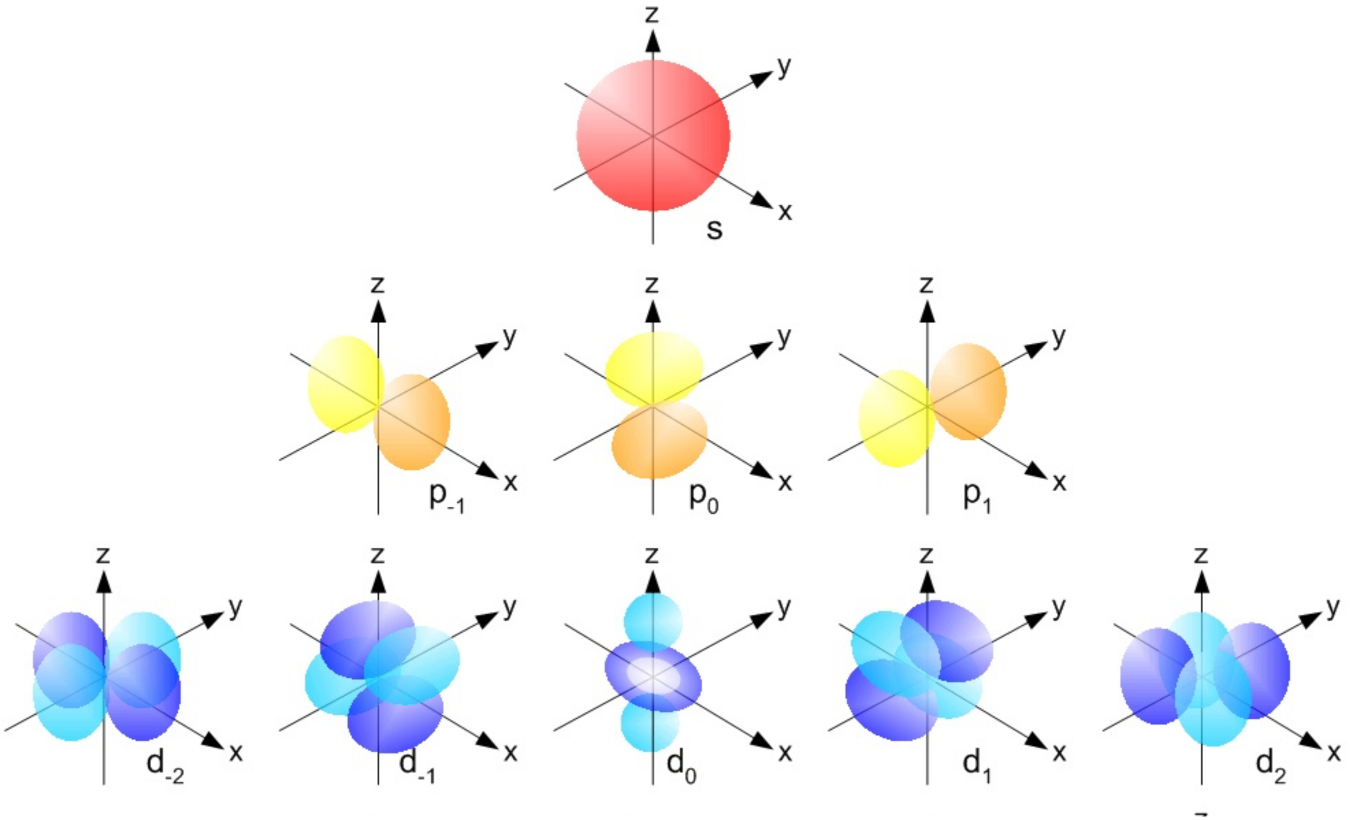
