§ 6 Structures of polyatomic molecules (II)

Introduction:

- In chapter 5, we focused on the (localized and delocalized) σ- and π-bonds within polyatomic molecules in terms of hybrid orbital theory (VB) and MO theory as well as the symmetry rules for chemical reactions of polyatomic molecules.
- In this chapter, we will discuss ***multi-center bonds in electron-deficient molecules*** (e.g., boranes and carboranes) and the chemical bonds in coordination compounds.

§ 6 Structures of polyatomic molecules (II)

6.1 Multi-center bonds in electron-deficient systems

6.2 Chemical bonds in coordination compounds

6.3 Ligand Field Theory (LFT)

6.4 Transition-metal cluster compounds

6.5 Carbon clusters and nanotubes

Qualitative description of Chemical bonding within a molecule: VB vs. MO

- ***VB:*** Valence AOs or hybridized orbitals of each atom(s)

→ Forming 2c-2e σ-/π-bonds with AOs of surrounding atoms.

→ If necessary, resonance of VB structures are used to account for electron delocalization (e.g., the Π_6^6 bond in benzene)!

- **MO: LCAO-MO**

→ Formation of bonding & nonbonding MOs.

* Both hybridization & electron delocalization (e.g., Π_a^b bond) are inherently taken into account.

A molecule/an aggregate of atoms can have several isomers. How to quickly predict its structure/bonding pattern?

Qualitative description of Chemical bonding within a molecule: VB vs. MO

A molecule/an aggregate of atoms can have several isomers. How can one quickly predict its structure/bonding pattern?

1. Chemical bondings occur between the valence atomic orbitals (VAOs) (and valence electrons (VEs)) of the constituent atoms within a molecule.
2. The more VEs and VAOs involved in chemical bondings, the more stable is a molecule.

→ A molecule prefers the bonding pattern/structure that involves as many bonding VEs & VAOs as possible!

A brief summary on the electronic structures of molecules we have learnt

(MO & VB)

A polyatomic molecule with a closed-shell electronic configuration has **m**(=even) **VE**s and **n** VAOs.

1) If ***m = n***,

VB: ***n/2*** 2c-2e (σ-/π-) bonds (σ first!);

MO: ***n/2 bonding MOs*** (occupied!) & ***n/2 antibonding MOs.***

Then if necessary can electron delocalization be considered.

C_2H_2: 10 VAOs/VEs = 2x4 (C) + 2x1(H)

→ VB: 3 σ-bonds & 2 π-bond.

→ MO: **3 σ- & 2 π-bonding MOs .**

A brief summary on the electronic structures of molecules we have learnt

(MO & VB)

2) If $m > n$,

VB: (m-n) lone pairs & ***($2n$-m)/2 2c-2e*** bonds;

MO: (***m-n) nonbonding*** MOs & ***($2n$-m)/2 bonding*** MOs.

Then if necessary can electron delocalization be considered.

H_2O: **4** VAOs(O) + **2** 1s(H) + **8**VE → VB: 2 LPs & 2 σ-bonds.

→ MO: 2 nonbonding, 2 σ-bonding MOs (occupied)

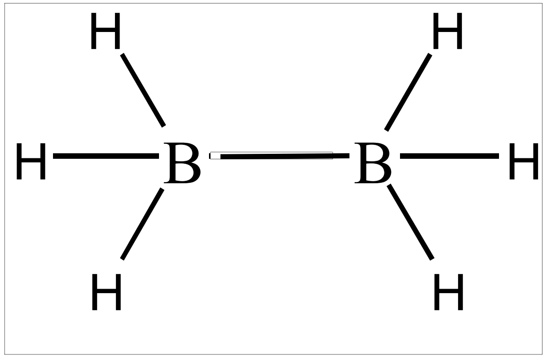
& 2 antibonding MOs (unoccupied!)

3) If ***$m < n$***, ? (to be learnt in this chapter).

6.1 Multi-center bonds in electron-deficient systems

6.1.1 Boranes and their relatives

i. B_2H_6

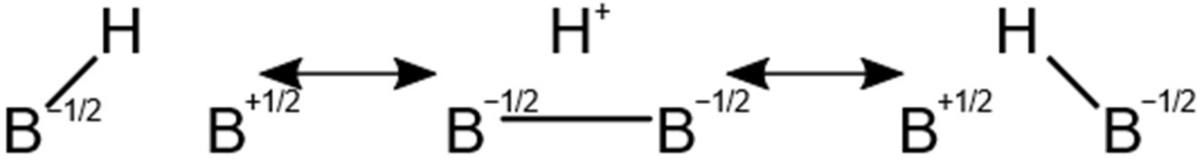


VAO = 4 (B) x2 + 1(H) x6 = 14

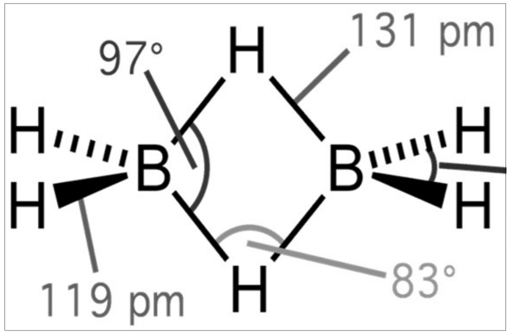
VE = 3 (B) x2 + 1(H) x6 = 12

- An ethane-like structure having 7 2c-2e bonds needs 14 VEs. Lack of two VEs!

- To make full use of all VAOs, two three-center two-electron (3c-2e) B-H-B bonds are formed.

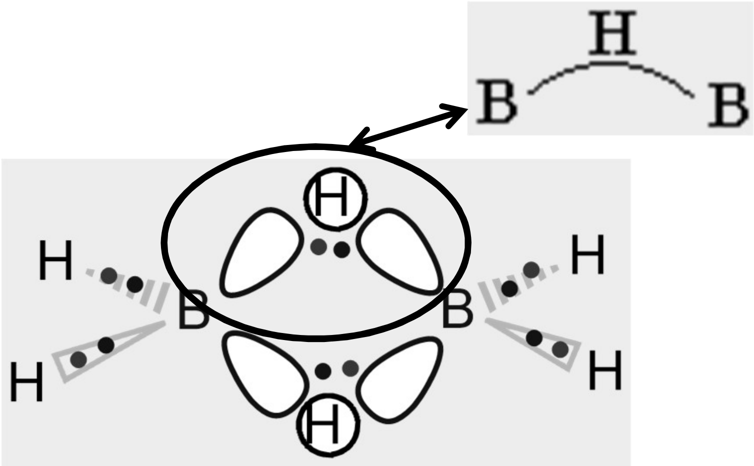


Resonance structures of 3c-2e bond in diborane (***VB description***)



i. B_2H_6

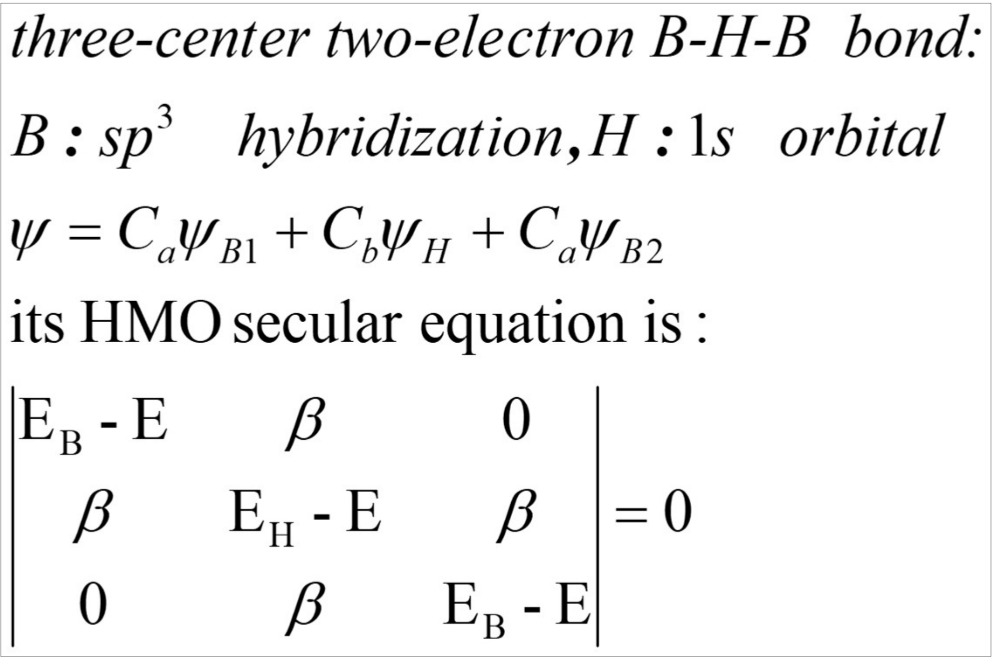
Localized MO description



For a B atom: sp^3-hybridization

- 2 VEs used by 2 terminal B-H bonds

- One VE&HO is used to form a B-H-B bond with a H 1s and a HO of another B atom!



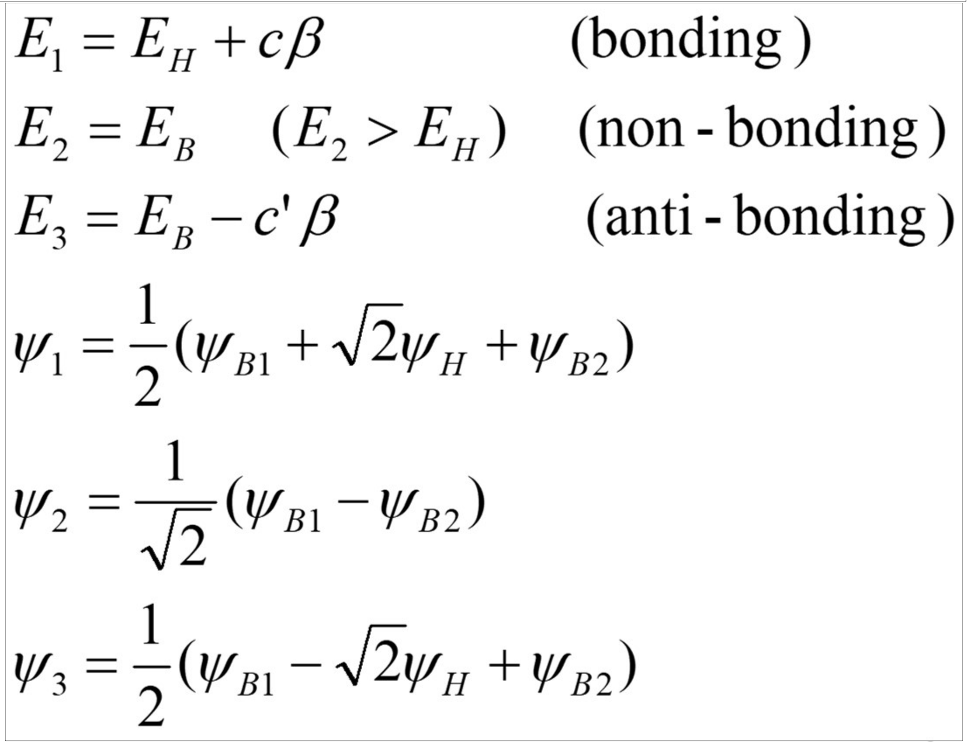
three-center two-electron B-H-B bond:

$B : sp^3$ *hybridization*, $H : 1s$ *orbital*

$$\psi = C_a\psi_{B1} + C_b\psi_H + C_a\psi_{B2}$$

its HMO secular equation is :

$$\begin{vmatrix} E_B - E & \beta & 0 \\ \beta & E_H - E & \beta \\ 0 & \beta & E_B - E \end{vmatrix} = 0$$



$$E_1 = E_H + c\beta \qquad \text{(bonding)}$$

$$E_2 = E_B \quad (E_2 > E_H) \qquad \text{(non-bonding)}$$

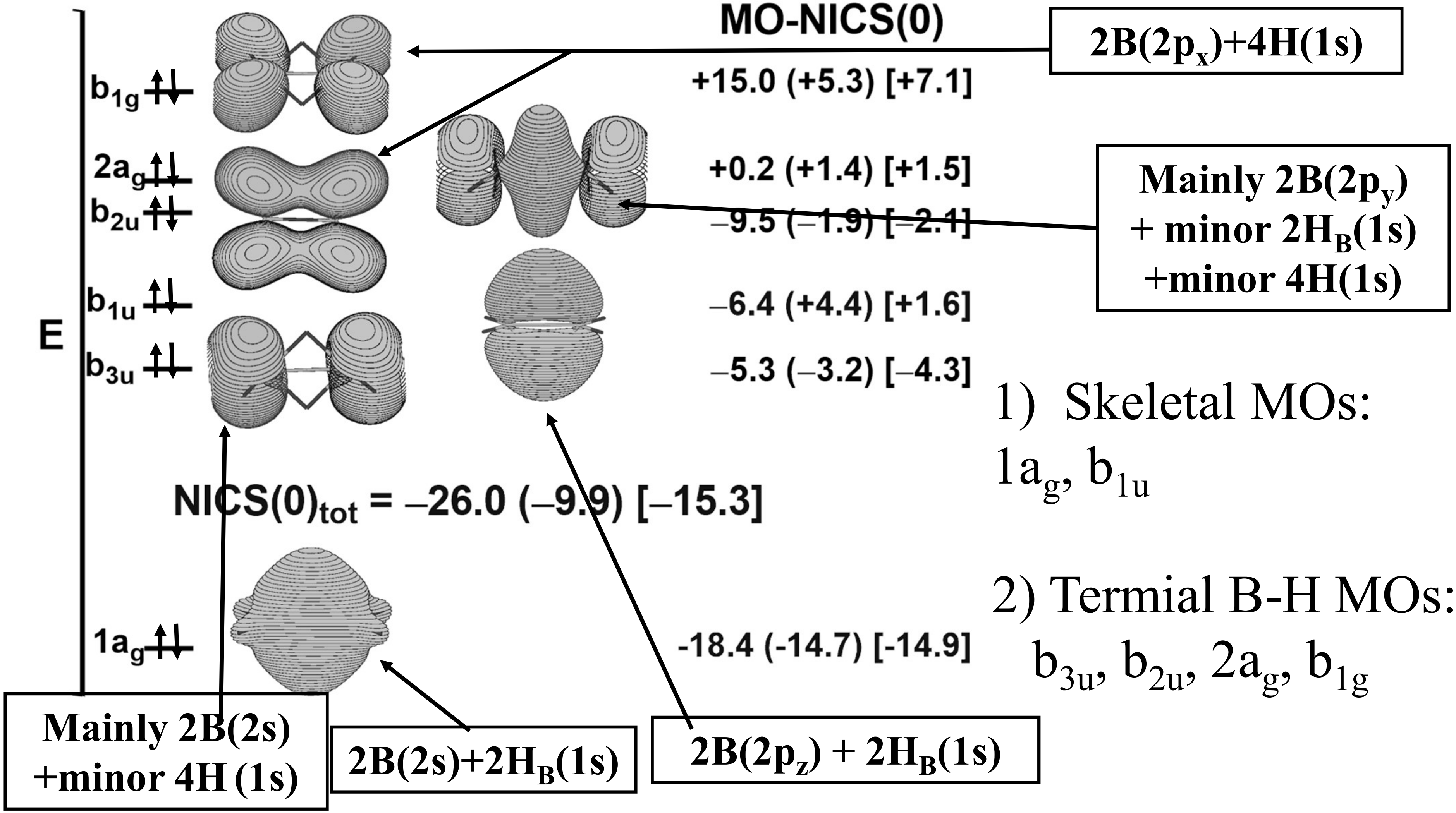
$$E_3 = E_B - c'\beta \qquad \text{(anti-bonding)}$$

$$\psi_1 = \frac{1}{2}(\psi_{B1} + \sqrt{2}\psi_H + \psi_{B2})$$

$$\psi_2 = \frac{1}{\sqrt{2}}(\psi_{B1} - \psi_{B2})$$

$$\psi_3 = \frac{1}{2}(\psi_{B1} - \sqrt{2}\psi_H + \psi_{B2})$$

B_2H_6: canonical valence molecular orbitals



$2B(2p_x)+4H(1s)$

Mainly $2B(2p_y)$
+ minor $2H_B(1s)$
+minor $4H(1s)$

Mainly $2B(2s)$
+minor $4H\ (1s)$

$2B(2s)+2H_B(1s)$

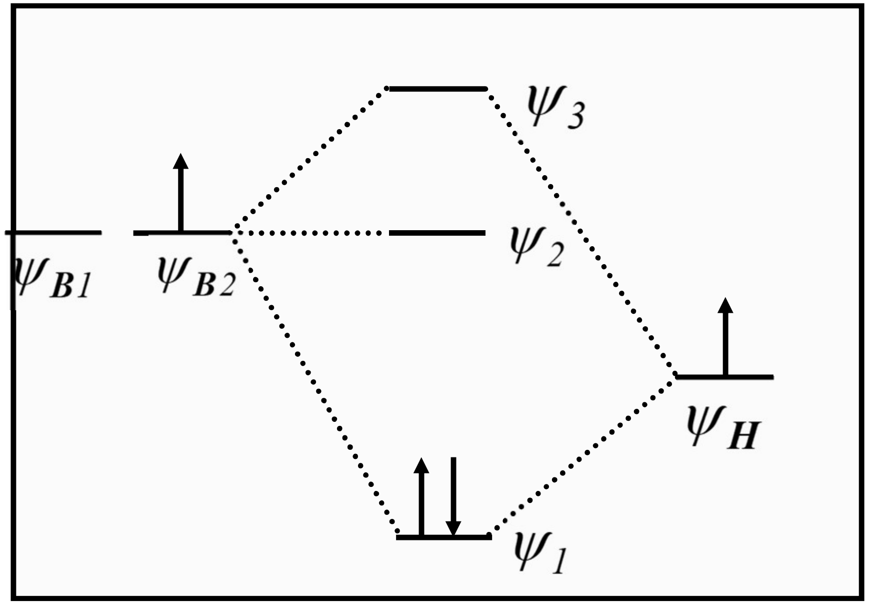
$2B(2p_z) + 2H_B(1s)$

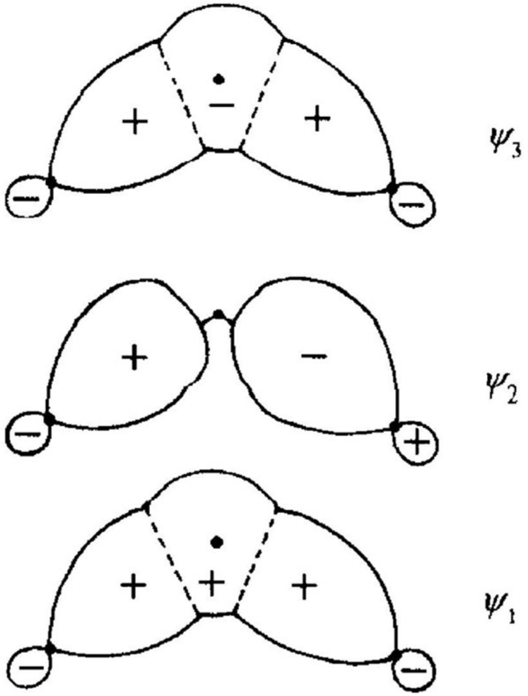
1) Skeletal MOs:
$1a_g$, b_{1u}

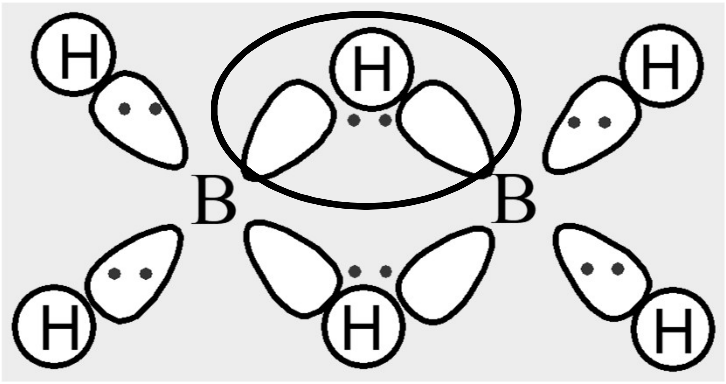
2) Termial B-H MOs:
b_{3u}, b_{2u}, $2a_g$, b_{1g}

Note: The CMOs can be transformed into LMOs, two of which are the 3c2e LMOs!

Three-center two-electron (3c-2e) B-H-B bond:





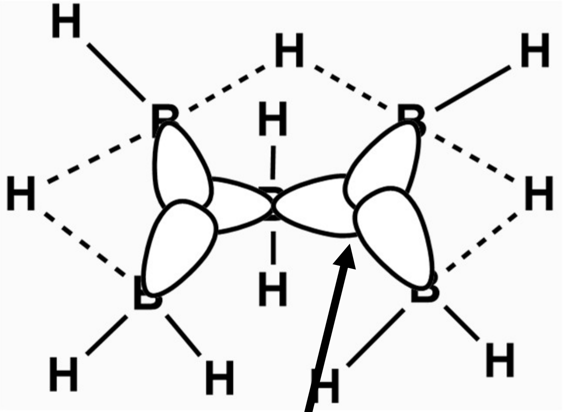


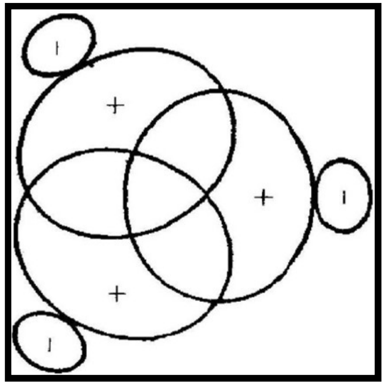
- B_2H_6 , actually having 14 VAOs and 12 VEs, has to form two 3c-2e BHB bonds to involve all VAOs into bonding MOs.

ii. B_5H_{11} **Nido structure**

Electron-deficient multi-center bonds

- VAO= 5x4(B) + 11(H) = 31 (needs 31VE)
- VE= 15(B) + 11 (H) = 26
- Actually having 8 BH σ-bonds, 3 BHB 3c-2e bonds, and **2 BBB 3c-2e bonds!**





Triangular BBB 3c-2e bond

HMO treatment

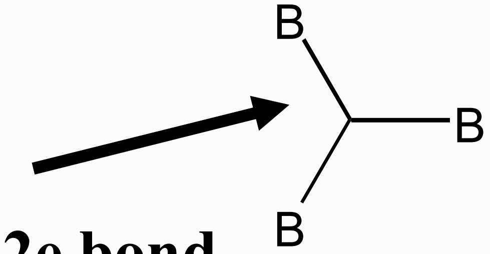
$$\begin{vmatrix} E_B - E & \beta & \beta \\ \beta & E_B - E & \beta \\ \beta & \beta & E_B - E \end{vmatrix} = 0$$

solve seqular equation

$$E_1 = E_B + 2\beta$$

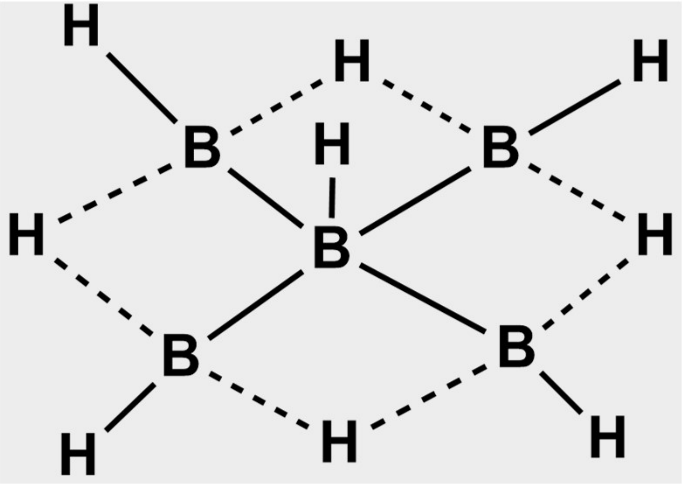
$$E_2 = E_3 = E_B - \beta$$

$$\psi_1 = \frac{1}{\sqrt{3}}(\psi_a + \psi_b + \psi_a)$$



BBB 3c-2e bond

iii. B_5H_9 **Nido structure**



Electron-deficient multi-center bonds

- VAO=5x4(B) + 9(H) = 29
- VE=5x3(B) + 9x1(H) = 24e

1) 5 B-H σ-bonds; (10e)

2) 4 BHB 3c-2e bonds; (8e)

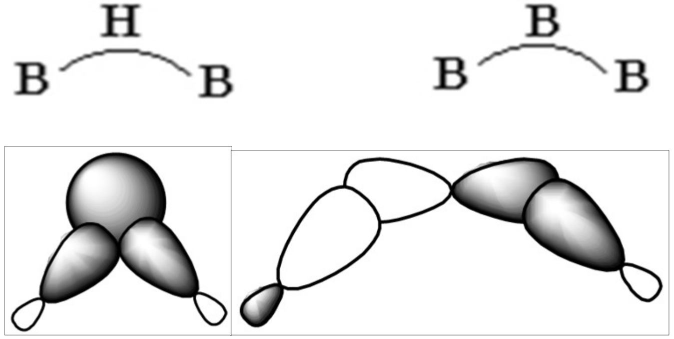
3) a **B_5 5c-6e bond**. (6e)

- Each peripheral B atom contributes one sp^3-HO and one electron.
- The central B atom contributes three sp^3-HOs and 2e.

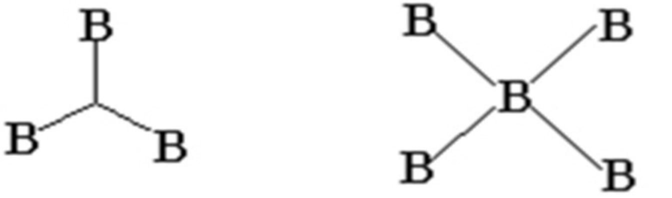
Types of Chemical bonds in Boranes

(a) Single σ-bond (2c-2e): B-H and B-B

(b) 3c-2e bond:



(c) Other polycenter-polyelectron bond

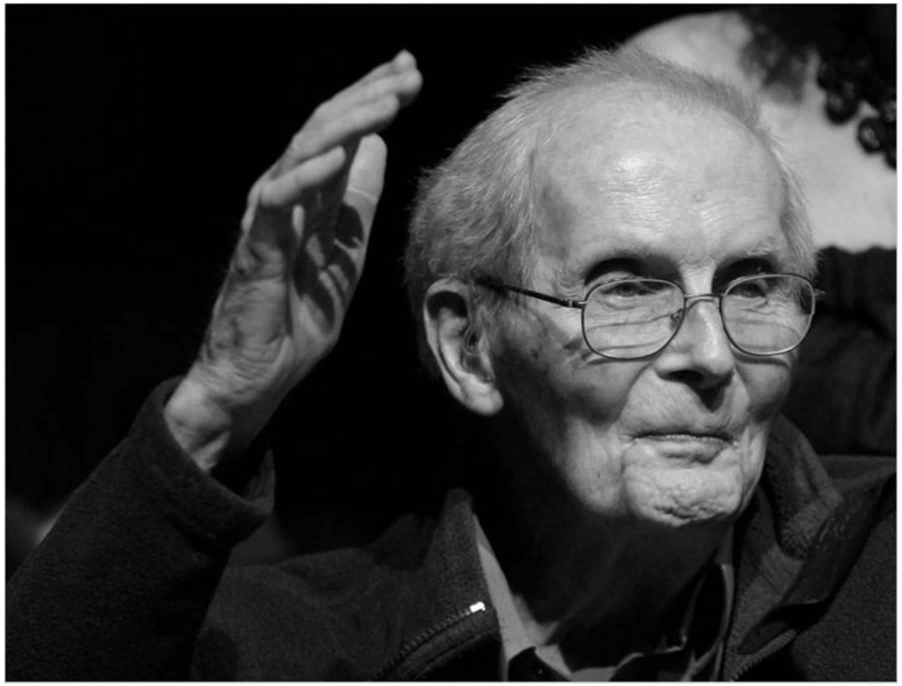


Question arisen:

How to determine the geometric and electronic structures of more complicated boranes?

6.1.2 B_nH_{n+m} with an open-framework structure (including nido- and arachno-type) and Lipscomb's *styx* method.

In mid 1950s, Lipscomb proposed the ***styx method*** to predict the topological structures of boranes B_nH_{n+m} with open-framework structures.



Linus Pauling
(1954&1962 Nobel Prize winner)

William Lipscomb
(1976 Nobel Prize winner)

Roald Hoffmann
(1981 Nobel prize winner)

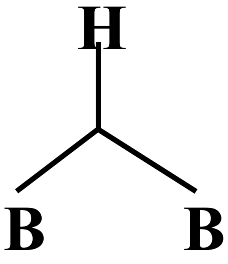
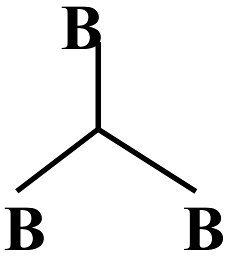
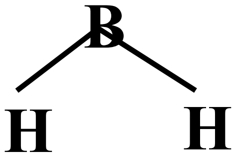
Boranes and their chemical bonding: William Lipscomb

Won Nobel prize,1976; Passed away on Apr. 14, 2011.

B_nH_{n+m} with an open-framework structure

n: the number of B atoms, thus the minimal number of B-H bonds

m: the number of extra H atoms.

Type	BHB 3c-2e	BBB 3c-2e	BB 2c-2e	Extra B-H
				
Number	s	t	y	x

The condition for a stable borane:

$x = m-s$ or $m = x+s$

$t = n-s$ or $n = s+t$ $\Longrightarrow$ ***p*** **sets of** ***styx*** $\Longrightarrow$ ***p*** **isomers**

$y = (2s-m)/2$

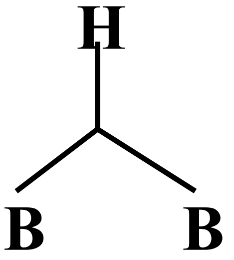
- To differentiate the isomers, each isomer can be labeled by a set of (***styx***).

Why do the three equations define a stable structure?

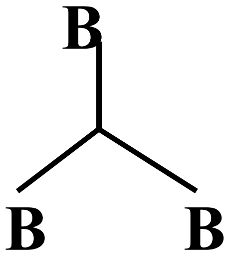
a) A $\mathbf{B_nH_{n+m}}$ molecule has ***(5n+m)*** valence AOs and ***(4n+m)*** valence electrons, yet being short of ***n*** electrons in order to form a normal (2c-2e)σ-bonded molecule.

(5n+m) AOs → **(5n+m)/2** 2c-2e bonding σ-bonds.

b) Thus requiring the formation of ***n*** 3c-2e bonds to make the whole molecule stable, meaning ***n = s + t*** or ***t = n - s***.

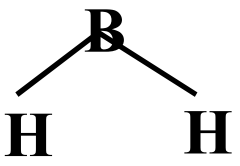


s



t

y



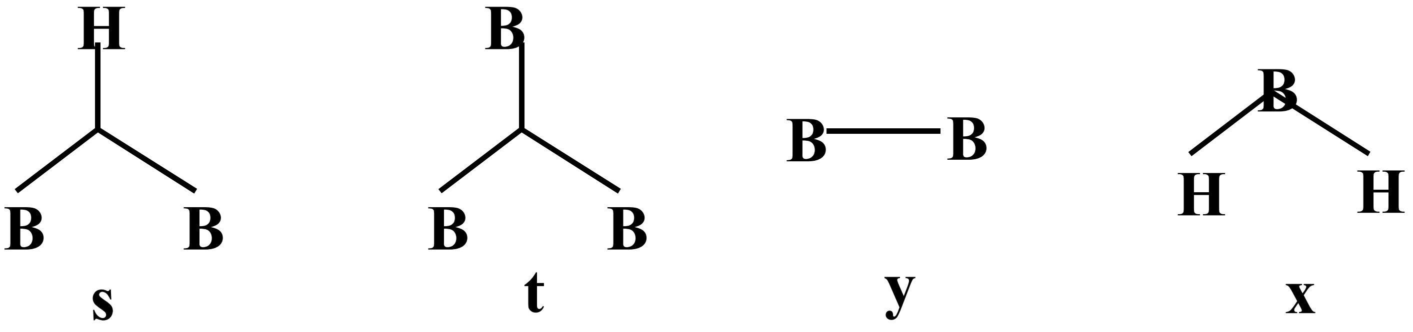
x

t = n-s or n = s+t

Why do the three equations define a stable structure?

c) Except the minimal n terminal B-H σ-bonds, the extra m H atoms are used to form s 3c-2e B-H-B bonds and x extra B-H σ-bonds, meaning $m = s + x$ or $x = m - s$.

d) The total electrons are all used to form various types of bonds, meaning $4n + m = 2n + 2(s + t + y + x) \rightarrow y = (2s-m)/2.$



$x = m-s$ or $m = x+s$
$t = n-s$ or $n = s+t$
$y = (2s-m)/2$

⟹ p **sets of** $styx$ ⟹ p **isomers**

To differentiate the isomers, each isomer can be labeled by a set of (***styx***).

