		**0**	**2**	**n/a**	**n/a**
Amide	$M-NR_2$	**-1**	**2**	**0**	**1**
Isonitrile	$M-\overset{+}{N}\equiv\overset{-}{C}$	**0**	**2**	**n/a**	**n/a**
Nitrosyls		**-1**	**2**	**0**	**1**
	$M-N\equiv O^{+}$	**+1**	**2**	**n/a**	**n/a**
Nitro		**-1**	**2**	**n/a**	**n/a**
Nitrito		**-1**	**2**	**0**	**1**
Phosphine	$M-PR_3$	**0**	**2**	**n/a**	**n/a**
Phosphide	$M-PR_2$	**-1**	**2**	**0**	**1**
Halide (e.g. Cl)	$M-Cl$	**-1**	**2**	**0**	**1**

η^1-coordination	**Formal charge**	**# of e- donated**
 η^1-aryl	-1	2
 η^1-alkenyl	-1	2
 η^1-alkynyl	-1	2
 η^1-Cp (cyclopentadienyl)	-1	2
 η^1-allyl	-1	2
 η^1-acetate	-1	2

η^x-coordination	**Formal charge**	**# of e- donated**
 η^6-arene	0	6
 η^2-alkene	0	2
 η^2-alkyne	0	2
 η^5-Cp (cyclopentadienyl)	-1	6
 η^3-allyl	-1	4
 η^2-acetate	-1	4

- **Common unsaturated π donating ligands encountered in organotransition-metal chemistry together with the respective numbers of electrons relevant to the application of the 18 VE rule.**

Bridging ligands (multidentate non-chelating)

		ionic model	
		formal charge	# of e^- donated
μ-hydride	M—H—M	**-1**	**1/metal**
μ-oxo		**-2**	**2/metal**
μ-alkoxide		**-1**	**2/metal**
μ-halide		**-1**	**2/metal**
μ-CO		**0**	**1/metal**
μ-en **(ethylene diamine)**		**0**	**2/metal**
μ-pyrazine		**0**	**2/metal**
μ-4,4'-bipyridine		**0**	**2/metal**
μ-dppe **[1,2-bis(diphenyl phosphino)ethane]**		**0**	**2/metal**

- When applying the 18VE rule the following should be considered

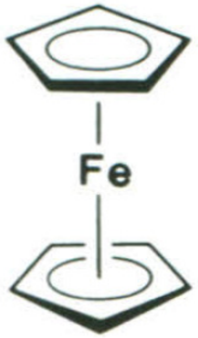
1. The intramolecular partitioning of the electrons has to ensure that the total charge of the complex remains unchanged *(ionic or covalent model).*

2. A M–M bond contributes one electron to the total electron count of a single metal atom.

3. The electron pair of a bridging ligand donates one electron to each of the bridged metal atoms.

1. **The intramolecular partitioning of the electrons has to ensure that the total charge of the complex remains unchanged.**

Di(cyclopentadienyl)iron $Fe(C_5H_5)_2$:



	$2(C_5H_5^-)$	$12e$
	Fe^{2+}	$6e$
		$18e$
or:	$2(C_5H_5\cdot)$	$10e$
	Fe^0	$8e$
		$18e$

$2^- + 2^+ = 0$

2. **A M–M bond contributes one electron to the total electron count of a single metal atom.**

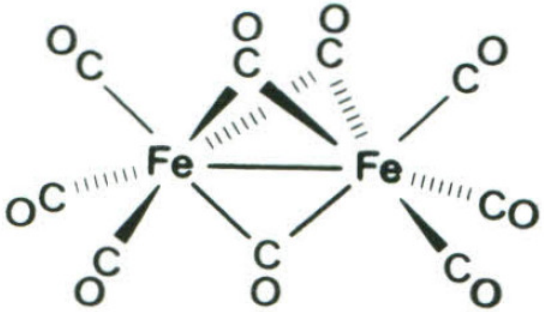
Decacarbonyldimanganese $Mn_2(CO)_{10}$

5(CO)	10 *e*
Mn^0	7 *e*
Mn – Mn	1 *e*
	18 *e*

What is the d electron count of Mn in the unstable $(CO)_5Mn$ monomer?