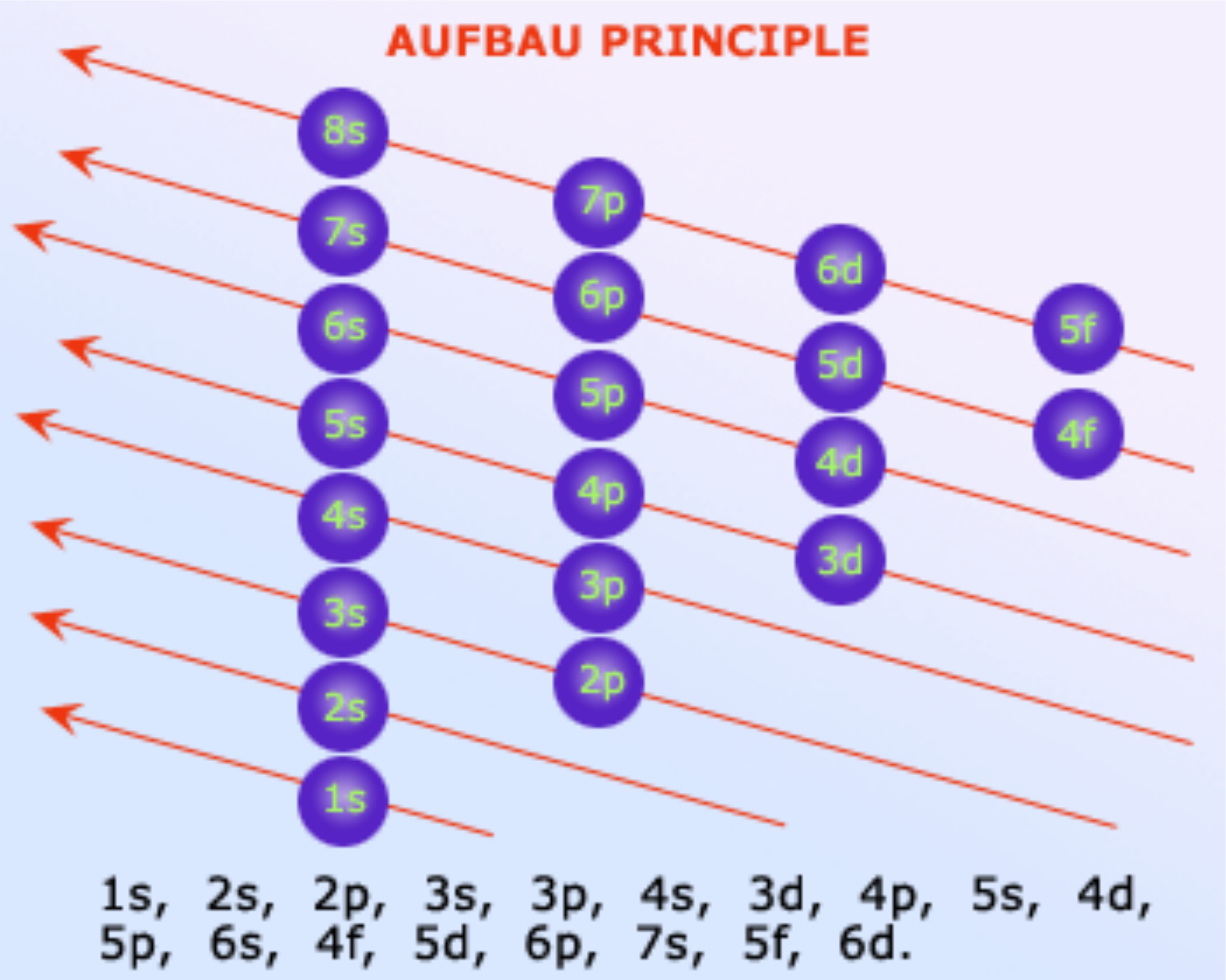
THE BASICS