Example 1: B_4H_{10} (2 isomers)

$S_{max} = 4$

n=4, m=6

$x = m - s$

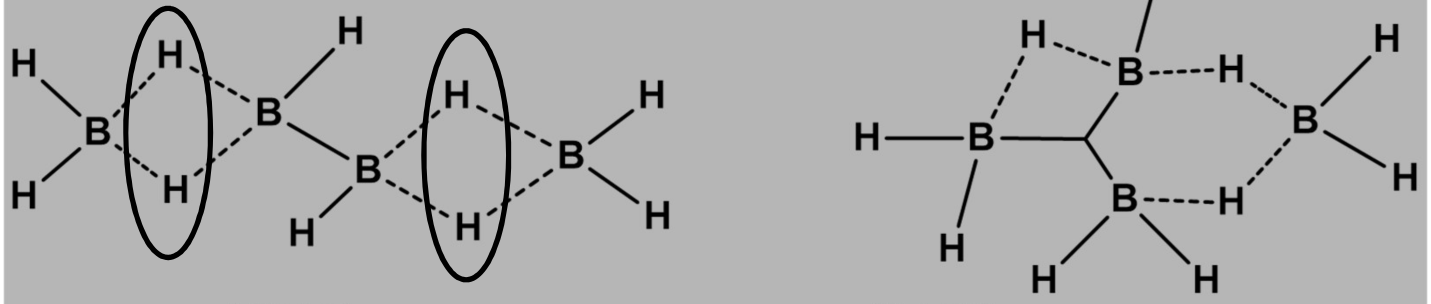
$t = n - s$

$y = (2s - m)/2$

$S_{min} = 3$

Solution 1		Solution 2
$s=4$	BHB	$s=3$
$t=0$	BBB	$t=1$
$y=1$	B-B	$y=0$
$x=2$	$B\text{-}H_{extra}$	$x=3$

Expt. Structure



(4012)

(3103)

Example 2: The topological structure of B_6H_{10} (3 isomers)

n=6, m=4

$x = m-s$

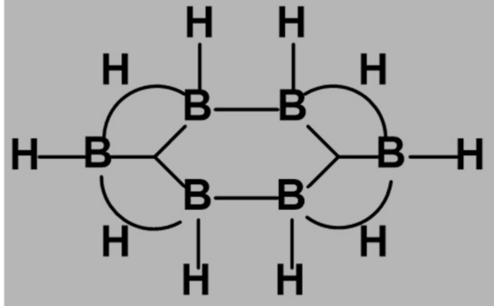
$t = n-s$

$y = (2s-m)/2$

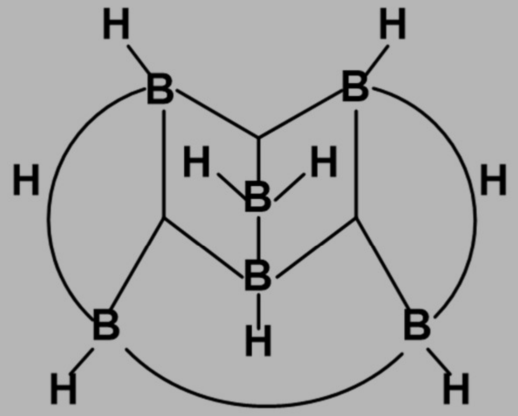
$S_{max} = 4$

$S_{min} = 2$

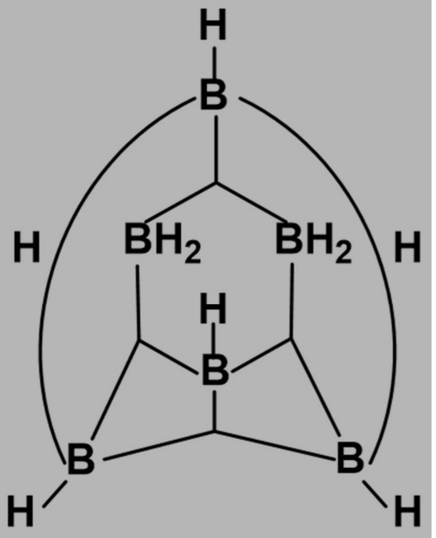
Solution 1	Solution 2	Solution 3	
$s=4$	$s=3$	$s=2$	BHB
$t=2$	$t=3$	$t=4$	BBB
$y=2$	$y=1$	$y=0$	B-B
$x=0$	$x=1$	$x=2$	B-H_{extra}



(4220)



(3311)



(2402)

Example 3: B_5H_9 (3 isomers)

n=5, m=4

S_{max} =4

$x = m-s$

$t = n-s$

$y = (2s-m)/2$

S_{min} =2

⇨

	Solution 1	Solution 2	Solution 3
BHB	$s=4$	$s=3$	$s=2$
BBB	$t=1$	$t=2$	$t=3$
B-B	$y=2$	$y=1$	$y=0$
$B\text{-}H_{extra}$	$x=0$	$x=1$	$x=2$
	Expt. Structure		

Example 4: B_5H_{11} (3 isomers)

n=5, m=6

S_{max} =5

$x = m-s$

$t = n-s$

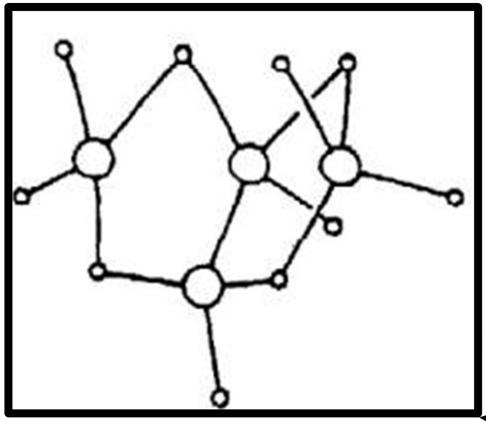
$y = (2s-m)/2$

S_{min} =3

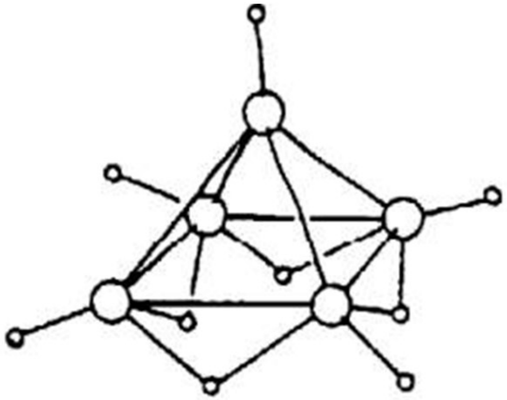
⇨

	Solution 1	Solution 2	Solution 3
BHB	$s=5$	$s=4$	$s=3$
BBB	$t=0$	$t=1$	$t=2$
B-B	$y=2$	$y=1$	$y=0$
$B\text{-}H_{extra}$	$x=1$	$x=2$	$x=3$
			Expt. Structure

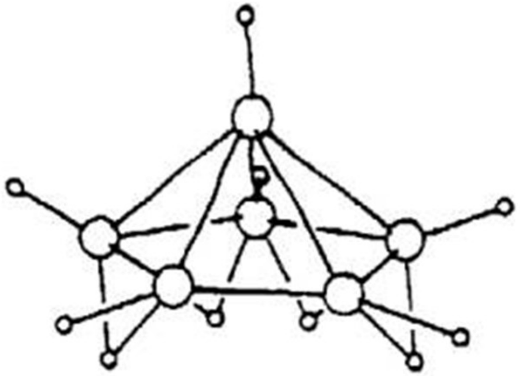
Structures of Boranes: Three types/series



B_4H_{10}



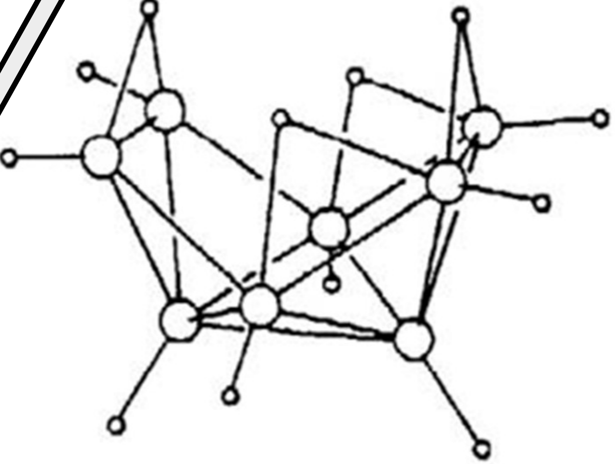
B_5H_9



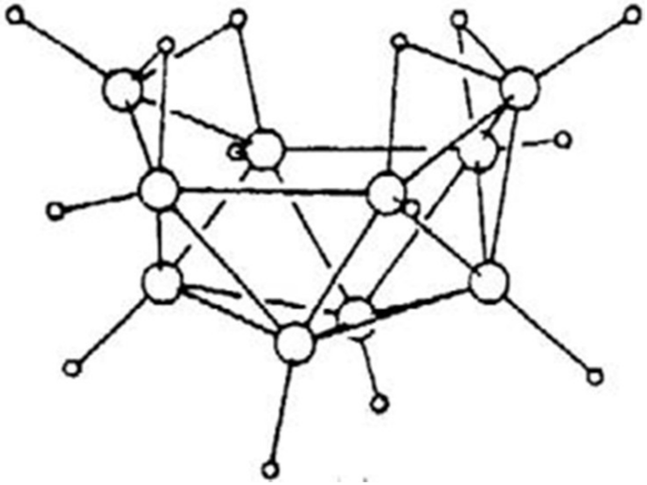
B_6H_{10}

Arachno-type
B_nH_{n+6}

Nido-type
B_nH_{n+4}



B_8H_{12}



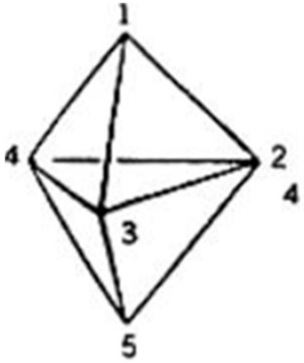
$B_{10}H_{14}$

Closo-type (Cage): $B_nH_n^{2-}$

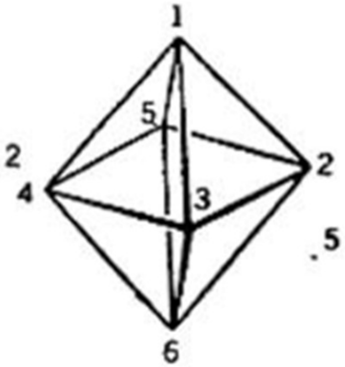
6.1.3 Borohydride anions $B_nH_n^{2-}$ and carboranes $C_{n'}B_nH_{(n+n'+m)}$ with closo-structures and the Wade's rule

$B_nH_n^{2-}$(closo):

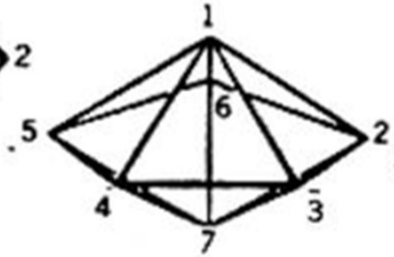
- $B_6H_6^{2-}$ (octahedral)
- $B_8H_8^{2-}$ (dodecahedral)
- $B_{12}H_{12}^{2-}$ (icosahedral)



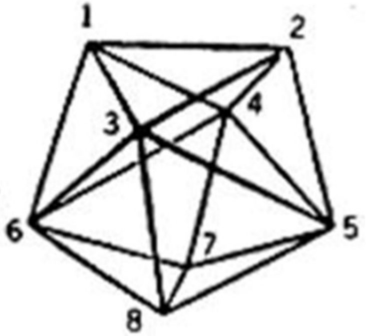
$B_5H_5^{2-}$ (D_{3h})



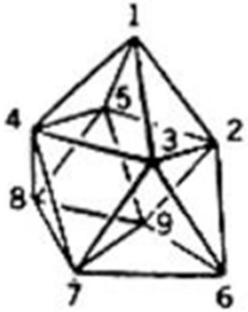
$B_6H_6^{2-}$ (O_h)



$B_7H_7^{2-}$ (D_{5h})

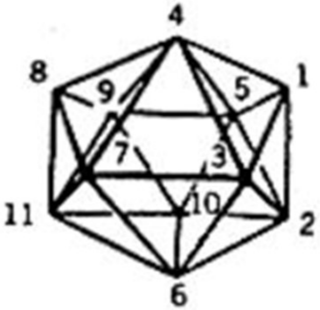


$B_8H_8^{2-}$ (D_{2d})



$B_9H_9^{2-}$ (C_{2v})

$B_{10}H_{10}^{2-}$ (D_{4d})



$B_{11}H_{11}^{2-}$ (C_{2v})

$B_{12}H_{12}^{2-}$ (I_h)

◆ There is little tendency to add H^+ and form neutral species.

polyhedra with n vertices

trigonal bipyramid
N = 5

octahedron
N = 6

pentagonal bipyramid
N = 7

dodecahedron
N = 8

tricapped trigonal prism
N = 9

bicapped square antiprism
N = 10

octadecahedron
N = 11

icosahedron
N = 12

16.8

"Closo" series - formula $B_nH_n^{2-}$

- Total valence electrons:

  N_{VE}(Total) = **3n** (B) + **n** (H) + **2** (charge) = **4n+2**

- Total valence atomic orbitals:

  N_{VO}(Total) = **4n** (B) + **n** (H) = **5n**

- Each B-H bond uses **2** electrons. (2c-2e σ-bond)

  → N_{VE}**(B-H)** = ***2n*** & N_{VO}**(B-H) = 2n**

- The skeletal VEs (for the polyhedral framework):

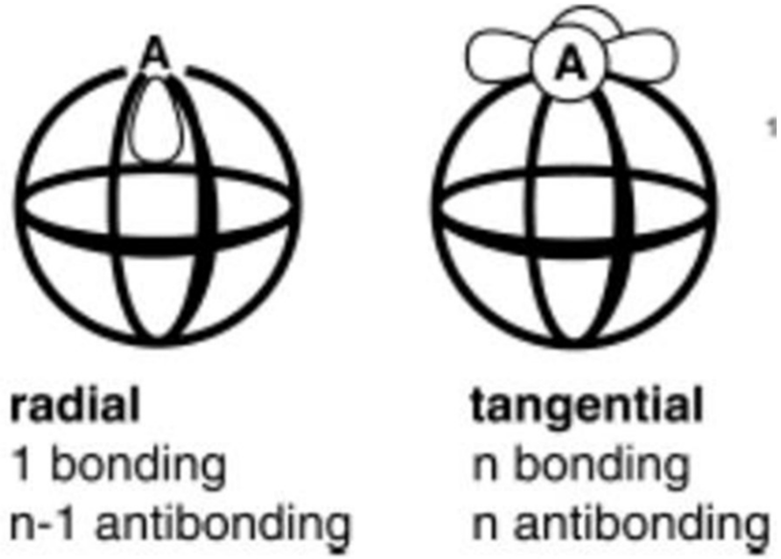
  N_{VE} **(skeletal) = (4n + 2) - 2n = 2(n+1) =** N_{FE}

  N_{VO}**(skeletal) = 5n – 2n = 3n**

MOs in "closo"-series $B_nH_n^{2-}$

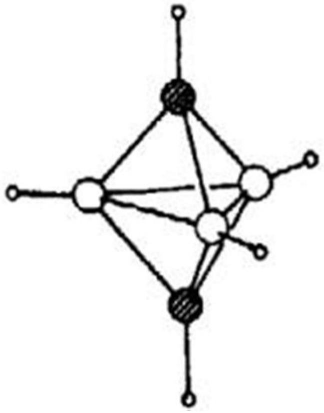
- Each B atom is sp-hybridized, forming an exocentric B-H bond.
- Each B atom contributes a radial hybrid orbital to form a total of ***n*** radial skeletal MOs with the only one bonding MO being occupied.
- Each B atom has two tangential AOs. These AOs form ***2n*** tangential skeletal MOs, half of which are bonding orbitals and doubly occupied.
- **A *n*-vertice *closo*-borane anion or carborane has in total of (n+1) bonding skeletal MOs.**

Wade's (n+1) rules

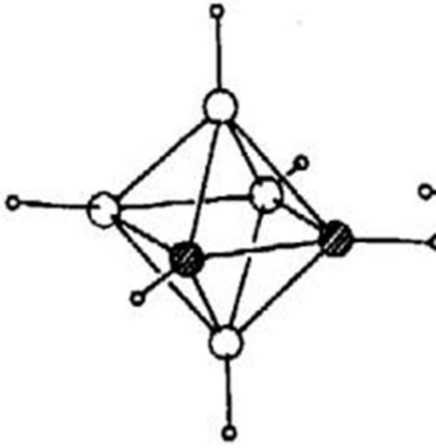


- 3n skeletal AOs/MOs
- n+1 bonding skeletal MOs
- 2n-1 antibonding skeletal MOs
- **N_{FE}= 2n + 2**

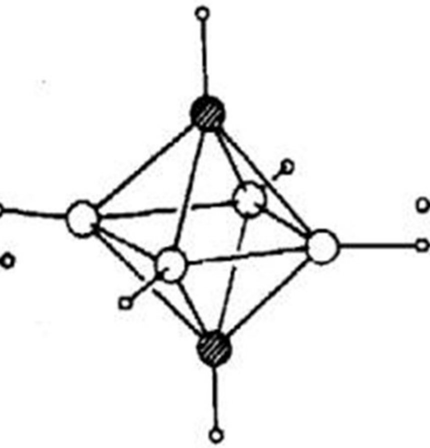
Structure of Carboranes



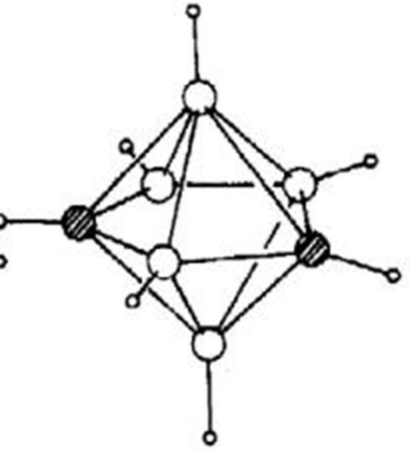
1,5-$C_2B_3H_5$



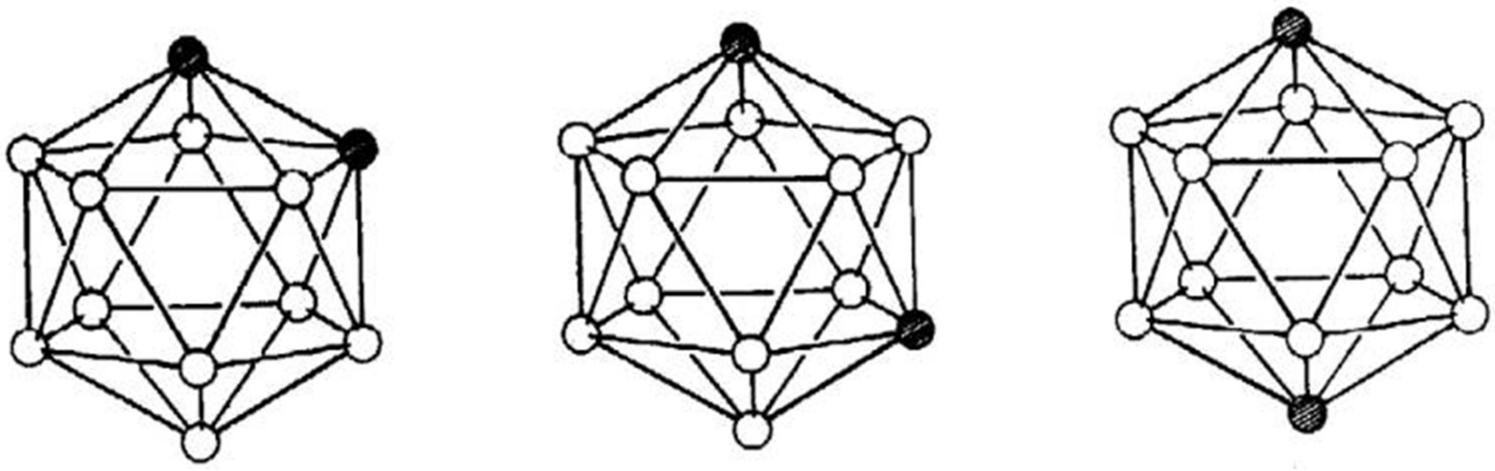
1,2-$C_2B_4H_6$



1,6-$C_2B_4H_6$



2,4-$C_2B_5H_7$



3 isomers of $C_2B_{10}H_{12}$ (with hydrogen omitted)

Note: Herein the topological atom-atom linkage does not mean the presence of a 2c-2e σ-bond! (3D aromaticity!)

Tang’s rule

- For a *closo*-borane/carborane with a *n*-vertice triangular polyhedral structure, its total bonding MOs amount to ***BMO = 4n – F***, with ***F = f + 3(s+1).***

(***f*** is the number of faces in the polyhedron, ***s*** is the number of defected vertices. For a closo-structure, ***s=0***).

e.g., for octahedral $B_6H_6^{2-}$, F=8 + 3 =11, BMO = 4x6-11=13.

(6 B-H bonds, 7 skeletal bonding MOs.)

- **This rule also works for *nido*- and arachno-boranes by supposing the number of defected vertices being 1 and 2, respectively.**

e.g. nido-C_5H_9, ***f*** = 8, ***s*** = -1, **F** = 8, **BMO** = 4x5-8 = 12

5 B-H bonds, 7 skeletal BMOs (i.e., 4 BHB 3c2e bonds, 3 BBB 3c2e bonds).

“Nido” series – formula $B_nH_{(n+4)}$

- Total valence electrons(VEC) = **3n (B) + n(H) + 4** (extra H) = **4n + 4**
- Framework electrons (NFE) = **2n + 4**

 (i.e., **n+2** pairs).

- The structure of the “nido” compound is based on the “closo” polyhedron with one more vertex than the “nido” compound.

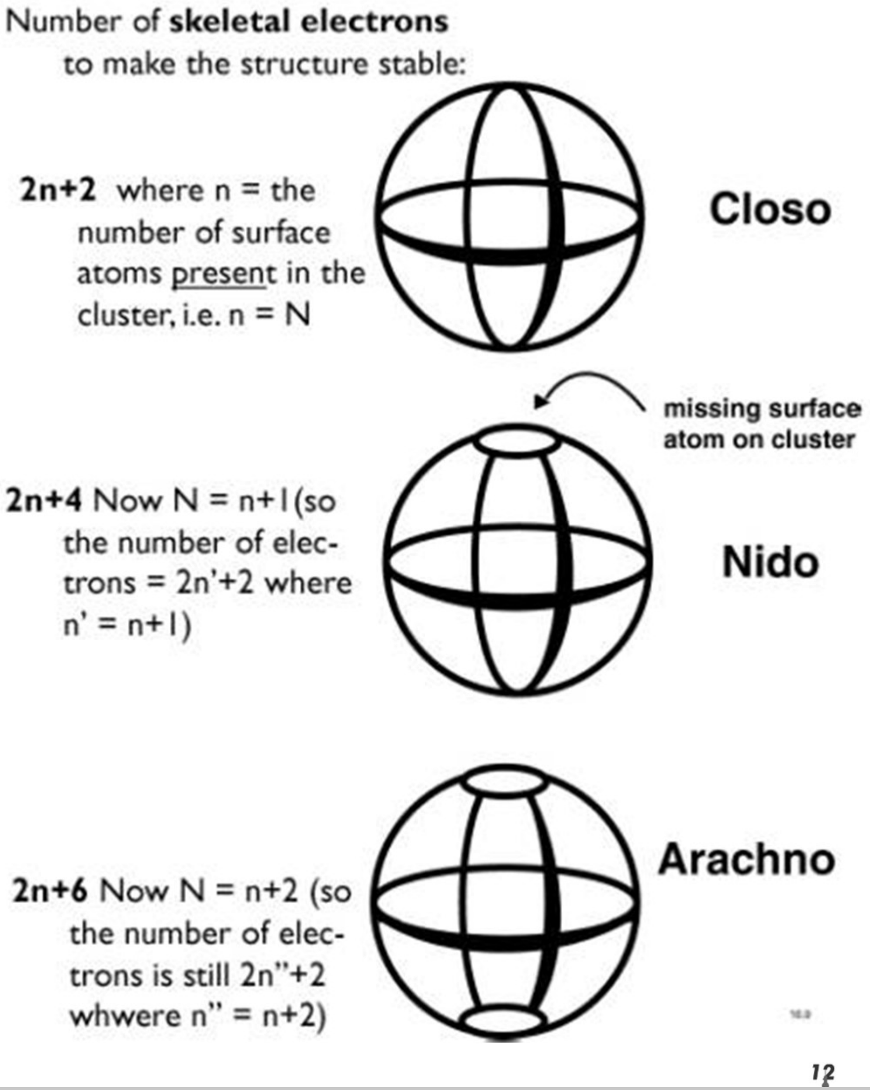
“Arachno” series – formula $B_nH_{(n+6)}$

- Total valence electrons(VEC) = **4n + 6**
- Framework electrons (NFE) = **2n + 6**

 (i.e., **n+3** pairs).

- The structure of the “nido” compound is based on the “closo” polyhedron with two more vertices than the “nido” compound.

BMO = 4n – F
F = f +3(s+1).


Number of **skeletal electrons** to make the structure stable:

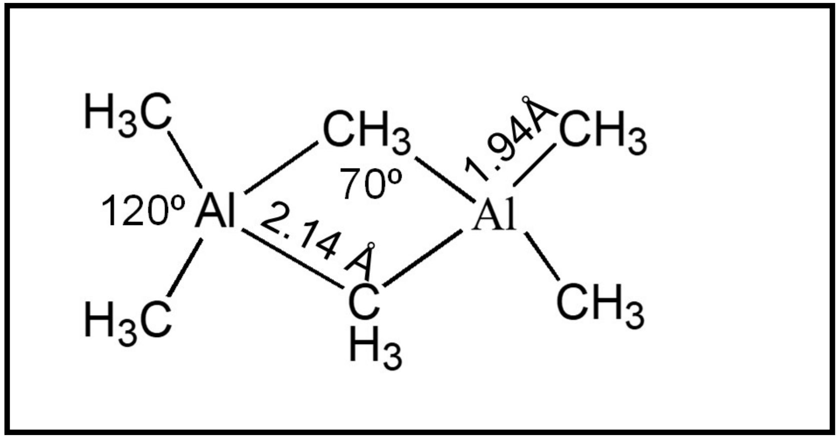
2n+2 where n = the number of surface atoms present in the cluster, i.e. n = N

2n+4 Now N = n+1 (so the number of electrons = 2n'+2 where n' = n+1)

2n+6 Now N = n+2 (so the number of electrons is still 2n''+2 whwere n'' = n+2)

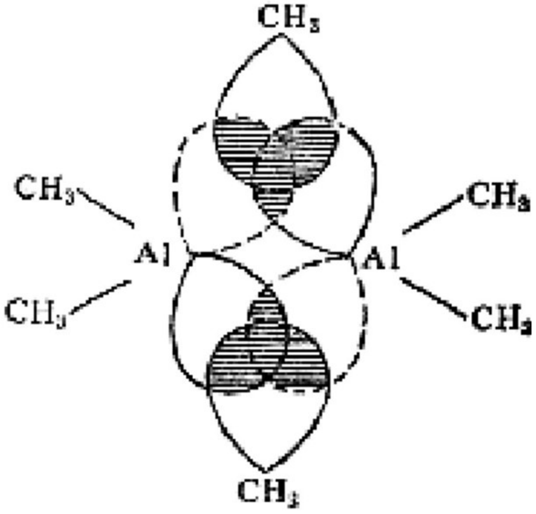
6.1.4 other electron-deficient compounds

Boron group **B、Al、Ga、In、Tl**



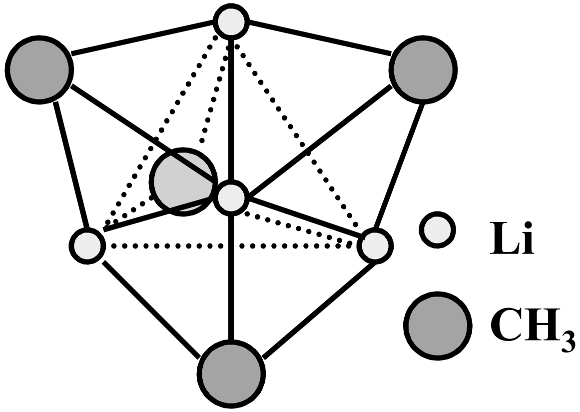
Gas-phase: monomer

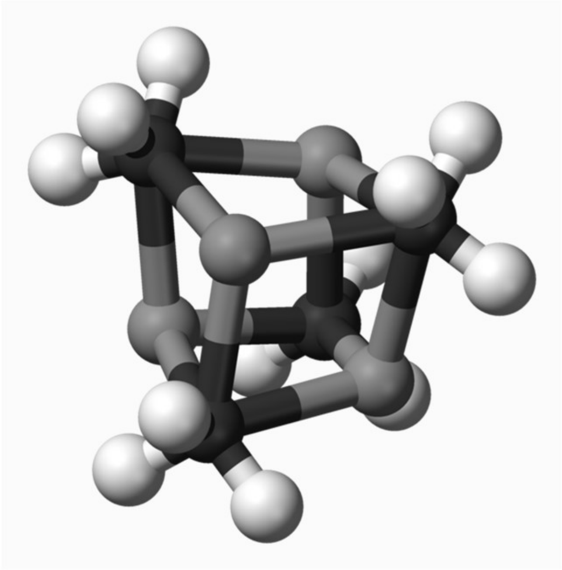
Solid state: dimer or polymer

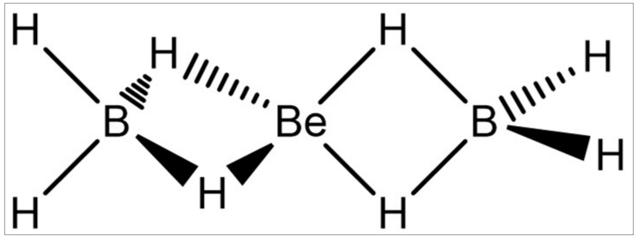


Alkali metal and alkali earth metal alkylides

$[Li(CH_3)]_4$



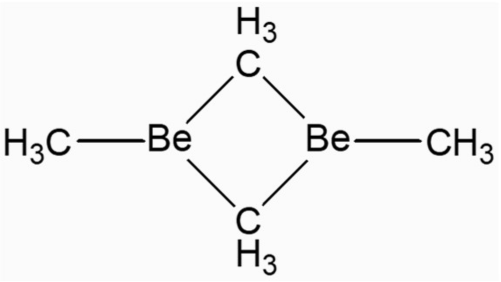




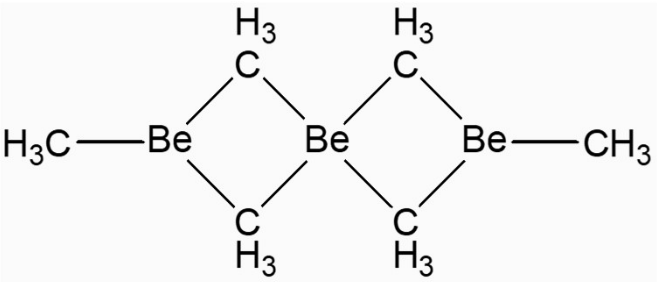
BeB_2H_8

R(Li-Li) = 2.68 Å
R(Li-CH_3) = 2.31 Å

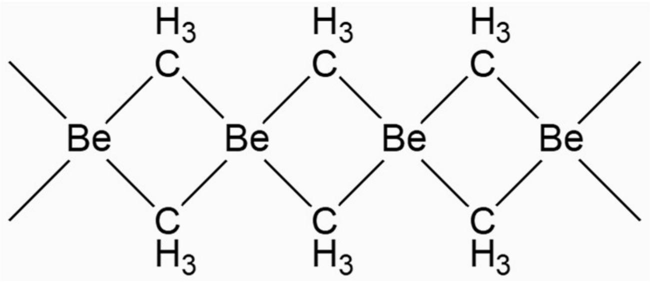
$Be(CH_3)_2$



dimer



trimer

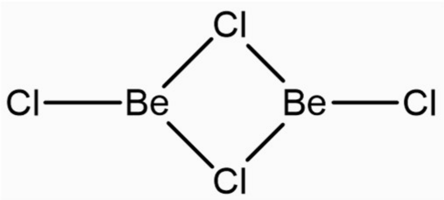


polymer

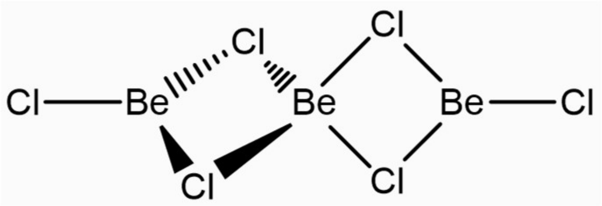
Multicenter bond can also exist in transition-metal cluster compounds!

Is there any 3c-2e bond in the following compounds?

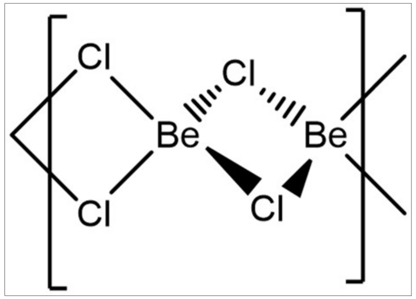
$BeCl_2$



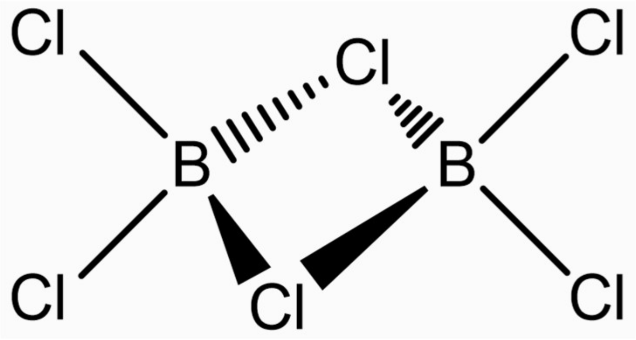
dimer



trimer



polymer Solid $BeCl_2$



Dimer of BCl_3

There is no 3c-2e bond in these compounds!

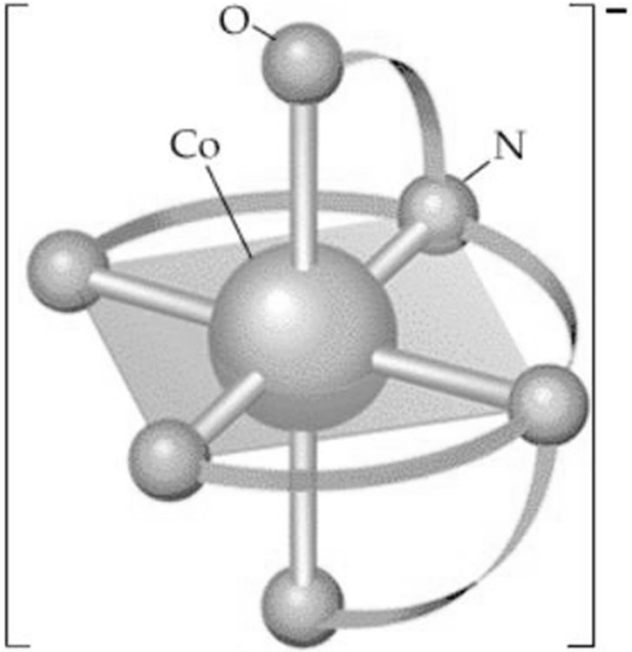
They just have normal & dative 2c-2e bonds!

