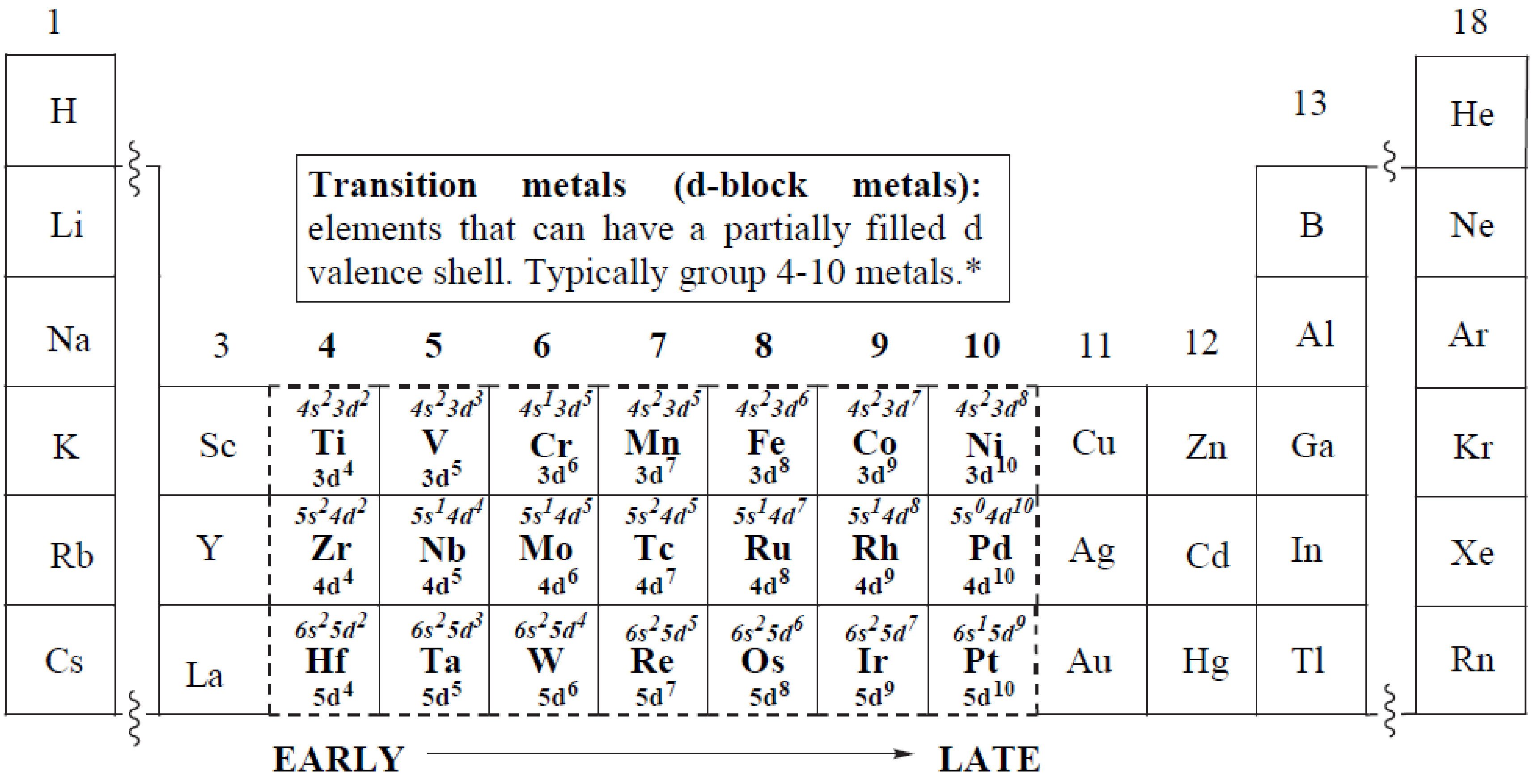
The Transition Metals



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.**

Electronegativity

Electronegativity (χ) is a chemical property that describes the ability of an atom to attract electron density towards itself in a covalent bond.

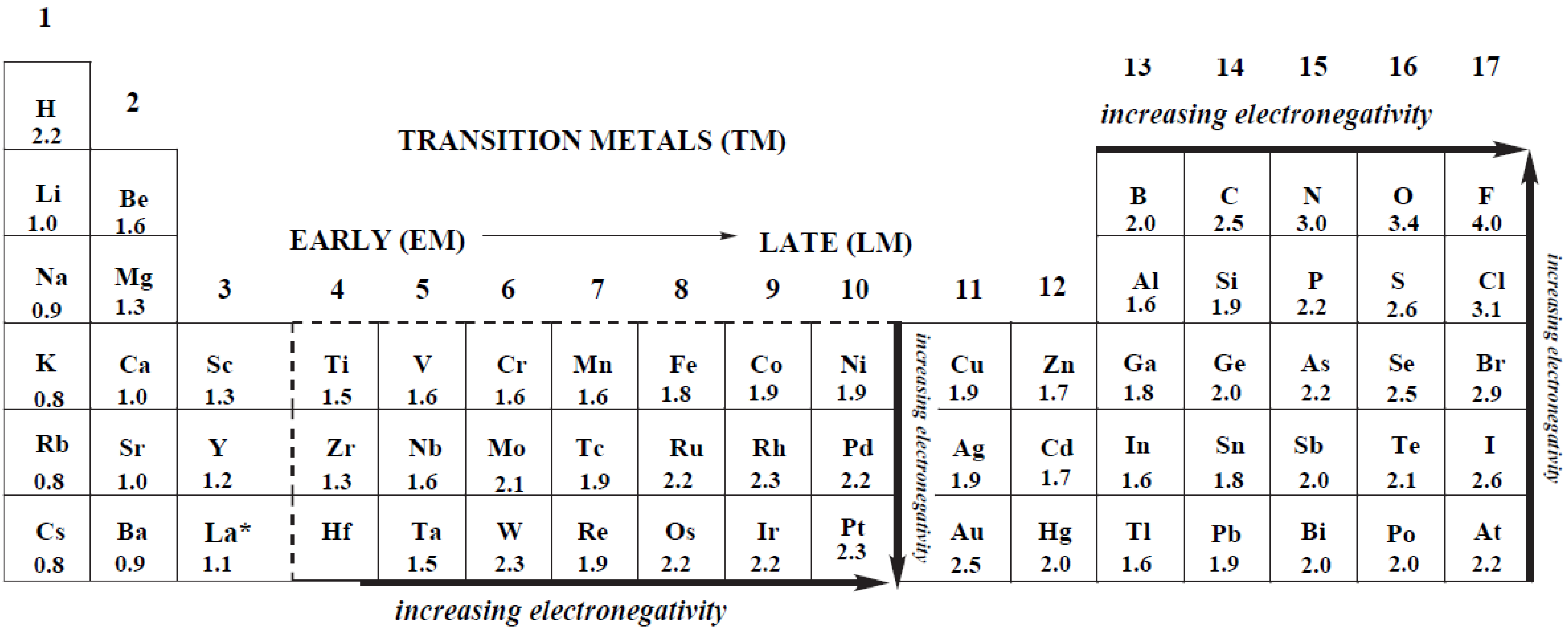
- The electronegativity is ***dependent on the hybridization*** of the atom.
  - s orbitals experience stronger nuclear charge than p orbitals of same principal quantum number, therefore χ(C) increases with higher s character of hybrid orbital:

$$\chi(\mathrm{Csp^3}) = 2.5; \qquad \chi(\mathrm{Csp^2}) = 2.9; \qquad \chi(\mathrm{Csp}) = 3.95$$

[note: values may vary dependent on method of calculation]

  - χ of an element ***increases with increasing oxidation number*** of that element

