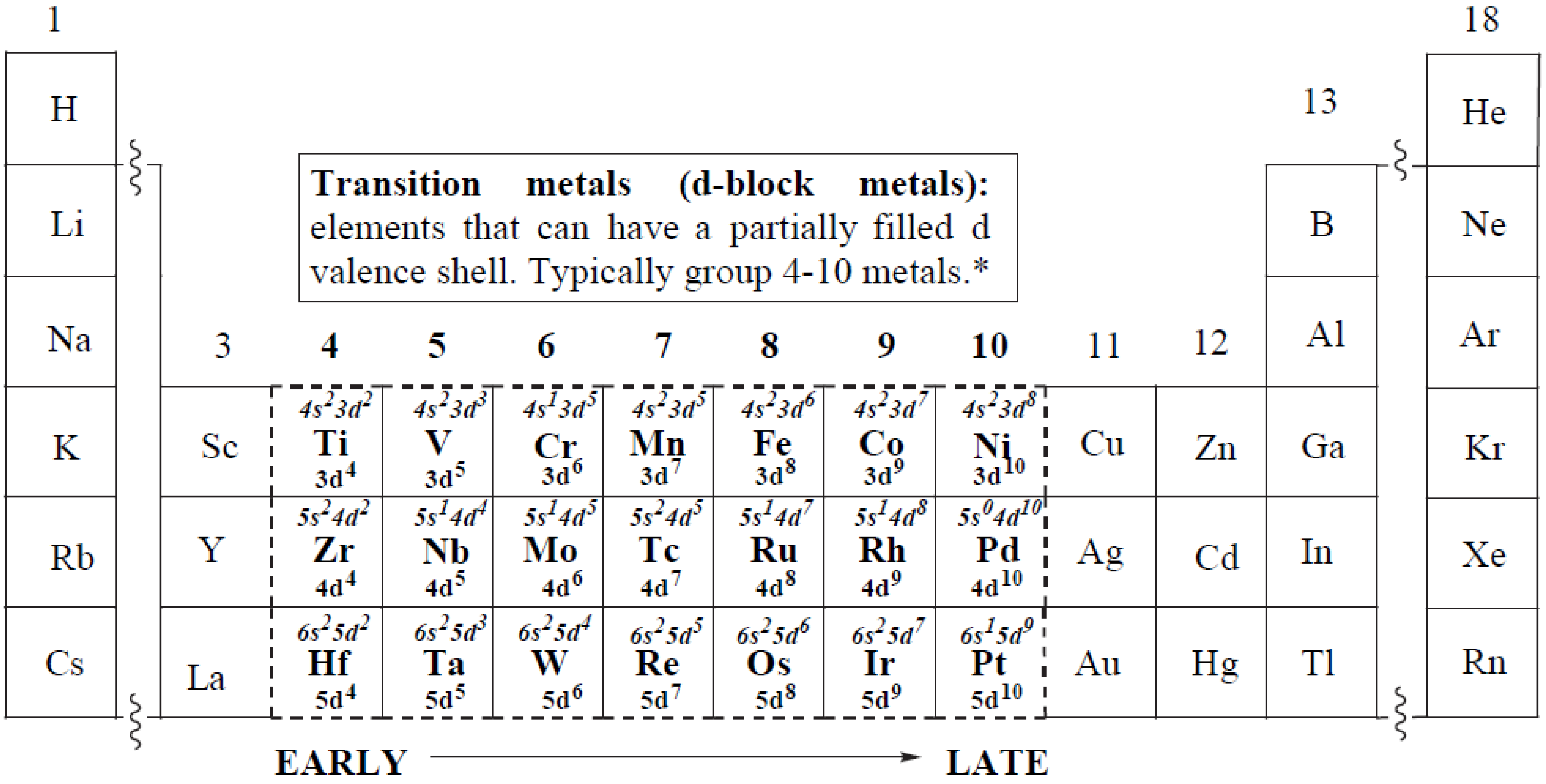
The Transition Metals



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

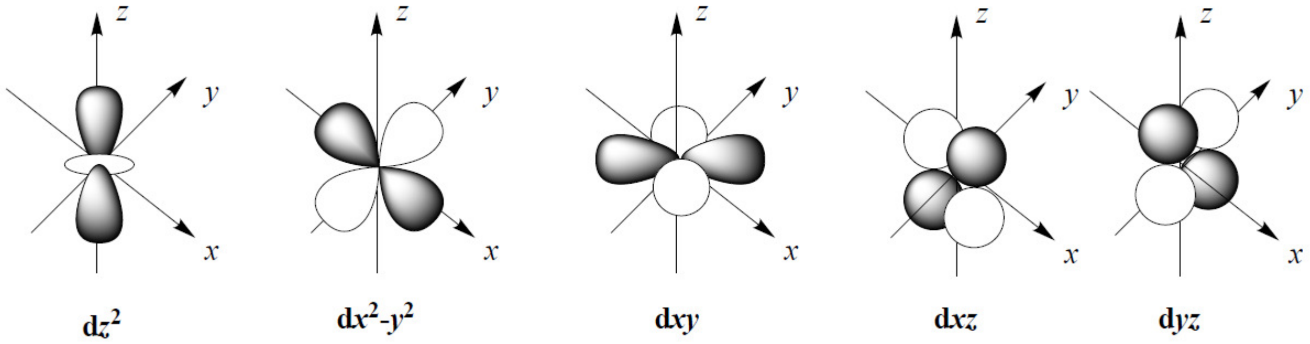
1	3	4	5	6	7	8	9	10	11	12	13	18
H												He
Li											B	Ne
Na											Al	Ar
K	Sc	$4s^2 3d^2$ **Ti** $3d^4$	$4s^2 3d^3$ **V** $3d^5$	$4s^1 3d^5$ **Cr** $3d^6$	$4s^2 3d^5$ **Mn** $3d^7$	$4s^2 3d^6$ **Fe** $3d^8$	$4s^2 3d^7$ **Co** $3d^9$	$4s^2 3d^8$ **Ni** $3d^{10}$	Cu	Zn	Ga	Kr
Rb	Y	$5s^2 4d^2$ **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**