6.2 Chemical bonds in coordination compounds

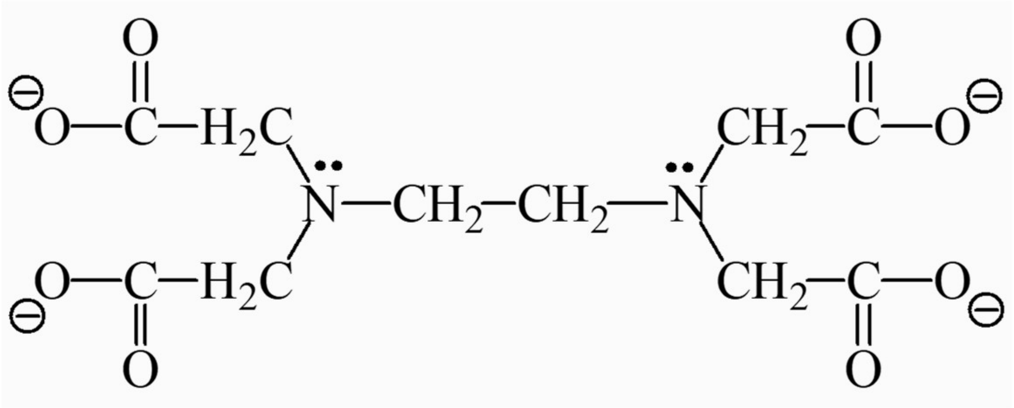
Definition of Coordination compound:

Composed of a metal atom or ion and one or more ligands.

- Ligands usually donate electrons to the metal
- Includes organometallic compounds



$CoEDTA^-$



ethylenediaminetetraacetate ($EDTA^{4-}$)
(hexadentate ligand)

Theories to describe the bonding within coordination compounds.

1) Valence bond theory: developed by Pauling in early 1930s to explain the coordination number, geometry and magneticity of coordination compounds. (**Hybrid Orbital + Dative Bond**!)

2) Crystal field theory: developed by ***Bethe*** and ***van Vleck*** in early 1930 to explain the spectra of coordination compounds, but not their chemical bonding!

3) Molecular orbital Theory: qualitative description, also can be computationally approached by *ab initio* calculations.

4) <u>Ligand field theory</u>: a combination of CFT and MOT.

6.2.1 Coordination polyhedron: (VB description)

molecule	C.N.	**hybridization Of metal**	Symmetry	Geometry
$Ag(NH_3)^{2+}$	2	sp		linear
$CuCl_3^-$	3	sp^2	D_{3h}	triangular
$Ni(CO)_4$	4	sp^3	T_d	tetrahedral
$PtCl_4^{2-}$	4	dsp^2	D_{4h}	square planar
$Fe(CO)_5$	5	dsp^3	D_{3h}	Trigonal bipyramidal
	5	d^2sp^2	C_{4v}	square pyramid
FeF_6^{4-}	6	d^2sp^3	O_h	octahedral
others	8		D_{4h}	tetragonal
	8		D_{4d}	Antisquare pyramidal
	10			Bicapped square antiprism
	12		I_h	icosahedral

Coordinate covalent bond & Coordinate ionic bond

Coordinate covalent bond & Coordinate ionic bond

Coordinate covalent bond:

To form dative covalent bonds, the central transition metal ion has to rearrange its *n*d-AO electrons to empty some of its d-AOs for hybridization!

→ Central transition metal ion adopts a low-spin state.

Coordinate ionic bond: M-L bond is ionic (electrostatic)!

→ Central transition metal ion adopts a high-spin state.

6.2.2 Crystal Field Model

Mainly focuses on the energy splitting of *d* (or f) orbitals (belonging to the central TM atom). .

Assumptions:

1. Ligands are regarded as negative point charges or point dipoles.
2. Metal-ligand bonding is supposed to be entirely ionic.

The otherwise degenerate (n-1)d-orbitals of the central metal atom are split into two or more groups of different energies and symmetries in the electrostatic field exerted by the surrounding ligands.

- Strong-field: large splitting of *d* orbitals → low-spin
- Weak-field: small splitting of *d* orbitals → high-spin

Perturbation Theory

$$\hat{H} = \hat{H}_0 + \hat{H}' \text{(Crystal Field)}$$

Hamiltonian of metal atom (central force field)

Potential energy operator arising from the crystal field.

Spherical symmetry

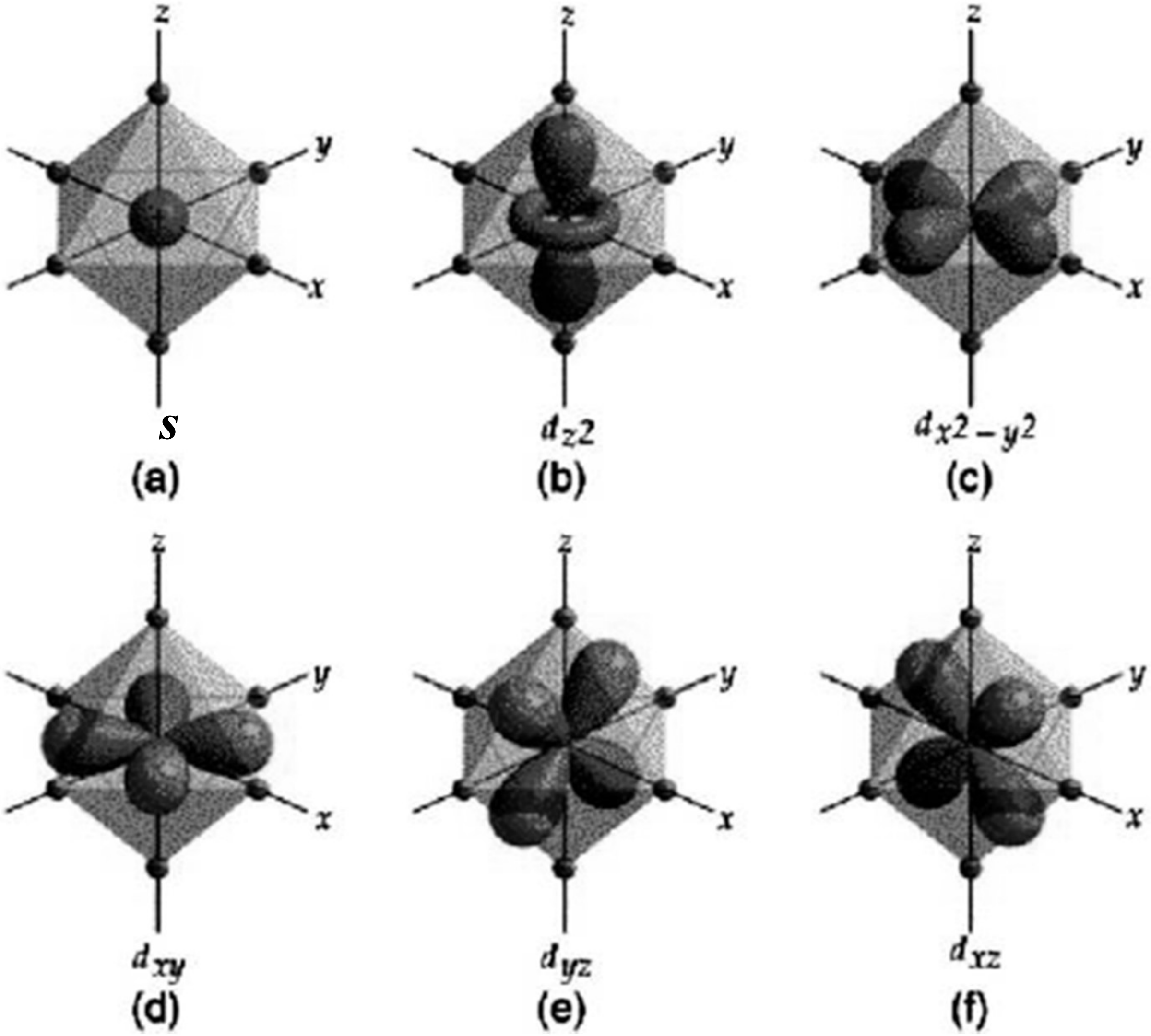
Non-spherical symmetry

- The AOs' symmetries of the central atom now depend on the symmetry of the crystal field.

- The energy gap between the otherwise degenerate atomic orbitals (e.g., ***d AOs)*** is dependent on the strength of the crystal field.

CFT A. Crystal-field splitting of d orbitals

Example 1: octahedral field

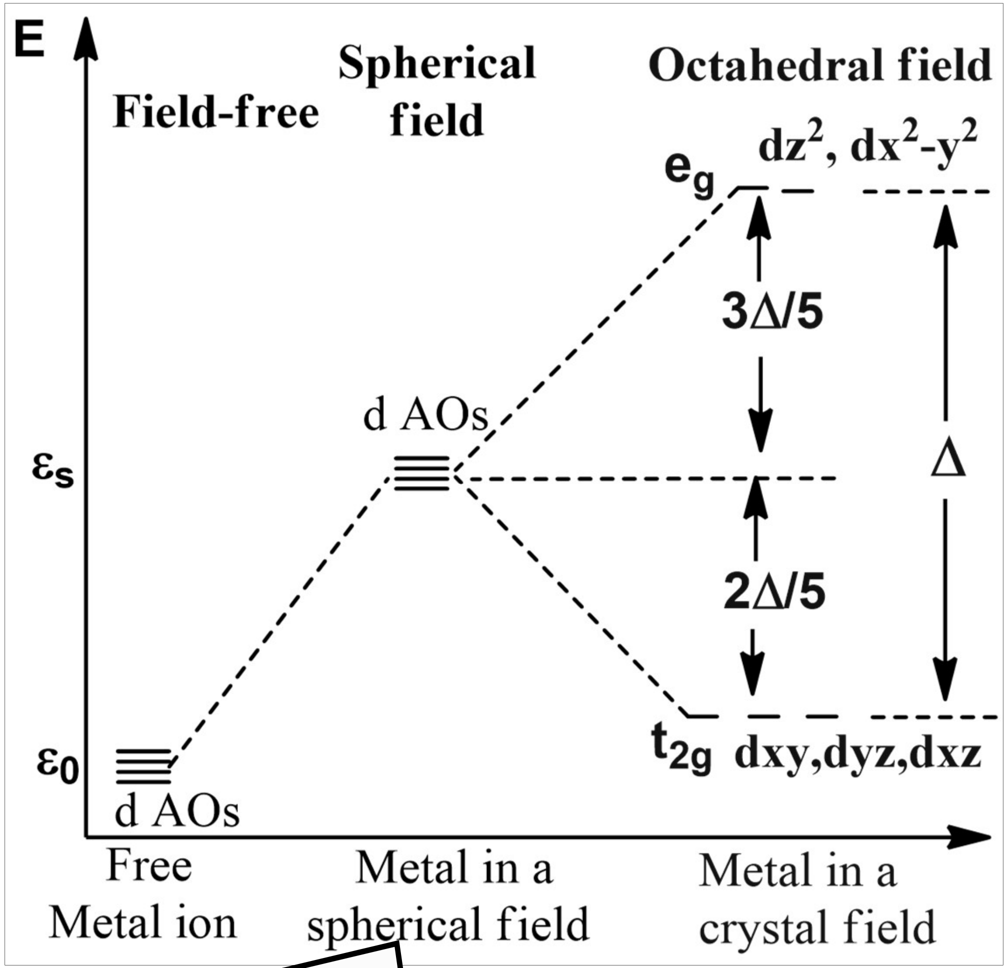


s and d-orbitals of a transition-metal atom.

- CF: octahedrally distributed negative charges.
- A qualitative picture:

The dz^2 and $d(x^2-y^2)$ orbitals of the central atom suffer from stronger repulsion from the ligands than do the other three d-orbitals.

Octahedral field: Semi-quantitative picture



A hypothetic field by supposing the negative charges of ligands are evenly distributed over the shell.

Stronger CF results in:

i) Larger ε_s - ε_0 gap.

ii) Larger crystal-field splitting energy Δ.

$$\because 6E_{t_{2g}} + 4E_{e_g} = 10\varepsilon_s$$

Suppose $\varepsilon_s = 0$, and

$$\Delta = E_{e_g} - E_{t_{2g}} = 10D_q$$

$$\Rightarrow 6E_{t_{2g}} + 4E_{e_g} = 10\varepsilon_s = 0$$

$$\Rightarrow E_{e_g} = \frac{3}{5}\Delta = 6\mathrm{D}_q$$

$$E_{t_{2g}} = -\frac{2}{5}\Delta = -4D_q$$

Crystal-field stabilization energy (CFSE):

For a ***d^n*** ion in a crystal field (e.g., an octahedral field), the CFSE is defined as,

$$\mathrm{CFSE} = E(d^n)_{CF} - E(d^n)_{MSF}$$

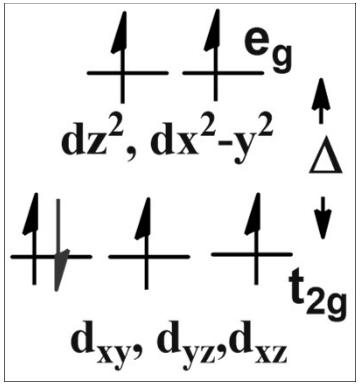
Sum of electronic energy in CF with d-splitting.

Sum of electronic energy in a mean spherical field without d-splitting.

$E(d^n)_{\mathrm{MSF}} = \boldsymbol{n}\boldsymbol{\varepsilon}_{\boldsymbol{s}} = 0$ (Let $\boldsymbol{\varepsilon}_{\boldsymbol{s}} = 0$)

e.g., Fe (d^6) in a weak field, $(t_{2g})^4(e_g)^2$

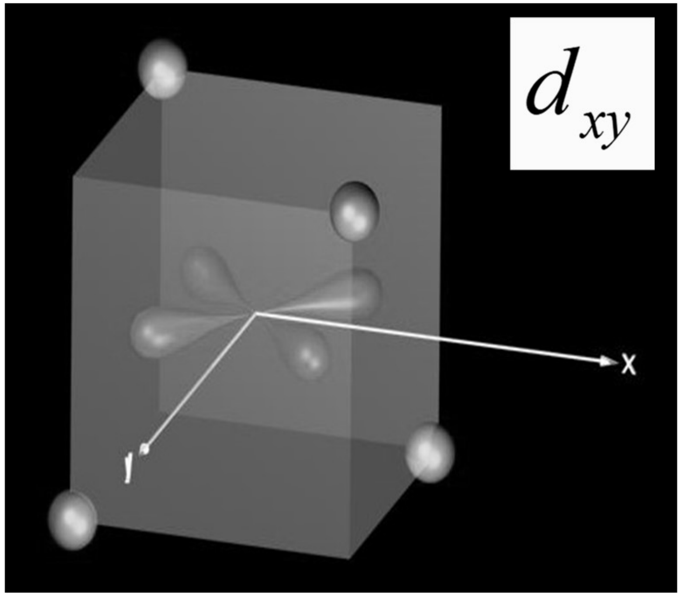
$$\mathrm{CFSE} = 4E_{t_{2g}} + 2E_{e_g} = 4\left(-\frac{2\Delta}{5}\right) + 2\left(\frac{3\Delta}{5}\right) = -\frac{2\Delta}{5}$$

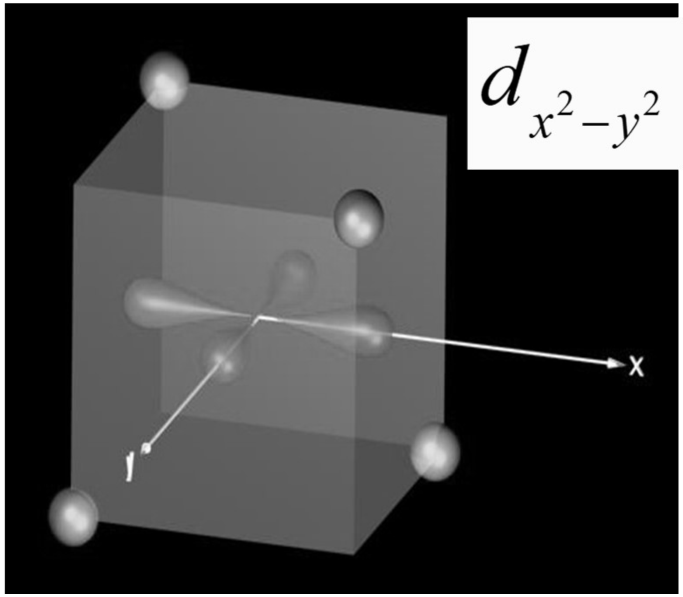


Question: Please derive the pattern of d-orbital splitting in a cubic field (also being O_h-symmetric)?

A. Crystal-field splitting of d orbitals

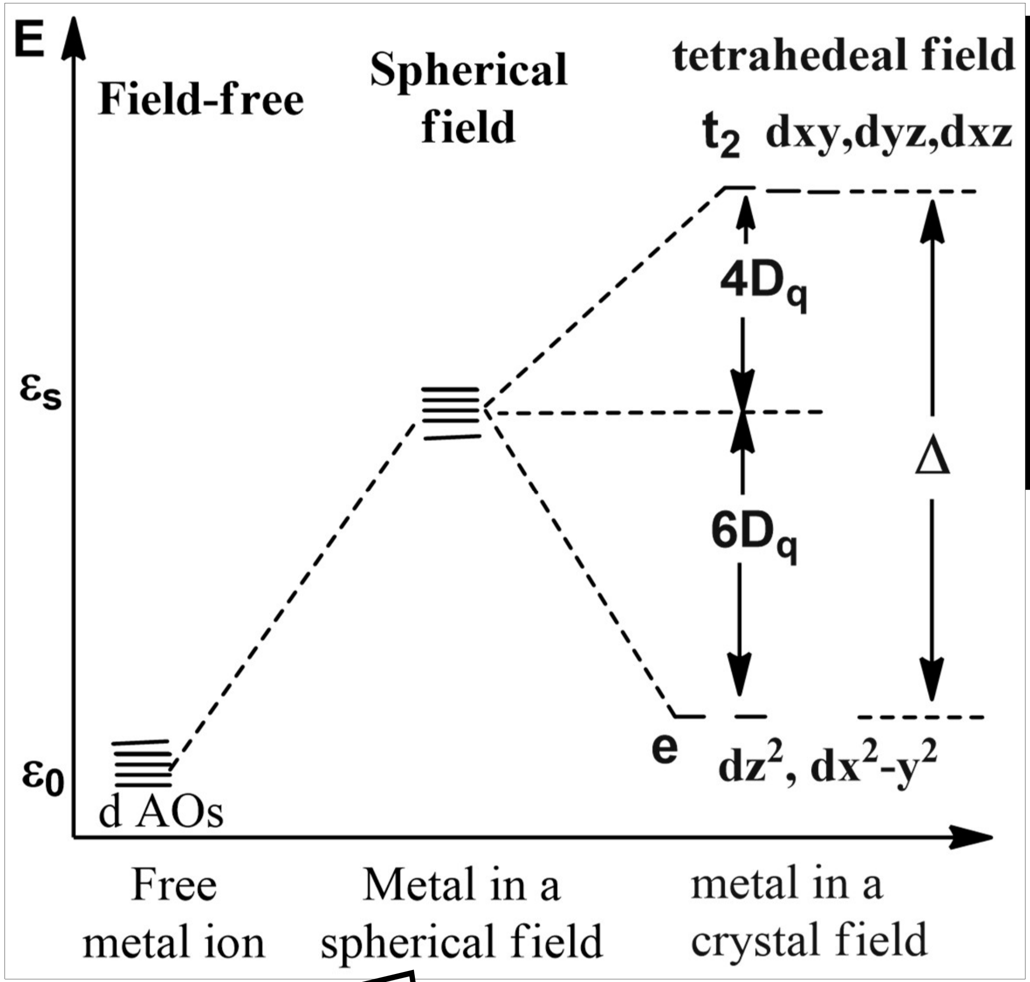
Example 2: tetrahedral field - qualitative analysis





- The distance between dxy (also dyz, dxz) and ligands is shorter than that between d(x^2-y^2) (also dz^2) and ligands.
- Accordingly, the d_{xy}, d_{yz}, and d_{xz} suffer stronger repulsion of the ligands than do the d(x^2-y^2) & dz^2 orbitals.

Example 2: tetrahedral field – A semiquatitative picture



A hypothetic field by supposing the negative charges of ligands are evenly distributed over the shell.

Stronger CF results in:

i) Larger ε_s - ε_0 gap.

ii) Larger crystal-field splitting energy Δ.

$$\because 6E_{t_2} + 4E_e = 10\varepsilon_s$$

Suppose $\boldsymbol{\varepsilon_S = 0}$, and

$$\Delta = E_{t_2} - E_e = 10D_q$$

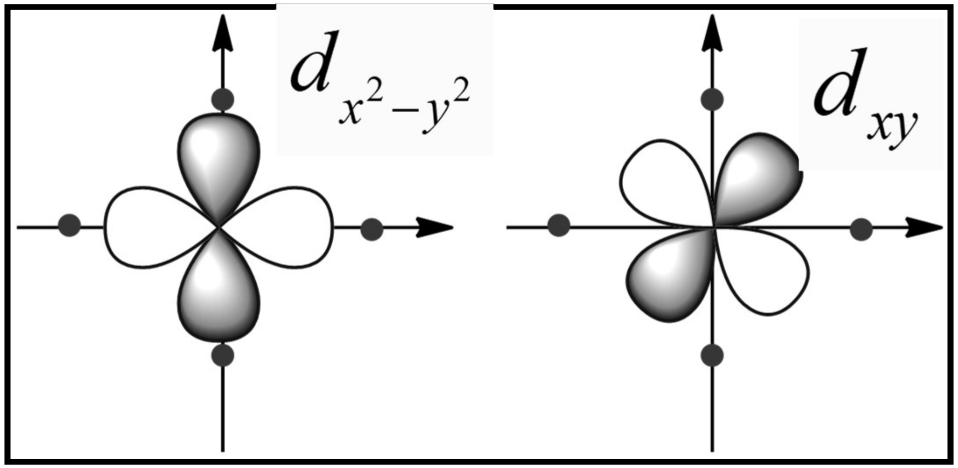
$$\Rightarrow 6E_{t_2} + 4E_e = 10\varepsilon_s = 0$$

$$\Rightarrow E_e = -6D_q = -\frac{3}{5}\Delta$$

$$E_{t_2} = 4D_q = \frac{2}{5}\Delta$$

A. Crystal-field splitting of d orbitals

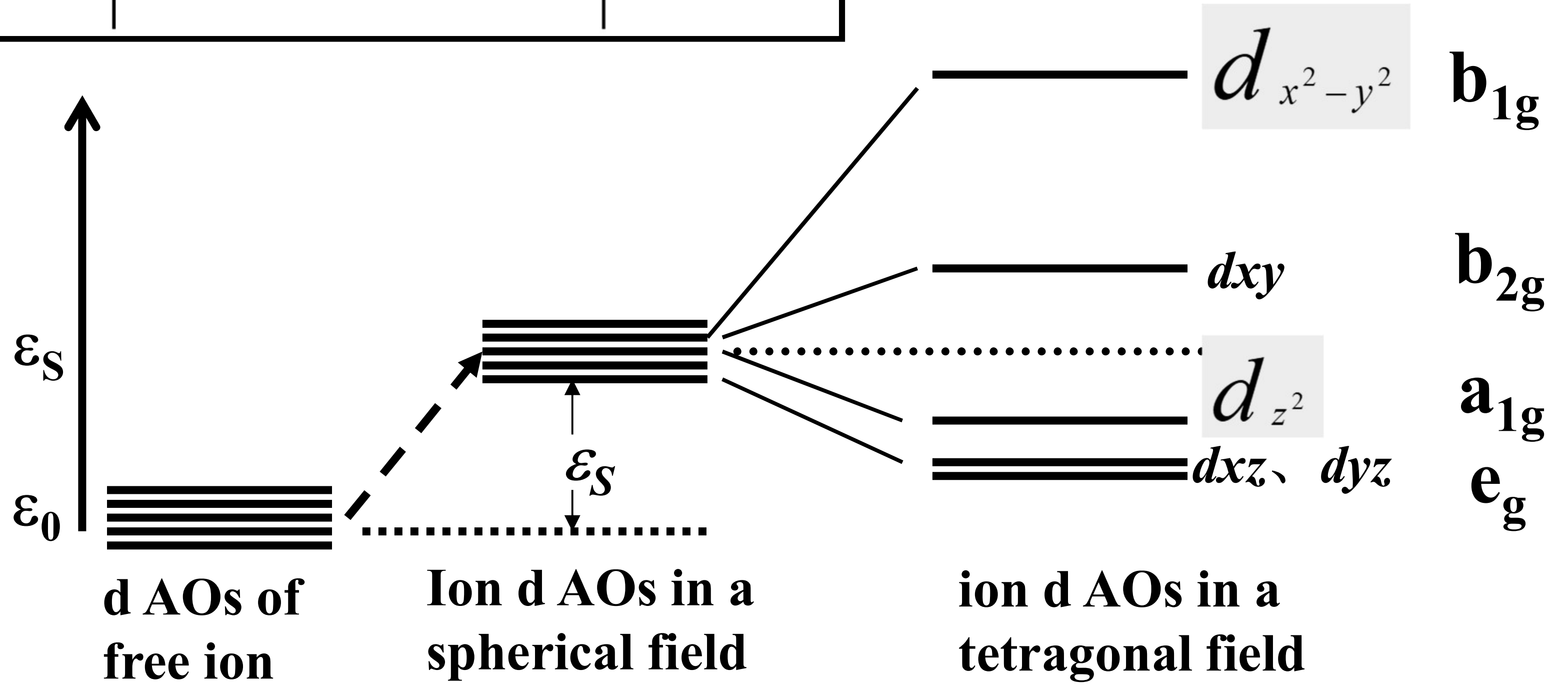
Example 3: Planar tetragonal (D_{4h}) field



- Repulsion of ligands:

  $d(x^2-y^2)$ > dxy > dz^2

  > $dxz = dyz$



Different types of crystal field induce different patterns of d-orbital splitting.

l	AOs	O_h (octahedral)	T_d	D_{4h}
0	*s*	a_{1g}	a_1	a_{1g}
1	*p*	t_{1u}	t_2	$a_{2u} < e_u$
2	*d*	$t_{2g} < e_g$ ($t_{2g} > e_g$ in a cube)	$e < t_2$	$e_g < a_{1g} < b_{2g} < b_{1g}$
3	*f*	$a_{2u} + t_{1u} + t_{2u}$		

Question: Why are the three *p* orbitals degenerate in a crystal field of O_h- or T_d-symmetry, but non-degenerate in a crystal-field of D_{4h}-symmetry?

B. Effects of Crystal-field splitting

B1. spectrochemical series

$CN^- > NO_2^- > en > NH_3 > H_2O > C_2O_4^{2-} > OH^- > F^- > Cl^- > Br^- > I^-$

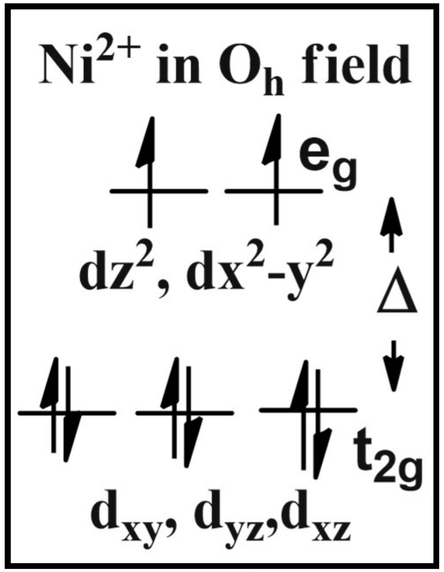
strongest CF → weakest CF

largest Δ   smallest Δ

Ni^{2+}: $t_{2g} \rightarrow e_g$

d-d excitation:

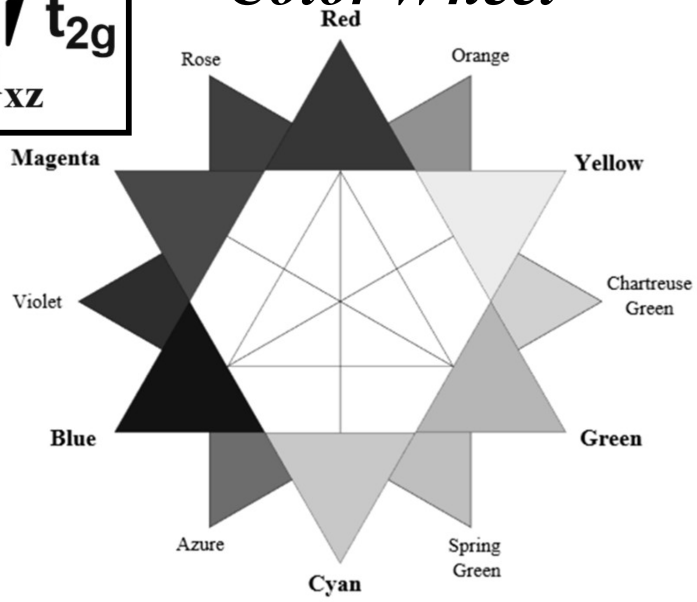
$\Delta E = h\nu$ ~visible region (UV-vis)



ROYGBV

lower E   higher E

Color Wheel



	absorbs	appears
weakest $Ni(H_2O)_6^{2+}$	<R	GB
$Ni(NH_3)_6^{2+}$	O	B
$Ni(en)_3^{2+}$	G	V
Strongest $Ni(CN)_4^{2-}$	BV	Yellow

en=ethylenediamine

B. Effects of Crystal field splitting

charge on metal

- **greater charge ⇒ larger Δ**
  (ligands held more closely, thus interacting more strongly with *d* orbitals, and exerted a stronger crystal field.)

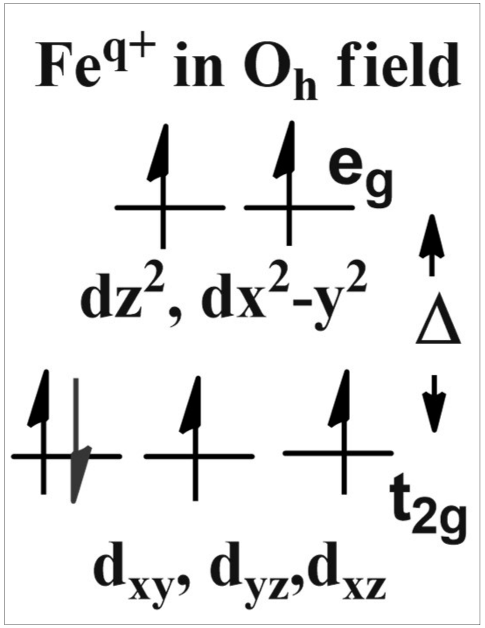
	absorbs	appears
$Fe(H_2O)_6^{2+}$	Red	Green
$Fe(H_2O)_6^{3+}$	Violet	Red-Orange

ROYGBV
lower E higher E

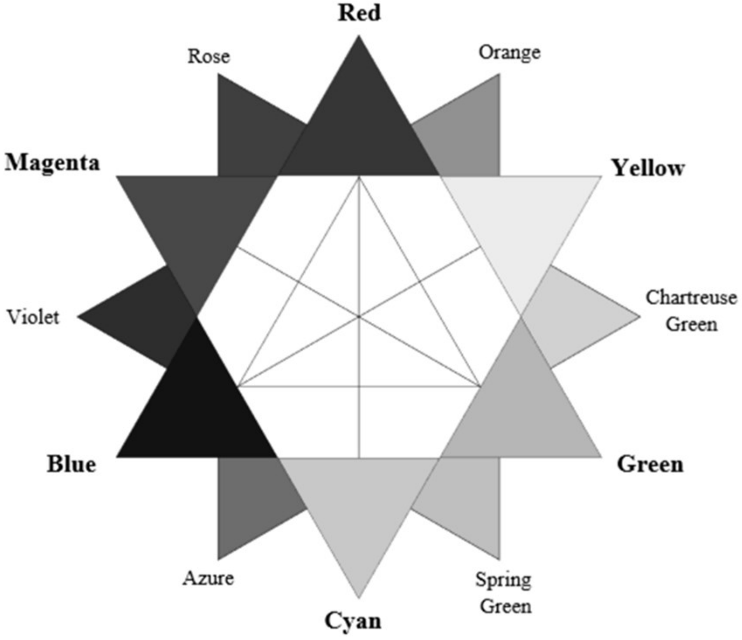
hν

Fe^{q+}: $t_{2g} \rightarrow e_g$

(q=2, $3d^6$)
(q=3, $3d^5$)



Color Wheel

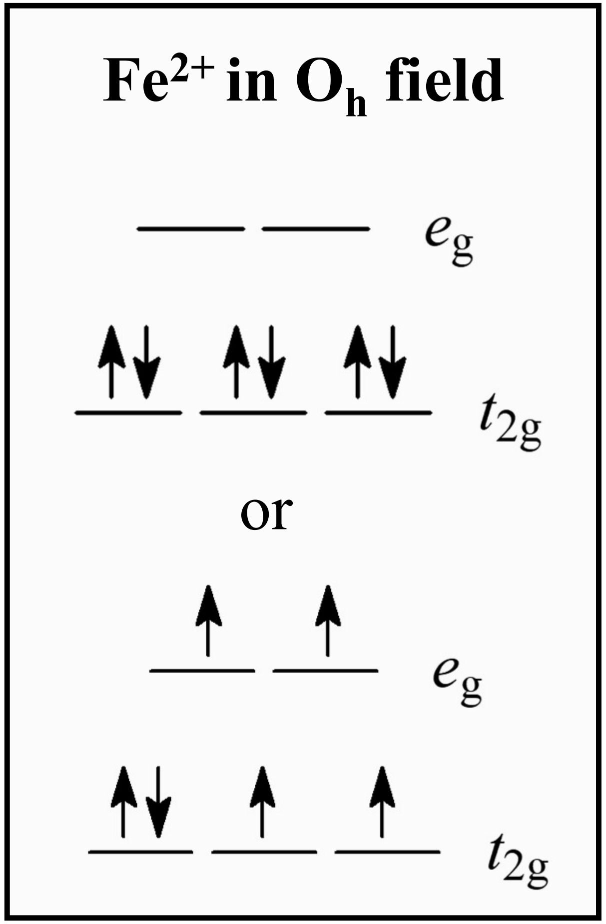


B2. Magnetic properties

No unpaired electrons, S = 0, diamagnetic

unpaired electrons, S ≠ 0, paramagnetic, ESR active!