    e.g., $\chi(\mathrm{Fe^{III}}) > \chi(\mathrm{Fe^{II}})$



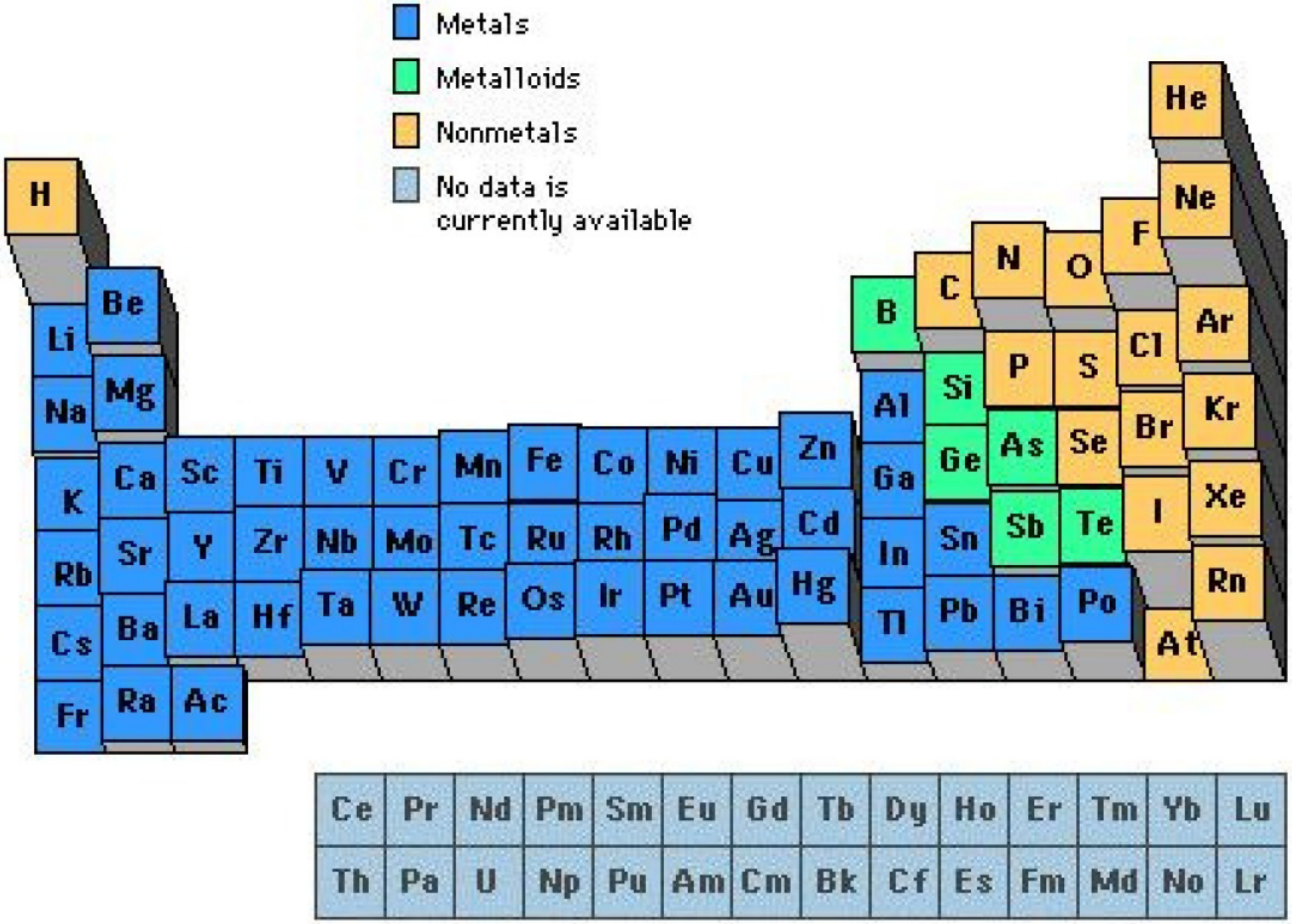
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
H 2.2																
Li 1.0	Be 1.6											B 2.0	C 2.5	N 3.0	O 3.4	F 4.0
Na 0.9	Mg 1.3											Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.1
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.6	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.7	Ga 1.8	Ge 2.0	As 2.2	Se 2.5	Br 2.9
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.3	Nb 1.6	Mo 2.1	Tc 1.9	Ru 2.2	Rh 2.3	Pd 2.2	Ag 1.9	Cd 1.7	In 1.6	Sn 1.8	Sb 2.0	Te 2.1	I 2.6
Cs 0.8	Ba 0.9	La* 1.1	Hf	Ta 1.5	W 2.3	Re 1.9	Os 2.2	Ir 2.2	Pt 2.3	Au 2.5	Hg 2.0	Tl 1.6	Pb 1.9	Bi 2.0	Po 2.0	At 2.2

- **The electronegativity of the elements increases substantially in progressing from left to right (early to late transition metals) across the periodic table**
  – increased penetration effect (stronger effective nuclear charge)

- **The electronegativity of main group elements increases in progressing up a column**
  – decreased shielding effect (stronger effective nuclear charge)

- **The electronegativity of transition metal elements increases in progressing down a column**
  - poor shielding from diffuse d orbitals

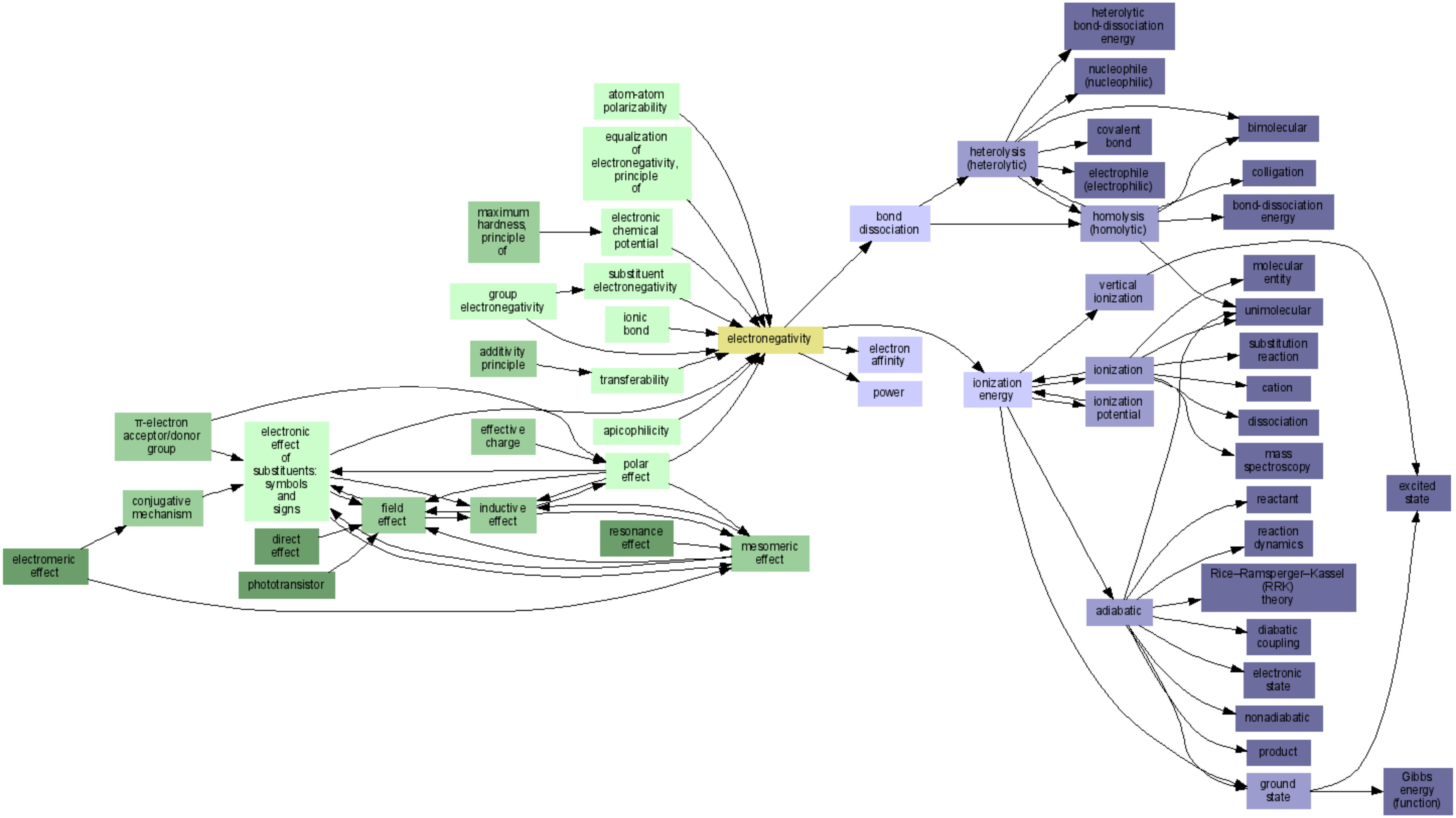
$\chi_M = (IP + EA)/2$



- **Ionization energies decrease down a group and increase across a period**

  (metals have higher ionization energies than non-metals)

http://goldbook.iupac.org/Graphs/E01990.3.map.html



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**

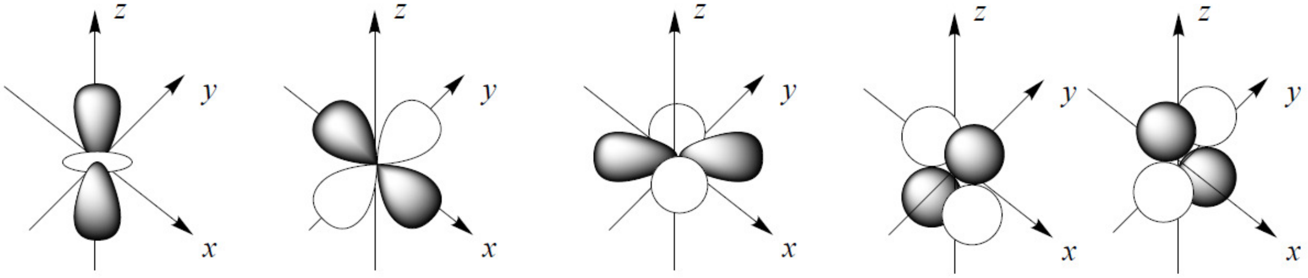
  ➢ ***$EN(L_5M)$ increases with π acceptor (and decreasing π donor) strength of L.***

- 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)