Basic shapes of atomic orbitals



Aufbau principle

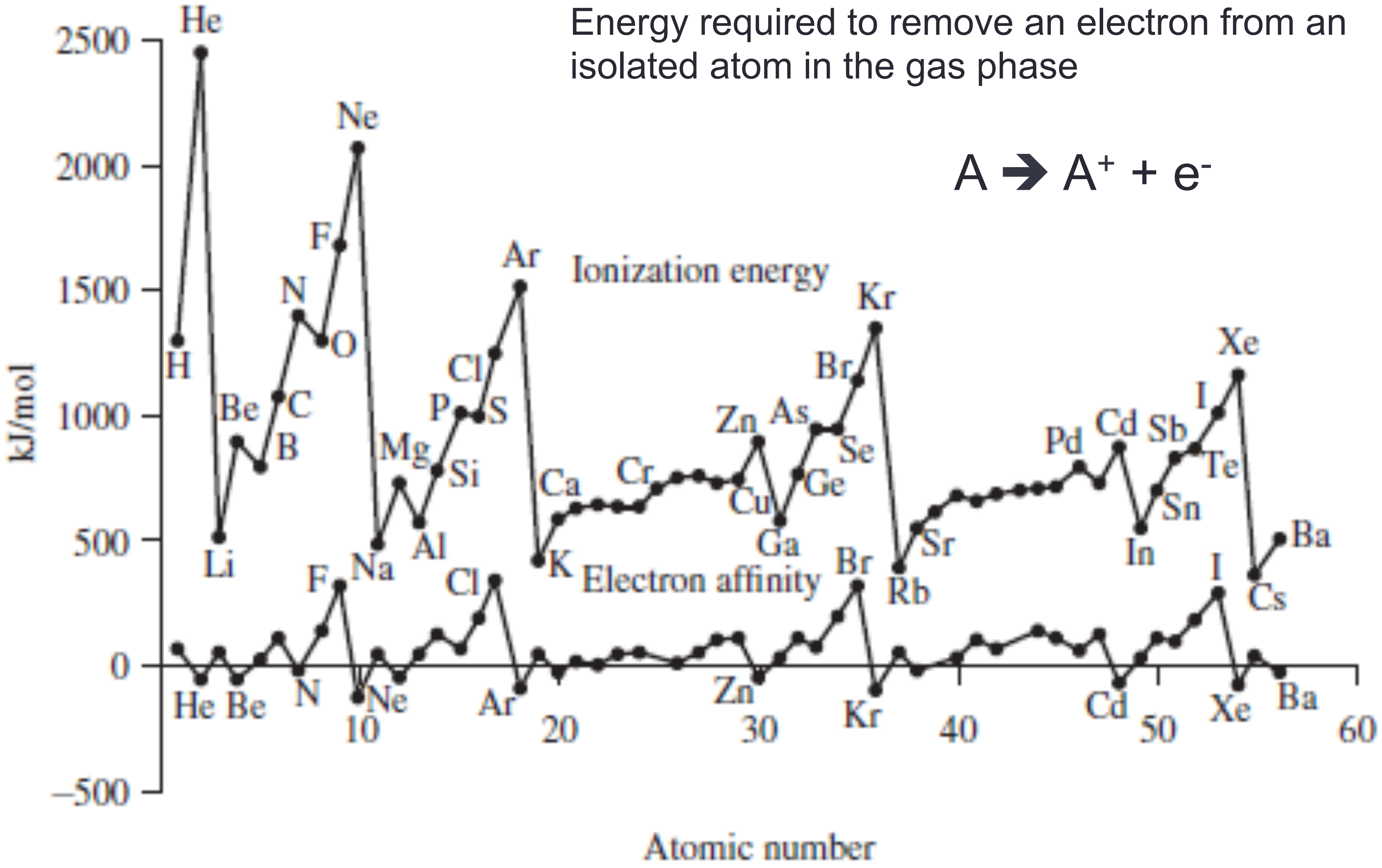


1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d.