Magnetic momentum $$\mu_m = 2\sqrt{S(S+1)}\,\mu_B = \sqrt{n(n+2)}\,\mu_B$$ ***n***: number of spin-unpaired electrons



Fe^{2+} in O$_h$ field

e.g., **Fe(H$_2$O)$_6$$^{2+}$** **(Fe^{2+} = *d*^{6})**

weak-field ligands !

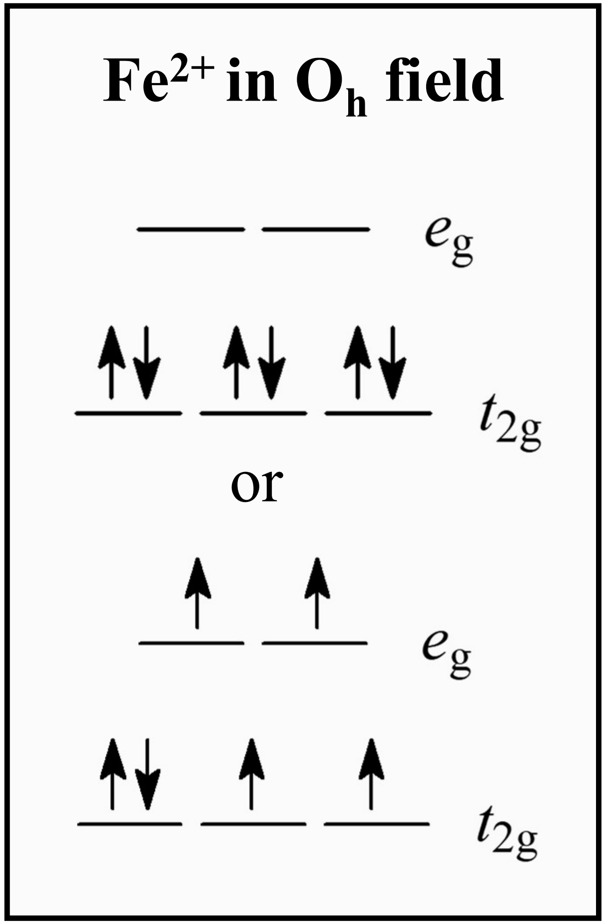
Case I: low-spin
(maximum pairing)
diamagnetic

Case II: high-spin ← **found experimentally**
(minimum pairing)
paramagnetic

S=2， μ ≈ 4.9μ$_B$

B2. Magnetic properties

e.g., **$Fe(NH_3)_6^{2+}$** **($Fe^{2+} = d^6$)** Strong-field ligands


Fe^{2+} in O_h field

Case I: low-spin ← found experimentally!
(maximum pairing)
diamagnetic
S=0

Case II: high-spin
(minimum pairing)
paramagnetic

B2. Magnetic properties

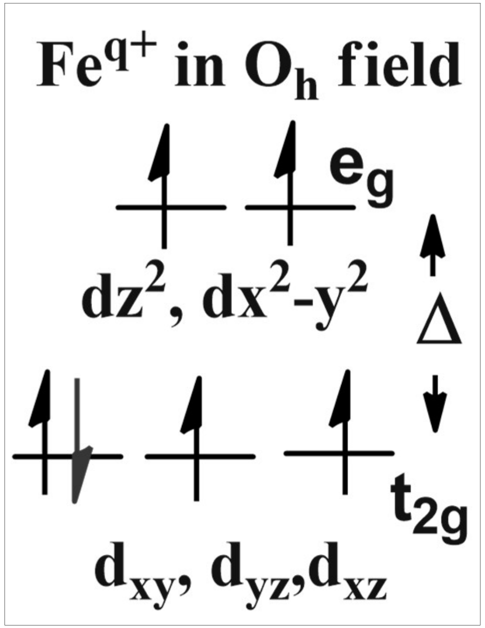
Competition between:

crystal-field splitting (Δ) vs electron pairing energy ($P>0$)

enhanced e-e repulsion!

when $\Delta < P \Rightarrow$ high-spin complex

when $\Delta > P \Rightarrow$ low-spin complex



In General,

d^1, d^2, d^3: always high-spin

d^4, d^6: high-spin with ligands $\leq H_2O$

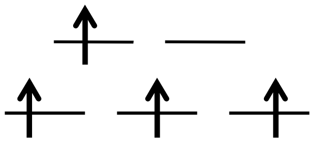
low-spin with ligands $> H_2O$

d^5: high-spin with all ligands except CN^-

d^7-d^{10} always low-spin

B2. Magnetic properties

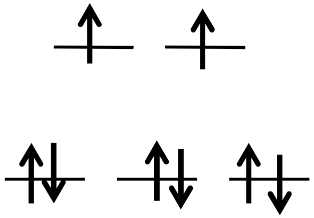
e.g., $[Cr(H_2O)_6]^{2+}$ $3d^4$ weak CF



→ high-spin

→ S=2

e.g., $[Ni(NH_3)_6]^{2+}$ $3d^8$ strong CF



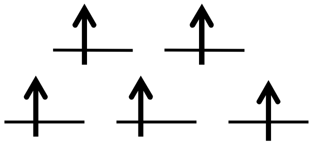
→ low-spin (too many electrons)

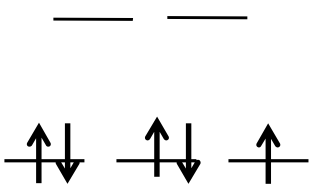
→ S=1

e.g., $[Fe(H_2O)_6]^{3+}$ vs $[Fe(CN)_6]^{3-}$ $3d^5$

weak field

Very strong field





S=5/2, $\mu \approx 5.9\mu_B$

S=1/2, $\mu \approx 1.7\mu_B$

Question: Is it possible to design such a coordination compound that has comparable energy in its high- and low-spin states?

- **Spin crossover (SCO)/Spin transition (ST)** ***Entropy-driven!***

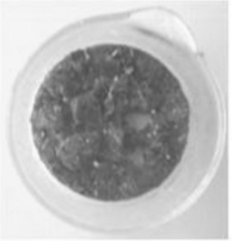
1) M^{q+}: d^4-d^7; 2) $\Delta E(\text{HS-LS}) \approx k_BT$; 3) Mostly six-coordinated.

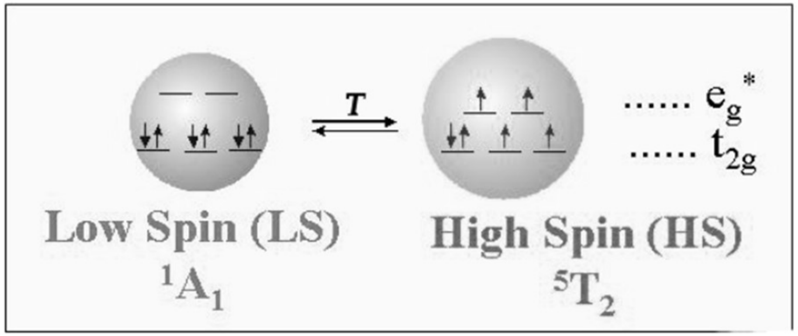
$\Delta S(\text{HS-LS}) > 0$ & $\Delta H(\text{HS-LS}) \approx \Delta E(\text{HS-LS}) > 0$

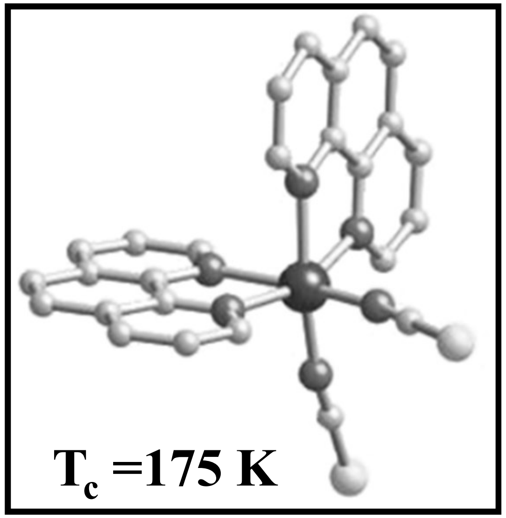
$\Delta G(\text{HS-LS}) = \Delta H - T\Delta S \approx \Delta E - T\Delta S$;

When $T > T_c$, $\Delta G \leq 0$; → $\mathbf{T_c = \Delta E/\Delta S}$ **&** $\mathbf{\Delta E(HS\text{-}LS) \approx k_BT}$

HS state:
weaker CFT! →
Longer M-L distance!
→ higher S!

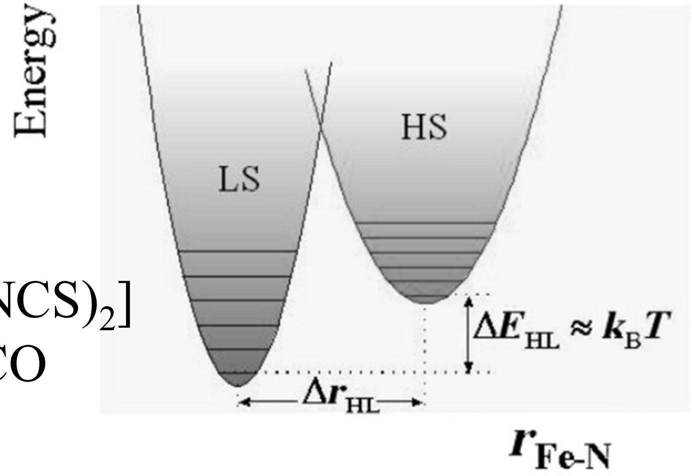






T_c =175 K

[Fe(phen)$_2$(NCS)$_2$]
--the first SCO
compound



Madeja, K.; König, E. *J. Inorg. Nucl. Chem.* **1963,** *25,* 377–385.

External stimuli for spin crossover：

1) Variation of Temperature
2) Variation of pressure
3) Light irradiation
4) Influence of a magnetic field

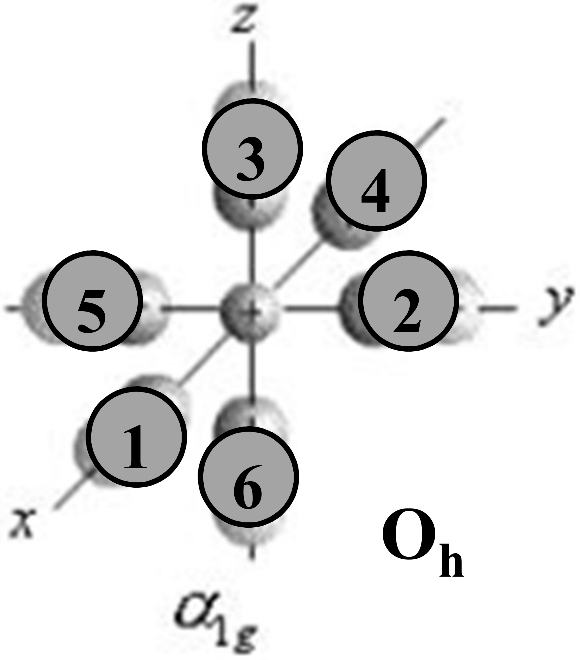
Methods of Study:

SQUID(Magnetic susceptibility), Mössbauer Spectroscopy, X-ray crystallography, UV-vis, Raman etc.

6.2.3 σ ligands and σ bond: A Molecular orbital (MO) theory description

Example:

Octahedral coordination complex



Categories of central metal valence orbitals:

σ type: s (A_{1g}); p_x, p_y, p_z(T_{1u}); $d_{x^2-y^2}$, d_{z^2}(E_g)

π type: d_{xy}, d_{xz}, d_{yz} （T_{2g})

6 ligands contribute 6 lone pairs:

$\{\sigma_1, \sigma_2, \sigma_3, \sigma_4, \sigma_5, \sigma_6\}$ $\Longrightarrow$ $\Gamma_{\sigma 1\text{-}6} = A_{1g} \oplus T_{1u} \oplus E_g$

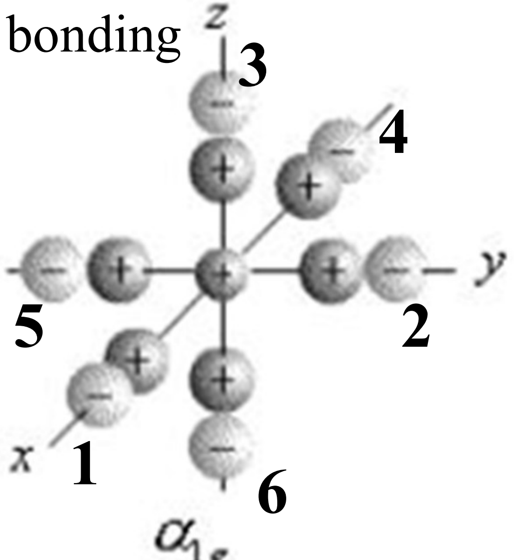
$\Longrightarrow$ *(Projection operator!) 6 SALCs formed by the 6 lone pairs)*

➔ **A total of 12 σ-type AOs give rise to 12 σ-type MOs,**

i.e., 6 bonding (occupied) + 6 antibonding (empty) !

6.2.3 σ ligands and σ-bonding MO′s

Symmetry-adapted linear combination (SALC) of MOs:



α_{1g}

$$\psi_1 = \varphi_{4s} \pm \frac{1}{\sqrt{6}}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)$$

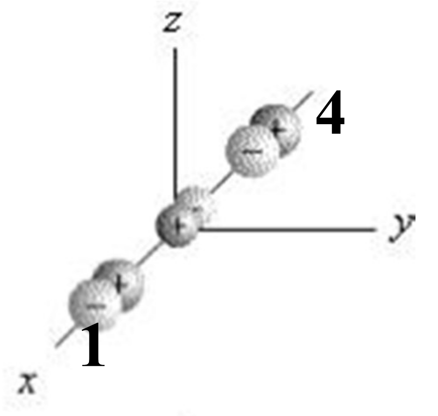
a_{1g}

t_{1u}

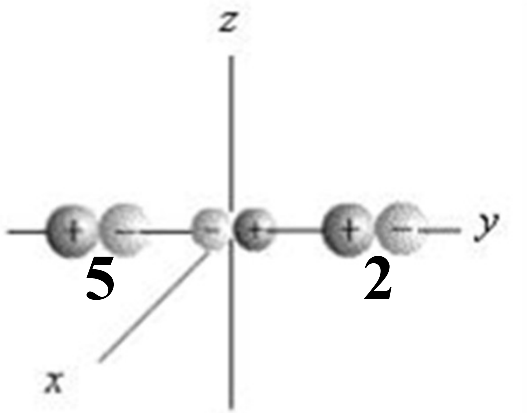
$$\psi_2 = \varphi_{4px} \pm \frac{1}{\sqrt{2}}(\sigma_1 - \sigma_4)$$

$$\psi_3 = \varphi_{4py} \pm \frac{1}{\sqrt{2}}(\sigma_2 - \sigma_5)$$

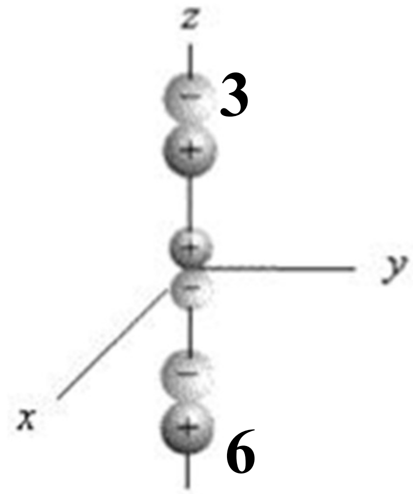
$$\psi_4 = \varphi_{4pz} \pm \frac{1}{\sqrt{2}}(\sigma_3 - \sigma_6)$$



t_{1ux}



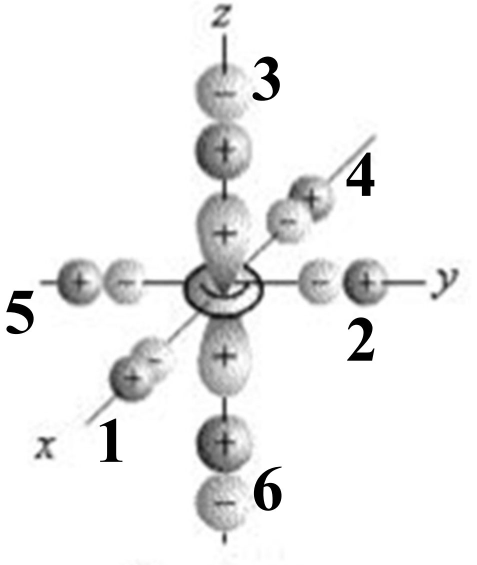
t_{1uy}



t_{1uz}

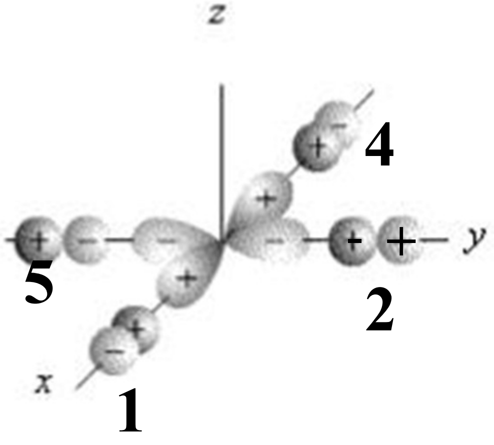
e_g

$$\psi_5 = \varphi_{3dz^2} \pm \frac{1}{2\sqrt{3}}(2\sigma_3 + 2\sigma_6 - \sigma_1 - \sigma_2 - \sigma_4 - \sigma_5)$$

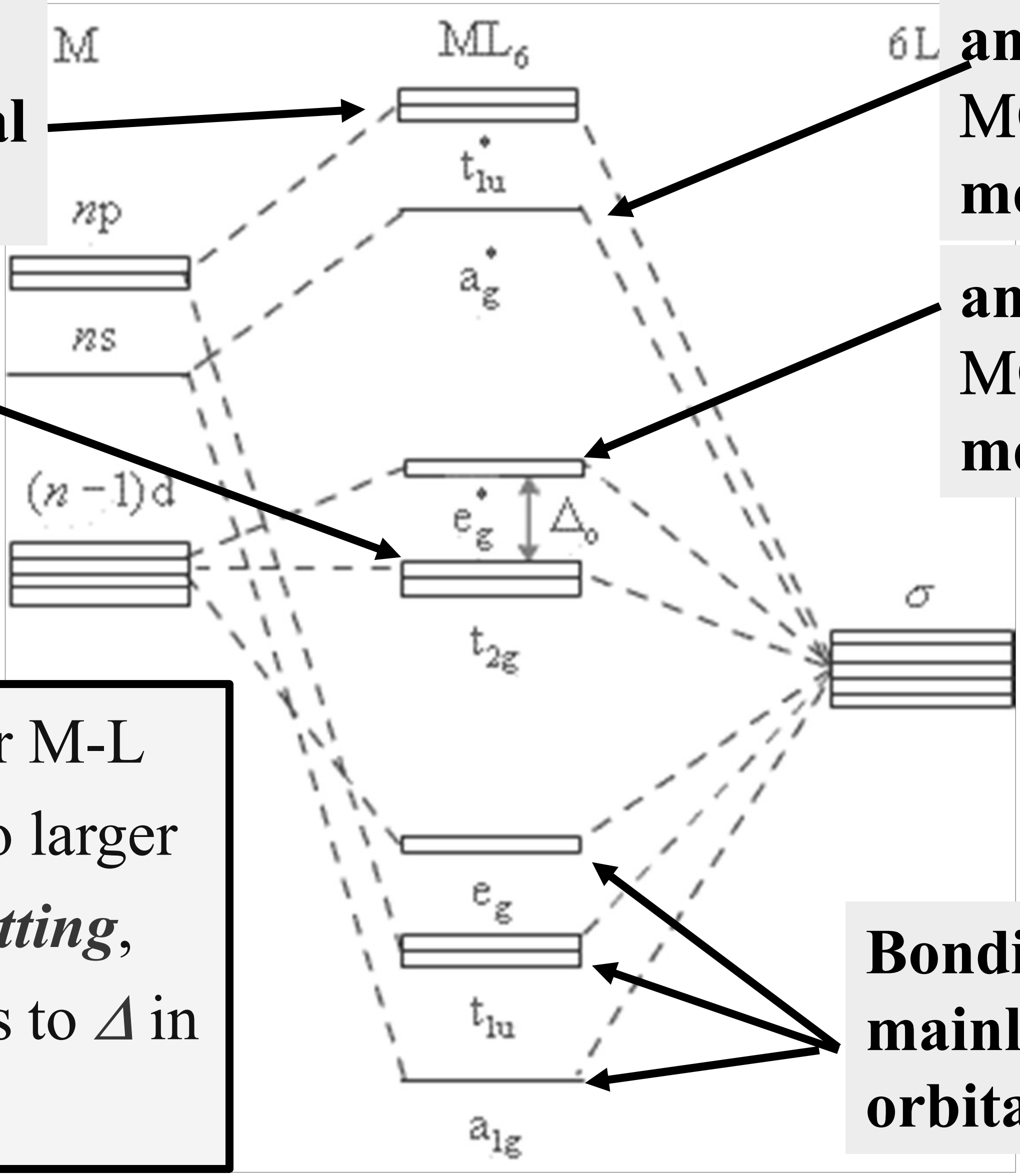


$e_{g(3z^2-r^2)}$

$$\psi_6 = \varphi_{3dx^2-y^2} \pm \frac{1}{2}(\sigma_1 - \sigma_2 + \sigma_4 - \sigma_5)$$



$e_{g(x^2-y^2)}$



anti-bonding σ–MOs/ mainly metal np orbitals

anti-bonding σ–MOs / mainly metal ns orbitals

anti-bonding σ–MOs / mainly metal d_σ orbitals

Non-bonding d_π orbitals of metal.

Bonding σ–MOs/ mainly ligands σ orbitals

Note: The stronger M-L σ-bonding leads to larger *e_g*-t_{2g} energy splitting*, which corresponds to *Δ* in the CF theory.

Energetic diagram of σ molecular orbitals

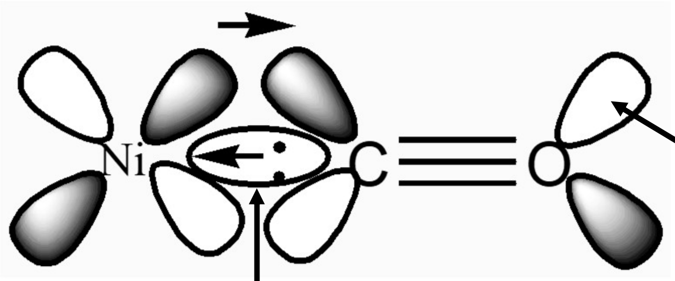
6.2.4 **Metal-ligand π – Bonding**

In addition to the aforementioned σ-bonding interactions, metal-ligand π-bonding may present in some metal complexes.

- A π-donor ligand donates electrons to the metal center in an interaction that involves a filled ligand orbital and an empty metal orbital.
  - **Cl^-, Br^-, and I^- donates p_π electrons to the metal center**
- A π-acceptor ligand accepts electrons from the metal center in an interaction that involves a filled metal orbital and an empty ligand orbital.
  - **CO, N_2, NO, and alkenes accept d_π-electrons into their vacant anti-bonding π*-MOs.**
  - **π-acceptor ligands can stabilize low oxidation state metal complexes.**

$Ni(CO)_4$ Ni($3d^{10}$: sp^3 hybridization)

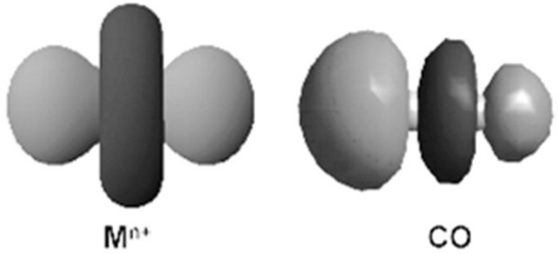
CO $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^2\mathbf{(5\sigma)^2(2\pi^*)^0}$



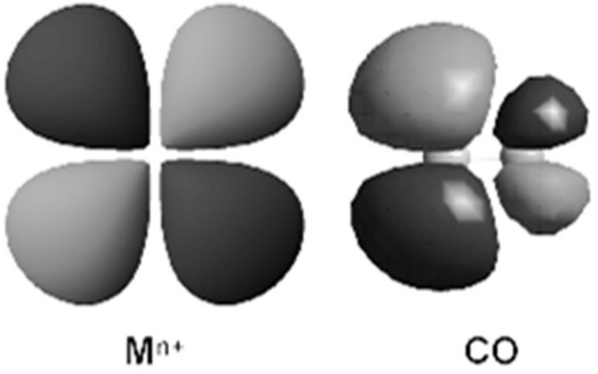
2π*-MO of ligand

(d_{xy}, d_{xz}, d_{yz}) σ bond/σ-donation

Metal d-AO **CO 5σ/HOMO**



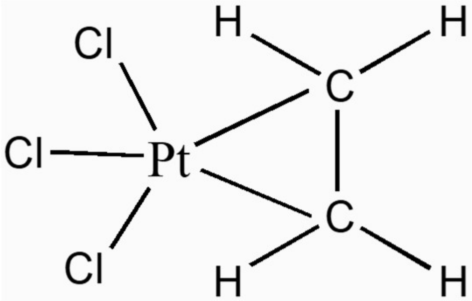
Metal dπ **CO 2π*/LUMO**

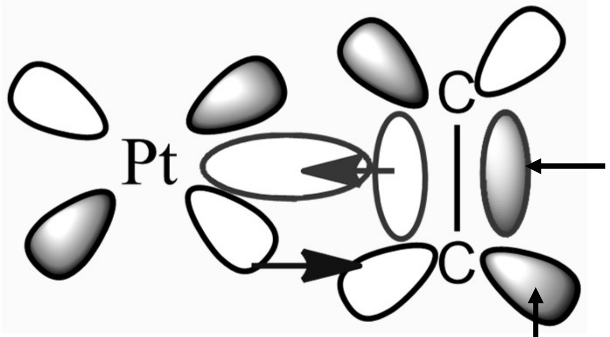


d_π-π* bonding/back-donation

CO bond weakened

$[PtCl_3(C_2H_4)]^-$ Pt^{2+}($3d^8$): dsp^2





π bonding orbital

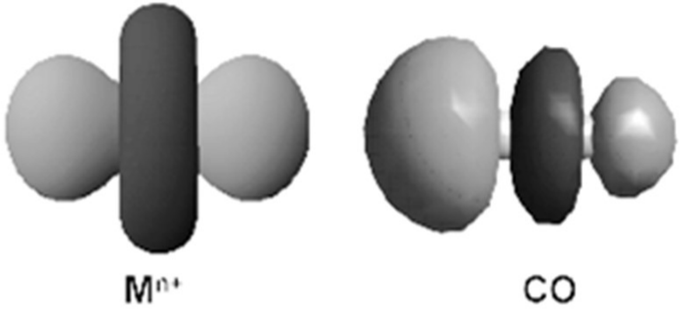
π* anti-bonding orbital

Dewar-Chatt-Duncanson complexation model

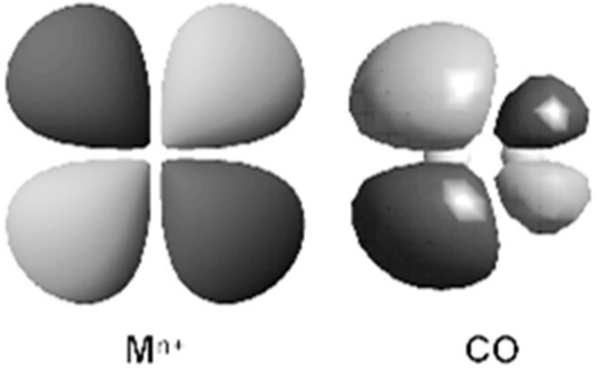
Bonding and charge transfer between transition metal and Ligands:

1. σ-bonding results in σ-donation from ligand to empty AO/HO of TM.
2. π-bonding, if available, gives rise to π-backdonation from dπ of TM to the empty π* of ligands.

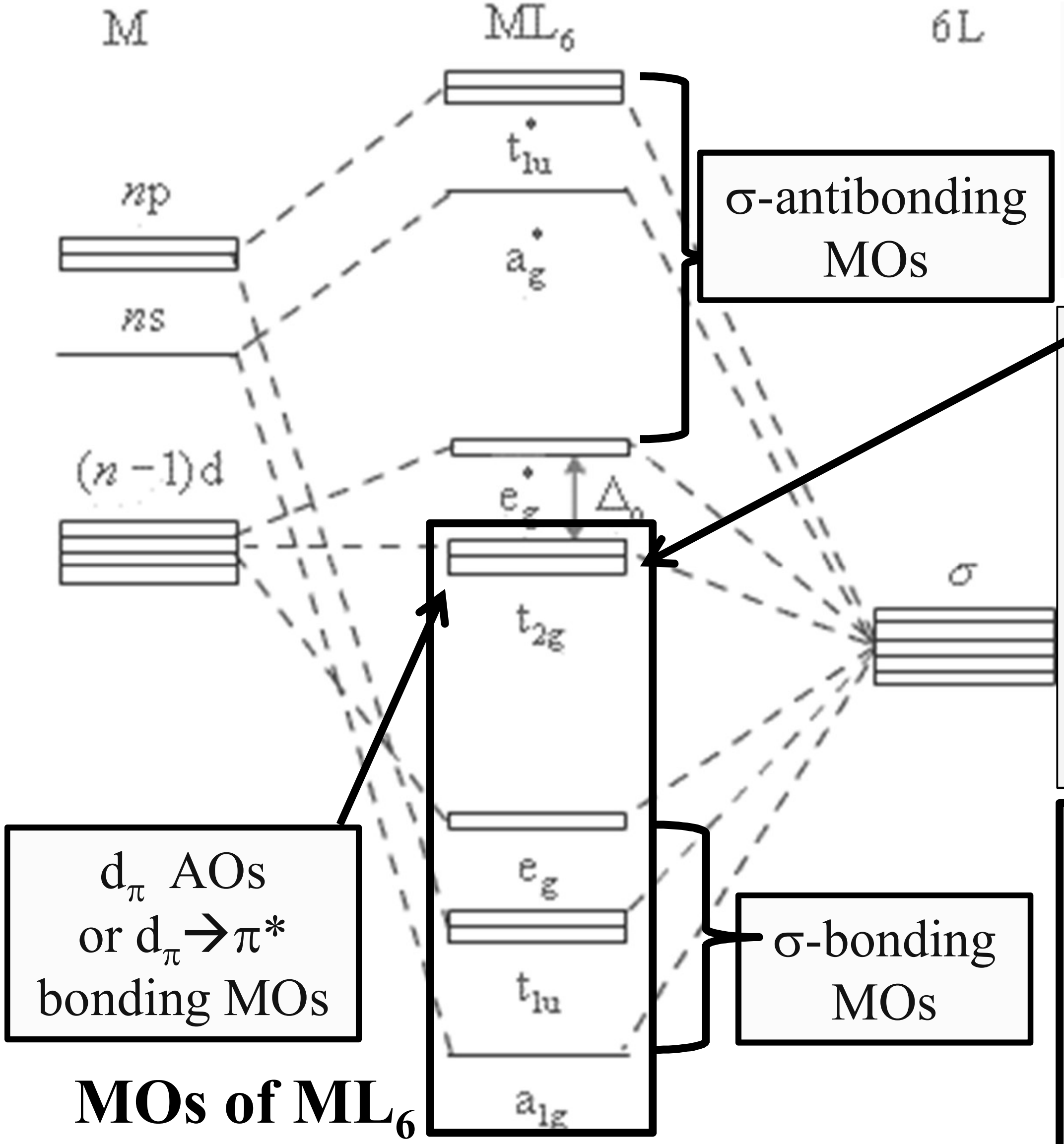
$d^m sp^n$ hybridized orbital ← 5σ (CO HOMO)



$d_\pi \rightarrow 2\pi^*$ (CO LUMO)



σ-donation and π-backdonation in metal carbonyl complexes



σ-antibonding MOs

σ-bonding MOs

d_π AOs or $d_\pi \rightarrow \pi^*$ bonding MOs

MOs of ML$_6$

- To maintain metal-ligand $d_\pi \rightarrow \pi^*$ bonding, the metal-ligand σ-bonding should be covalent!

6 bonding + 6 anti-bonding σ-MOs

- The t_{2g} d_π-orbitals are substantially stabilized upon $d_\pi \rightarrow \pi^*$ interactions, which in turn enlarges the energy gap Δ_0 and ensures a low-spin state of the metal ion!

- The as-formed metal-ligand σ-bonding and non-bonding (mostly π-bonding) MOs amount to ***nine***, ***acquiring a total of 18 VEs***!

→ 18-electron rule of transition metal complexes !

6.2.5 18-electron rule

- First proposed by ***Irving Langmuir*** in 1921.
- For a ***low-oxidation-state*** organometallic complex (mostly containing π-acceptor ligands), the metal center tends to acquire 18 electrons in its valence shell, i.e***., (n-1)dnsnp***.
- Combination of the ***9*** atomic orbitals, ***(n-1)dnsnp***, of a TM atom with ligand orbitals creates ***9 occupied molecular orbitals*** that are either metal-ligand bonding or non-bonding.