3. **The electron pair of a bridging ligand donates one electron to each of the bridged metal atoms.**

Nonacarbonyldiiron $Fe_2(CO)_9$

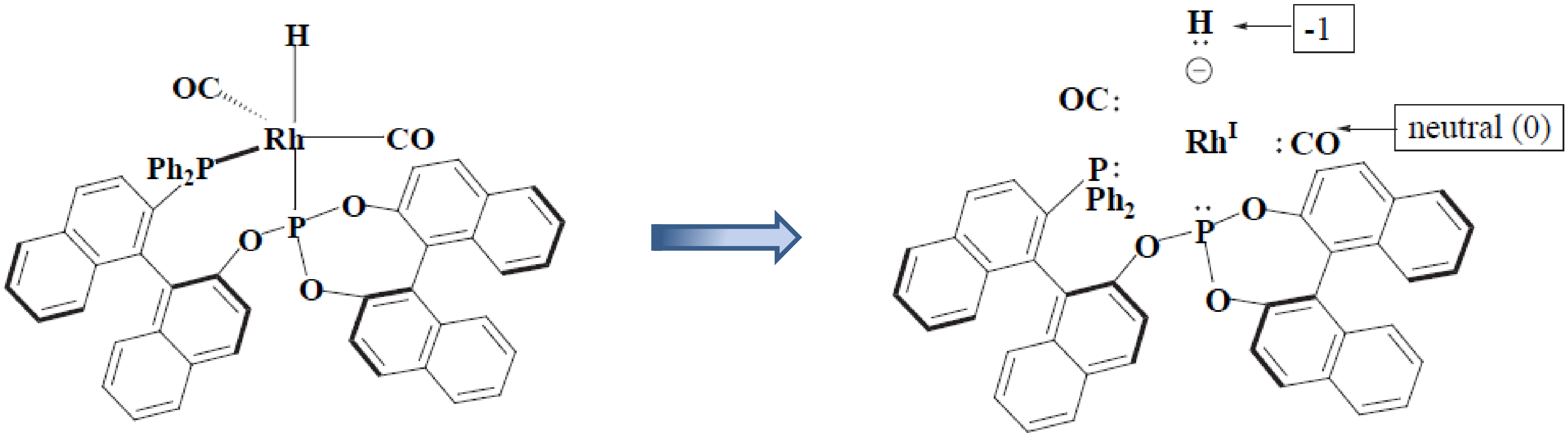


3(CO)	6 *e*
3(μ-CO)	3 *e*
Fe^0	8 *e*
Fe – Fe	1 *e*
	18 *e*

Electron Counting contd.