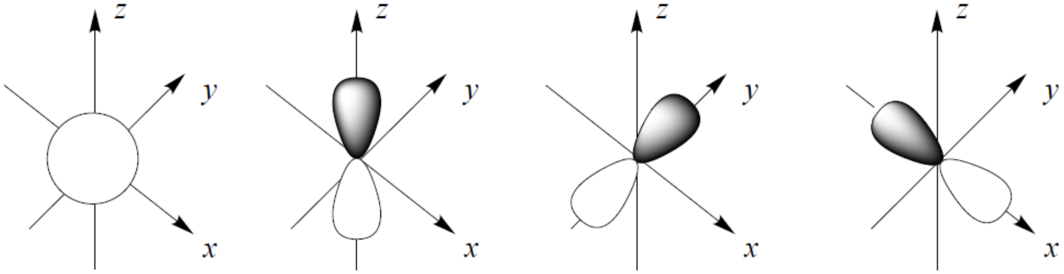
$$\chi_M = (IP + EA)/2$$

Transition Metal Valence Orbitals

- *n*d orbitals



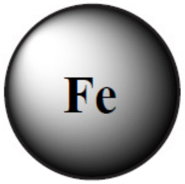
- (*n* + 1)s and (*n* + 1)p orbitals



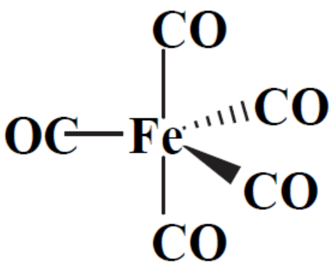
- dx^2-dy^2 and dz^2 (e_g) lobes located on the axes
- dxy, dxz, dyz lobes (t_{2g}) located between axes

- 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)

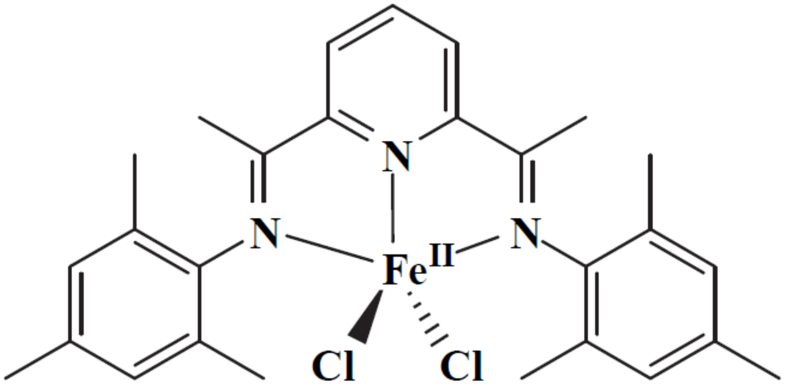


$4s^2 3d^6$

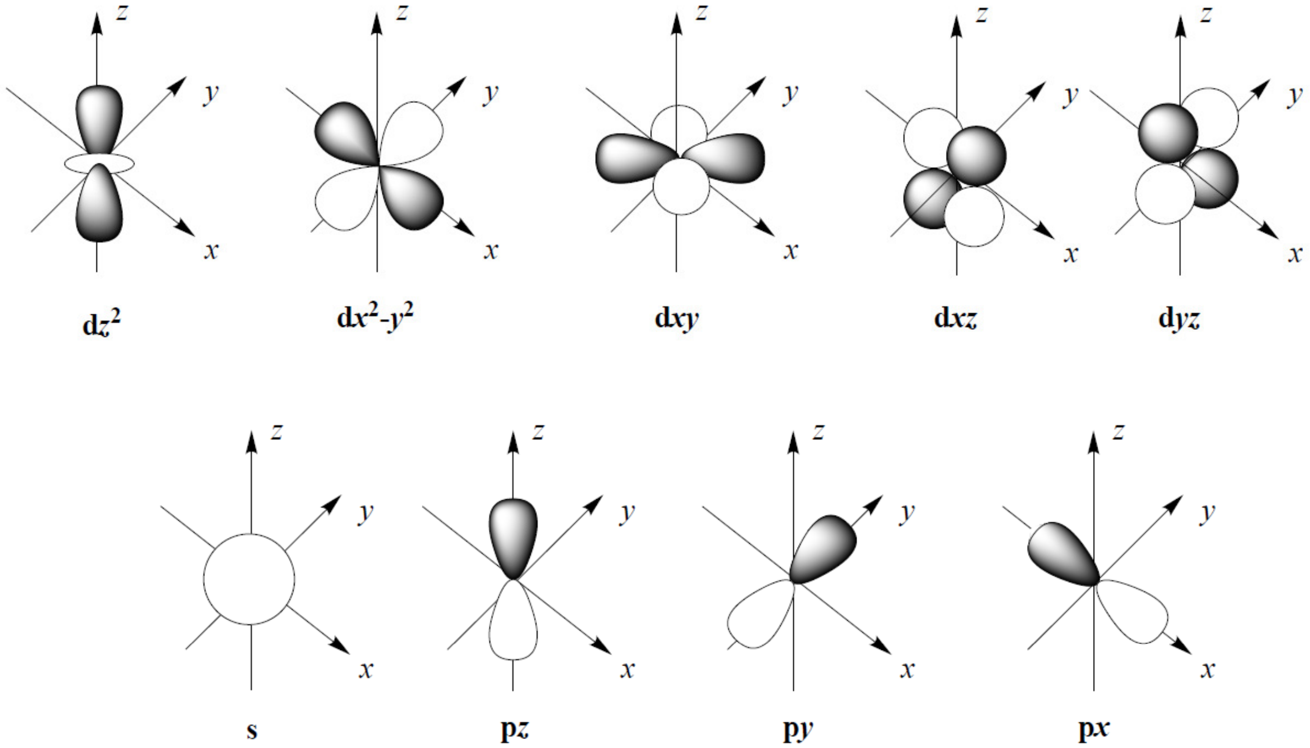


$3d^8$

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



$3d^6$



- 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

Geometry of Transition Metals

***Coordination Geometry* – arrangement of ligands around metal centre**

- Valence Shell Electron Pair Repulsion (VSEPR) theory is generally not applicable to transition metals complexes (ligands still repel each other as in VSEPR theory)

- For example, a different geometry would be expected for metals of different d electron count

$[V(OH_2)_6]^{3+}$ d^2

$[Mn(OH_2)_6]^{3+}$ d^4 } **all octahedral geometry !**

$[Co(OH_2)_6]^{3+}$ d^6

Coordination geometry is, *in most cases*, independent of ground state electronic configuration

- **Steric:** M-L bonds are arranged to have the maximum possible separation around the M.

- **Electronic:** d electron count combined with the complex electron count must be considered when predicting geometries for TM complexes with non-bonding d electrons
***e.g.* CN = 4, d^8 (16 e^-) prefers square planar geometry**

  d^{10} (18e^-) prefers tetrahedral geometry

Coordination number

Coordination Number **(CN)**

– the number of bonding groups at metal centre

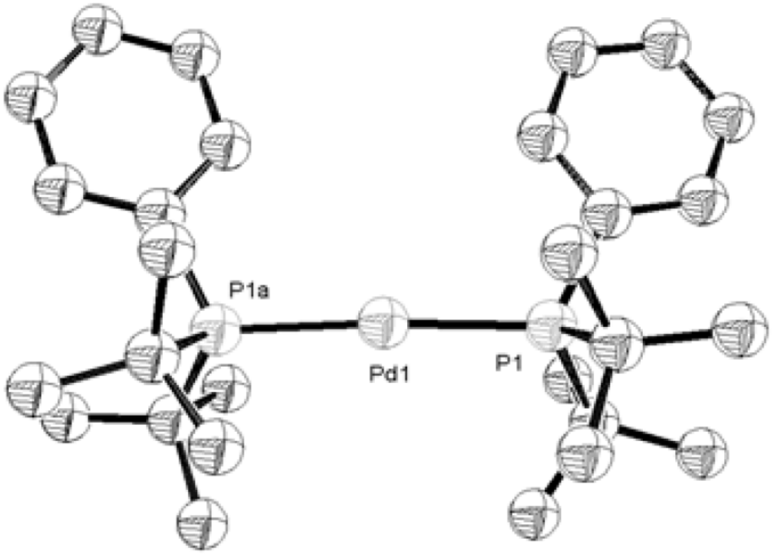
Influenced by:

- **Size** of the central atom
- **Steric** interactions between ligands
- **Electronic** interaction between the central atom & the ligands

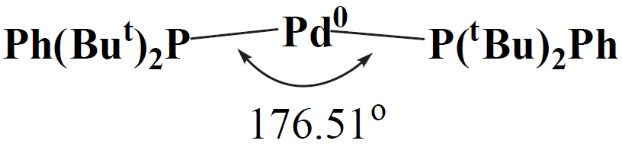
- ***Coordination Number* (CN) – the number of bonding groups at metal centre**
  - ***Low CN favored by:***

    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.