– metal is electron rich (low oxidation number)

– ligands are good π-acceptors (CO, NO) → strong dπ-π* bonding enhances M-L σ–bonding → larger Δ.

– mostly *6-coordinated* complexes with large splitting energy, i.e., the *M* atom adopts d^2sp^3 *hybridization*. (More convenient VB description).

How to use the 18e rule:

- Treat the ligand as neutral entity.
- The number of valence electrons for a zero-valent metal center is equal to the group number. e.g., Cr(6e) in $Cr(CO)_6$. $Cr(CO)_6$-- d^2sp^3 + $3d^6$ vs. $3d^54s^1$ (free Cr)
- Rearrangement of valence-shell electrons, if necessary, occurs on the central TM atom.

$Fe(CO)_5$: square pyramidal, Fe($3d^8$ + dsp^3 hybridization)

(free Fe atom--$3d^64s^2$)

$Ni(CO)_4$: tetrahedral, Ni ($3d^{10}$ + sp^3 hybridization).

(free Ni atom--$3d^84s^2$)

Alternatively, you may treat the metal and its ligands in their valence states.

18-electron rule

Many ligands donate more than 1 electron. How to count the electrons donated by ligands?

a) 1-electron donor:

$H^{\bullet}$(in any bonding mode), and terminal $Cl^{\bullet}$, $Br^{\bullet}$, $I^{\bullet}$, $R^{\bullet}$ (e.g. R=alkyl or Ph), and $RO^{\bullet}$;

b) 2-electron donor:

π-MO as ligand orbital.

CO, PR_3, $P(OR)_3$, $R_2C{=}CR_2$ (η^2-alkene), R_2C: (carbene)

c) 3-electron donor:

η^3–$C_3H_5^{\bullet}$(allyl radical), RC(carbyne), μ_2-$Cl^{\bullet}$, μ_2-$Br^{\bullet}$, μ_2-$I^{\bullet}$, μ_2-$R_2P^{\bullet}$;

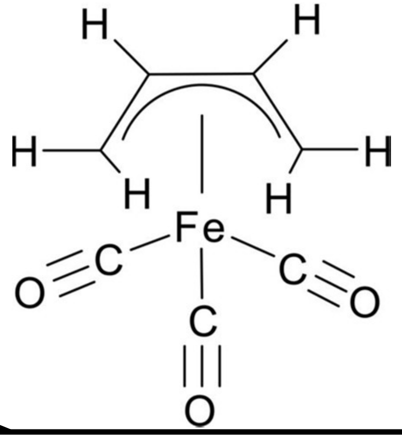
π-MOs as ligand orbitals.

+Lone pair as ligand orbital.

18-electron rule

d) 4-electron donor:

η^4–diene, η^4–C_4R_4 (cyclo-butadienes);



e) 5-electron donor:

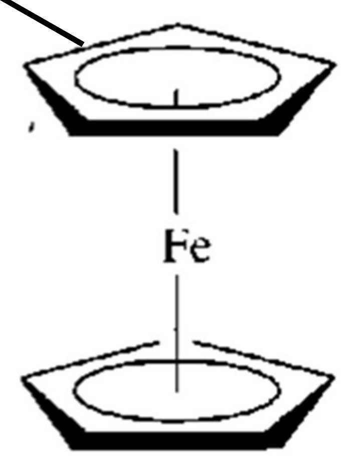
μ_3-Cl$^\bullet$, μ_3-Br$^\bullet$, μ_3-I$^\bullet$, μ_3 - $R_2P^\bullet$, η^5 **–$C_5H_5^\bullet$**;

π-MOs as ligand orbitals.

f) 6-electron donor:

η^6 –C_6H_6 , η^6 –C_6H_5Me;

g) 1- or 3-electron donor: **NO**



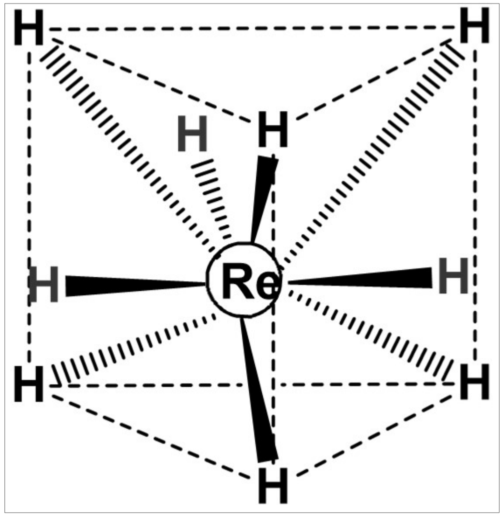
Example: Ferrocene

Some examples:

- **$[ReH_9]^{2-}$**: 7e (Re) + 9e (9H) + 2e = 18e

  Nine-coordinated! Tricapped trigonal prism!

  All *(n-1)*d*n*s*n*p AOs of metal are used to form M-L bonds!

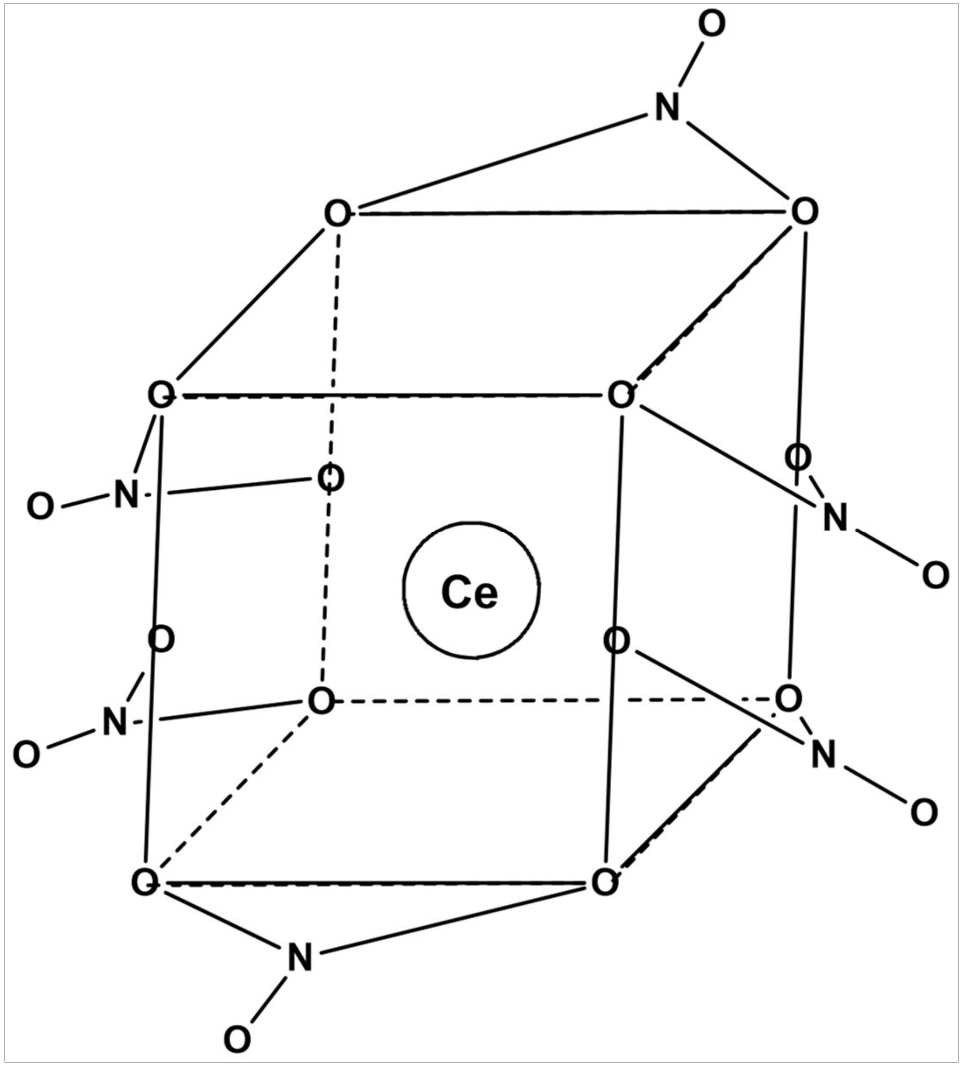


- **All lanthanides can form nine-coordinated aquo-ions.**

  $[Ln(H_2O)_9]^{3+}$; Ln 4f AOs are not involved in the dative bonding**.**

- In situation where covalency is important, ***nine*** would be the limiting coordination number of TM metals!

- However, many of the complexes involving small, nonpolarizable main-group ligand atoms have high-degree ionic characters and coordination numbers greater than ***9***.



- $[Ce(NO_3)_6]^{2-}$ 12-coordinate

Some exceptions:

- If there is no possibility to stabilize the t_{2g} level via π-bonding

→ complexes with less than 18 electrons

Examples: WCl_6^{2-} (14 e), $OsCl_6^{2-}$ (16 e), TcF_6^{2-} (15 e)

- Or if Δ is small, e_g^* orbitals may be occupied,

Examples: $Co(H_2O)_6^{2+}$ (19 e), $Ni(en)_3^{2+}$ (20e), $Cu(NH_3)_6^{2+}$ (21e)

[It is not essential for weaker CFT complexes to fulfill the 18e rule!]

- "Left side" metals: 18 electron valence shell would require too many ligands (steric repulsion)

→ complexes with less than 18 electrons are very common

Examples: TiF_6^{2-} (12 e), $Cr(NCS)_6^{3-}$ (15 e), VCl_6^{2-} (13 e)

- Square planar complexes: "16 electron rule" (all bonding orbitals are occupied, 18 e complex would have 2 e in antibonding orbitals)

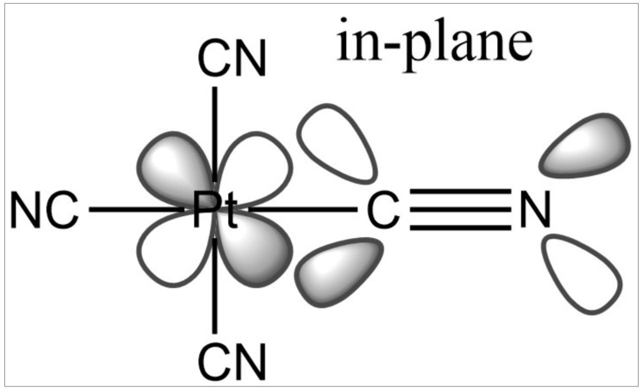
Some exceptions:

- **$[PtCl_3(C_2H_4)]^–$** : **10e (Pt) + 3e (3Cl) + 2e (C_2H_4) + e = 16e**

(Pt is dsp^2-hybridized with one $6p_z$ orbital being unoccupied. However, this unhybridized $6p_z$ orbital can interact with the p_π orbitals of such π-donor ligands as Cl, Br, I etc.)

- **$[Au(Cl)_4]^–$** : **11e (Au) + 4e (4Cl) + e = 16e**
- **$[M(CN)_4]^{2–}$** (M= **Pt, Ni**): **10e (M) + 4e (4CN) + 2e = 16e**

(involving in-plane and out-of-plane $d\pi$-π^* bondings!)



A more general rule accounts for such exceptions!

6.3 Ligand Field Theory (LFT)

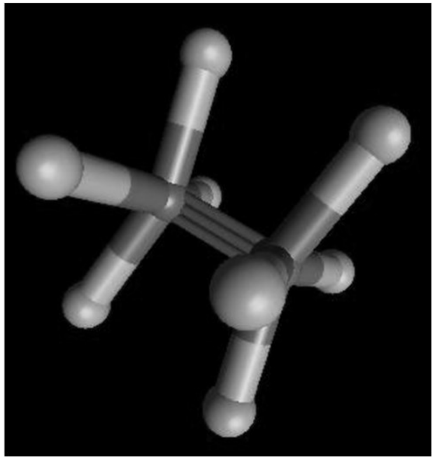
- A combination of the crystal field theory, MO theory, and group theory, but focusing on the energy splitting, spectral terms of metal ion in coordination compounds.
- Two factors influence the d-orbital splitting of a metal atom in a ligand field,

1) The interaction between d-orbital electrons;

2) The bonding between the metal and ligands.

- A strong ligand field is formed in case type **2** interaction is stronger than type **1**. Otherwise, the ligand field is a weak field.
- This rule also helps us to understand the strong and weak crystal fields defined in the crystal field theory.

6.4 Transition-metal cluster compounds
6.4.1 Metal-metal multiple bonds



$Re_2Cl_8^{2-}$ Re-Re 2.24Å(2.76 Å in Re crystal)

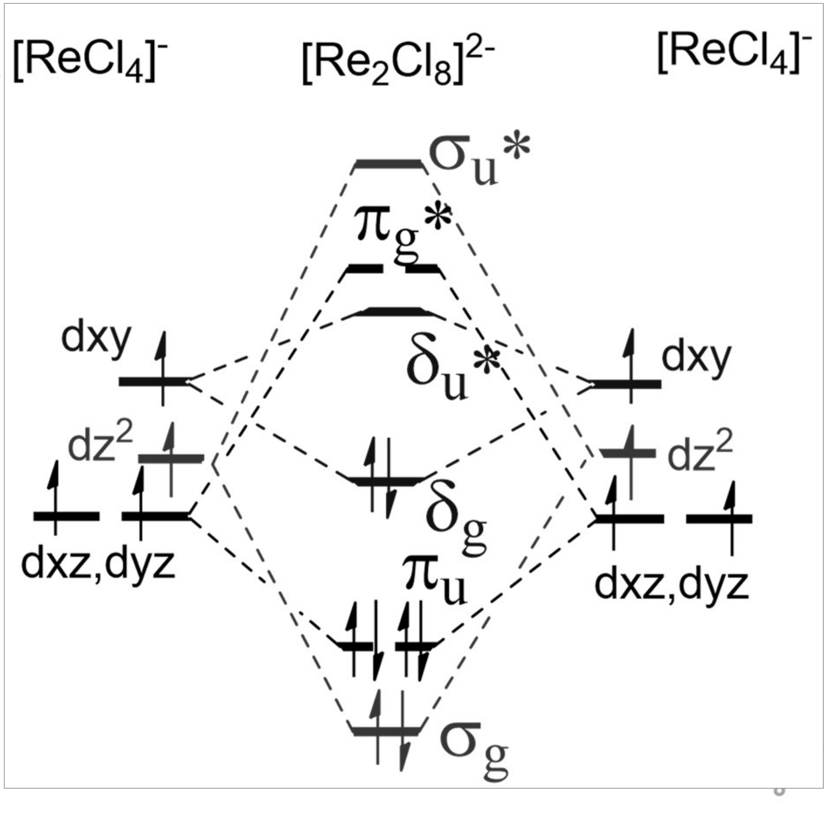
$ReCl_4^-$: Re^{3+}-$5d^4$, dsp^2, {$5dx^2$-y^2, 6s, $6p_x$,$6p_y$};

- Each HO forms a dative Re←Cl bond.
- The rest four 5d AO′s (+4e) of Re^{3+} are used to form Re-Re quadruple bonds with another Re^{3+}.

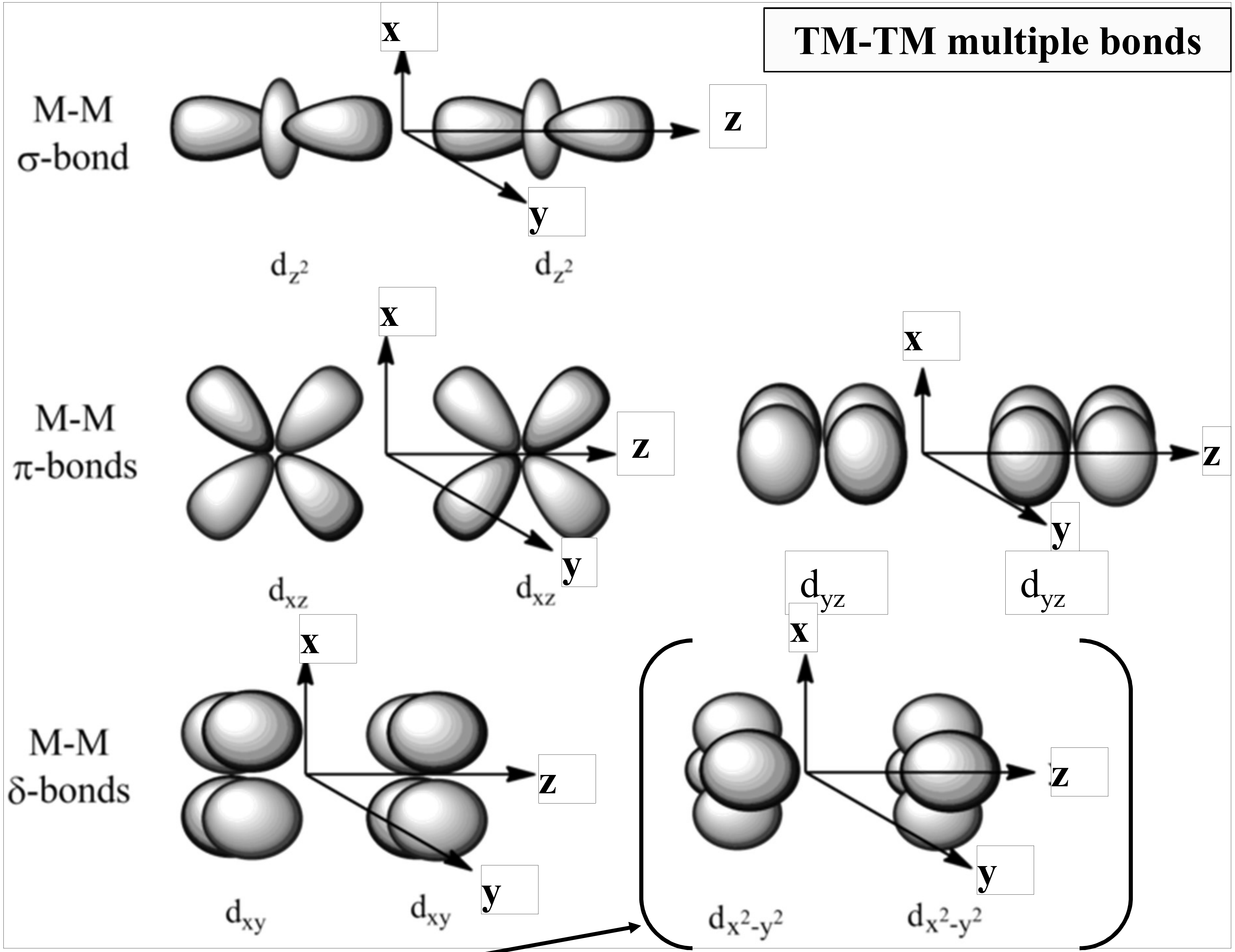
Quadruple Bond

$$\boxed{\sigma_g^{\ 2}\pi_u^{\ 4}\delta_g^{\ 2}}$$

Analog: $Mo_2(O_2CR)_4$ and $Cr_2(O_2CR)_4$

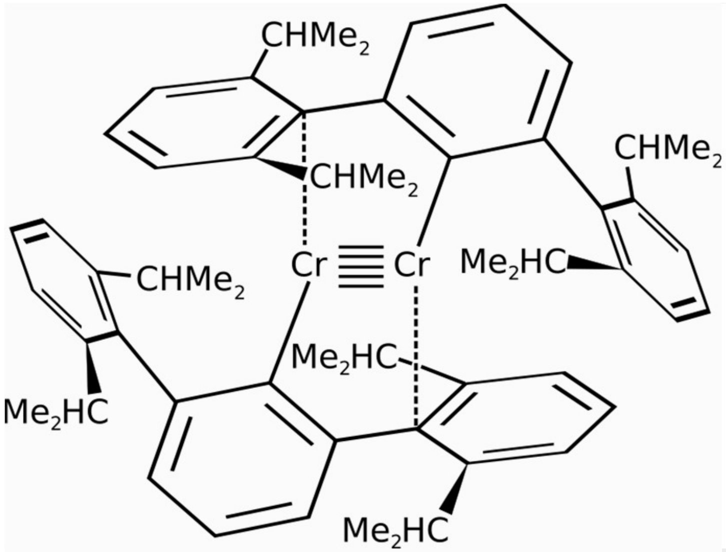


TM-TM multiple bonds



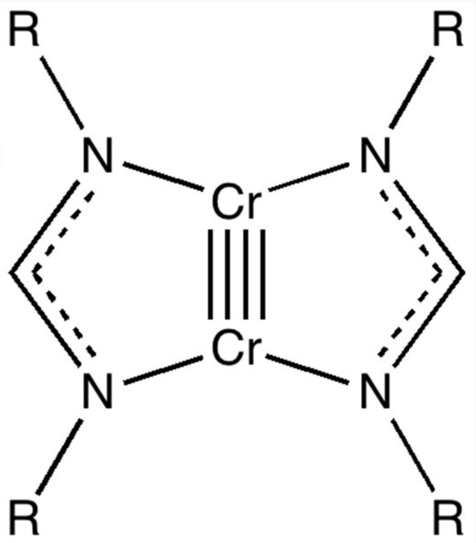
Note: This is not involved in the Re-Re quadruple bond.

- Extremely, a TM-TM bond can be a **quintuple bond** by making use of all ***(n-1)d*** orbitals, e.g., in **Cr(I)-Cr(I)** and **Mo(I)-Mo(I)** complexes.



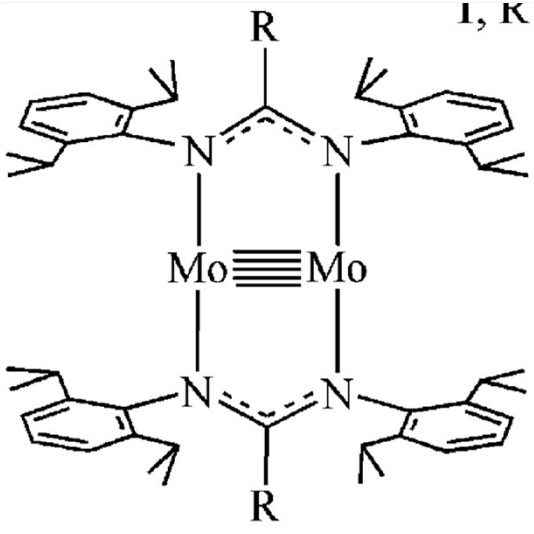
Cr_2(terphenyl)$_2$
(Cr-Cr = 1.86 Å)

P. Powers et al,
Science,
2005, 310, 844



R=Phenyl
(Cr-Cr = 1.74 Å)

Y.-C. Tsai *et al*,
Angew Chem Int Ed,
2008, 47, 9933.



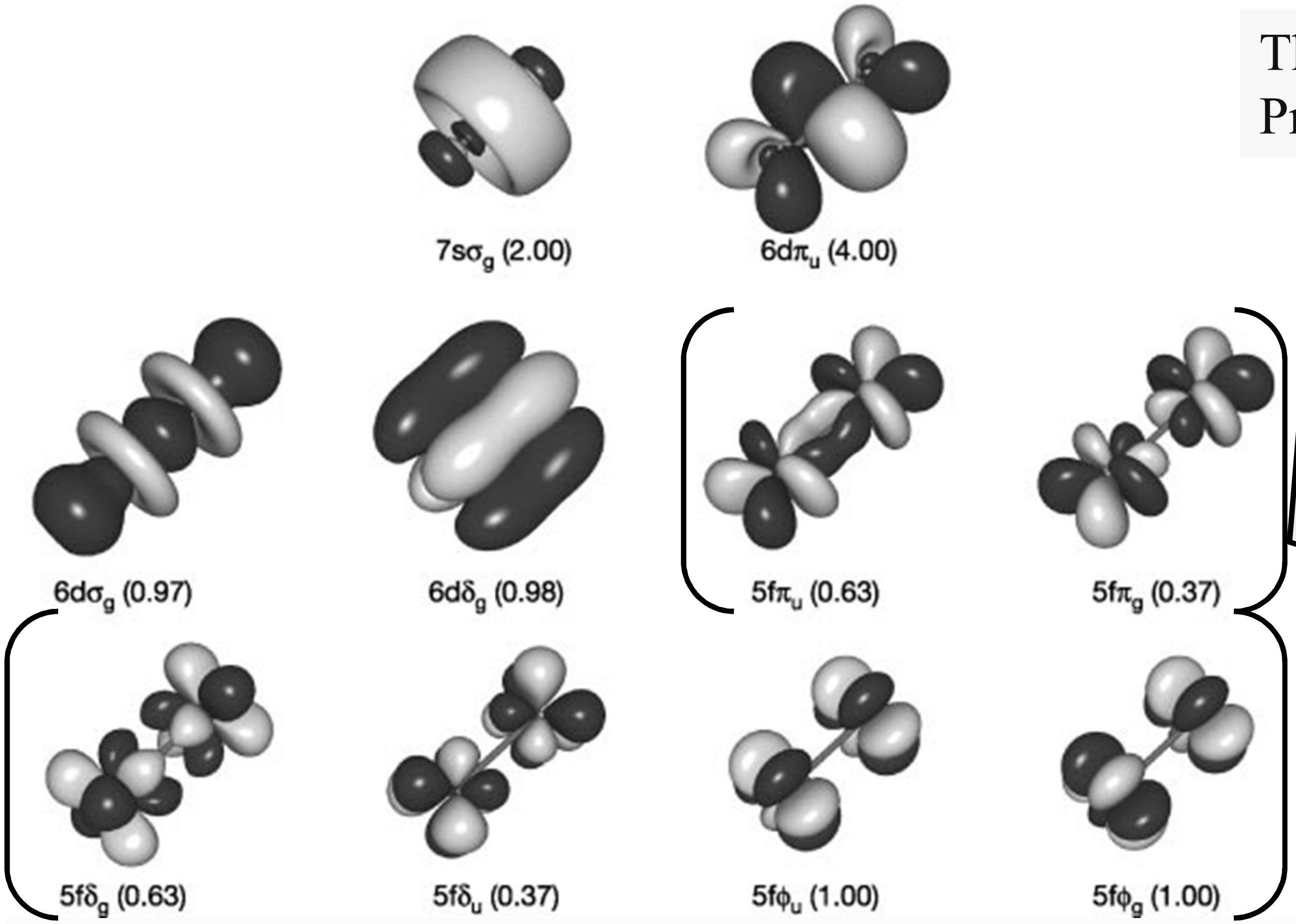
R=Phenyl, H
(Mo-Mo = 2.02 Å)

Y.-C. Tsai *et al*,
J. Am. Chem. Soc.,
2009, 131, 12534.

$$\boxed{\sigma^2\pi^4\delta^4}$$

- Similarly, two f-series metals (Ln-series or Am-series metal) can form f-orbital-based multiple M-M bond, i.e., U_2

Theoretical Prediction!



$7s\sigma_g$ (2.00) $6d\pi_u$ (4.00)

$6d\sigma_g$ (0.97) $6d\delta_g$ (0.98) $5f\pi_u$ (0.63) $5f\pi_g$ (0.37)

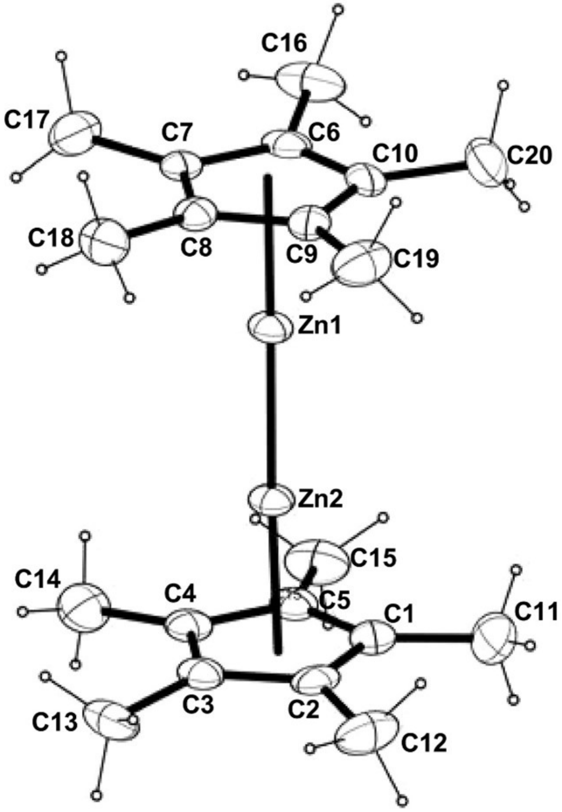
$5f\delta_g$ (0.63) $5f\delta_u$ (0.37) $5f\phi_u$ (1.00) $5f\phi_g$ (1.00)

s-, d- and f-based bonding orbitals of U_2 that has a quintuple U-U bond.

However, owing to the quite strong exchange-correlation effects, the 5f-derived π-, δ- and ϕ-type MOs are weakly bonding or even non-bonding!

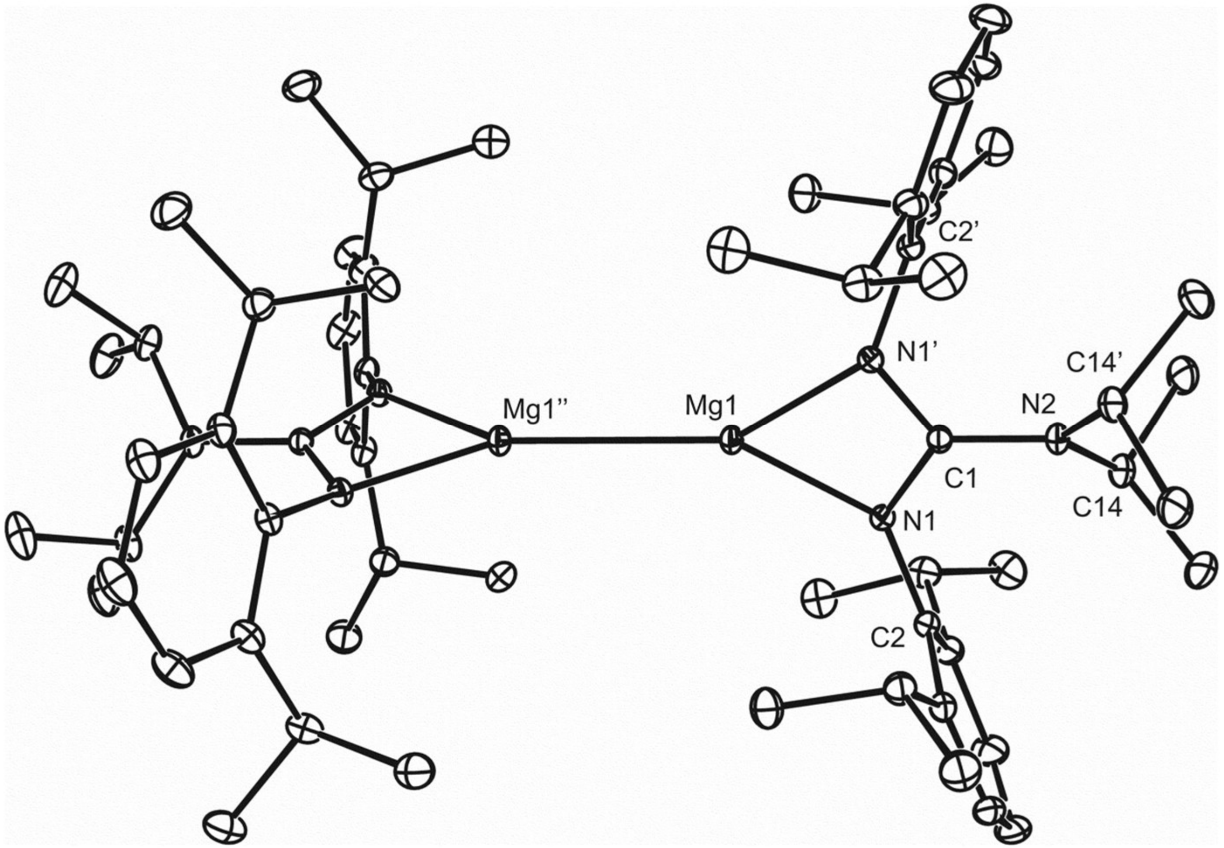
- Gagliardi and Roos, *Nature*, 2005, 433, 848.

- A M-M bond also can be formed between ***ns*** AOs of two metal atoms, e.g., in Zn(I)-Zn(I) and Mg(I)-Mg(I) complexes.