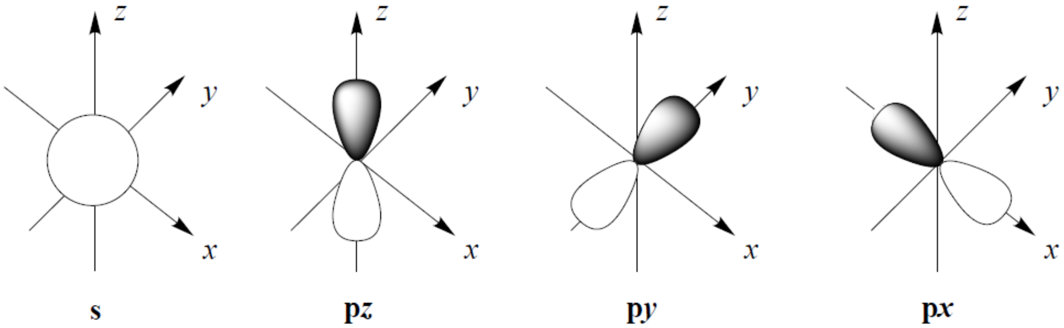
- **d electrons in group 3 are readily removed *via ionization*.**
- **d electrons in group 11 are stable and generally form part of the core electron configuration.**

Transition Metal Valence Orbitals

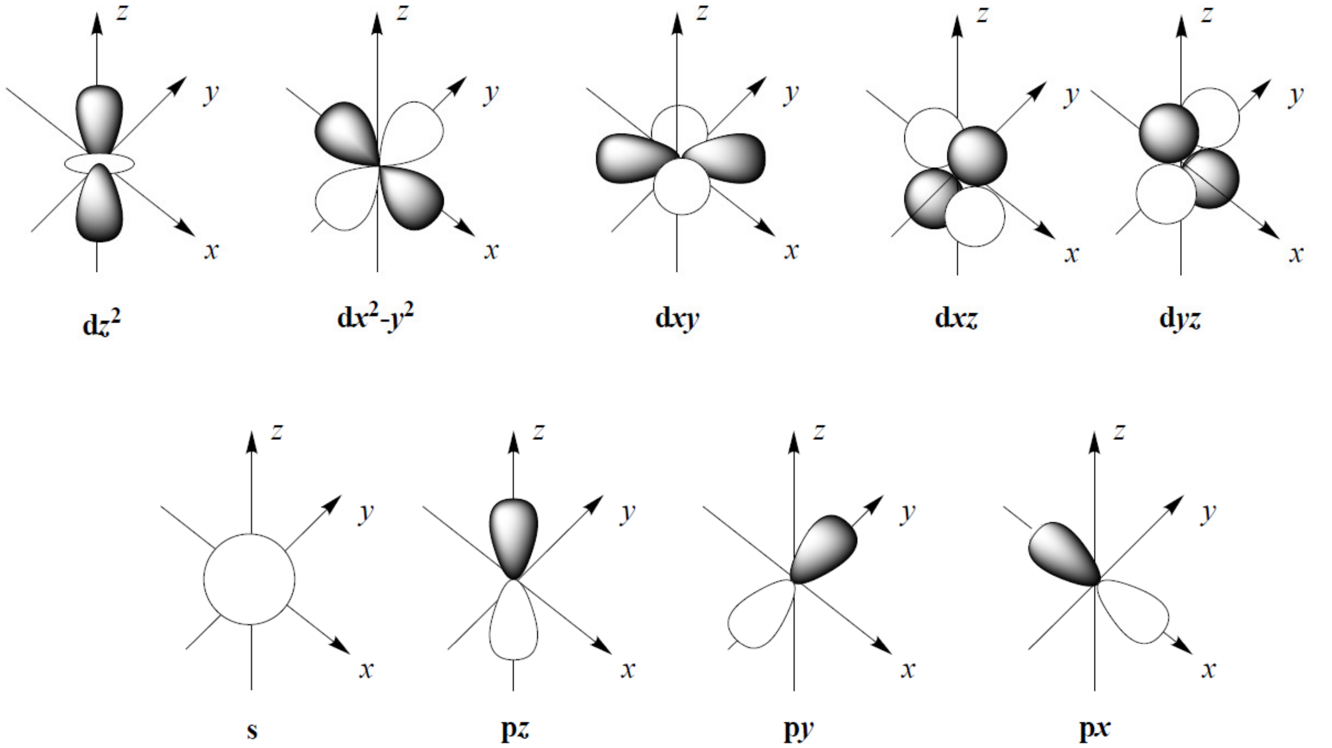
- ***n*d orbitals**



- **(*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**



- orbitals oriented orthogonal wrt each other creating unique possibilities for ligand overlap.

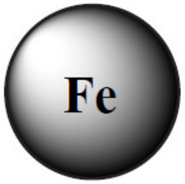
- Total of ***9 valence orbitals available*** for bonding (2 x 9 = 18 valence electrons!)

- For an σ bonding only O_h complex, ***6 σ bonds*** are formed and the remaining d orbitals are *non-bonding*.

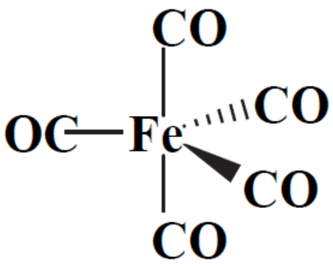
- It's these non-bonding d orbitals that give TM complexes many of their unique properties

- 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)

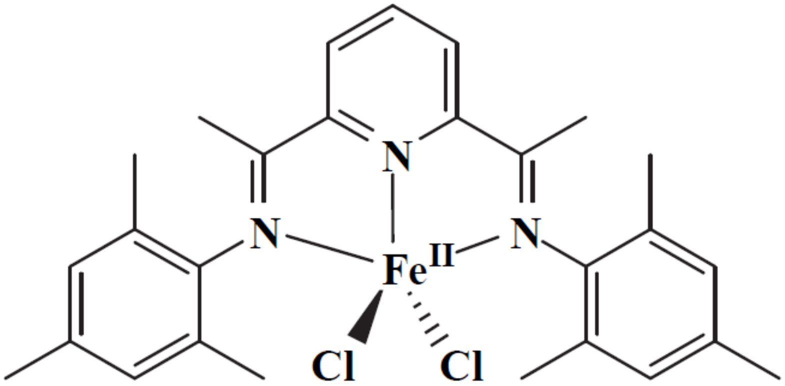


$4s^2 3d^6$



$3d^8$

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



$3d^6$

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

$$\left.\begin{array}{l} [V(OH_2)_6]^{3+}\ d^2 \\ [Mn(OH_2)_6]^{3+}\ d^4 \\ [Co(OH_2)_6]^{3+}\ d^6 \end{array}\right\}$$

all octahedral geometry !