$$Ph(Bu^t)_2P—Pd^0—P(^tBu)_2Ph \quad 176.51^o$$

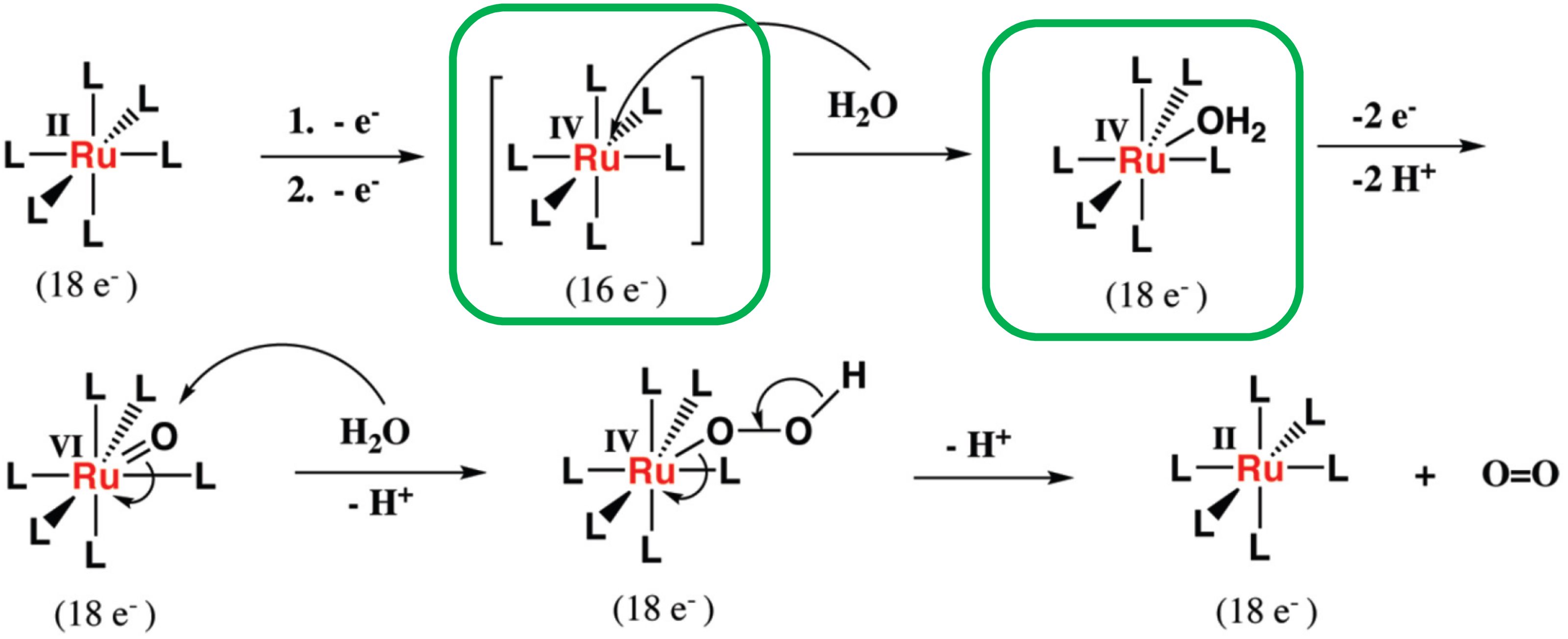
What is the d electron count for Pd?

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.

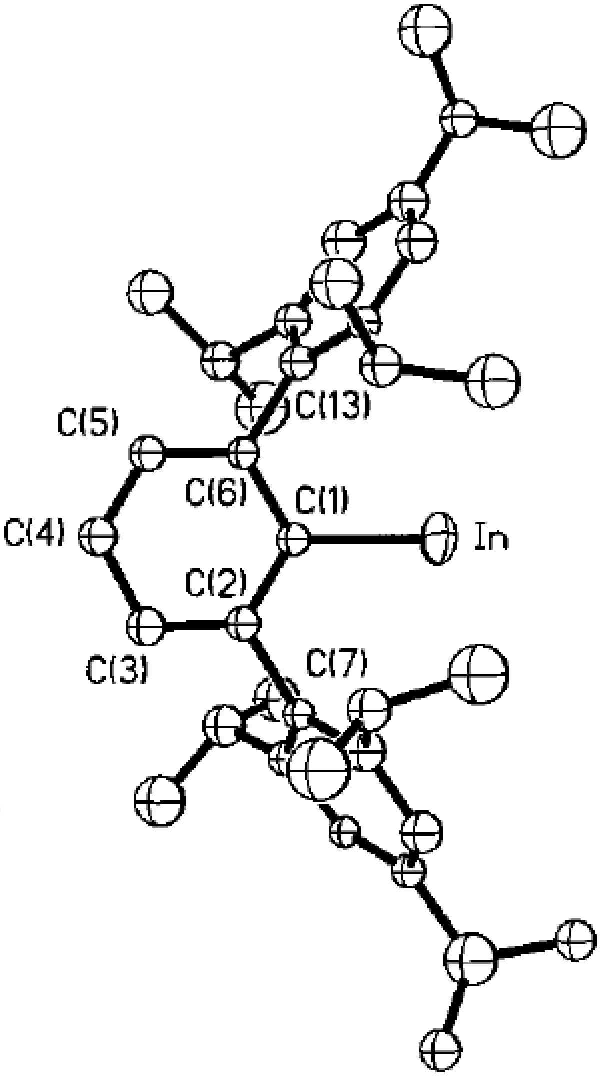
    2. Small ligands.



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

Muckerman & Thummel *Inorg. Chem.* 2008

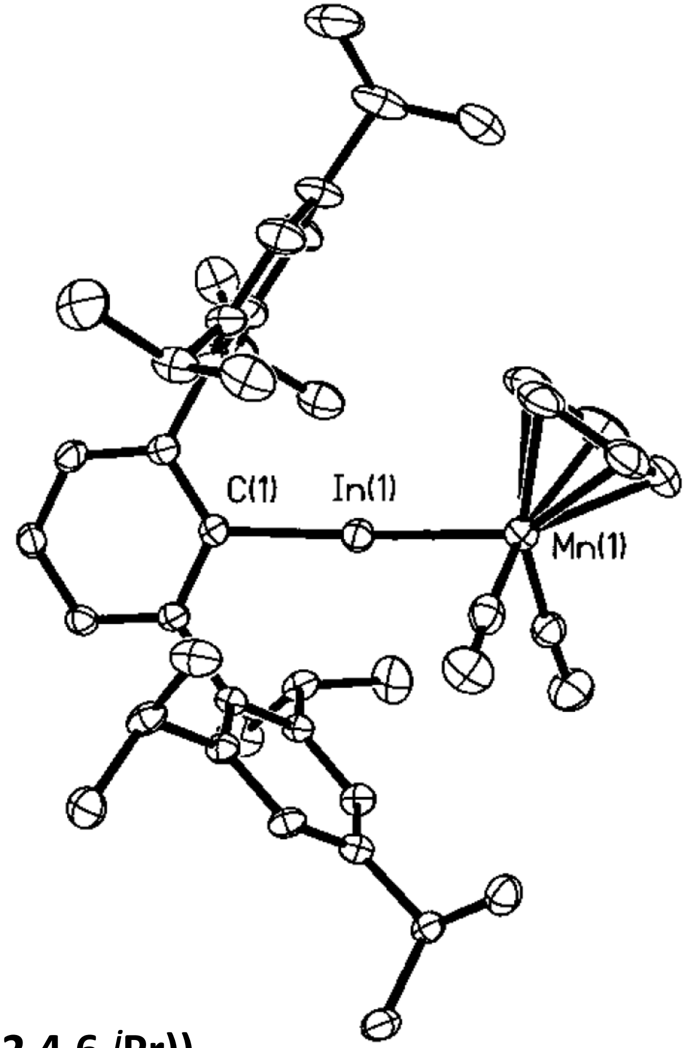
- **CN # 1**
  - Very rare



In(C_6H_3-2,6-(C_6H_2-2,4,6-^{i}Pr))

Haubrich S. T.; Power P. P. J. Am. Chem. Soc. **1998, 120, 2202-2203**

- **CN # 2**
  - Relatively rare



$(\eta^5\text{-Cp})(CO)_2MnIn(C_6H_3\text{-}2,6\text{-}(C_6H_2\text{-}2,4,6\text{-}^iPr))$

Oxidation state of Mn?

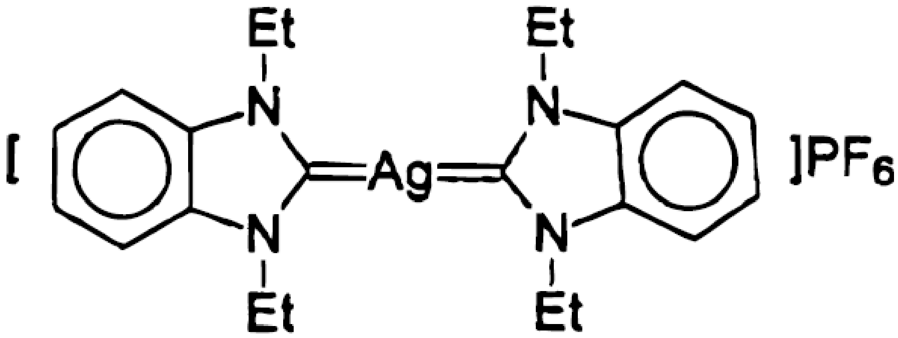
Do steric effects really play a part here?

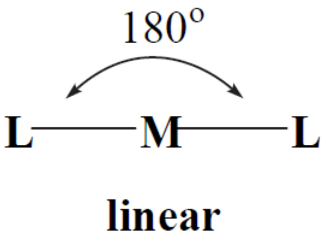
Haubrich S. T.; Power P. P. J. Am. Chem. Soc. **1998, 120, 2202-2203**

- **CN # 2 contd.**

  - Relatively rare, occurring mainly with +1 cations of Cu, Ag and Au
  - **Coordination geometry is linear**

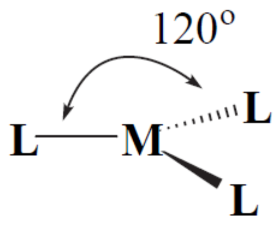
  e.g. $[H_3N\text{-}Ag\text{-}NH_3]^+$, $[NC\text{-}Ag\text{-}CN]^-$, $[Cl\text{-}Au\text{-}Cl]^-$



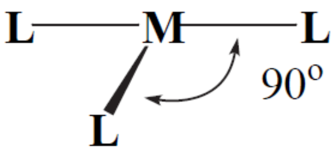


Oxidation state of Ag?