Periodic trends: ionization energy

Energy required to remove an electron from an isolated atom in the gas phase

$A \rightarrow A^+ + e^-$



Periodic trends: Atomic size

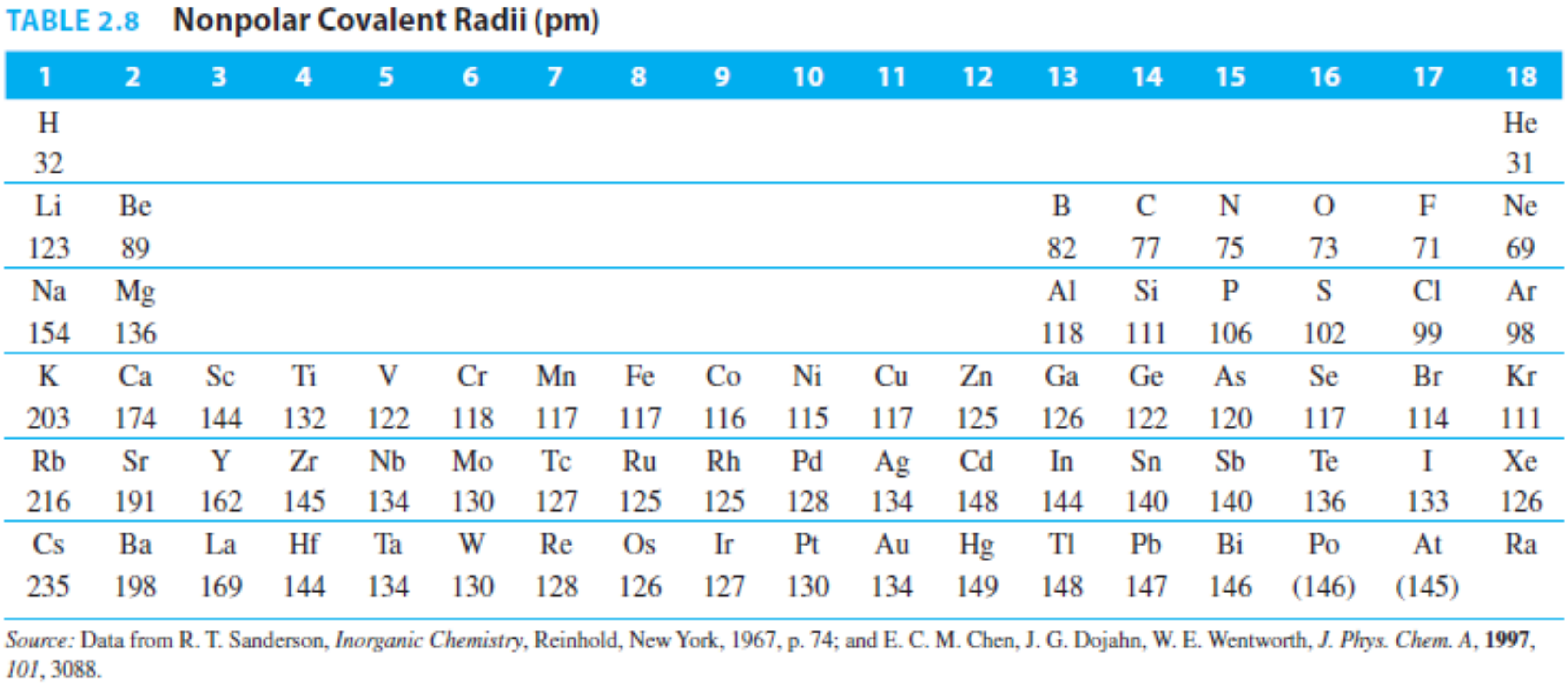
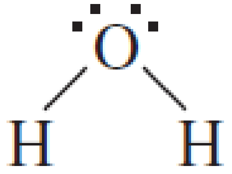