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

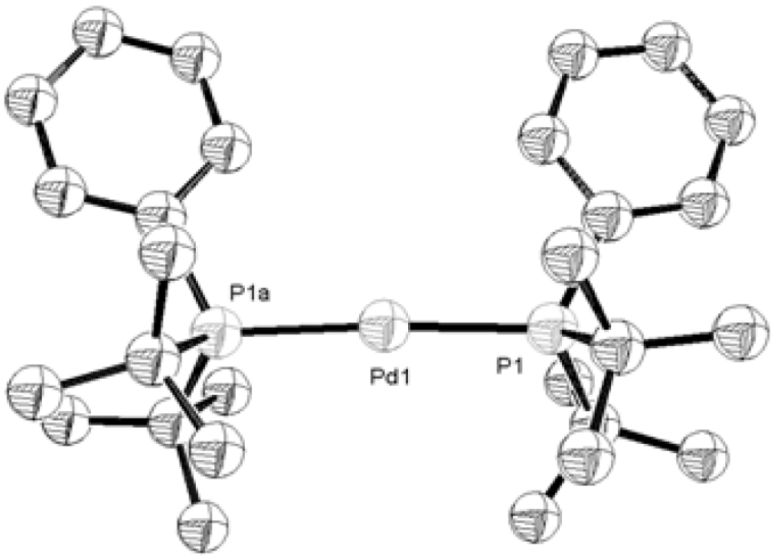
Influenced by:

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

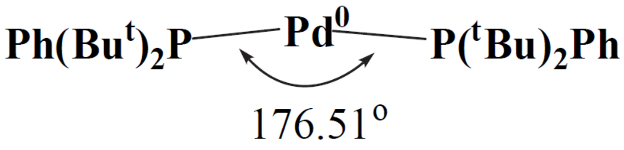
- ***Coordination Number*** **(CN) – the number of bonding groups at metal centre**
  - ***Low CN favored by:***

    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—$P(^tBu)_2Ph$

176.51°

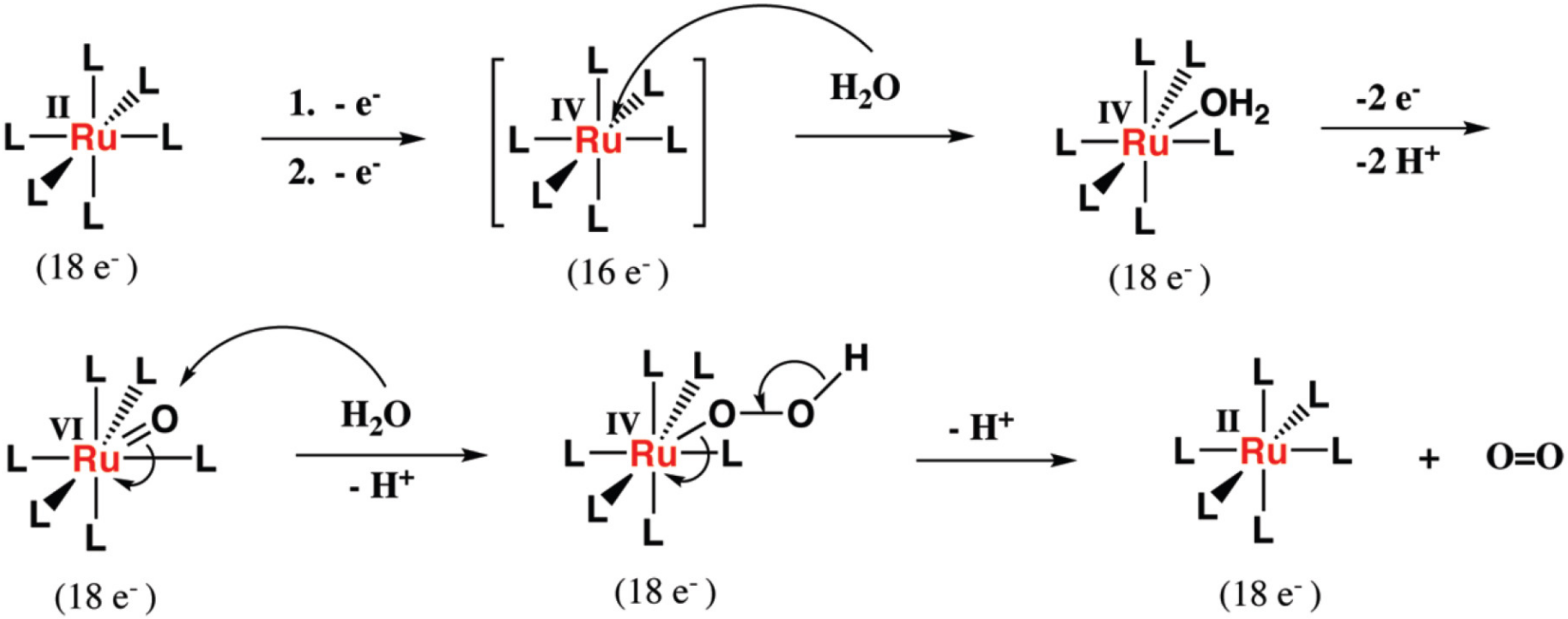
What is the d electron count for Pd?