- **CN # 3**
  - CN of three is extremely rare
  - $[HgI_3]^-$, $K[Cu(CN)_2]$ in the solid state.
  - ions are arranged at the corner of a distorted triangle.



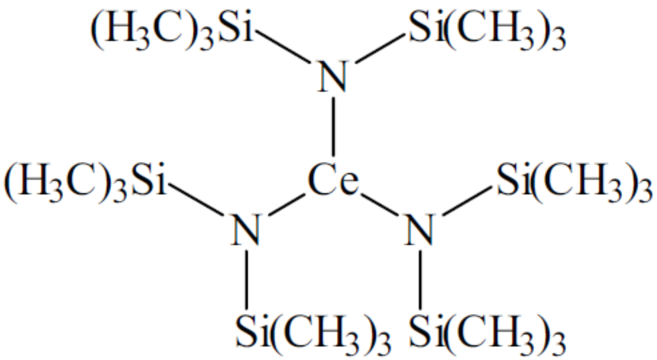
trigonal planar

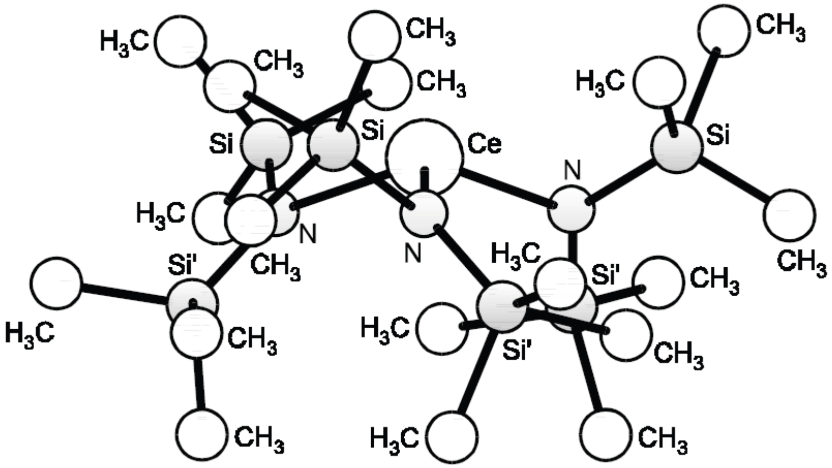


T-shaped

- **CN # 3 contd.**

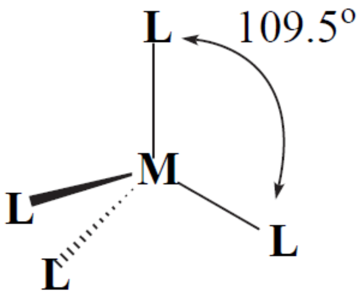
  - The use of the very ***bulky bis(trimethylsilylamido) ligand*** has allowed the characterization of Ce(III) in the coordination number 3.



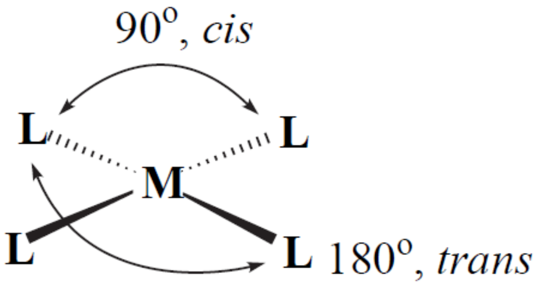


- **CN # 4**

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



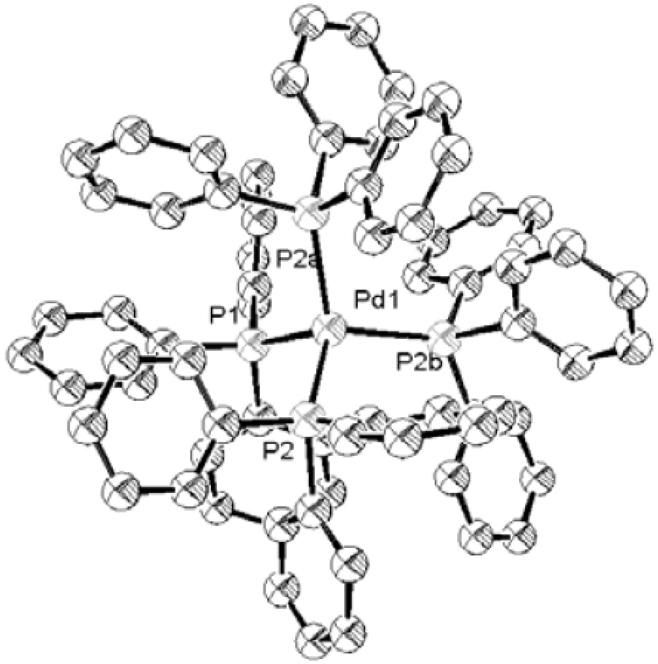
tetrahedral

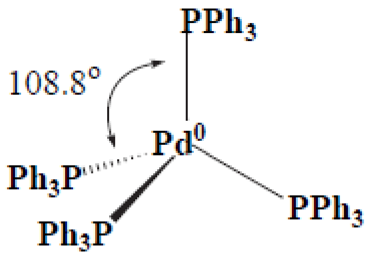


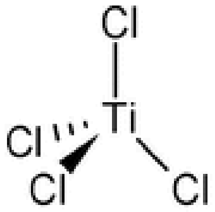
square planar

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}





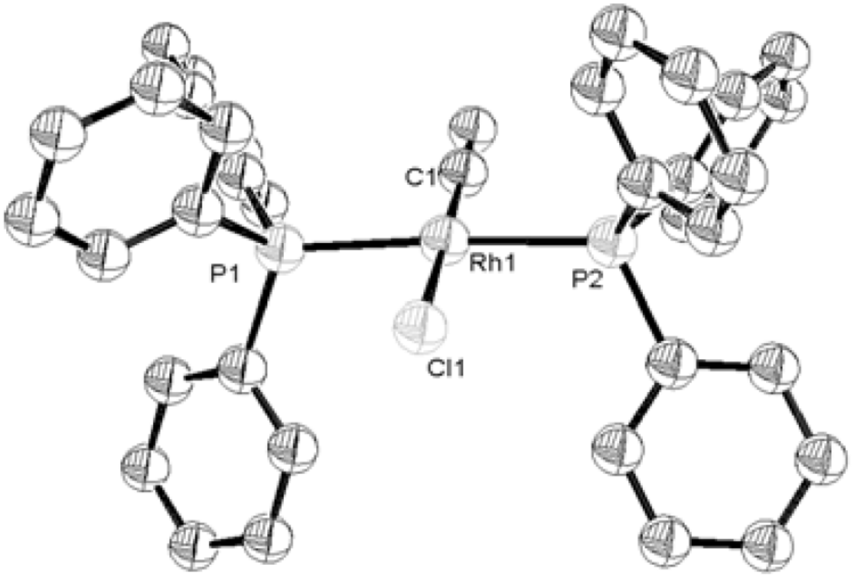


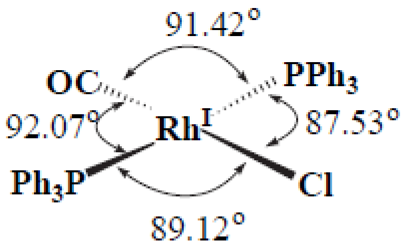
Oxidation state of Ti?

- **CN # 4 contd.**

  - ➢ d^8 electron configuration usually leads to square planar geometries

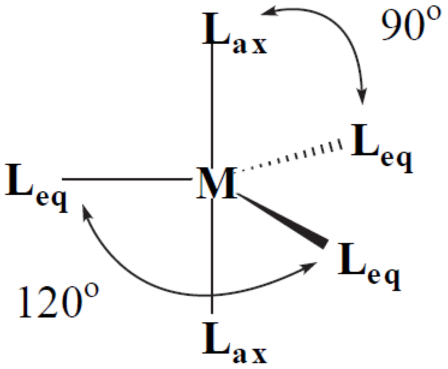
    (as only one d-orbital required for forming the 4 metal ligand s-bonds)



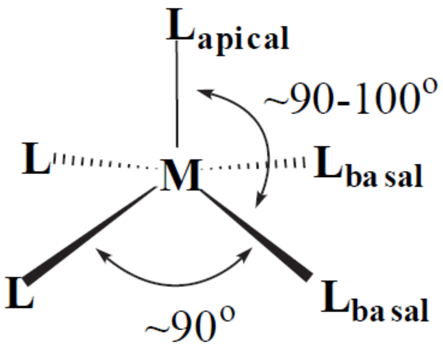


- **CN # 5**

  - Trigonal bipyramidal and square pyramidal exist



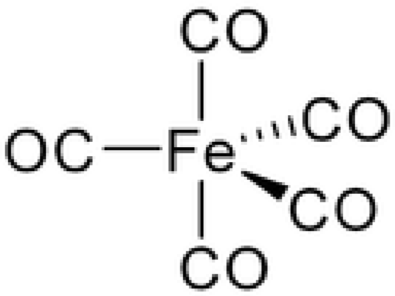
trigonal bipyramidal



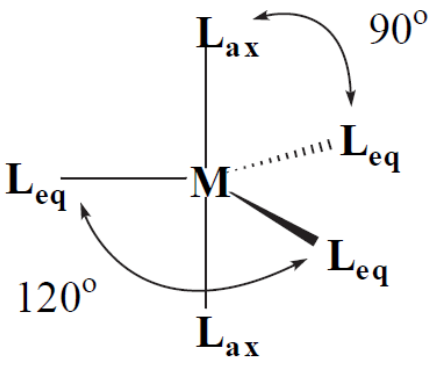
square pyramidal

  - This geometry is less common than 4 and 6.