$Zn_2(\eta^5\text{-}C_5Me_5)_2$

Resa et al. *Science* 2004, 305, 1136

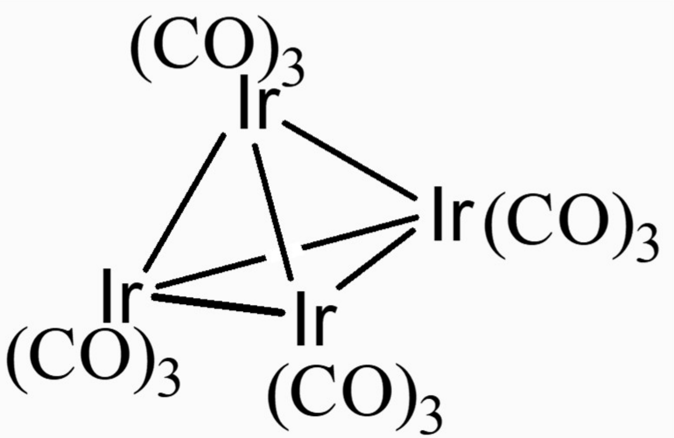


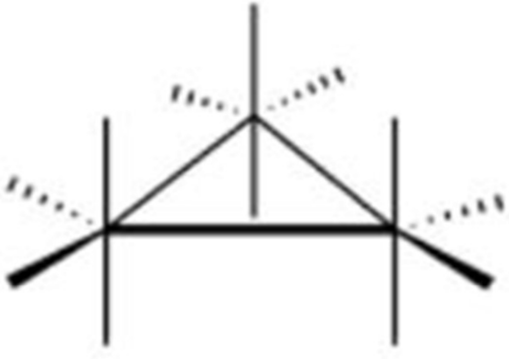
$Mg_2(N_2CR)_2$

S P Green et al. Science 2007;318:1754-1757

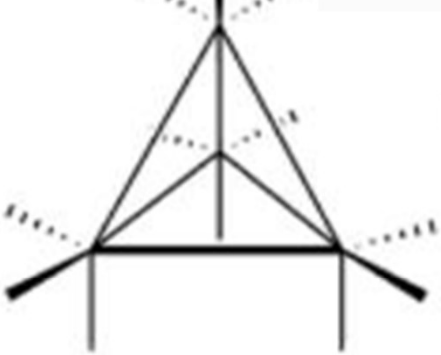
6.4.2 Cluster geometry

i. Structural polyhedron

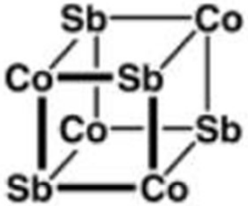




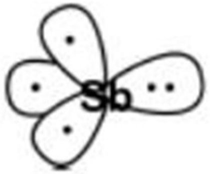
$Os_3(CO)_{12}$

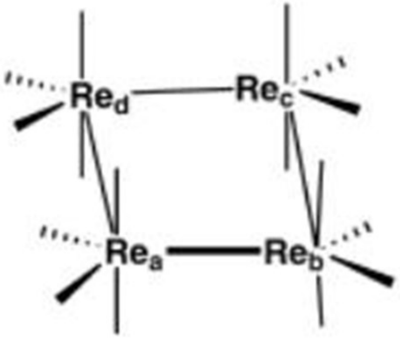


$Ir_4(CO)_{12}$



$Co_4(CO)_{12}Sb_4$





$Re_4(CO)_{16}{}^{2-}$

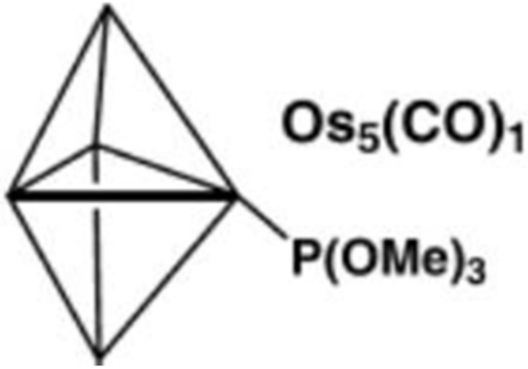
Re_a-Re_b = 3.01Å
Re_b-Re_d = 2.96Å
Re_a-Re_c = 5.23Å

$Co_6(CO)_{14}^{4-}$

$Ir_6(CO)_{15}^{2-}$

$Ir_6(CO)_{15}Cl^-$

$Ir_6(CO)_{15}PPh_3$



$Os_5(CO)_{15}[P(OMe)_3]$

$Os_5(CO)_{15}I^+$

Note: The number of edges of such polyhedra do not necessarily correspond to the number of M-M bonds!

ii. Electron counting and metal-metal bonds

$$b = \frac{1}{2}(18n - g)$$

* Derived from the 18e rule for ***low-oxidation-state transition metal complexes***!

* Valid for low-oxidation-state metal clusters.

b: bond valence (i.e., total number of metal-metal bonds)

n: number of transition-metal atoms

g: total valence-shell electrons, including electrons from all

In a metal cluster, a $\boldsymbol{ML}_x$ fragment forms a suitable number of metal-metal covalent bond(s) with its neighboring $\boldsymbol{ML}_y$ fragments to attain 18 valence-shell electrons!

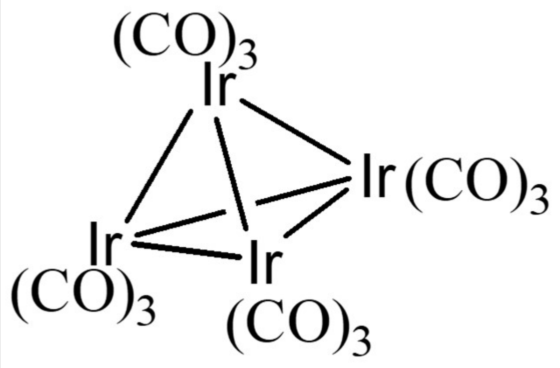
If a cluster involves main-group atoms,

$$b = \frac{1}{2}(18n_1 + 8n_2 - g)$$

$\boldsymbol{n_1}$: number of transition-metal atoms

$\boldsymbol{n_2}$: number of main-group atoms in the cluster polyhedron.

Examples:



VE = g = 4x9 (Ir: $5d^76s^2$)
+ 12x2 (CO) = 60

$\therefore$ b = (18n - g)/2
= (18x4 - 60)/2 = 6

$Ir(CO)_3$ **VAO (Ir) = 9 i.e., (n-1)d (5) + ns (1) + np (3)**

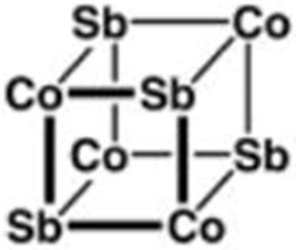
(Ir: $5d^76s^2$) **VE = 9 + 3x2 = 15**

→ Being lack of 3 VEs to fulfill the 18e rule!

→ The Ir atom in $Ir(CO)_3$ forms three covalent M-M bonds with other M centers to get three more electrons.

Full picture: In $Ir_4(CO)_{12}$, each Ir adopts d^2sp^3 hybridization with three VEs/HOs being used to form three M-M bonds, as well as three unhybridized 5d AOs doubly occupied.

Examples:



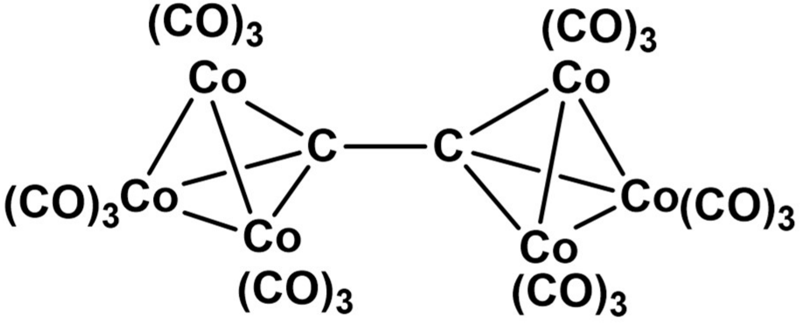
$Co_4(CO)_{12}Sb_4$

$n_1 = 4, n_2 = 4$

$$VE = g = 4x9\ (Co: 3d^7 4s^2) + 4x5 + 12x2\ (CO) = 80$$

$$\therefore\ b = (18n_1 + 8n_2 - g)/2 = (72 + 32 - 80)/2 = 12$$

$Co_6C_2(CO)_{18}$



$$VE = g = 6x9\ (Co: 5d^7 6s^2) + 2x4\ (C) + 18x2\ (CO) = 98$$

$$\therefore\ b = (18x6 + 8x2 - g)/2 = (124 - 98)/2 = 13$$

$n_1 = 6, n_2 = 2$

Problem: The metallocene Cp_2Ni reacts with $Ni(CO)_4$ to afford a binuclear complex: **$Cp_2Ni + Ni(CO)_4 \rightarrow [CpNiCO]_2 + 2CO$**
Please derive the Ni-Ni bond order and structure of this complex!
(Cp = cyclopentadienyl)

---

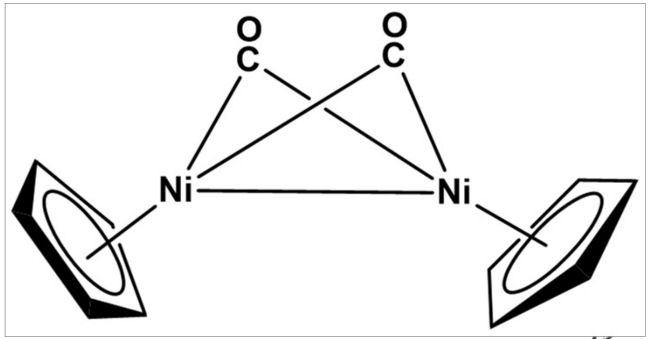
1) **VE = g = 2x10 (Ni: $3d^84s^2$) + 2x5 (Cp) +2x2 (CO) = 34**
b = (2x18- 34)/2 =1 (Ni-Ni bond order)

2)Key question: Are the CO ligands bridging or terminal?

Key point: Each Ni atom should follow the 18e rule.

Each Ni atom adopts d^2sp^3 hybridization, thus forming 6 σ-bonds with its surrounding atom/ligands:

- 3 of them are used by a Cp ligand.
- 1 of them is used by the Ni-Ni bond.
- 2 of them should be used by the CO ligands.
- Only two CO ligands are available.
- **➔ two μ_2-CO ligands!**

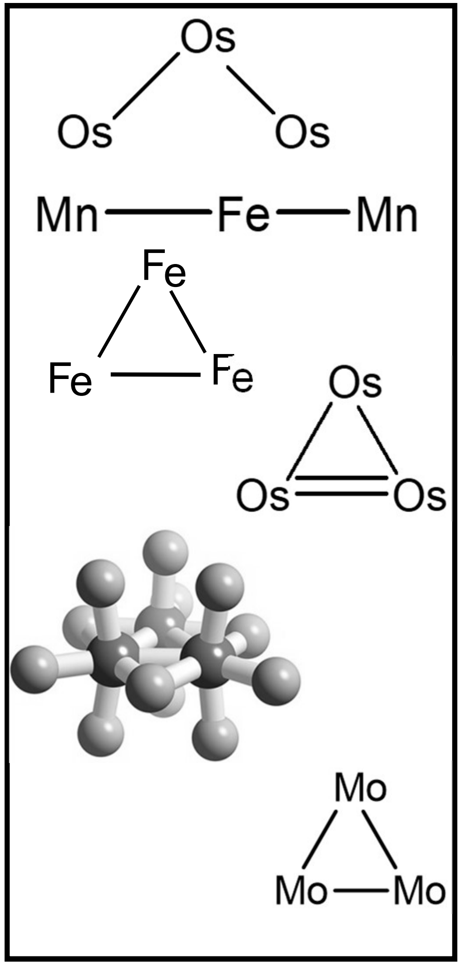


iii. Bond valence and cluster geometry

A. Tri-nuclear compounds

$$b = \frac{1}{2}(18n - g)$$

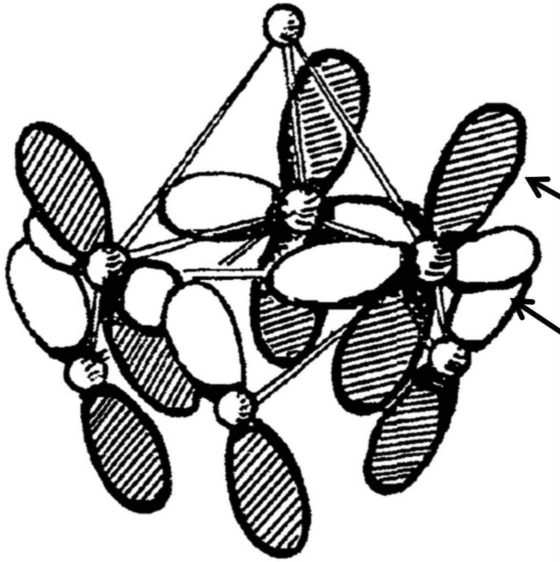
Metal cluster compounds	g	b	M-M/pm
$Os_3(CO)_9(\mu_3\text{-}S)_2$	50	2	Os-Os, 281.3
$Mn_2Fe(CO)_{14}$	50	2	Mn-Fe, 281.5
$Fe_3(CO)_{12}$	48	3	Fe-Fe, 281.5
$Os_3H_2(CO)_{10}$	46	4	Os-Os, 281.5 Os=Os,268.0
$[Re_3(\mu_2\text{-}Cl)_3Cl_9]^{3-}$ Re(III) ~ $5d^4$	42	6	Re=Re, 247
$[Mo_3(\mu_3\text{-}O)(\mu_2\text{-}O)_3F_9)]^{5-}$ Mo(IV) ~$4d^2$	42	6(expected) 3 (actually)	Mo-Mo,250.2

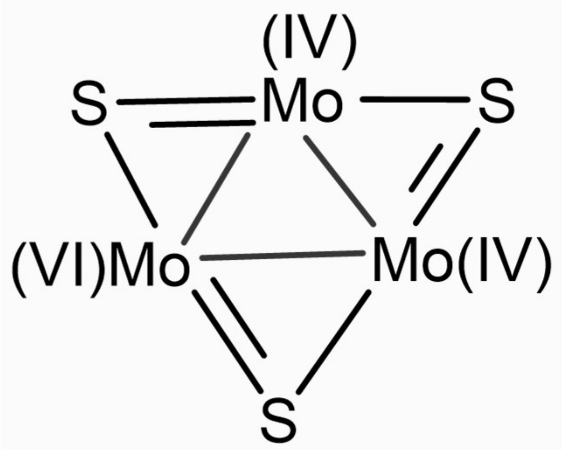


The last compound has such high-valent metal cations that are too electron-deficient to afford the hypothetic M-M bonds.

Special case: $[Mo_3(\mu_3\text{-}X)(\mu_2\text{-}X)_3]^{4+}$ (X= S, O) core with d-p π-conjugation & quasiaromaticity

$[Mo_3(\mu_3\text{-}O)(\mu_2\text{-}O)_3F_9)]^{5-}$





- Each 6-coordinate Mo(IV) is d^2sp^3-hybridized.
- Each Mo(IV) contributes two d-AO′s and two VE′s to afford three bonding skeletal MO′s.
- Each Mo (IV) has 16VE with an empty d-AO!

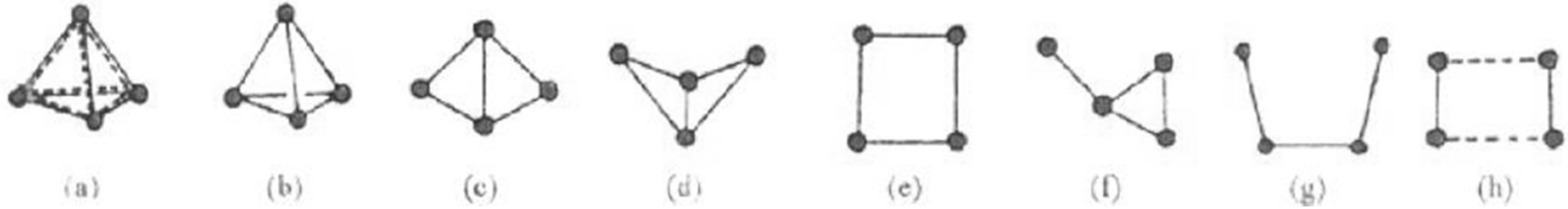
- The 6c-6e d(Mo)-p(S) π-conjugation within the puckered $[Mo_3S_3]^{6+}$ ring, i.e., **the so-called quasi-aromaticity**.
- Only upon inclusion of such p(S)→d(Mo) π-bonding can each Mo center approximately fulfill the 18e Rule.

Lu, J.X., Chen. Z.D, *Int. Rev. Phys. Chem.*, 1994, 13, 85.

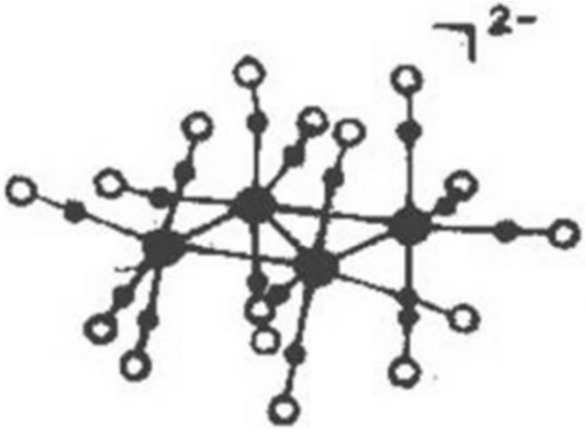
B. Tetranuclear compounds

$$\boxed{b=\frac{1}{2}(18n-g)}$$

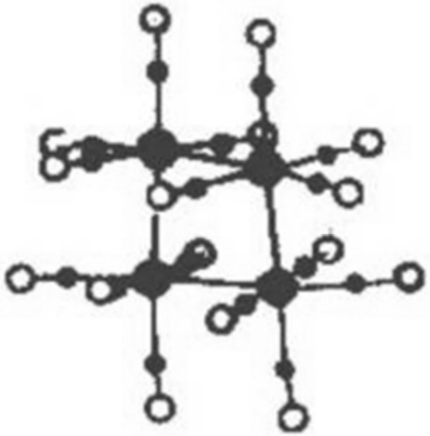
b= 6 6 5 5 4 4 3 3


(a) (b) (c) (d) (e) (f) (g) (h)

$Ir_4(CO)_{12}$



$Re_4(CO)_{16}^{2-}$



$Os_4(CO)_{16}$

g=4*9+12*2=60

b= (18*4-60)/2=6

g=4*7+16*2+2=62

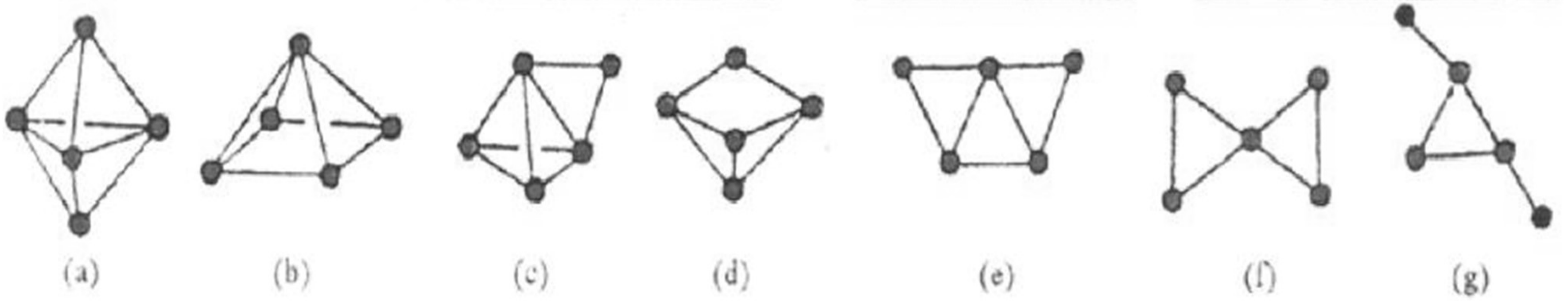
b= (18*4-62)/2=5

g=4*9+16*2=64

b= (18*4-64)/2=4

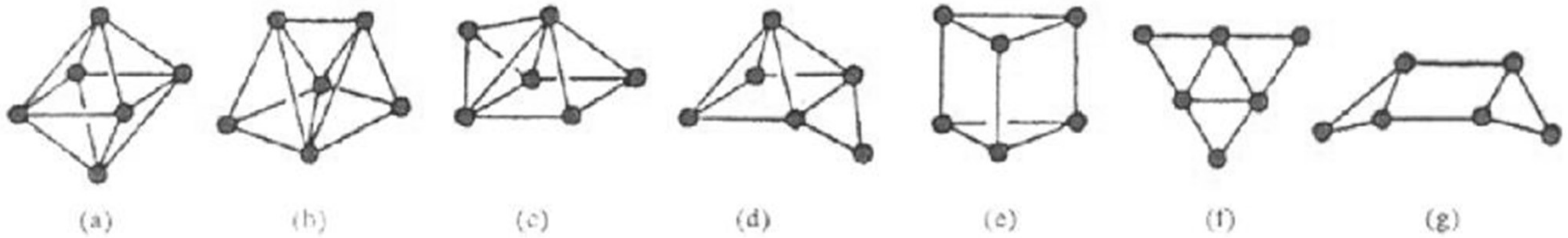
Pentanuclear compounds

b= 9 8 8 7 7 6 5

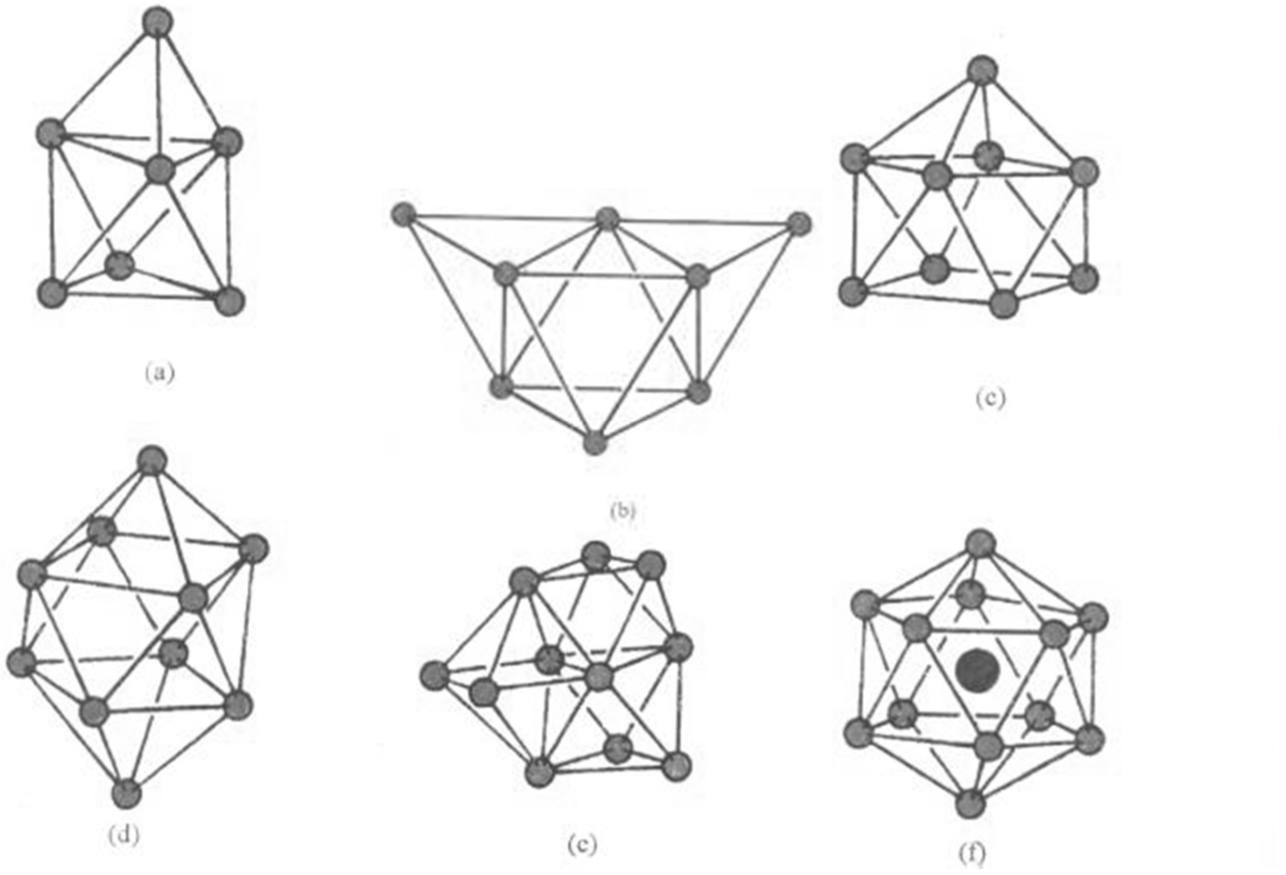


Hexanuclear compounds

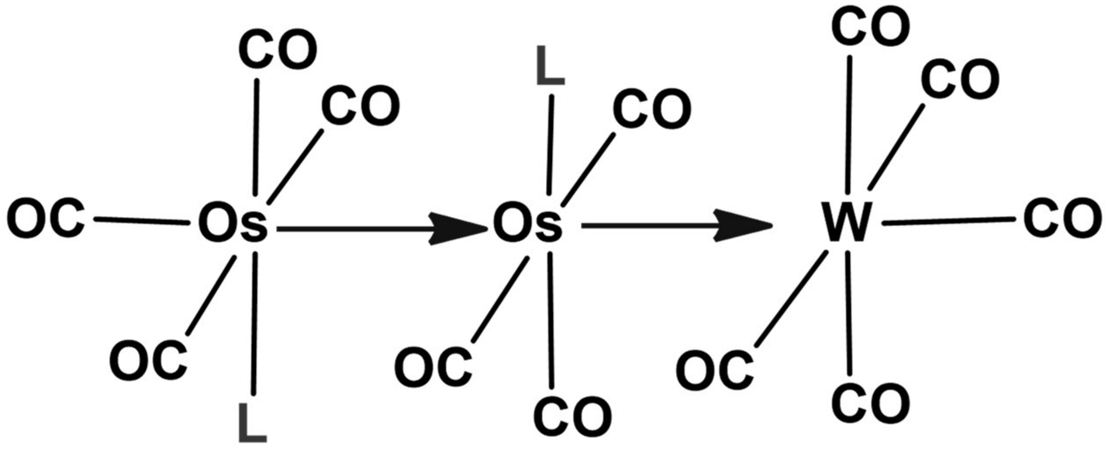
b= 12 12 11 10 9 9 8



Multi-nuclear (N>6) compounds



iii. Metal-metal dative bond

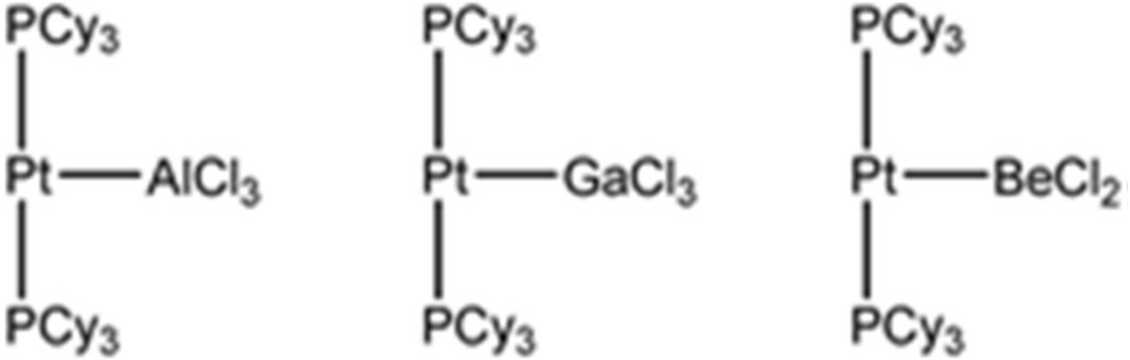


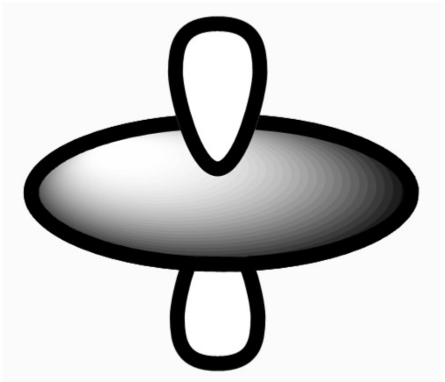
$L = Bu^tNC$

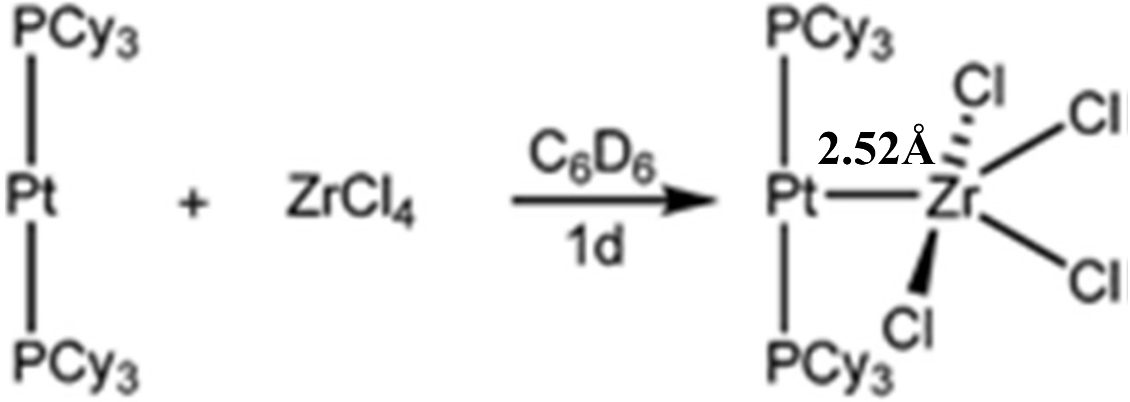
- VE or $g = (2x8+6+14x2) = 50$, $b = (18xn-g)/2 = 2$
- For the $Os(CO)_5L$, its Os1 atom fulfills the 18e rule. So this fragment works as a ligand of Os2.
- $W(CO)_5$ requires 2 extra electrons to fulfill the 18e rule.
- Both metal-metal bonds could be regarded as **dative bonds** for the metal atoms to achieve an 18e configuration.

see Pomeroy et al, ***Inorg. Chem***., 1992, 31, 3155.

Metal-metal dative bond: more examples





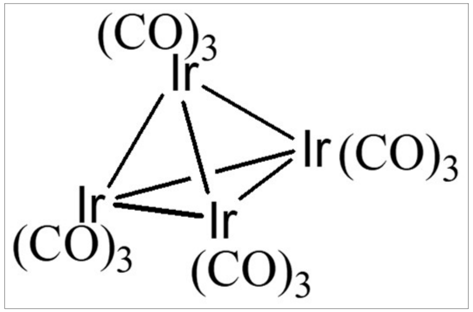


- Non-bonding sd$_\sigma$-hybridized orbital of Pt.
- It is electron-donative !

- Pt – sp-hybridization. Pt achieves a 14e configuration in $Pt(PCy_3)_2$.
  Or more exactly, Pt --sd$_\sigma$-hybridization, 3c4e σ-bond in $Pt(PCy_3)_2$.
- Thus in $Pt(PCy_3)_2$, the occupied Pt sd$_\sigma$ hybridized orbital has a high-degree of 6s contribution, and is diffusive and electron-donative!

see Braunschweig et al, ***Chem. Comm***., 2010, 46, 913.

6.4.3 Molecular fragment, Generalized octet rule, and Isolobal analogy



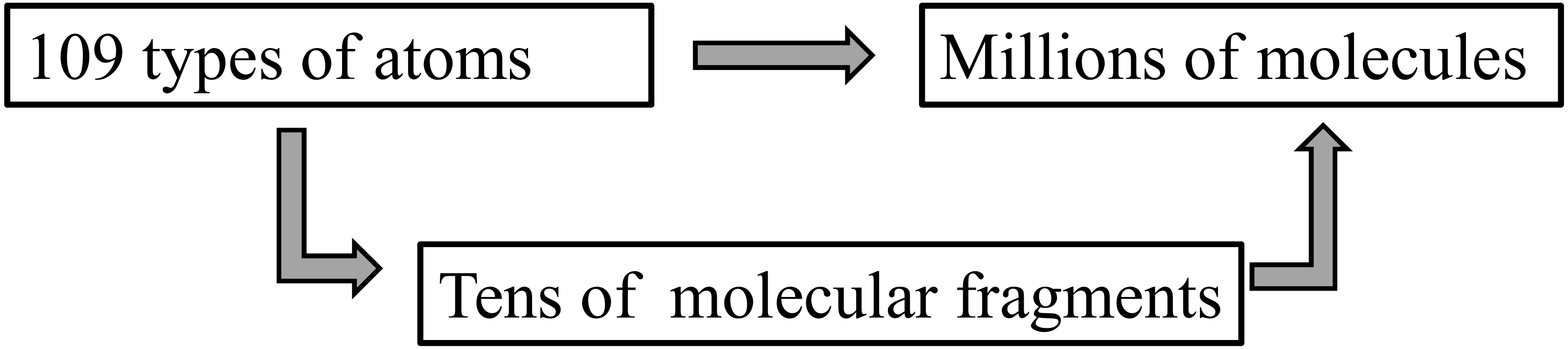
- **Molecular fragment --** the constitutive groups of atoms in a molecule, e.g., functional groups in organic chemistry, monomer of a polymer, $Ir(CO)_3$ in $Ir_4(CO)_{12}$.

- A molecule can be regarded as a combination of molecular fragments chemically bonded with each other. (Proposed by R. Hoffmann!)

e.g., $CH_3CH_2OH = (CH_3)(CH_2)(OH)$; $Ir_4(CO)_{12} = [Ir(CO)_3]_{4;}$

$H_2O_2 = (HO)_2$;

- This concept facilitates us to understand the construction of complicated molecules and to design new molecules.



109 types of atoms

Millions of molecules

Tens of molecular fragments

- In practice, a molecular fragment can be regarded as an atom with certain valence electrons (VEs) and unsaturated valence $\boldsymbol{V_i}$.

$$V_i = 2O_i - i \quad (\mathrm{V_i}: \textit{unsaturated valence} \text{ or covalency}; \; O_i: \textit{number of V}\mathrm{O's}; \; i: \textit{number of V}\mathrm{E's})$$

- For a given molecular fragment, we focus on the total VEs (***i***) & VOs of its central atom with unsaturated valence ($\boldsymbol{V_i}$), e.g., both CH_3 and OH have 7 VEs/4VOs and 1 free valence, CH_2 has 6 VEs and free valence of 2, $Ir(CO)_3$ has 15VEs/9VOs and free valence of 3, $Fe(CO)_4$ has 16 VEs and free valence of 2.