TABLE 2.8 **Nonpolar Covalent Radii (pm)**

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H 32																	He 31
Li 123	Be 89											B 82	C 77	N 75	O 73	F 71	Ne 69
Na 154	Mg 136											Al 118	Si 111	P 106	S 102	Cl 99	Ar 98
K 203	Ca 174	Sc 144	Ti 132	V 122	Cr 118	Mn 117	Fe 117	Co 116	Ni 115	Cu 117	Zn 125	Ga 126	Ge 122	As 120	Se 117	Br 114	Kr 111
Rb 216	Sr 191	Y 162	Zr 145	Nb 134	Mo 130	Tc 127	Ru 125	Rh 125	Pd 128	Ag 134	Cd 148	In 144	Sn 140	Sb 140	Te 136	I 133	Xe 126
Cs 235	Ba 198	La 169	Hf 144	Ta 134	W 130	Re 128	Os 126	Ir 127	Pt 130	Au 134	Hg 149	Tl 148	Pb 147	Bi 146	Po (146)	At (145)	Ra

Source: Data from R. T. Sanderson, *Inorganic Chemistry*, Reinhold, New York, 1967, p. 74; and E. C. M. Chen, J. G. Dojahn, W. E. Wentworth, *J. Phys. Chem. A*, **1997**, *101*, 3088.

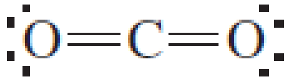
Lewis dot structures



H: 2 e^-s from O-H bond
O: 4 e^-s from 2 O-H bonds
    4 e^-s from 2 lone pairs

$H-C\equiv C-H$

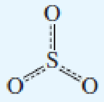
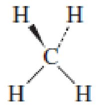
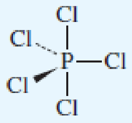
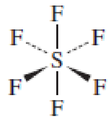
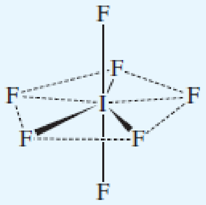
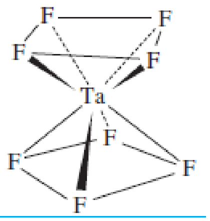
H: 2 e^-s from bonding pair
C: 2 e^-s from C-H bond
    6 e^-s from C$\underline{=}$C triple bond



O: 4 e^-s from C=O double bond
    4 e^-s from 2 lone pairs
C: 8 e^-s from 2 C=O double bond

VSEPR

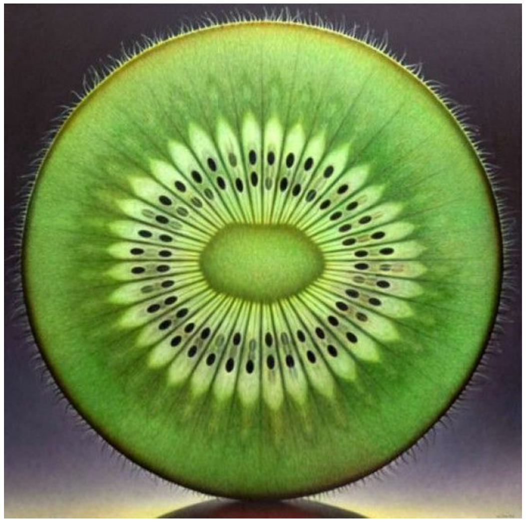
The systems in this table have the same groups surrounding the central atom

Steric Number	Geometry	Examples	Calculated Bond Angles	
2	Linear	CO_2	180°	$O{=}C{=}O$
3	Trigonal (triangular)	SO_3	120°	
4	Tetrahedral	CH_4	109.5°	
5	Trigonal bipyramidal	PCl_5	120°, 90°	
6	Octahedral	SF_6	90°	
7	Pentagonal bipyramidal	IF_7	72°, 90°	
8	Square antiprismatic	$[TaF_8]^{3-}$	70.5°, 99.6°, 109.5°	