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

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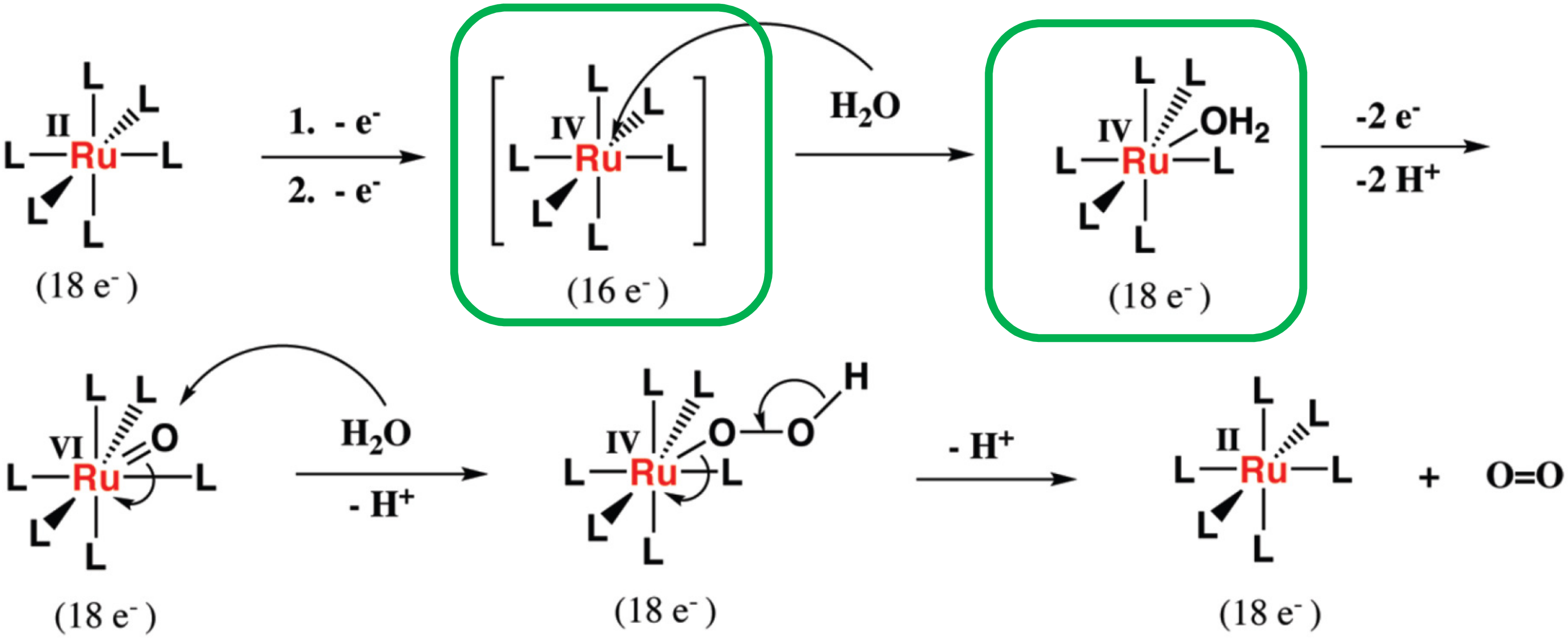
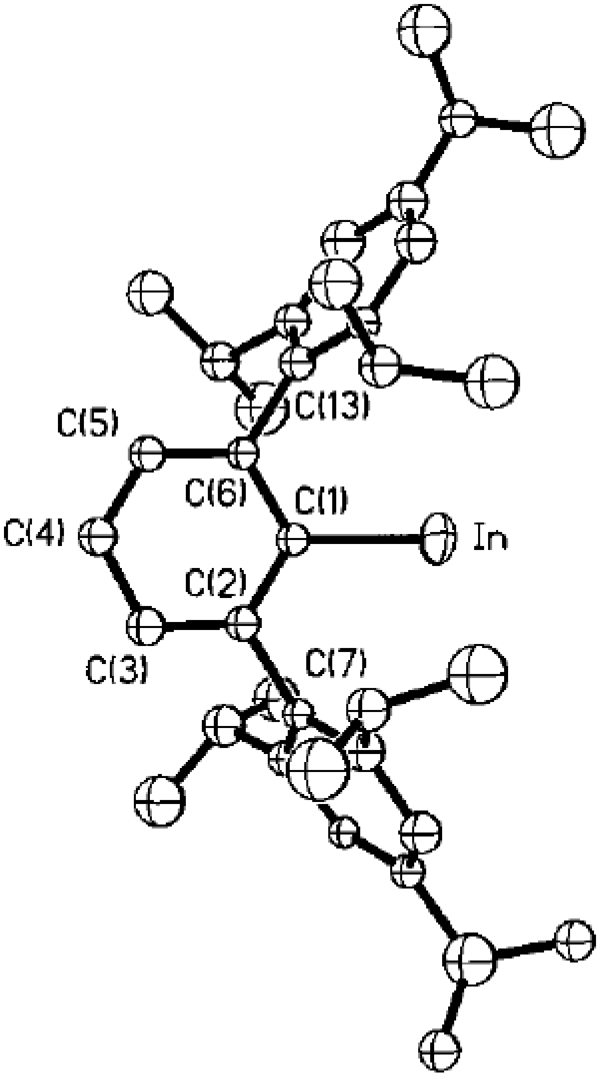


Water oxidation by mononuclear Ru complex involving a 7 coordinate Ru(IV) species.