Examples:

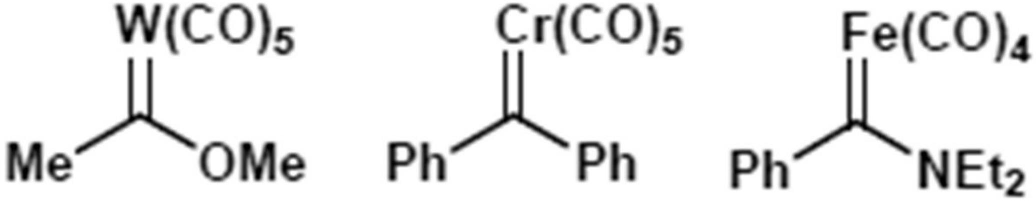
Carbene CR_2: O = 4, i(VE) = 6， V = 2

$M(CO)_x$: $Fe(CO)_4$, $Cr(CO)_5$, $W(CO)_5$

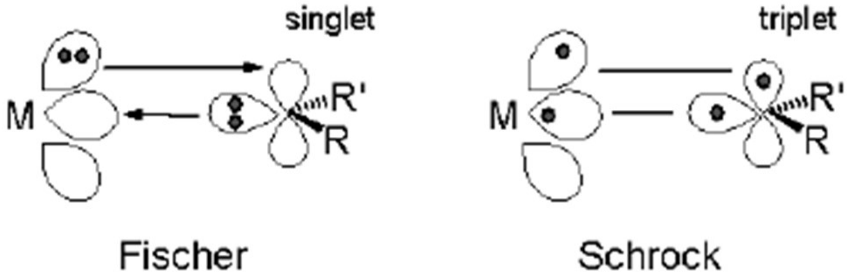
O = 9, i = 16, V =2

The fragments can form M=C double bond as in the following Fischer carbene complexes,

Representative Fischer Carbenes:



Comparision of Fisher Carbene and Schrock carbene:



Dative bond **Covalent bond**

How to understand the bond valence of a TM cluster compound in terms of molecular fragment theory?

$$b = \frac{1}{2}(18n - g)$$

- For the ***i***th fragment of a cluster compound, the unsaturated valence is

$$V_i = 2O_i - i \quad (\mathrm{V_i}: \textit{unsaturated valence} \text{ or covalency;}$$
$$O_i: \textit{number of V}\mathrm{O}'s; \quad i: \textit{number of V}\mathrm{E}'s)$$

→ The total free valence (***V***) of all fragments in a cluster compound can be saturated upon formation of M-M bonds (***b***), i.e., ***V*** = ***2b***.

$$V = \sum_i V_i = \sum_i 2O_i - \sum_i i = \sum_i 2O_i - g, \quad b = V/2 = (\sum_i 2O_i - g)/2$$

- For a TM cluster compound with ***n*** TM atoms, each TM center has $\boldsymbol{O_i}$ = ***9***. Then

$$\sum_{i=1}^{n} 2\mathrm{O_i} = 18n \Rightarrow \; b = (18n - g)/2$$

Generalized octet rule: proposed by Pearson

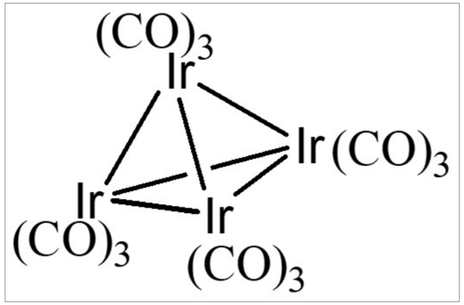
- If the total VEs (***i***) of a molecular fragment is **2** times of its total valence orbitals ($\boldsymbol{O_i}$), this molecule fragment has a closed-shell electronic configuration and can itself be an stable molecule.

$$i.e., i = 2O_i \Rightarrow V_i = 2O_i - i = 0$$

- **central atom = main-group element (O_i=4), i.e.,octet rule**

  central atom = transition metal (O_i=9), i.e., 18e rule

  ……



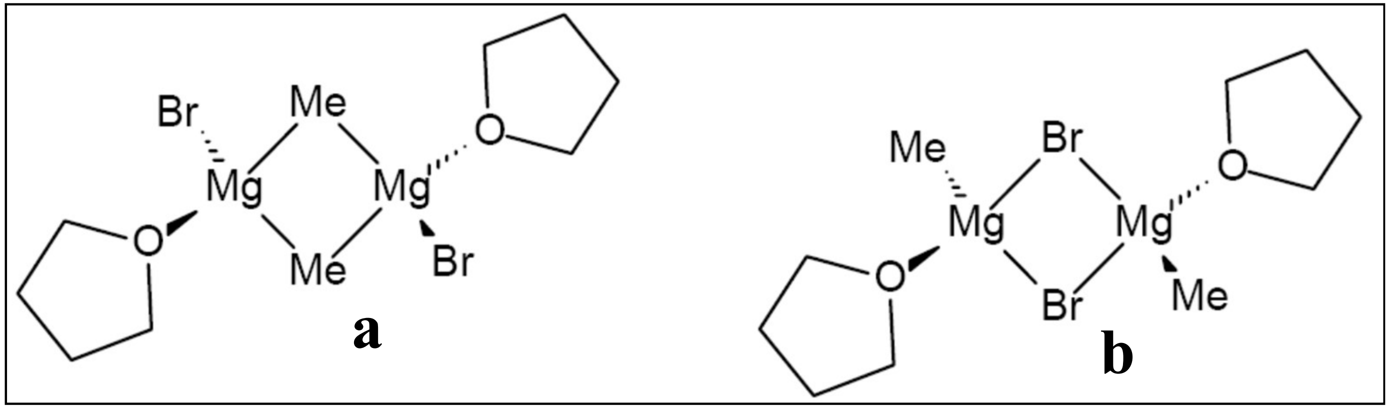
- This rule also governs the chemical bondings between molecular fragments, e.g., $Ir(CO)_3$ has 15 VEs and 9 VOs, being short of 3VEs. To fulfill the rule, it forms three 2c-2e M-M bonds with other $Ir(CO)_3$ fragments in $Ir_4(CO)_{12}$.

Generalized octet rule

Rules	O_i	i	VO′s	Examples
2e	1	2	s	LiH, LiR, Li2
4e	2	4	sp	BeR_2, R-Mg-Cl
6e	3	6	sp^2	BEt_3, $La(Ph)_3$
8e	4	8	sp^3	CH_4, NF_3, H_2O
10e	5	10	sp^3d	PF_5, SF_4, XeF_2
12e	6	12	sp^3d^2	SF_6, MoF_6, PF_6^-, SiF_6^{2-}
14e	7	14	sp^3d^3/d^5sp	IF_7/ AgI_2^-, $Au(CN)_2^-$
16e	8	16	d^5sp^2	Cp_2Cr, $Au(CN)_4^-$
18e	9	18	d^5sp^3	$Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$

Generalized octet rule (GOR): examples

- **Complexes fulfilling the octet rule**:



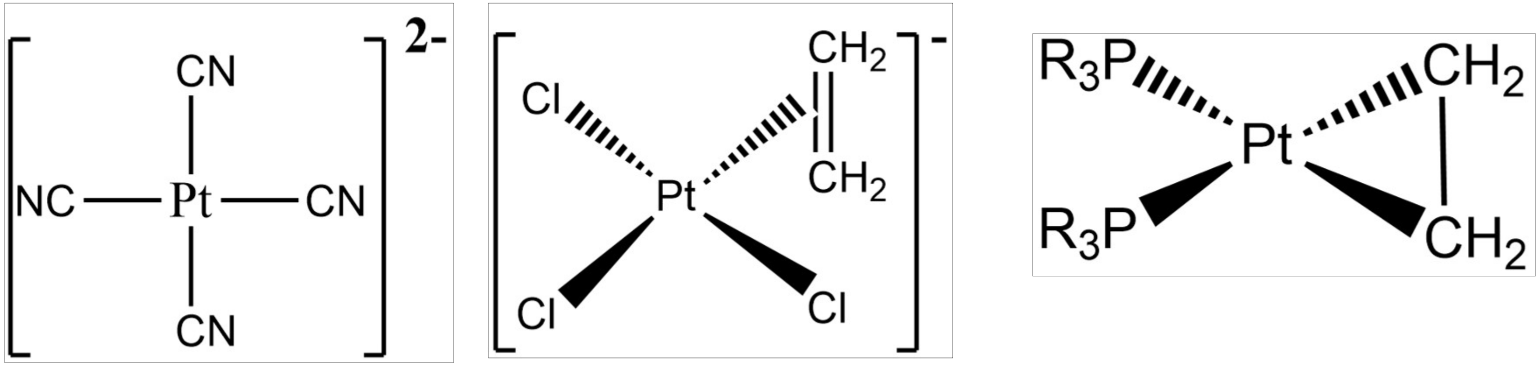
Why is isomer **b** more stable than isomer **a**?

Note: isomer **a**, has two Mg-Me-Mg 3c-2e bonds.

1) No metal-metal bond. **V = 8n-g=0 → g=8n =16!**
2) However, total skeletal bonding MO′s: 8 (**b**) > 6 (**a**). →
3) Total skeletal bonding electrons: g=16 (**b**) > 12 (**a**) (needs extra **4e**)
4) Isomer **a** conflicts with GOR. Isomer **b** having four more bonding skeletal electrons and fulfilling GOR is more stable!

Generalized octet rule: examples

- **16e complexes**:



1) The Pt^{2+} ($5d^8$) adopts dsp^2 hybridization in order to form the 4-coordinated planar complexes. Meanwhile, each ligand contributes a lone-pair orbital.

2) A total of **8** AOs are involved in the M-L bondings, forming **8** σ-MOs (4 bonding and 4 antibonding).

3) The total valence electrons around Pt: **8** (nonbonding $5d^8$) + **8** (4 bonding σ-MOs/dative bonds) = **16**.

Generalized octet rule: examples

Beyond 18e: Thorocene and Uranocene

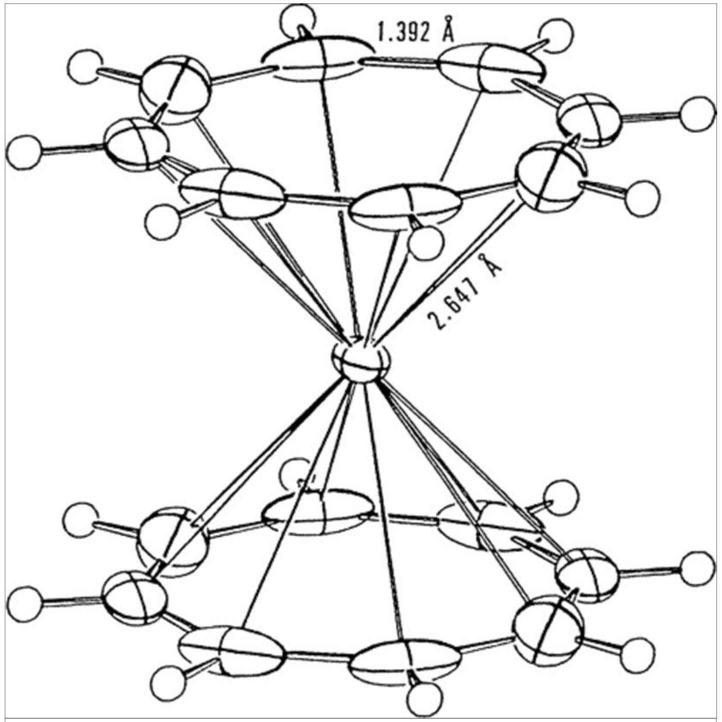
$[M(C_8H_8)_2]$, M= Th, U

1) Th ($5f^0 6d^2 7s^2$) and $2C_8H_8$ ($8\pi e$)
   → Th^{4+} and $2C_8H_8^{2-}$($10\pi e$).

2) D_{8h}-symmetry, VE = 20 .

3) **$(\sigma_g)^2 (\sigma_u^*)^2 (\pi_u)^4 (\pi_g^*)^4 (\delta_g)^4 (\delta_u^*)^4$**

4) A 5f AO of Th (U) is involved in the metal-ligand bonding!



Uranocene

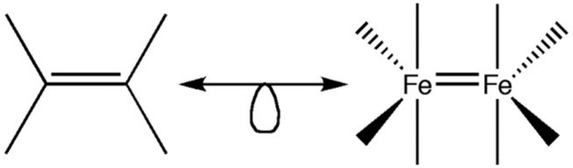
2L: 2x5 MO's
M: 10 AO's
$(n-2)f(n-1)d^5sp^3$

Prediction: Uranocene -- Fischer, R.D. *Theor. Chim. Acta*, **1963**, *1*, 418.
Synthesis: Uranocene -- Streitweiser A. Jr., *J. Am. Chem. Soc.* **1968**, *90*, 7364.
Thorocene-- Streitweiser A. Jr., *J. Am. Chem. Soc.* **1969**, *91*, 7528.

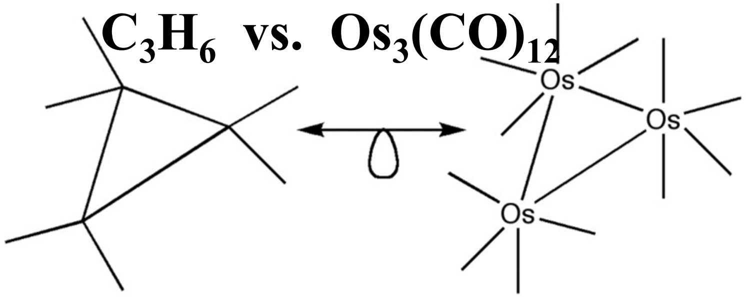
Isolobal Analogy : proposed by R. Hoffmann

- Molecular fragments having ***same number of VEs*** (or $\boldsymbol{VE_a = VE_b - 10}$) and ***similar frontier orbitals*** are isolobal.

  e.g., CH_2 (***VE = 6, V =2***) is isolobal to $Fe(CO)_4$ (***VE =16, V =2***).



$CH_2{=}CH_2$ vs. $Fe_2(CO)_8$



C_3H_6 vs. $Os_3(CO)_{12}$

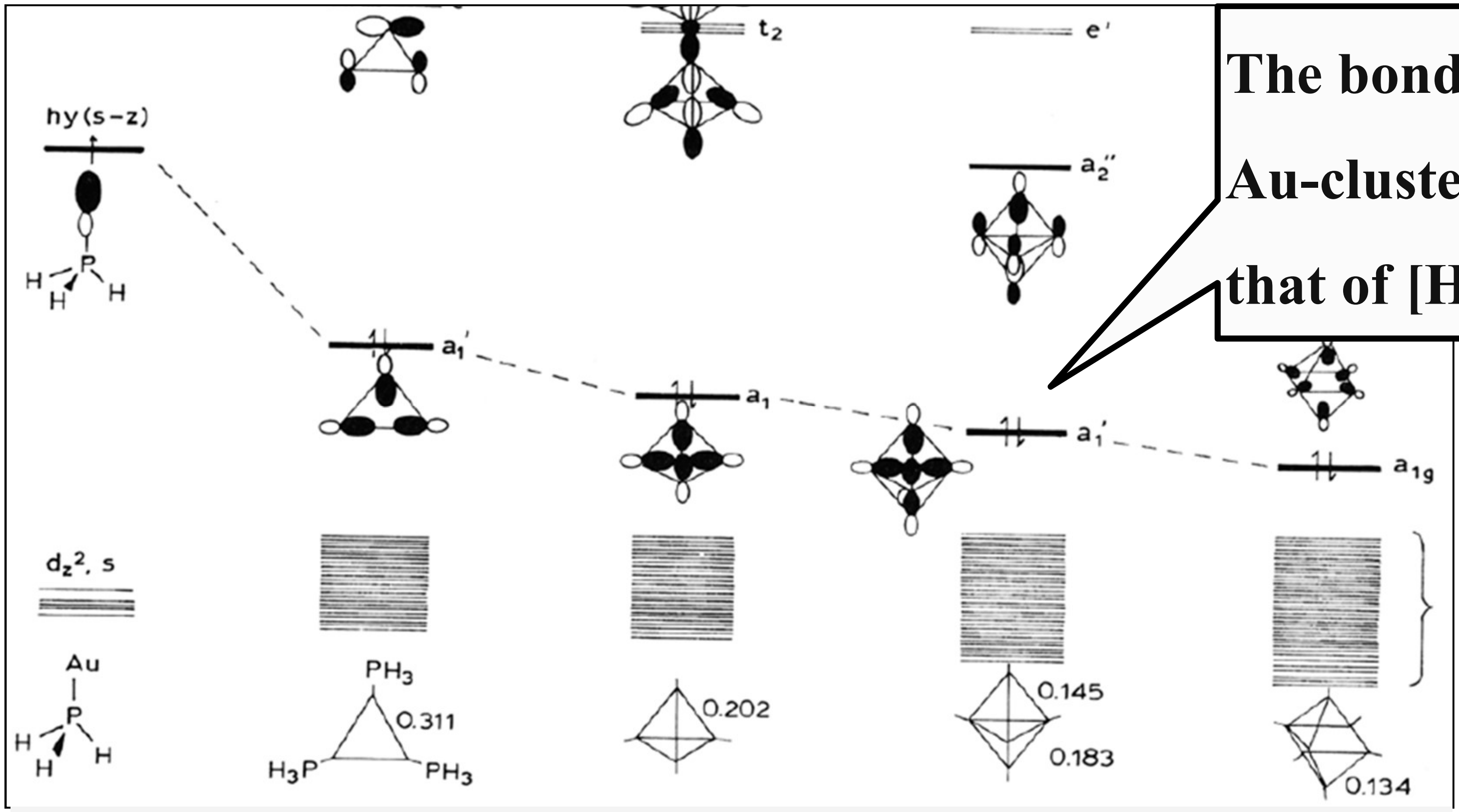
- A fragment in a molecule can be substituted with an isolobal fragment. e.g., **CR_2 vs $Fe(CO)_4$**, **$AuPR_3$ vs H**

  → Metal-carbene complexes: **$(L)_nM{=}CR_2$**

- Isolobal analogy has been widely exploited in synthetic chemistry and led to the production of numerous cluster compounds.

- One of the most widely exploited isolobal analogy is the isolobal analogy between $AuPR_3$ and H.

In 1970s, Mingos noticed the $AuPR_3$ ~ H analogy.



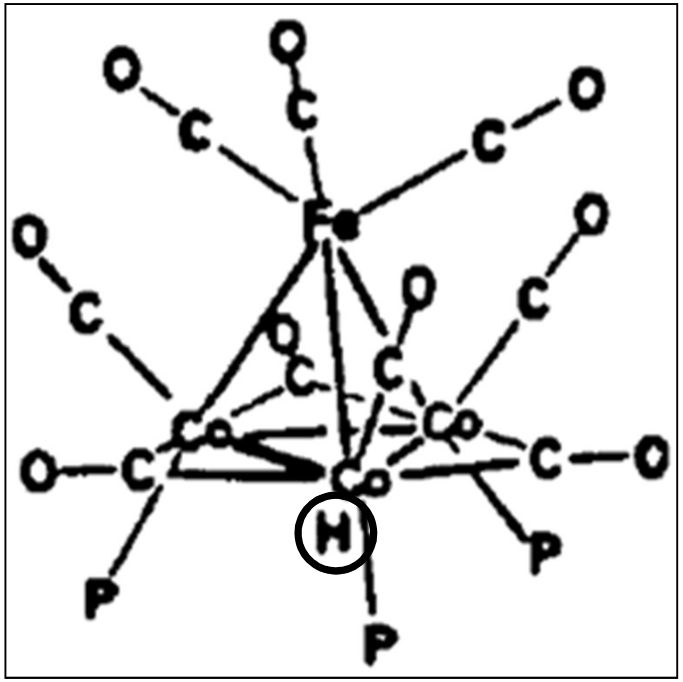
The bonding MO of the Au-clusters resembles that of $[H_n]^{(n-2)+}$.

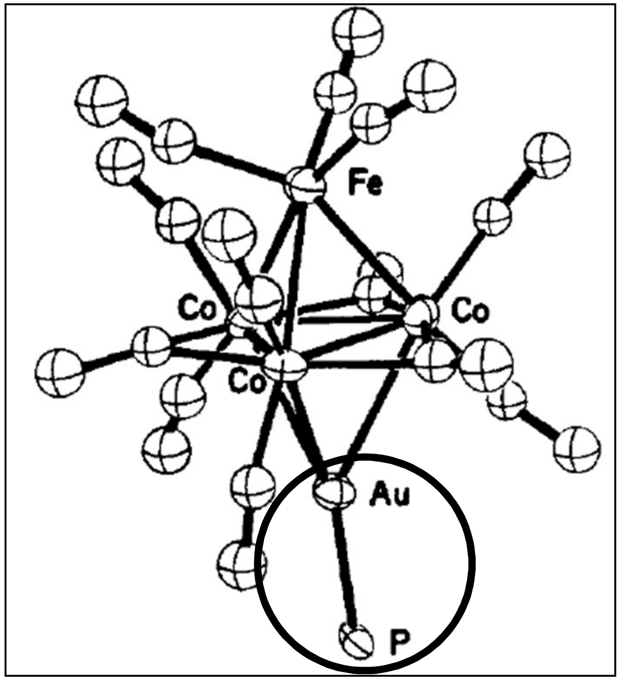
Skeletal MOs of $[(AuPR_3)_n]^{(n-2)+}$

- Mingos DMP, *J. Chem. Soc., Dalton Trans*, **1976**, 1163; *J. Organomet. Chem*. **1982**, *232*, 171.
- Hoffmann R, *Angew. Chem*., **1982**, *94*, 725.

Early experimental evidences of isolobal $AuPR_3$ ~H analogy.

- isostructural $[Co(CO)_4\mathbf{X}]$ ($\mathbf{X=H, AuPR_3}$)
- isostructural $[FeCo_3(CO)_{12}(\mu_3\text{-}\mathbf{X})]$ ($\mathbf{X=H, AuPR_3}$) compounds

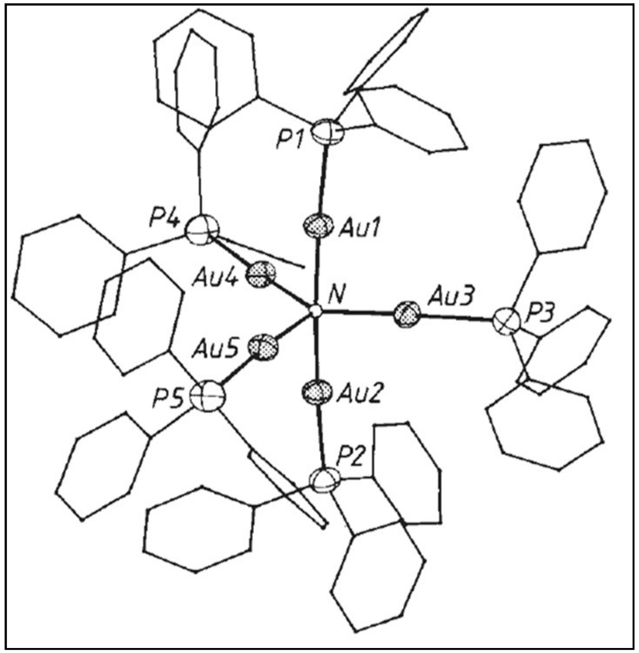


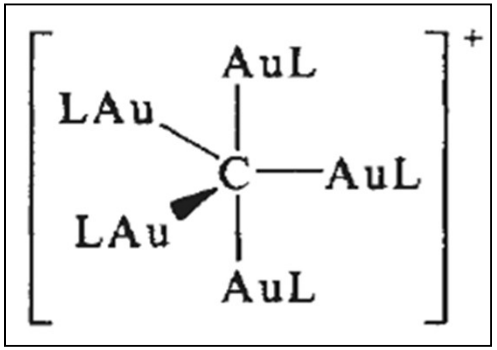


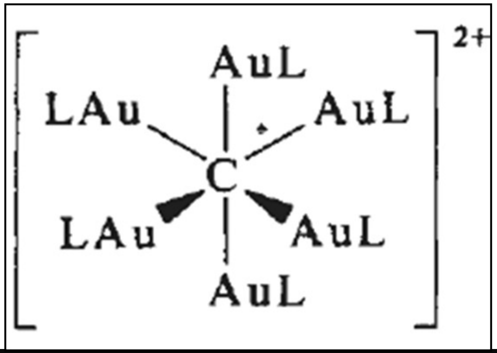
- Blundell and Powell, *J. Chem. Soc. A*, **1971**, 1685;
- McNeil and Scholer, *J. Am. Chem. Soc.* **1977**, *99*, 6243.
- Lauher and Wald, *J. Am. Chem. Soc.* **1981**, *103*, 7649.

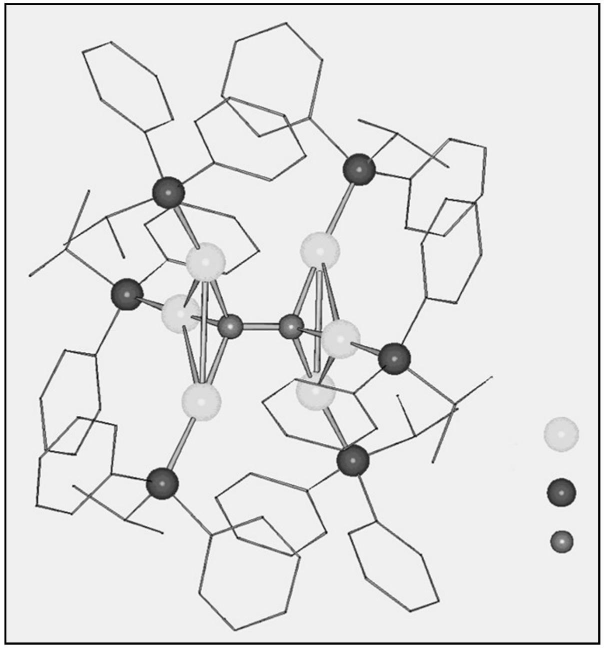
The Isolobal $AuPR_3$~H Analogy

The $AuPR_3$ synthon as H analogue has be widely exploited in bench chemistry, e.g., $\mathbf{[O(AuPR_3)_n]^{(n-2)+}}$ (n= 3-4); $\mathbf{[N(AuPR_3)_n]^{(n-3)+}}$ (n= 4-5); $\mathbf{[C(AuPR_3)_n]^{(n-4)+}}$ (n= 4-6); $\mathbf{[N_2(AuPR_3)_6]^{2+}}$……









- Schmidbaur, H. et al., *Nature,* **1990** , *345*, 140; **1991**, *352*, 141; **1995**, *377*, 503;
- Sharp P.R. et al . *Science*, **1997**, *275*, 1460.

- **$[O(AuPh_3)_n]^{(n-2)+}$** (n= *3-4*) ≈ **$[OH_3]^{+}$, $[OH_4]^{2+}$**
- **$[N(AuPh_3)_n]^{(n-3)+}$** (n= *4-5*) ≈ **$[NH_4]^{+}$, $[NH_5]^{2+}$**
- **$[C(AuPh_3)_n]^{(n-4)+}$** (n= *4-6*) ≈ **CH_4, $[CH_5]^{+}$, $[CH_6]^{2+}$**
- **$[N_2(AuPR_3)_6]^{2+}$** ≈ **$[H_3N\text{-}NH_3]^{2+}$** ;

In bench chemistry, the gold-hydrogen analogy is assisted exclusively by such type of ligands as PR_3!

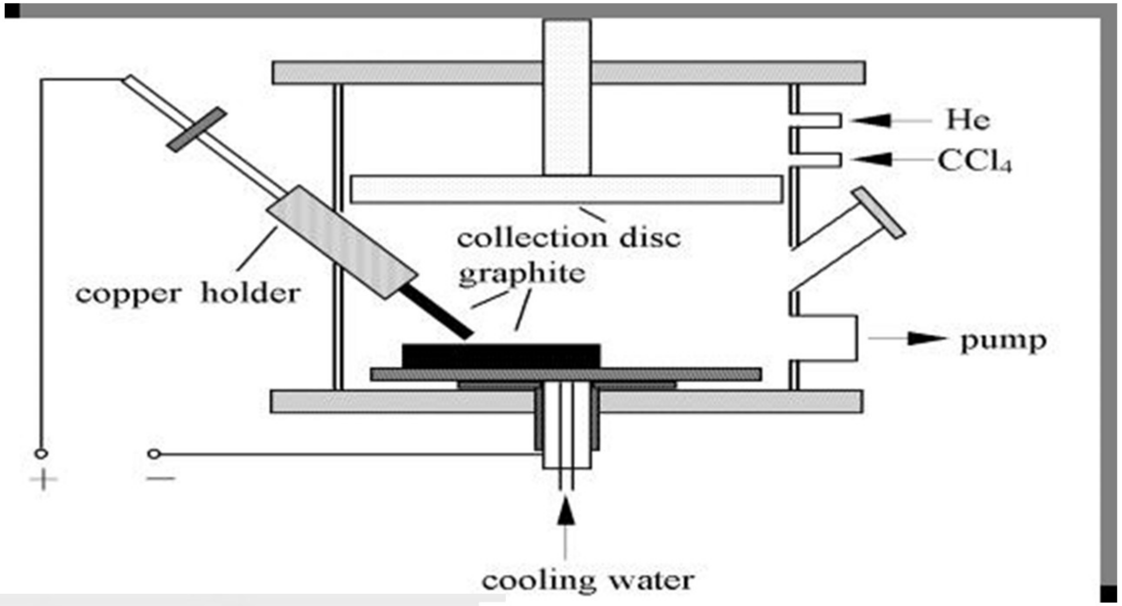
6.5 Carbon clusters and nanotubes

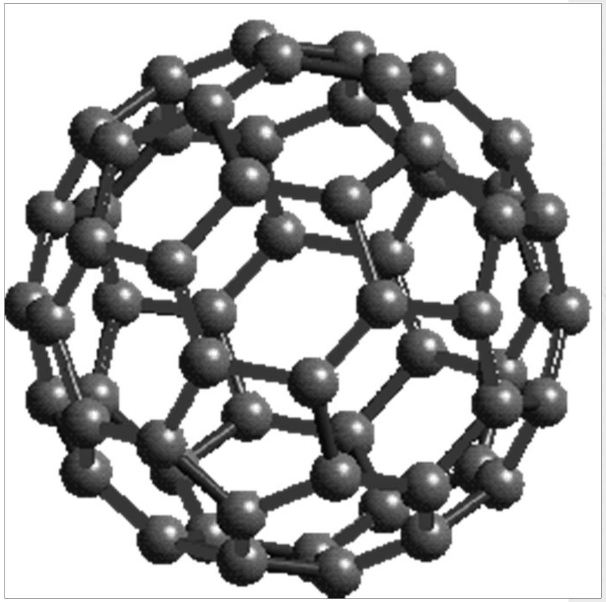
1. Fullerences

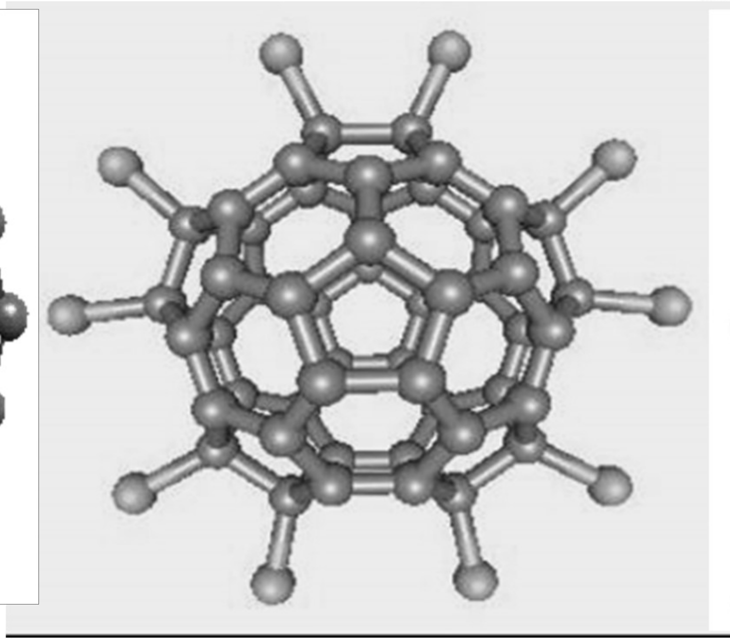
a. Without Cl, C_{60} , C_{70}…

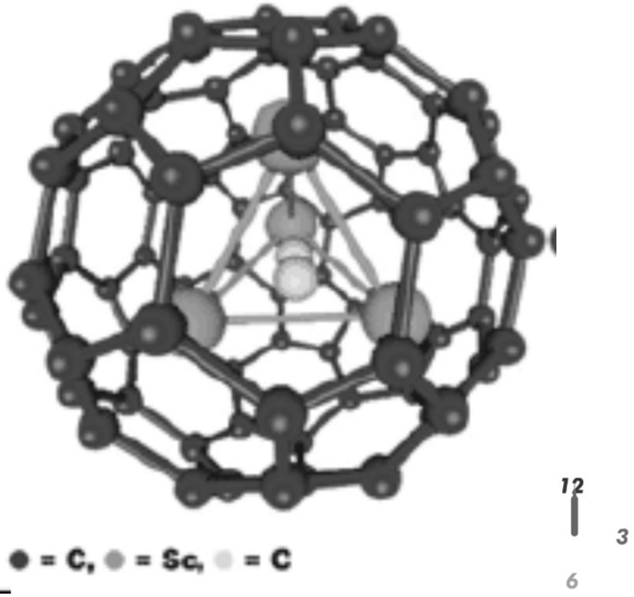
b. With Cl, $C_{50}Cl_{10}$…

c. With metal, $M_x@C_y$…







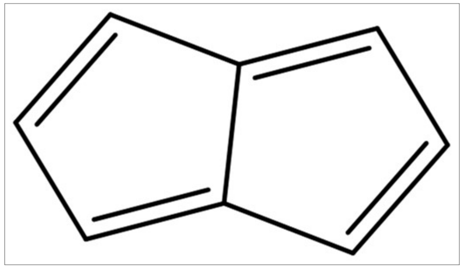


- **Fullerenes** are convex carbon cages comprising hexagons and exactly ***12*** pentagons.
- **Euler's Theorem** states that exactly 12 pentagons must be accommodated to allow closure of a carbon network consisting of ***n*** hexagons.
- **Isolated pentagon rule (IPR)**: the pentagons within the most stable fullerenes are surrounded by hexagons and, hence, isolated from each other.
- The smallest IPR-satisfying fullerene is C_{60} (I_h), immediately followed by C_{70}(D_{5h}). Those with a size smaller than C_{60} or between C_{60} and C_{70} do not obey IPR.
- *Lu X et al., Chem. Rev. 2005, 105, 3643.*

Non-IPR fullerenes with adjacent pentagons are always unstable. Why?

- Adjacent pentagons of a convex cage introduce enhanced steric strain (***steric effect***).

- Adjacent pentagons introduce antiaromatic destabilization pertaining to the pentalene-type **8π**-electron system (***electronic effect***).