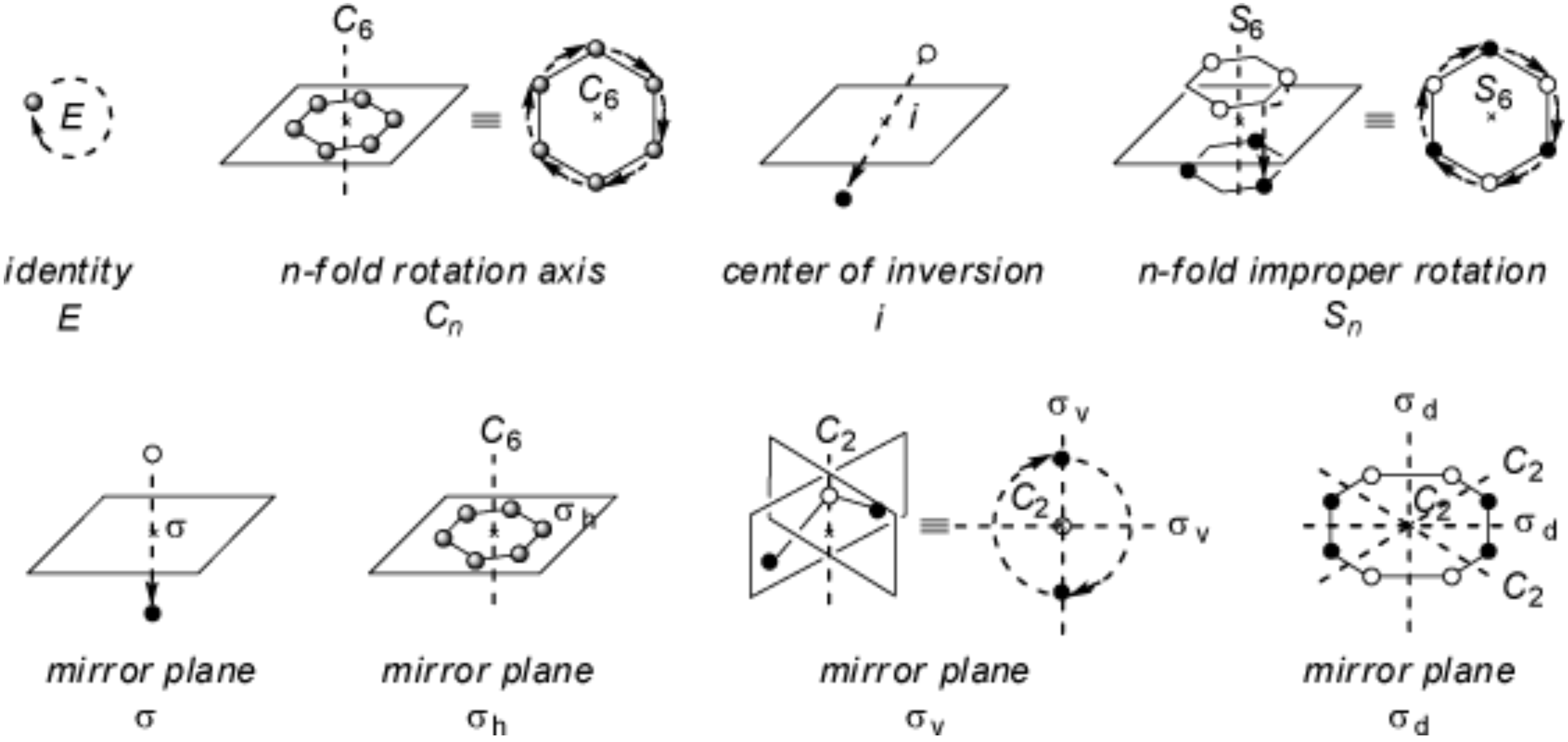
SYMMETRY

Symmetry all around us



Symmetry operations



identity
E

n-fold rotation axis