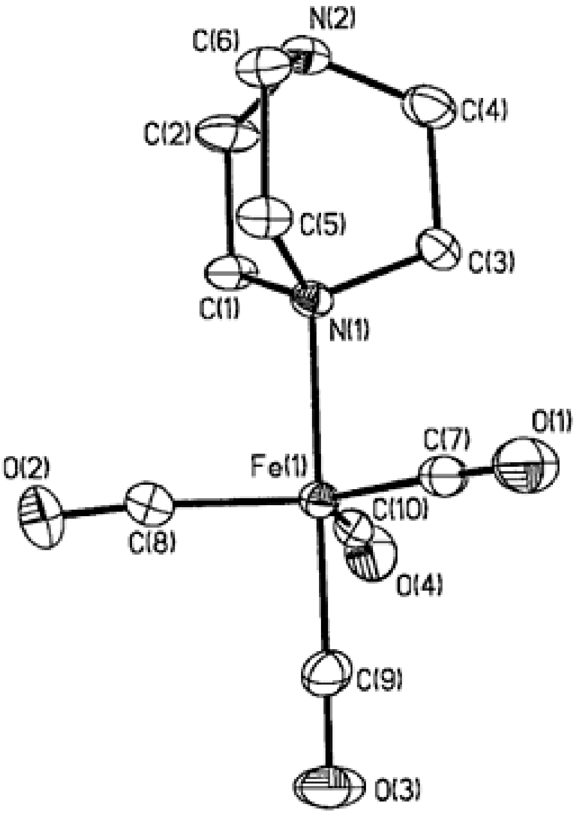
- **CN # 5 contd.**



Iron pentacarbonyl
very toxic !!!



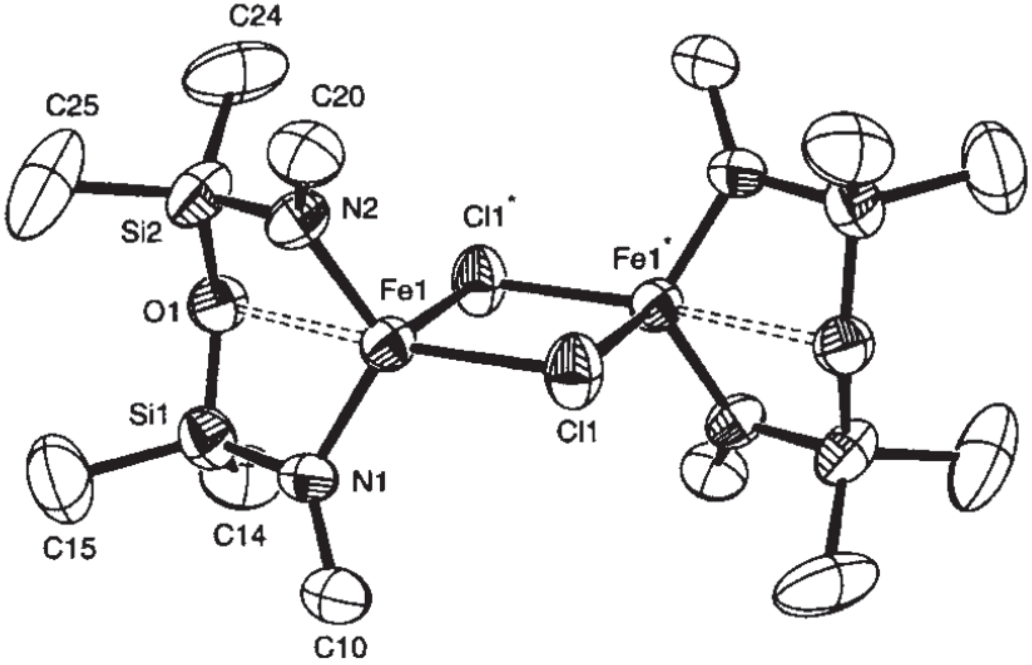
trigonal bipyramidal



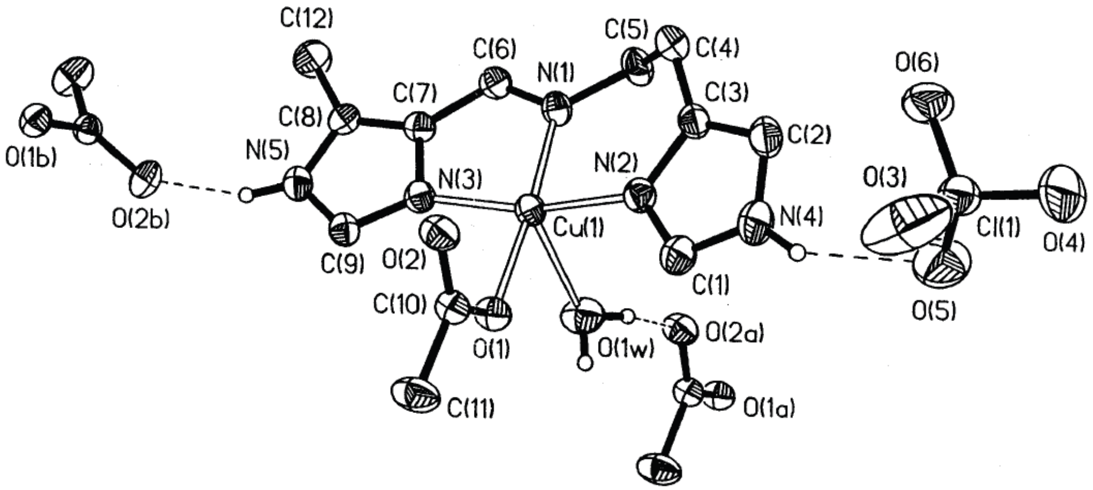
(DABCO)Fe(CO)$_4$
[DABCO = 1,4-diazabicyclo[2.2.2]octane]

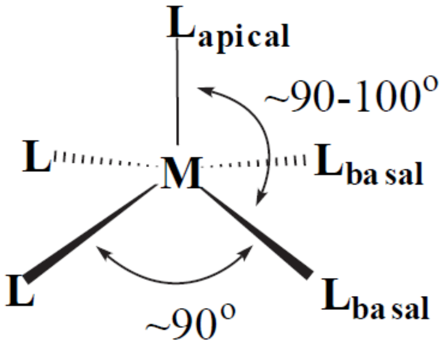
- **CN # 5 contd.**

  - **$\{FeCl[^tBuN(SiMe_2)]_2O\}_2$**



- **CN # 5 contd.**
  - Square pyramidal is less common



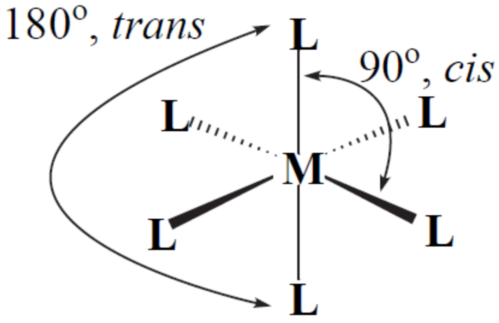


square pyramidal

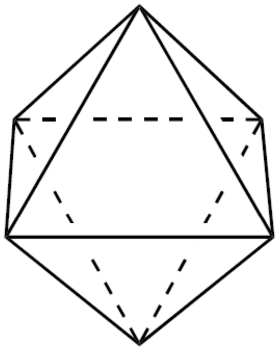
{acetatoaqua[[(4-methylimidazol-5-yl)methylene]histamine]-copper(II)} perchlorate

- **CN # 6**

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



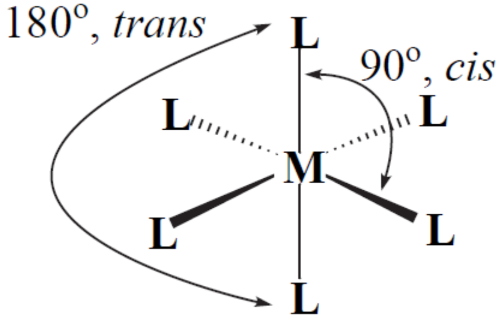
octahedral



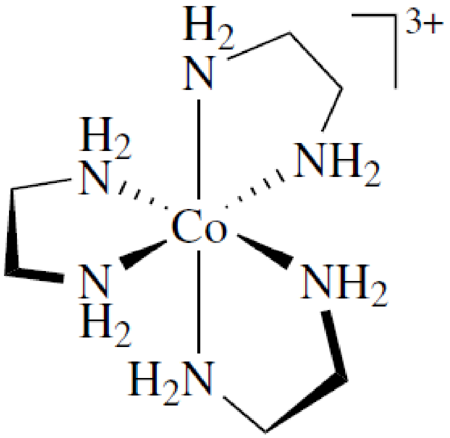
Octahedron

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.