Muckerman & Thummel *Inorg. Chem.* 2008

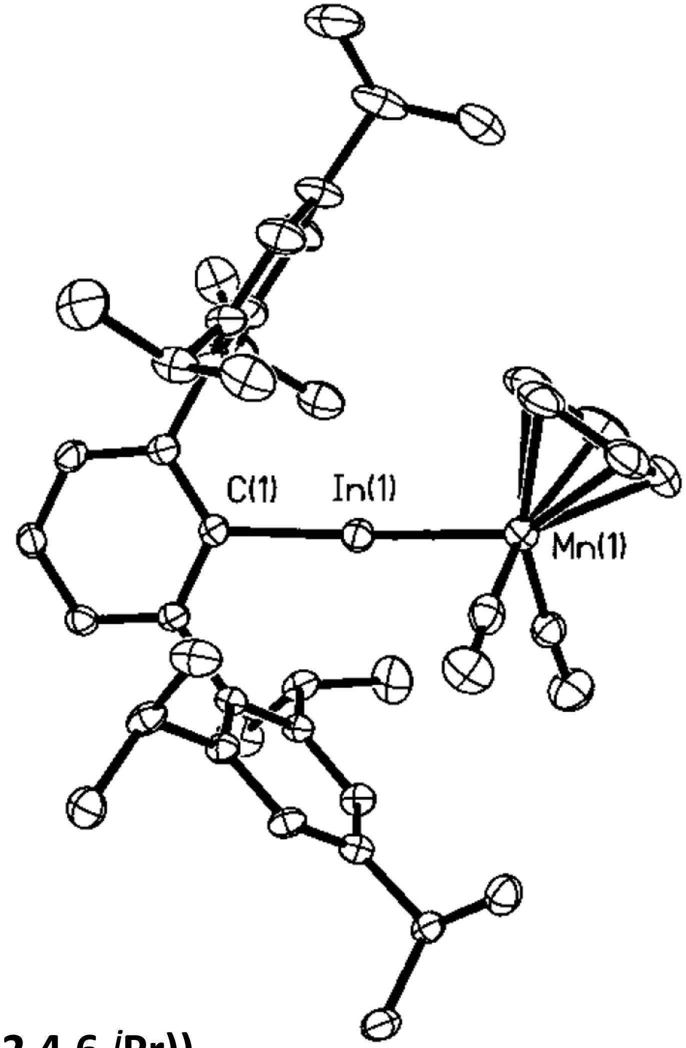
- **CN # 1**
  - Very rare



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



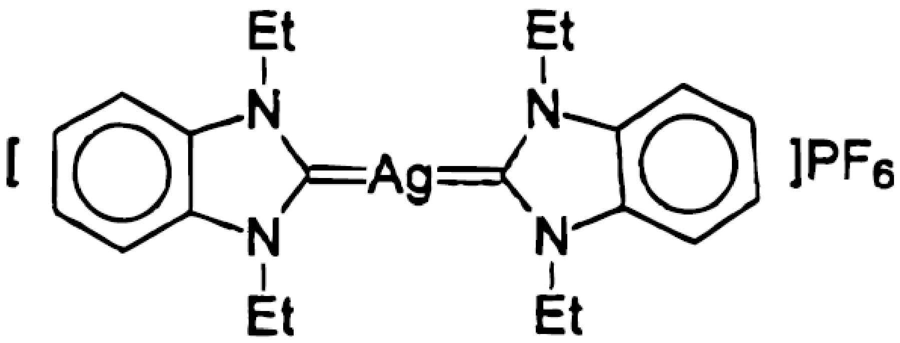
(η^5-Cp)(CO)$_2$MnIn(C$_6$H$_3$-2,6-(C$_6$H$_2$-2,4,6-^{i}Pr))

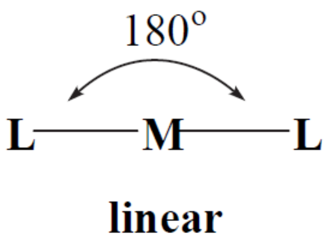
Haubrich S. T.; Power P. P. J. Am. Chem. Soc. **1998, 120, 2202-2203**

- **CN # 2 contd.**

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

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

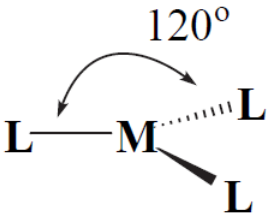




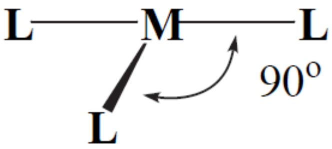
Oxidation state of Ag?

- **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.



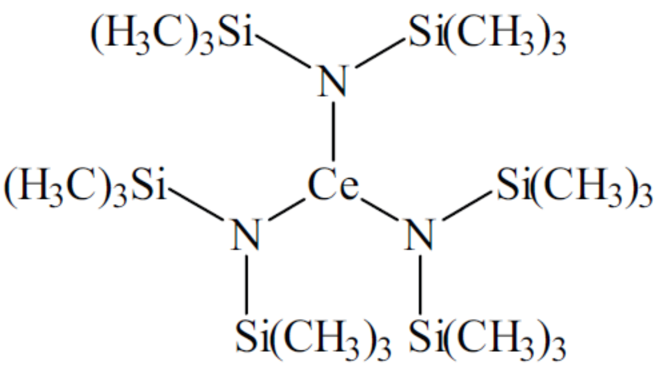
trigonal planar

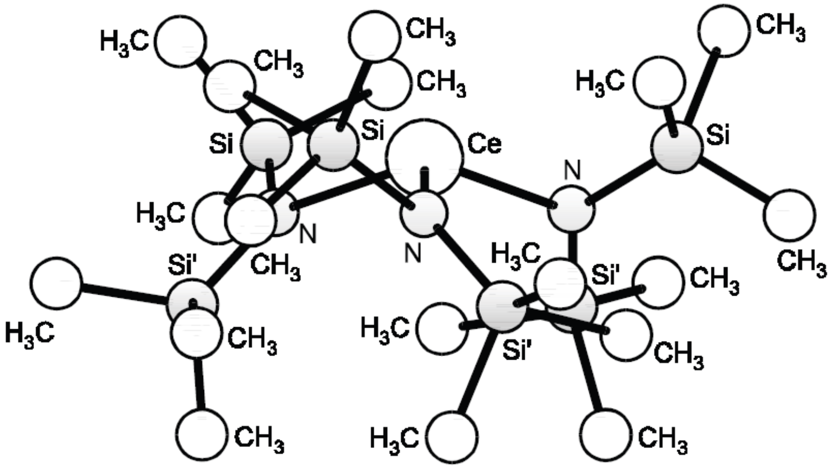


T-shaped

- **CN # 3 contd.**

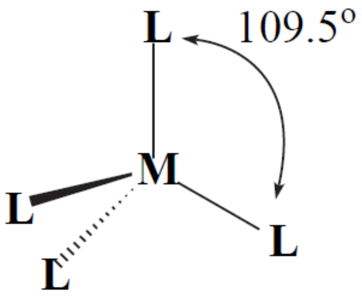
  - The use of the very ***bulky bis(trimethylsilylamido) ligand*** has allowed the characterization of Ce(III) in the coordination number 3.