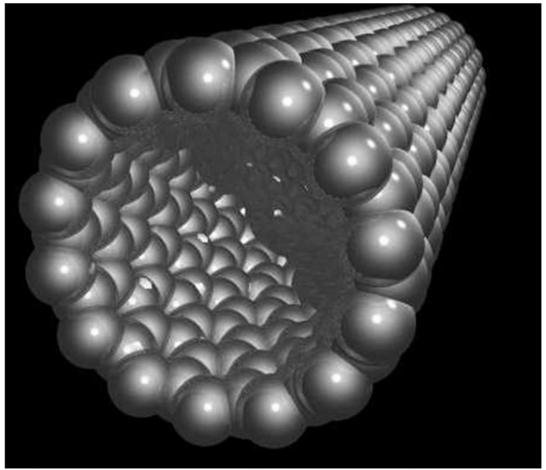


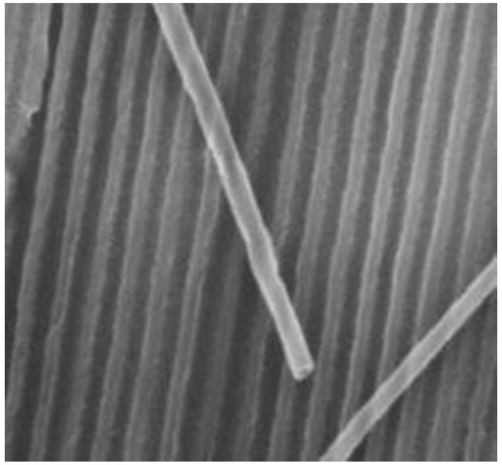
Antiaromatic pentalene

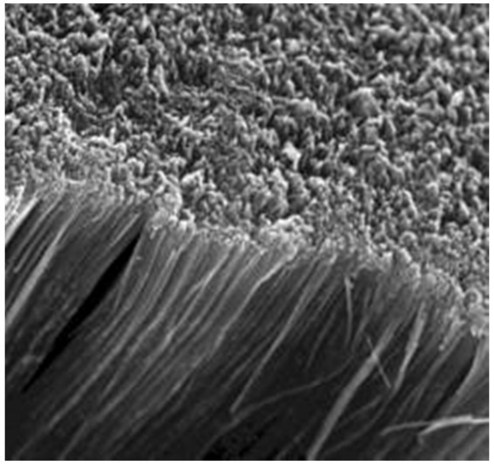
2. Carbon nanotubes

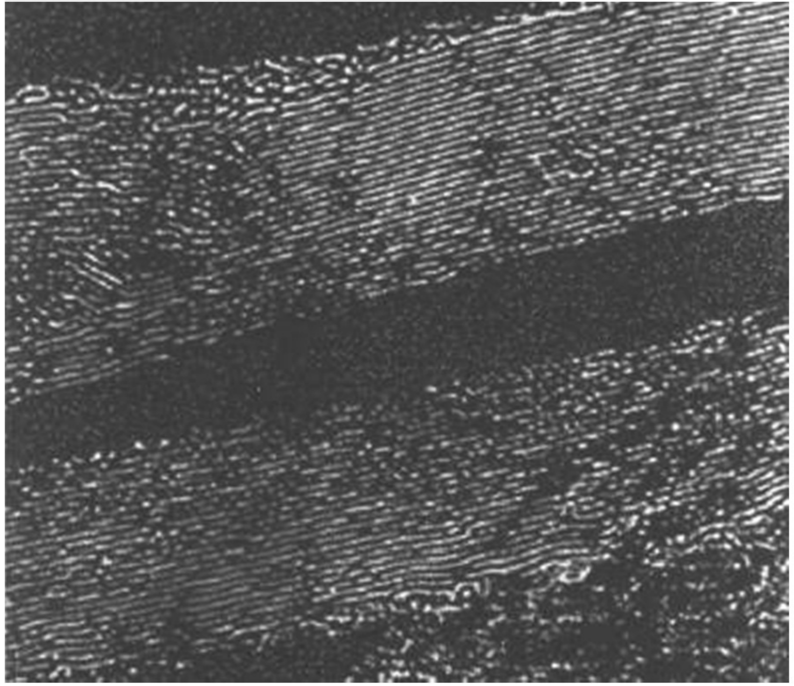
Discovered by Iijima (NEC, JPN) in 1991.

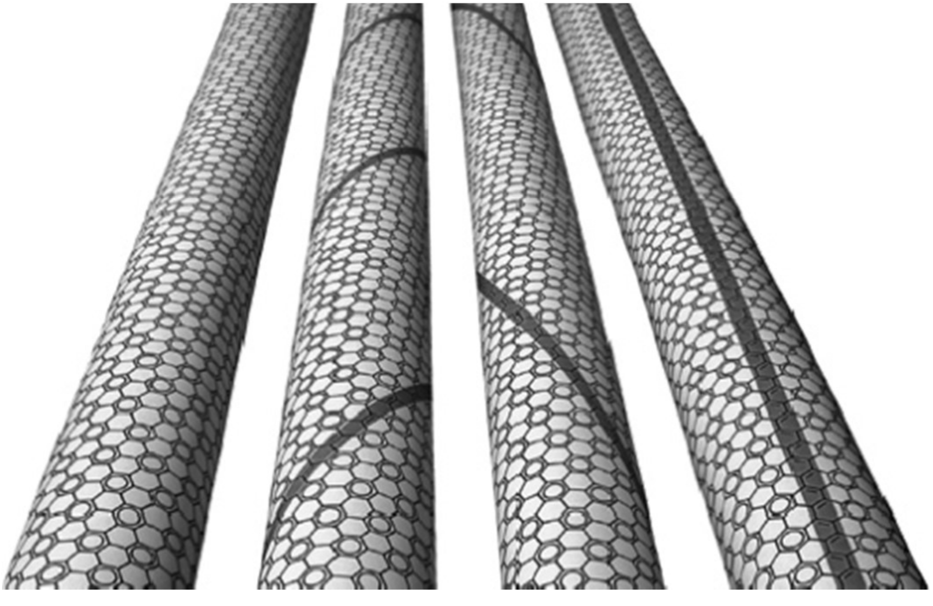
HRTEM











Single-walled carbon nanotube (SWCNT):

- The structure of a SWCNT can be uniquely defined by the roll-up vector, $\mathbf{C_h} = \boldsymbol{n}\mathbf{a_1} + \boldsymbol{m}\mathbf{a_2}$, and is designated by **(*n*,*m*).**

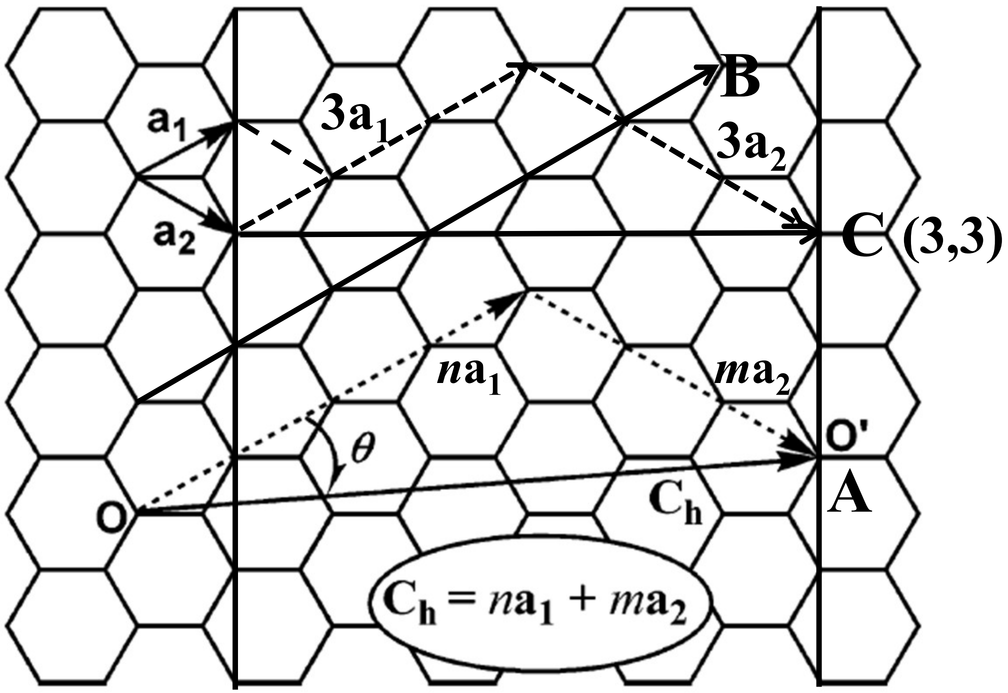


Figure 64. Roll-up vector $\mathbf{C}_h$ ($\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2$) and chiral angle θ for a (n,m) SWCNT (for this special case, $n = 4$, $m = 3$), where $\mathbf{a}_1$ and $\mathbf{a}_2$ are the primitive vectors of a graphene sheet.

Types:

A) $\mathbf{C_h} = n\mathbf{a_1} + m\mathbf{a_2}$

(n >m, m≠0),chiral (n,m).

B) $\mathbf{C_h} = n\mathbf{a_1}$

zigzag (n,0) – achiral

C) $\mathbf{C_h} = n\mathbf{a_1} + n\mathbf{a_2}$

armchair **(*n*,*n*)**-- achiral

e.g., The roll-up vectors **A**, **B** and **C** define the SWCNTs **(4,3)**, **(6,0)** and **(3,3)**, respectively.

Types:

a) Chiral (n,m) (n >m, m≠0).

b) Achiral zigzag (n,0).

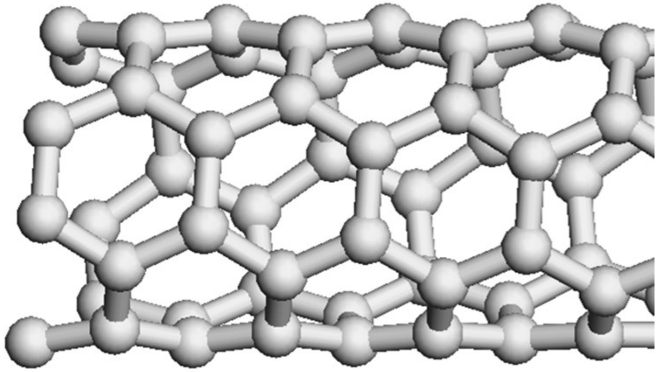
c) Achiral armchair (*n*,*n*).

Conductivity:

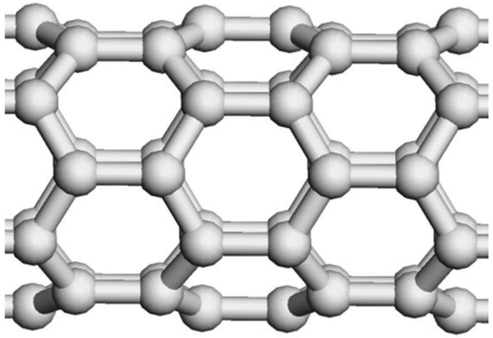
(n-m)/3 = k (k =0,1,2,…) --- metallic

(n-m)/3 ≠ k --- semiconductive

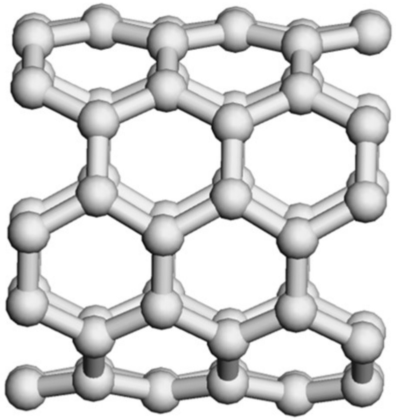
➔Metallic (n,n) and (3m,0)



(4,3)

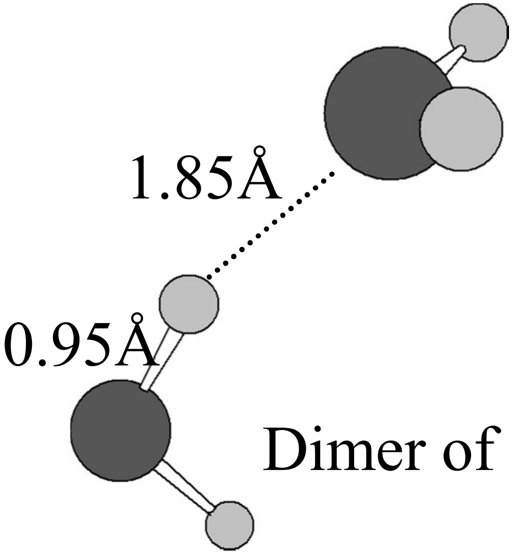


(6,0)

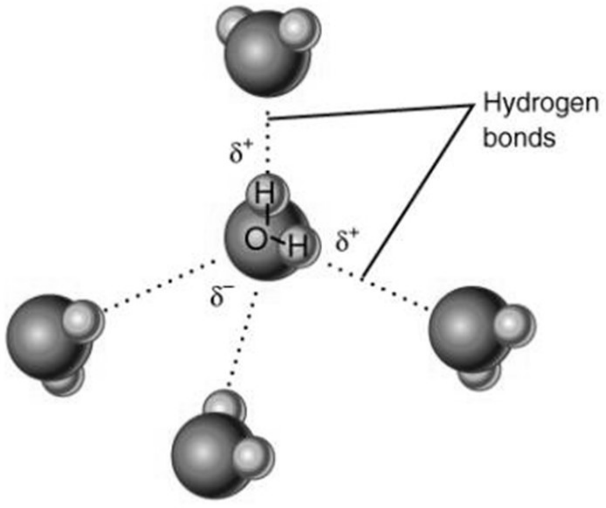


(5,5)

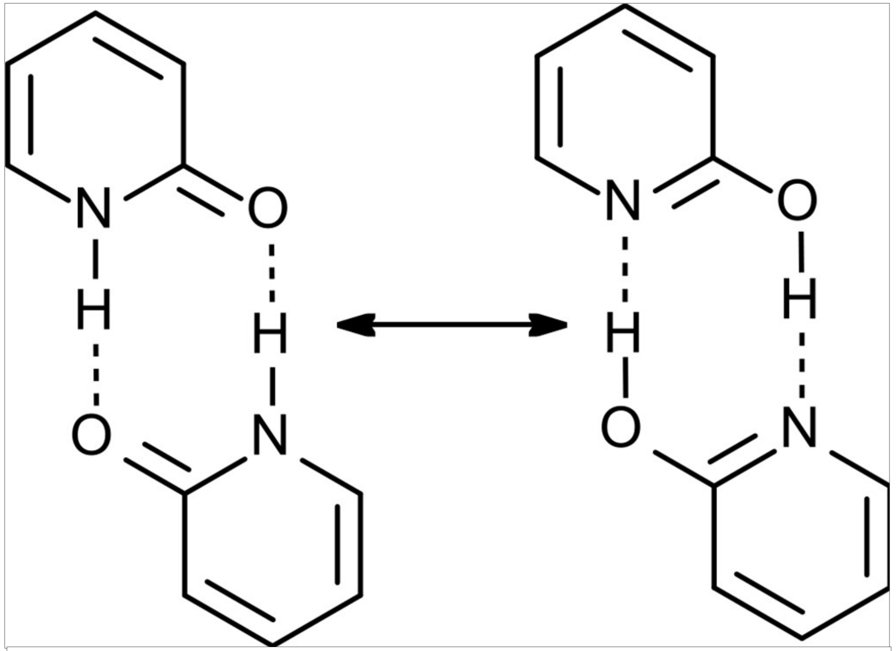
6.6 Hydrogen Bonding



Dimer of H_2O

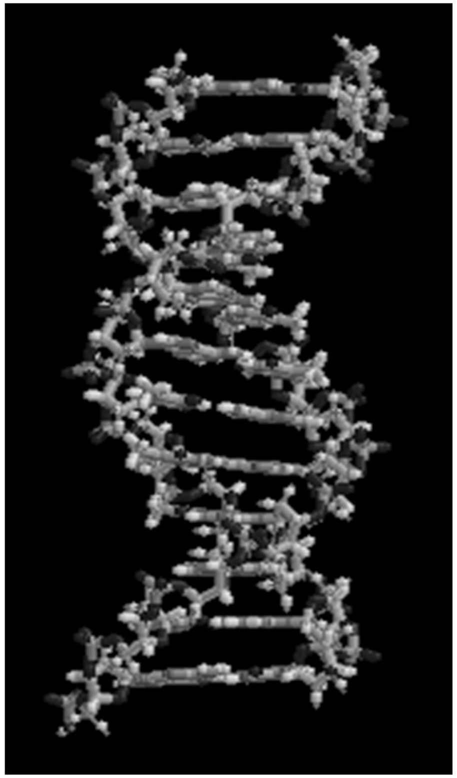


© John Wiley & Sons, Inc.

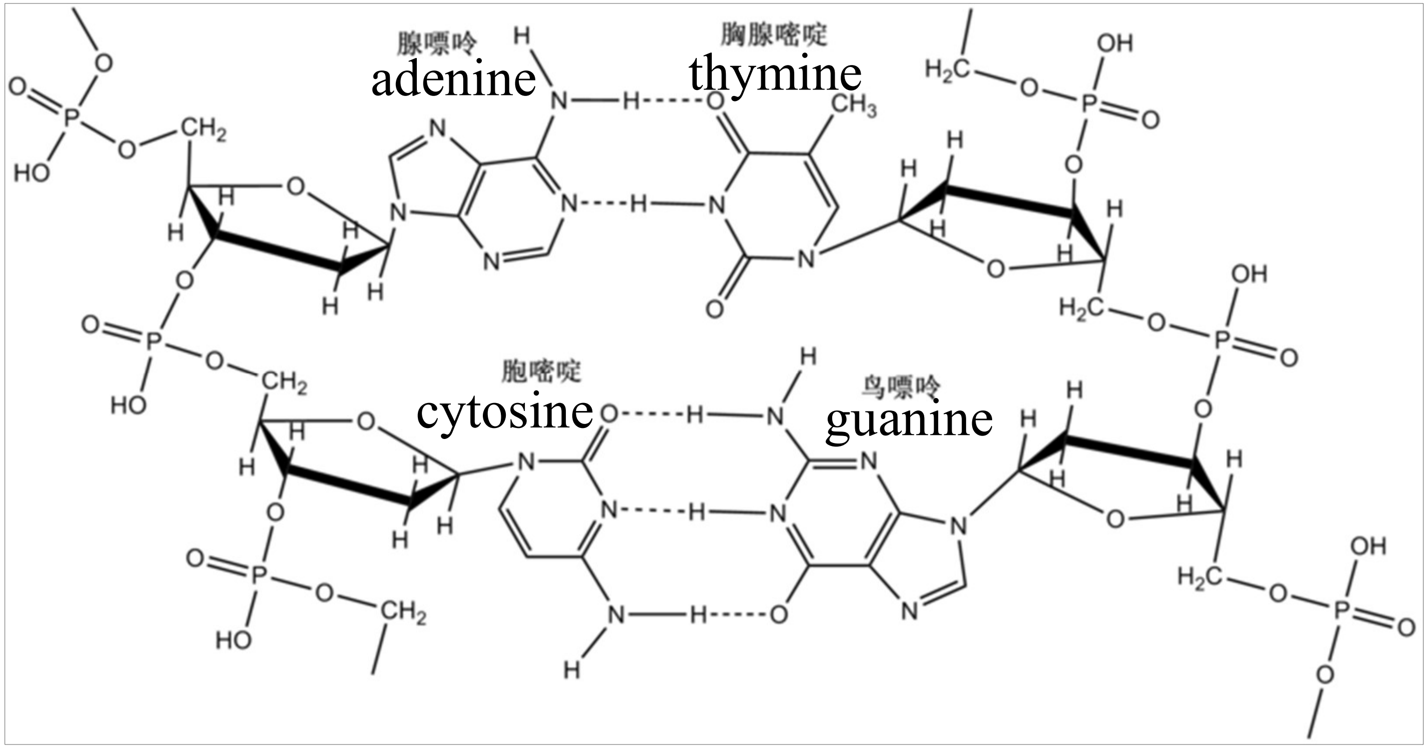


Dimer of 2-pyridone

Hydrogen bonds in DNA



part of DNA



- Hydrogen bonding within the base pairs of DNA

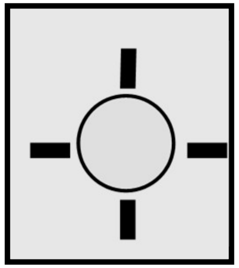
6.7 Prediction of structural features of inorganic iono-covalent compounds and tetrahedral anion complexes

Hume-Rothery’s 8 - N rule (1930/31)

Rule rationalizes observed structural features of (post-transition) main group elements. By forming the correct number of shared bonds with its neighbors each atom succeeds to complete its octet.

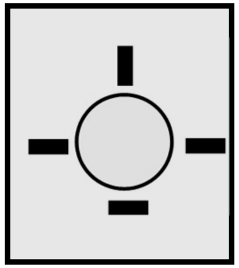
The number of bonds of an element is 8 - N where N is its column number in the periodic table (only for $4 \leq N \leq 8$).

Element structures which obey Hume-Rothery's 8 - *N* rule



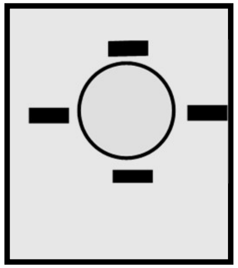
N = 4
4 bonds

C_D, Si, Ge, α-Sn



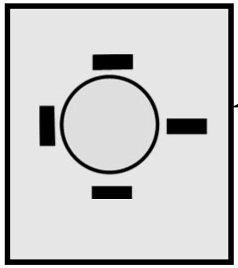
N = 5
3 bonds

P, As, Sb, Bi



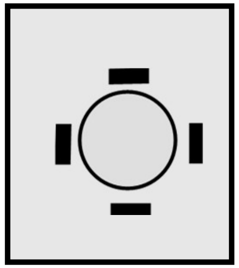
N = 6
2 bonds

S, Se, Te



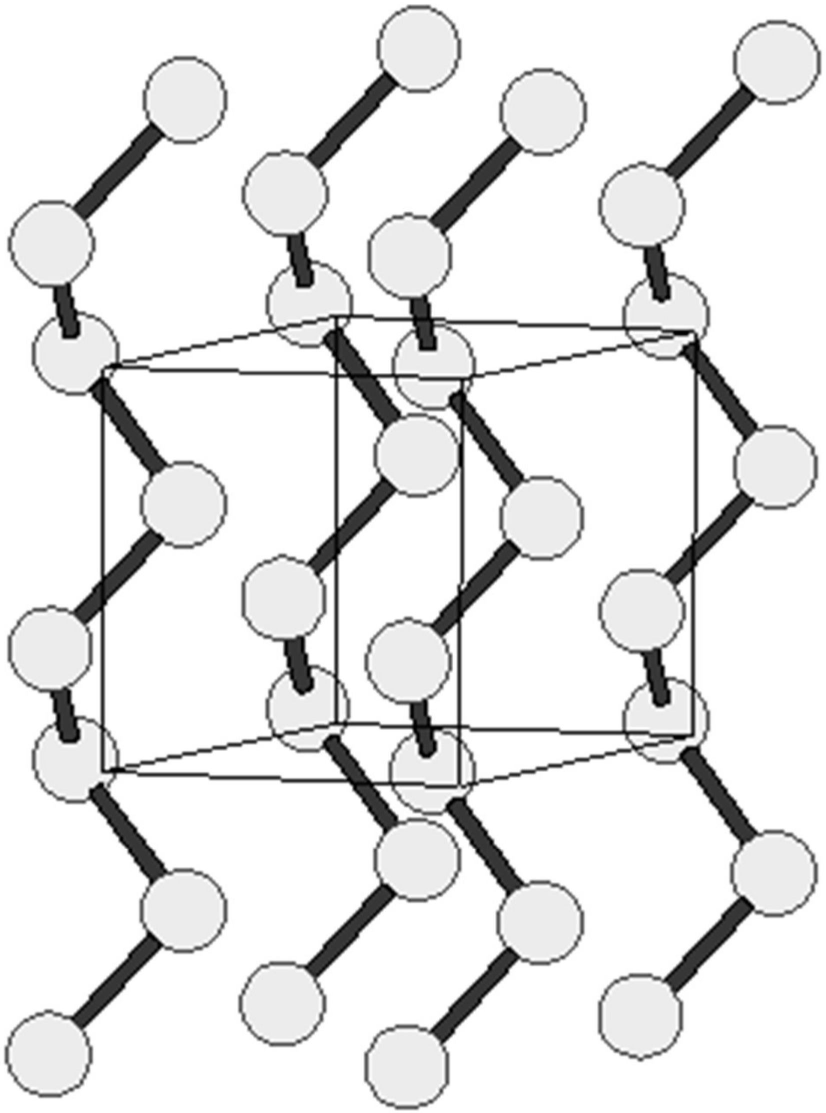
N = 7
1 bond

F, Cl, Br, I



N = 8
0 bonds

He, Ne, Ar, Kr, Xe, Rn



SELEN

Generalized 8 - *N* rule

Pearson (1964), Hulliger & Mooser (1965)

$$8 - \mathrm{VEC_A} = \mathrm{AA} - m\mathrm{CC}/n \qquad \text{for } C_mA_n$$

$\mathrm{VEC_A}$: Number of valence electrons per atom in anion.

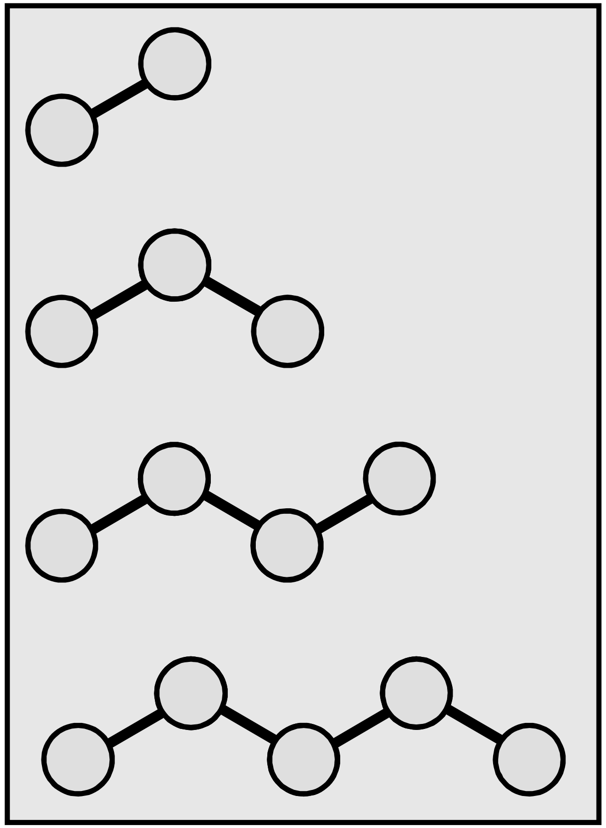
$\mathrm{VEC_A} < 8$, $\mathrm{AA}>0$, $\mathrm{CC}=0$ ⇨ Polyanionic val. comp.
$\mathrm{VEC_A} = 8$, $\mathrm{AA}=0$, $\mathrm{CC}=0$ ⇨ Normal valence compound
$\mathrm{VEC_A} > 8$, $\mathrm{AA}=0$, $\mathrm{CC}>0$ ⇨ Polycationic val. comp.

AA: Average number of A-A bonds per anion
CC: Average number of C-C bonds per cations and/or electrons used for inert-electron pairs on cations

Polyanionic valence compound (1)

$K_6Pd(II)Se_{20}$: VEC_A= 128/20=32/5, CC=0,

➔ AA=8/5, i.e., **$K_6Pd[Se_5]_4$**



AA = (2x1)/2
= 1

AA = (2x1 +2)/3
= 4/3

AA = (2x1 + 2x2)/4
= 6/4

AA = (2x1 +3x2)/5
= 8/5

$N_{A/M}$ = 2/(2 - AA)

$N_{A/M}$: Average number of atoms in a non-cyclic charged anion molecule

Polyanionic valence compounds (2)

- **LaAs$_2$** : VEC$_A$= 6.5; AA = 3/2; $N_{A/M}$ = 4
  La$_2$^[As$_4$] (LT) or La$_4$^[As$_3$] ^[As$_5$] (HT)
- **CsTe$_4$** : VEC$_A$= 6.25; AA = 7/4; $N_{A/M}$ = 8
  Cs$_2$^[Te$_8$]
- **Th$_2$S$_5$** : VEC$_A$= 7.6; AA = 2/5
- Th$_2$^[S$_2$][S]$_3$
- **Sr$_5$Si$_3$** : VEC$_A$= 7.33; AA = 2/3
- Sr$_5$^[Si$_2$][Si]

Polycationic valence compounds

- **HgCl** : $VEC_A = 9$; $CC = 1$
- $[Hg\text{-}Hg]Cl_2$
- **CCl_3** : $VEC_A = 8.33$; $CC = 1$
- $[C\text{-}C]Cl_6$
- **SiAs** : $VEC_A = 9$; $CC = 1$
- $[Si\text{-}Si]As_2$

Caution:

In most cases, the M-M bond valence of a cluster compound derived from the electron-counting rule may not be explicitly equal to the number of its M-M linkages!

Accordingly, it is better to make use of Wade's rule to count the number of skeletal bonding electron-pairs of a cluster compound!

- For each M center of a cluster compound that fulfills the 18e rule, it adopts supposedly d^2sp^3 hybridization with three non-hybridized d AOs unused.
- While some of the hybridized orbitals are used to form M-L dative bonds, the rest of the HOs are used to form the skeletal MOs of the cluster compound!
- Thus, the Wade's rule demands 2(n+1) bonding skeletal electrons for a ***n***-vertex polyhedron.

Example: $Fe_3(CO)_{12}$

A. Electron-counting rule: $g = 3\times8 + 12\times2 = 48$; $b=(3\times18-48)/2 = 3$

--seemingly adopts a triangular geometry with 3 M-M bonds!

B. Wade’s rule (MO theory):

i) Fe (8 VEs & 9 VAOs) in $Fe(CO)_4$ fragment:

- 3 non-bonding VAOs (doubly occupied d AOs, thus 6VEs used);
- 4 VAOs used for M-CO dative bonds; The rest 2VAOs (together with 2 VEs) contribute to the skeletal MOs of the cluster.

ii) Three $M(CO)_4$ fragments jointly form 3 bonding & 3 antibonding skeletal MOs.

In this case, predictions based on the simple electron-counting rule & Wade’s rule agree well with each other!

Cautions: The electron-counting rule even fails for some low-oxidation state TM compounds!

Example: $M_6(CO)_{18}$ (M = Fe, Ru, Os)

A. Electron-counting: g = 6x8 + 18x2 = 84; b=(6x18-84)/2 = 12

The cluster compounds seemingly have 12 M-M bonds, thus adopting an octahedral geometry! Is this prediction correct?

B. Wade’s rule (MO theory):

i) The M atom in a $M(CO)_3$ fragment has 8 VEs & 9 VAOs:

3VAOs used for M-CO bonds; 3 non-bonding d VAOs & 6VEs;

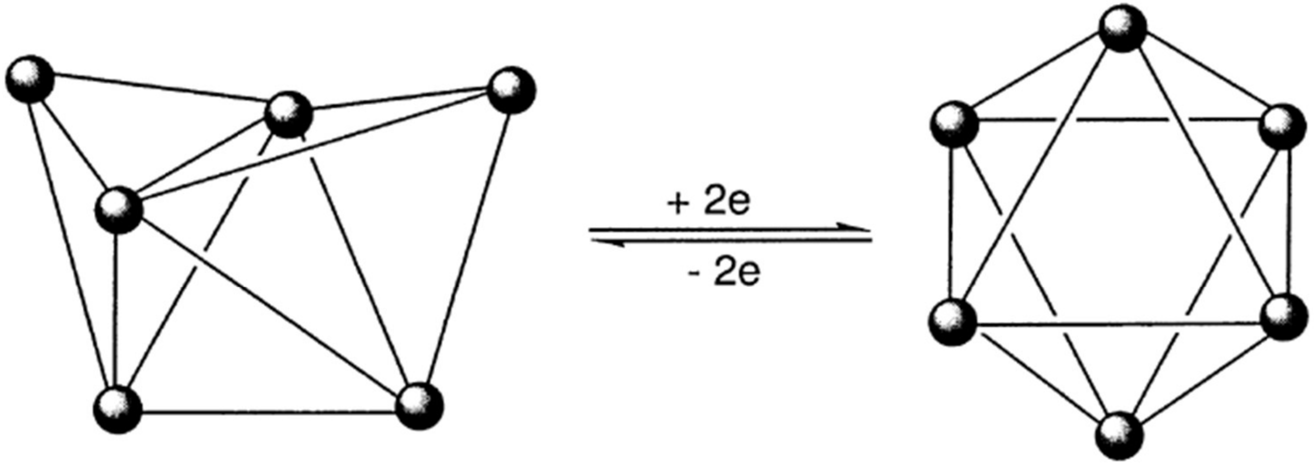
the rest 3VAOs, but only 2 VEs, used for the formation of the skeletal MOs of the cluster →

ii) The whole cluster has 12 VEs, i.e., 6 bonding skeletal MOs.

iii) However, **Wade’s rule** demands in total 7 bonding skeletal MOs (1 radial + 6 tangential MOs) for an octahedron.

v) The cluster is not ideally an octahedron, but actually a bicapped tetrahedron!

Instead, $[M_6(CO)_{18}]^{2-}$ is an octahedron with 7 bonding skeletal MOs!



$Os_6(CO)_{18}$
bicapped tetrahedron

$[Os_6(CO)_{18}]^{2-}$
octahedron

Validation of the simple electron-counting rule requires an in-depth analysis in light of the MO theory!

m VEs n VAOs	**VB description**	**MO description**
$m = n$	***m/2***(or n/2) 2c-2e bonds: (σ /+ π), e.g., 4 C-H bonds in CH_4	***m/2*** bonding MOs (σ /+ π) or plus Π_x^x (e.g., C_6H_6)
$m > n$	***(m-n)*** lone pairs & **(2n-m)/2** 2c-2e bonds, e.g., NH_3	***(m-n)*** non-bonding MOs & ***(2n-m)/2 bonding*** MOs or plus Π_x^x (e.g., pyridine)
$m < n$	Electron deficient! ?	(e.g., boranes, carboranes) 3c-2e or more delocalized σ-MOs.