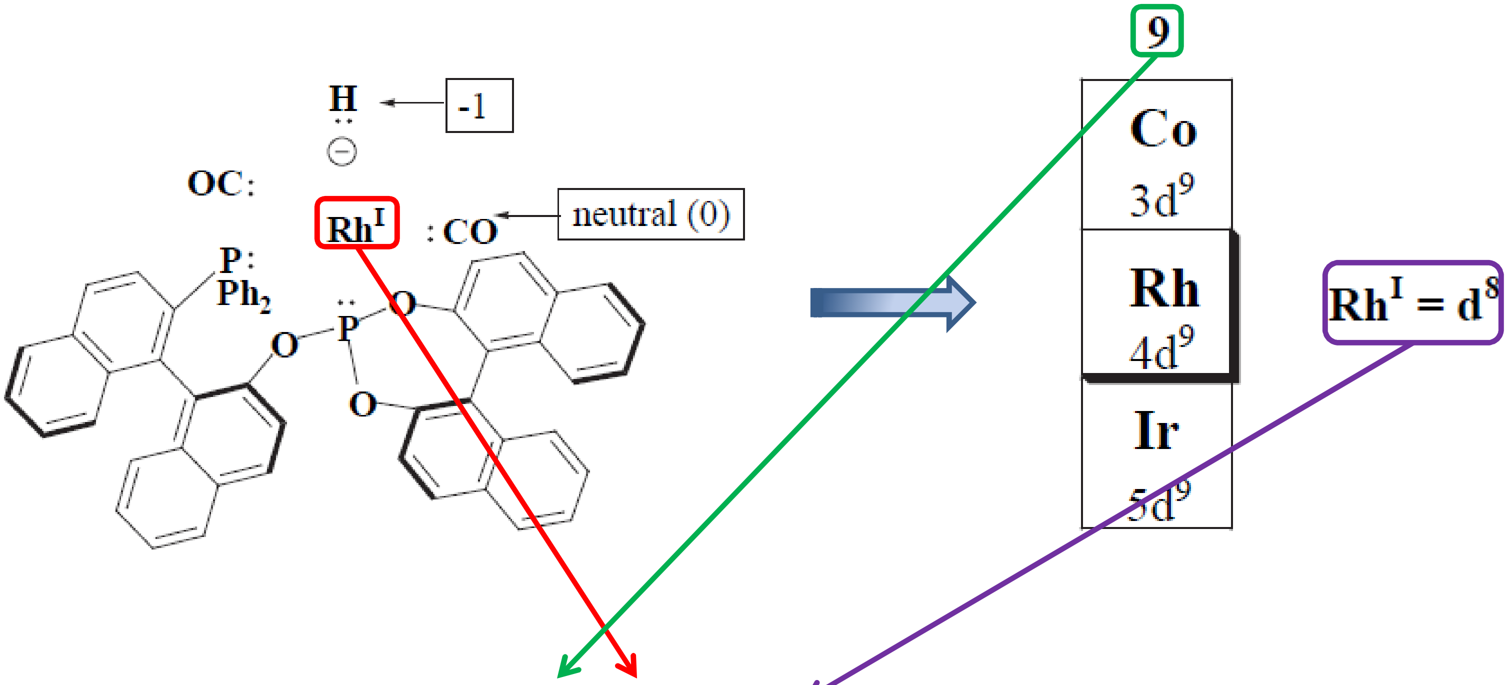
1. Determine the oxidation state of the metal.

- ➢ balance the ligand charges with an equal opposite charge on the metal.
- ➢ This is the metal's formal oxidation state.
- ➢ To determine ligand charges, ***create an ionic model*** by assigning each M-L electron pair to the more electronegative atom (L). This should result in stable ligand species or ones known as reactive intermediates in solution.



2. Determine the d electron count.

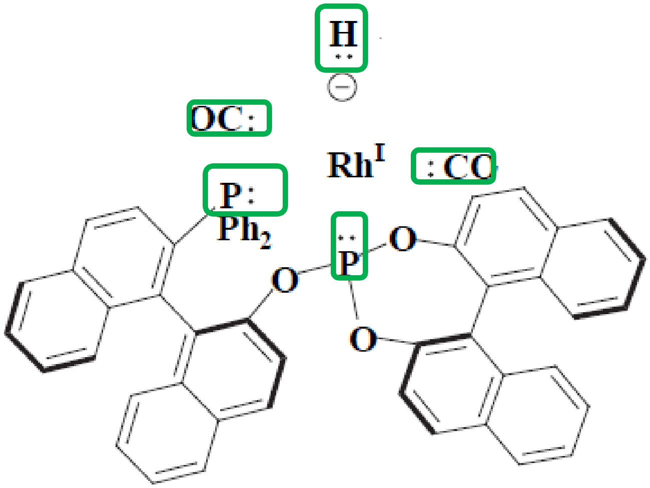
- Subtract the metal's oxidation state from its group #.



9 – 1 = 8

3. Determine the electron count of the complex

- by adding the # of electrons donated by each ligand to the metal's d electron count.