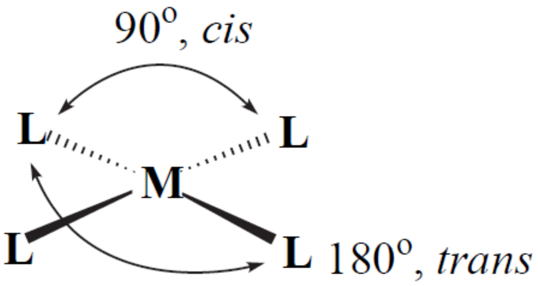


- **CN # 4**

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



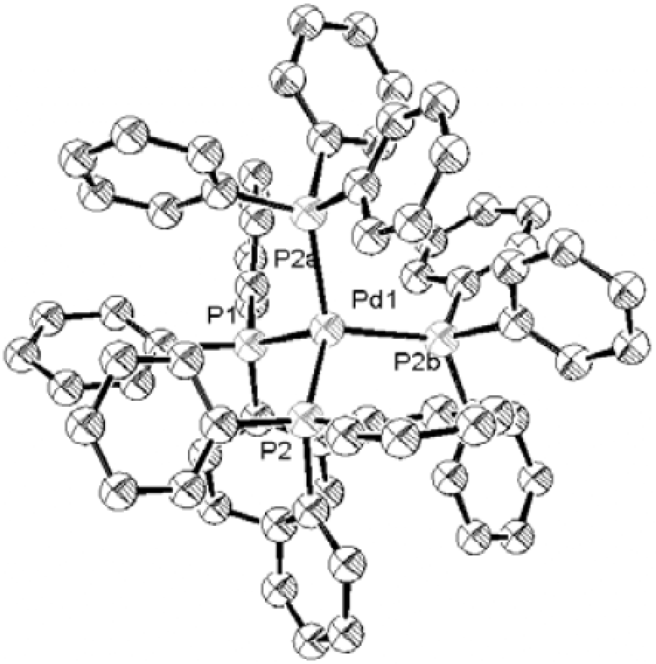
tetrahedral

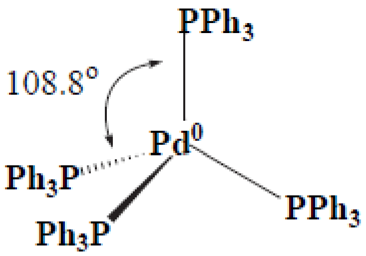


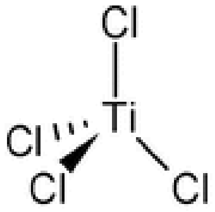
square planar

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}

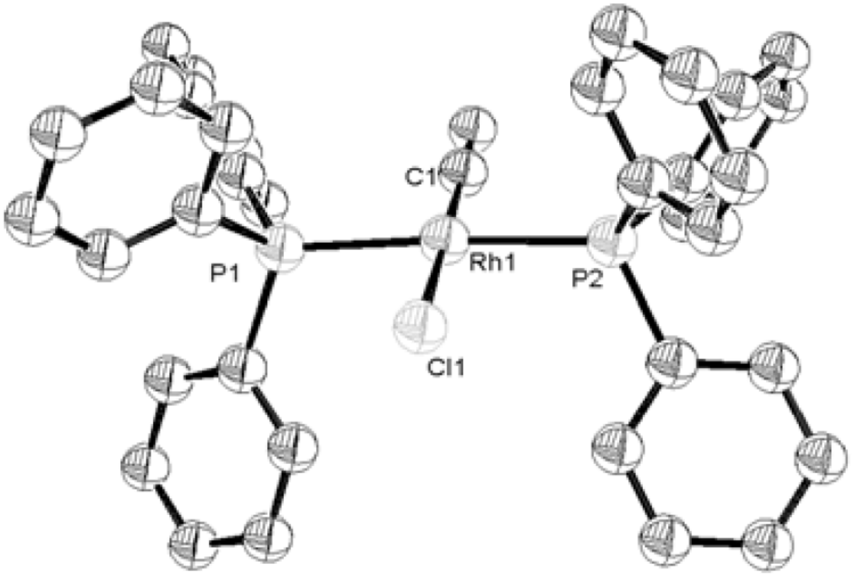


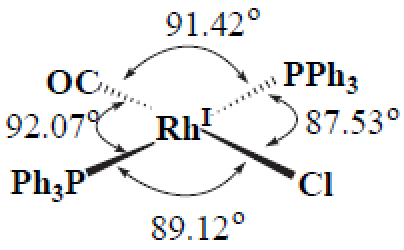




Oxidation state of Ti?

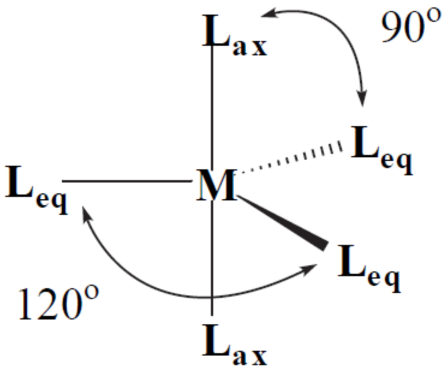
- **CN # 4 contd.**
  - ➢ d^8 electron configuration usually leads to square planar geometries (as only one d-orbital required for forming the 4 metal ligand s-bonds)



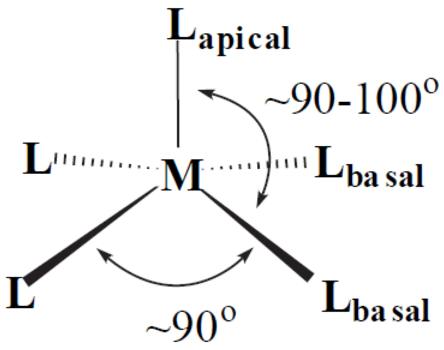


- **CN # 5**

  ➢ Trigonal bipyramidal and square pyramidal exist



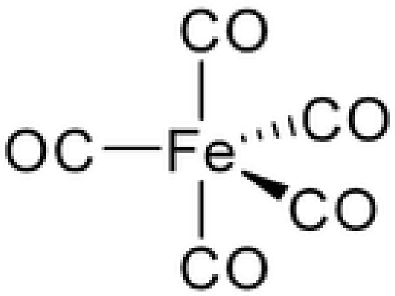
trigonal bipyramidal



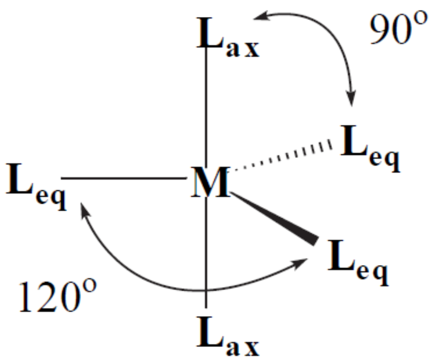
square pyramidal

  ➢ This geometry is less common than 4 and 6.