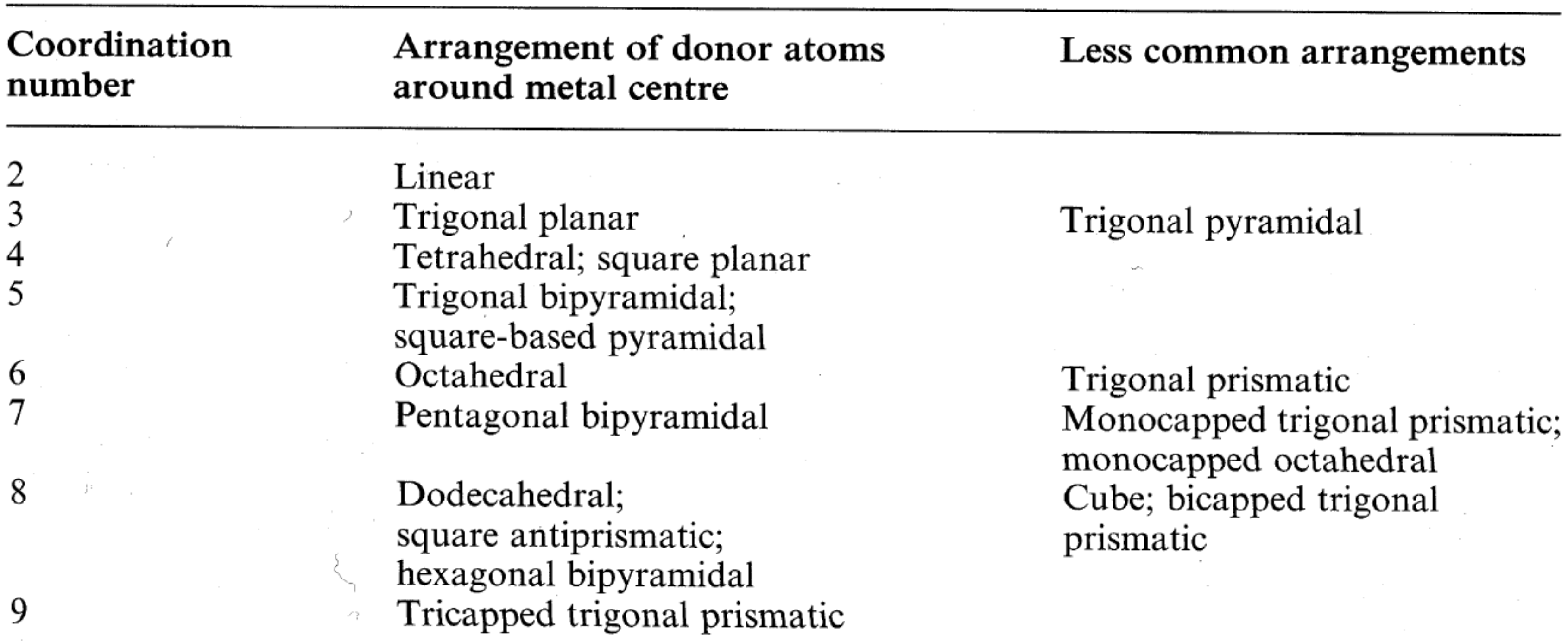
- **CN # 6**
  - Octahedral



octahedral



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

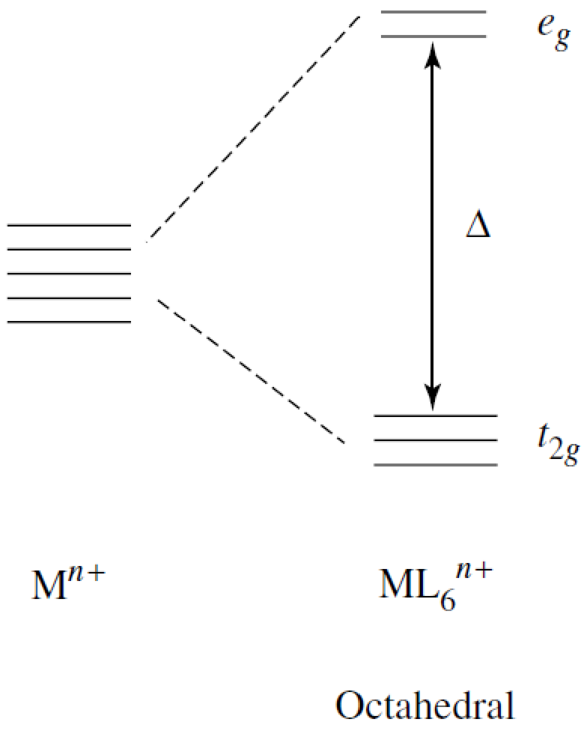


Coordination number	Arrangement of donor atoms around metal centre	Less common arrangements
2	Linear	
3	Trigonal planar	Trigonal pyramidal
4	Tetrahedral; square planar	
5	Trigonal bipyramidal; square-based pyramidal	
6	Octahedral	Trigonal prismatic
7	Pentagonal bipyramidal	Monocapped trigonal prismatic; monocapped octahedral
8	Dodecahedral; square antiprismatic; hexagonal bipyramidal	Cube; bicapped trigonal prismatic
9	Tricapped trigonal prismatic	

Correlation of *coordination number* and *coordination geometry* for transition metal complexes.

Crystal Field Theory

Describes how the *d orbitals of the transition metal are affected by the presence* of coordinating ligands.



- Imagine the metal ion isolated in space, then the d orbitals are degenerate.
- As the ligands approach the metal from the six octahedral directions ±x, ±y, and ±z, the ***degeneracy is broken***
- The d orbitals that point toward the L groups (dx2−y2 and dz2) are destabilized by the negative charge of the ligands and move to higher energy.
- Those that point away from L (dxy, dyz, and dxz) are less destabilized.
- The ***crystal field splitting energy*** (Δ - sometimes labeled 10Dq) depends on the value of the effective negative charge and therefore on the nature of the ligands.
- Higher Δ leads to stronger M−L bonds.

Spectrochemical series

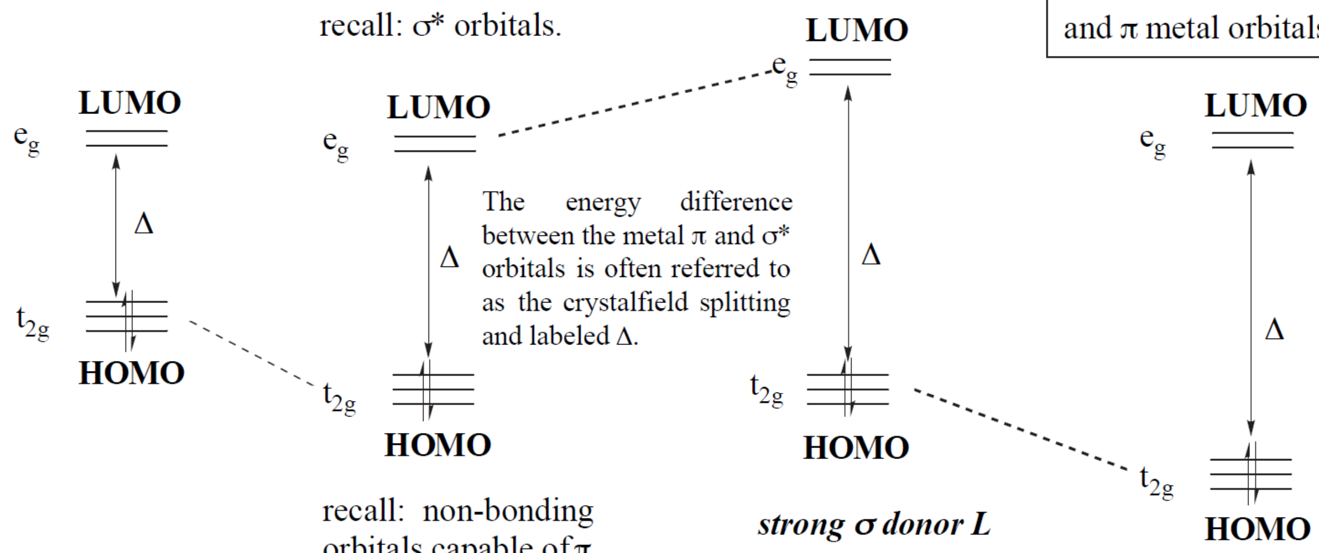
strong π donor ligand

Ligand to metal π donation increases the energy of the HOMO, making Δ smaller.

strong π acceptor L

π-backbonding lowers the energy of the HOMO and thus increases the energy difference Δ between the σ* and π metal orbitals.

recall: σ* orbitals.



The energy difference between the metal π and σ* orbitals is often referred to as the crystalfield splitting and labeled Δ.

recall: non-bonding orbitals capable of π bonding

strong σ donor L

Strong σ bonding orbitals are low in energy and have antibonding σ* orbitals that are proportionally high in energy .

Spectrochemical series The colors of TM complexes often arrise from the absorption of visible light that corresponds to the energy gap Δ. Electronic spectra (UV-vis) can often be used to measure Δ directly.