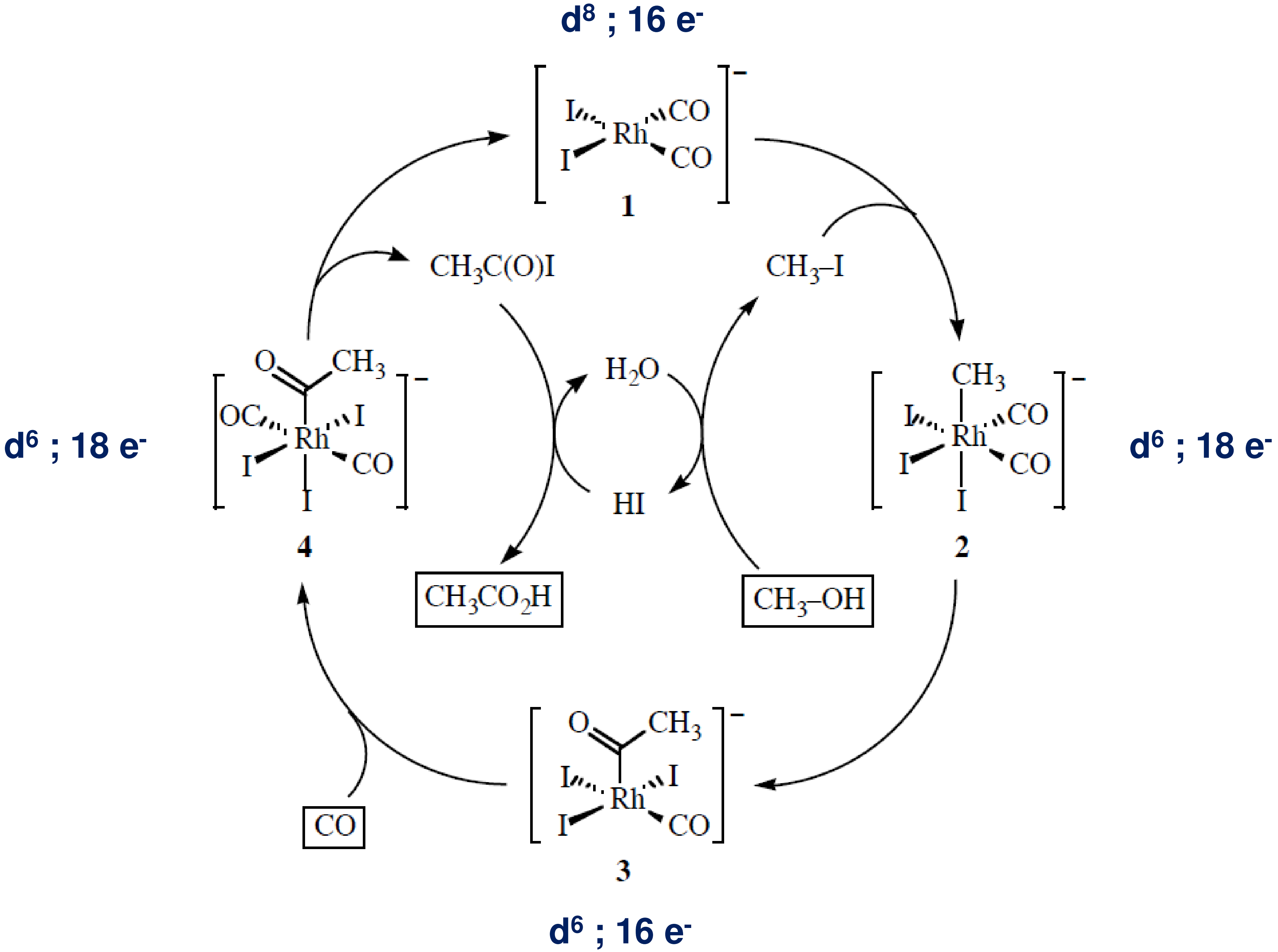


$5 \times 2e^- = 10e^-$

Metal : $8\ e^-$

Ligands: $10e^-$

Total: $18e^-$


d^8 ; 16 e$^-$
1
CH$_3$C(O)I
CH$_3$–I
H$_2$O
HI
d^6 ; 18 e$^-$
4
d^6 ; 18 e$^-$
2
CH$_3$CO$_2$H
CH$_3$–OH
CO
3
d^6 ; 16 e$^-$