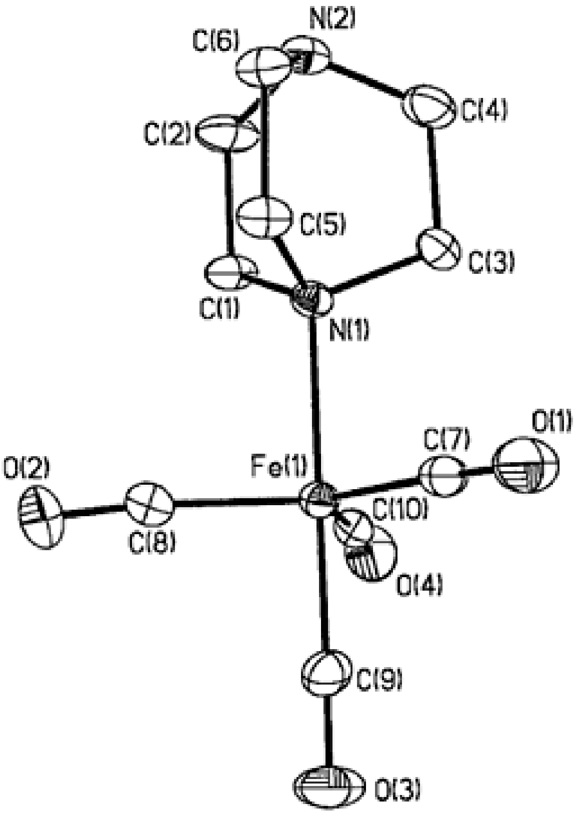
- **CN # 5 contd.**



Iron pentacarbonyl
very toxic !!!



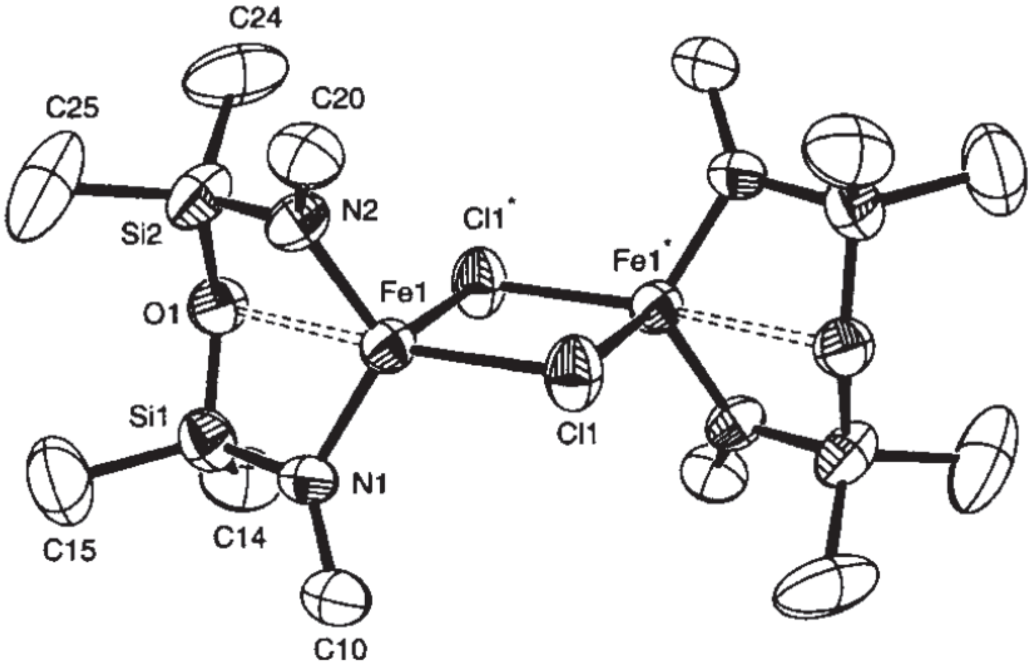
trigonal bipyramidal



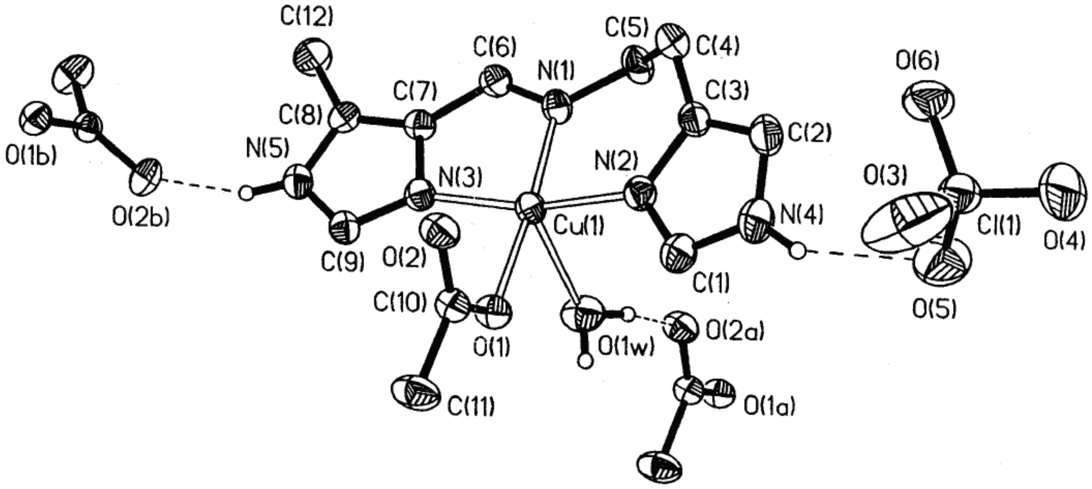
(DABCO)Fe(CO)$_4$
[DABCO = 1,4-diazabicyclo[2.2.2]octane]