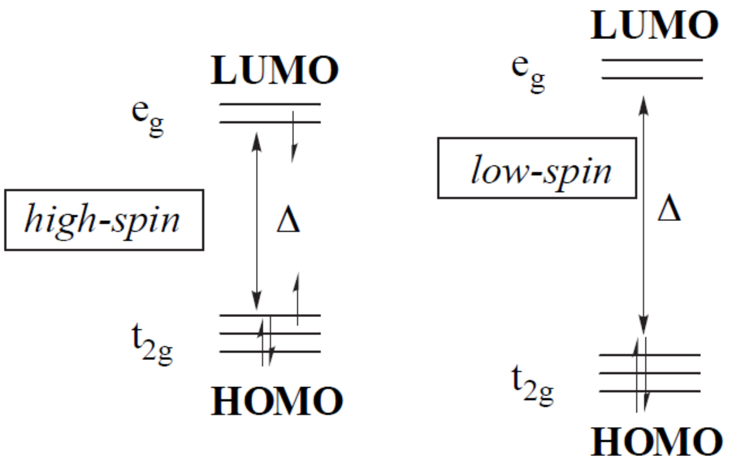
$\mathbf{I^- < Br^- < Cl^- < N_3^-, F^- < OH^- < O_2^- < H_2O < NCS^- < py, NH_3 < en < bpy, phen < NO_2^- < CH_3^-, C_6H_5^- < CN^- < CO, H^-}$

← π-donor
low Δ
"low field ligand"

π-acceptor/strong σ-donor →
high Δ
"high field ligand"

High spin *vs.* low spin electron configuration

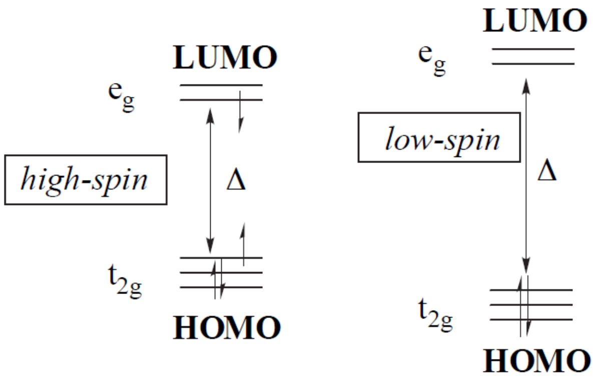
- If **Δ** is low enough, electrons may rearrange to give a "high spin" configuration to reduce electron- electron repulsion that happens when they are paired up in the same orbital.
- In 1st row metals complexes, low-field ligands (strong π - donors) favor high spin configurations whereas high field ligands (π-acceptors/ strong σ donors) favor low spin.
- The majority of 2nd and 3rd row metal complexes are low-spin irrespective of their ligands.



strong π donor L

strong σ donor L/ π-acceptor L

- **Low-oxidation state complexes also tend to have lower Δ than high-oxidation state complexes.**
- **High oxidation state→ increased χ →increased Δ → high-spin configuration**



strong π donor L

strong σ donor L/
π-acceptor L

$$\mathrm{Mn^{2+} < V^{2+} < Co^{2+} < Fe^{2+} < Ni^{2+} < Fe^{3+} < Co^{3+} < Mn^{4+} < Rh^{3+} < Ir^{3+} < Pt^{4+}}$$

← 1st row/low-valent
low Δ

2nd,3rd row/high-valent →
high Δ

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:

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

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

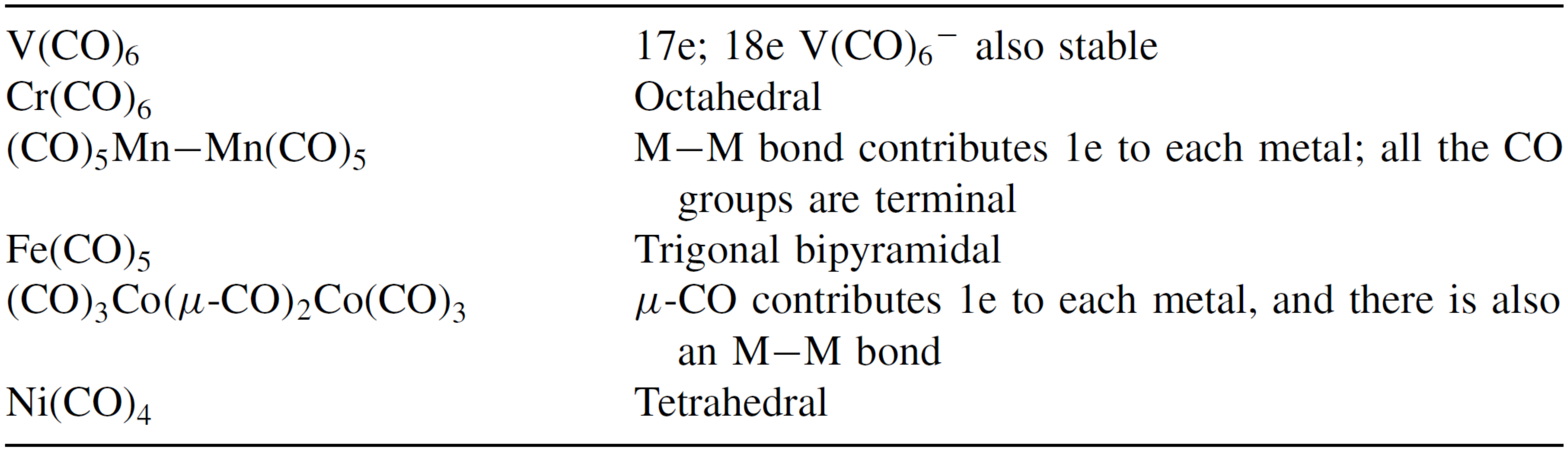
- An octet is appropriate for carbon, where one 2s and three 2p orbitals make up the valence shell; 8e⁻ fill four orbitals.
- Transition metal complexes follow the 18 electron rule, appropriate for an atom having 9 valence orbitals,

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

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

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

- First row transition metal carbonyls mostly obey the 18VE rule:
- Each metal contributes the same number of electrons as its group number.
- Odd electron metals attain 18 valence electrons through formation of M–M (Mn) bonds or through reduction.



$V(CO)_6$	17e; 18e $V(CO)_6^-$ also stable
$Cr(CO)_6$	Octahedral
$(CO)_5Mn{-}Mn(CO)_5$	M–M bond contributes 1e to each metal; all the CO groups are terminal
$Fe(CO)_5$	Trigonal bipyramidal
$(CO)_3Co(\mu\text{-}CO)_2Co(CO)_3$	μ-CO contributes 1e to each metal, and there is also an M–M bond
$Ni(CO)_4$	Tetrahedral

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).

- **Consider the case of carbon tetrachloride CCl_4**

- ***covalent model:***

$$C + 4Cl = CCl_4$$

$$(4 \text{ valence } e^-) + [4 \times (1 \text{ valence bonding } e^-)] = 8e^-$$

- ***ionic model:***

$$C^{4+} + 4Cl^- = CCl_4$$

$$(0 \text{ valence } e^-) + [4 \times (2 \text{ valence bonding } e^-)] = 8e^-$$

- **Now consider the case of the metal hydride complex $Mn(CO)_5H$**

- ***covalent model:***

$$Mn + 5CO + H = Mn(CO)_5H$$

(7 valence e^-) + [5 x (2 valence bonding e^-)] + (1 valence e^-) = $18e^-$

- ***ionic model:***

$$Mn^+ + 5CO + H^- = Mn(CO)_5H$$

(6 valence e^-) + [5 x (2 valence e^-)] + (2 valence e^-) = $8e^-$

- **Multidentate *or chelating* ligands can contribute multiple e-pairs:**

➢ Monodentate:	pyridine	$2e^-$
➢ Bidentate:	2,2’-bipyridine	$4e^-$
➢ Monodentate:	PPh_3	$2e^-$
➢ Bidentate :	dppe	$4e^-$

- **Bridging ligands contribute equally to both metals:**

➢ Bridging	4,4’-bipyridine	2 x $2e^-$
➢ Terminal CO:	CO	$2e^-$
Singly bridging CO:	μ^2-CO	2 x $1e^-$
➢ Terminal O_2	O_2	$4e^-$
Bridging O_2	μ^2-O_2	2 x $2e^-$

** Side-on CO can act as $4e^-$ or even $6e^-$ donor*

** Bridging halides act as 4e donors (2 x $2e^-$)*

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

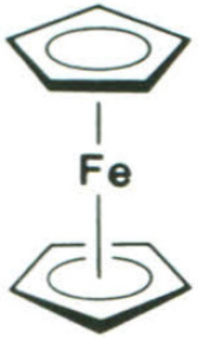
1. The intramolecular partitioning of the electrons has to ensure that the total charge of the complex remains unchanged *(ionic or covalent model).*

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.**

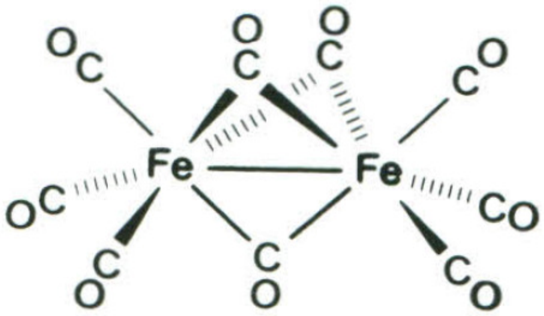
Decacarbonyldimanganese $Mn_2(CO)_{10}$

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*