- **CN # 5 contd.**

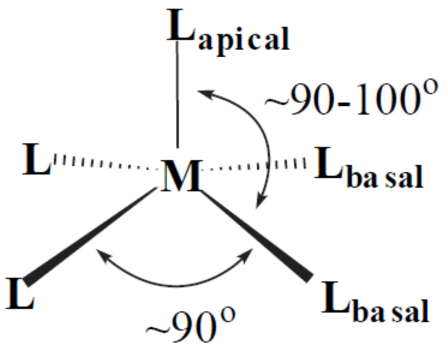
  - **$\{FeCl[^tBuN(SiMe_2)]_2O\}_2$**



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



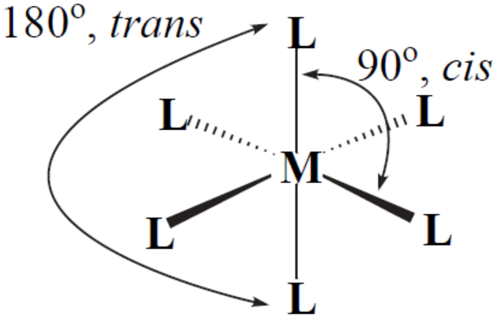
{acetatoaqua[[(4-methylimidazol-5-yl)methylene]histamine]-copper(II)} perchlorate



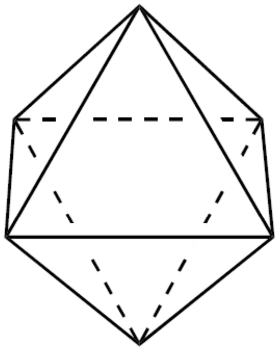
square pyramidal

- **CN # 6**

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



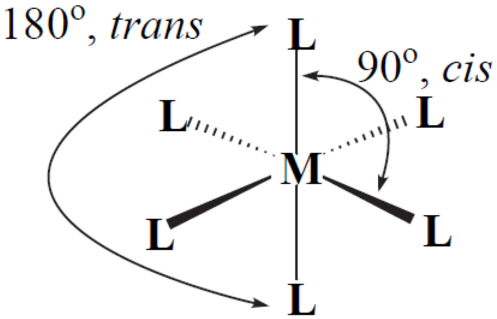
octahedral



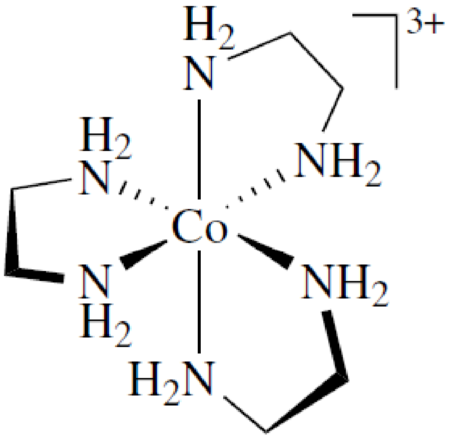
Octahedron

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.

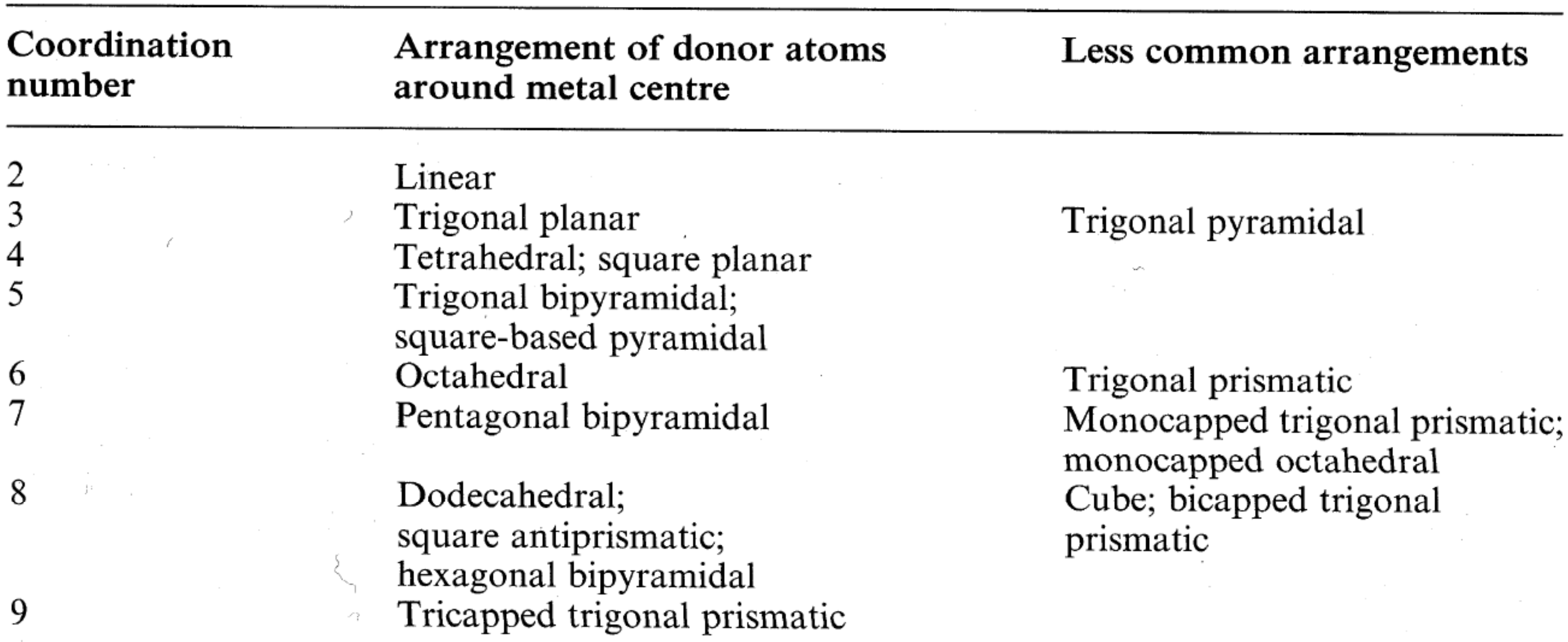
- **CN # 6**
  - Octahedral



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.