C_n

center of inversion
i

n-fold improper rotation
S_n

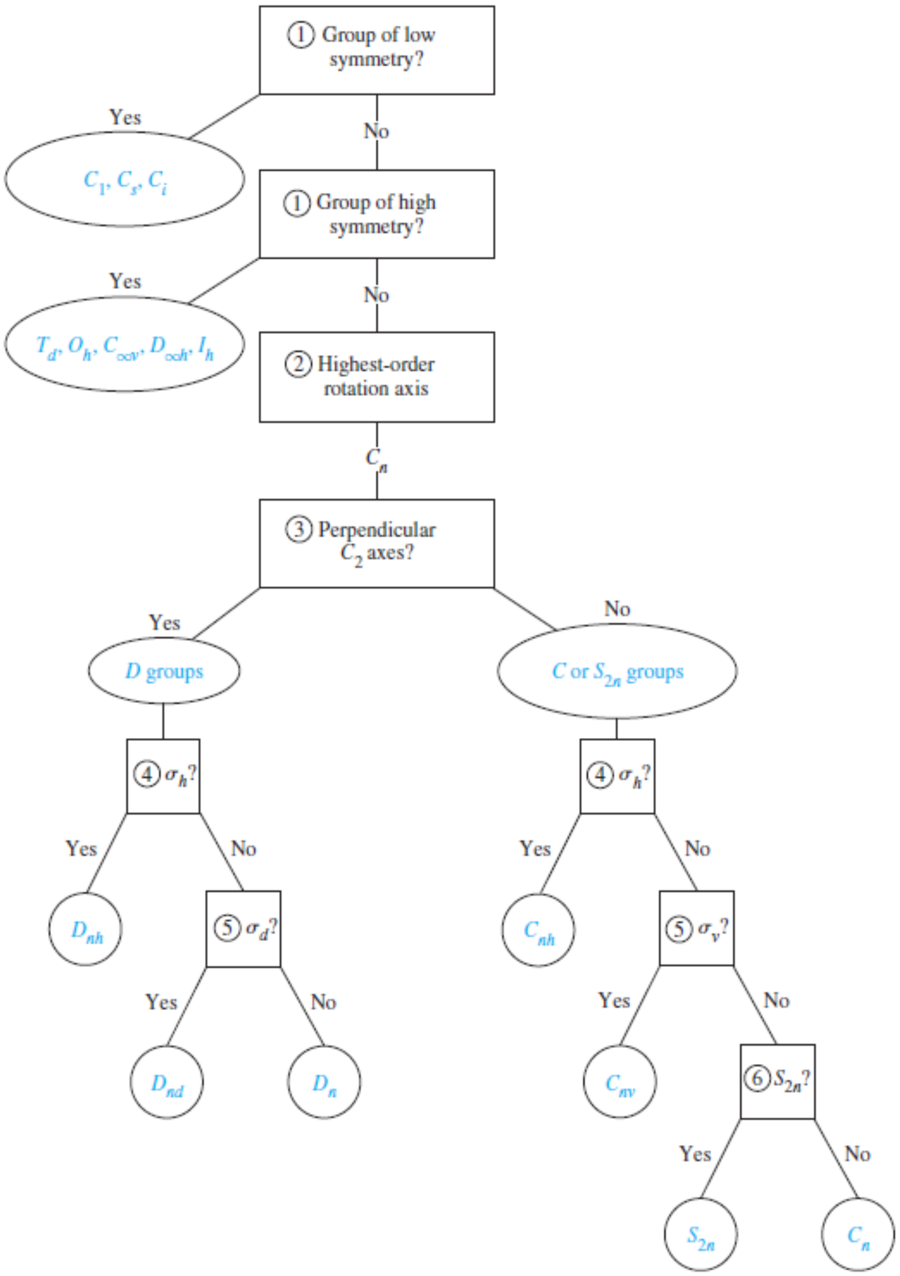
mirror plane
σ

mirror plane
σ_h

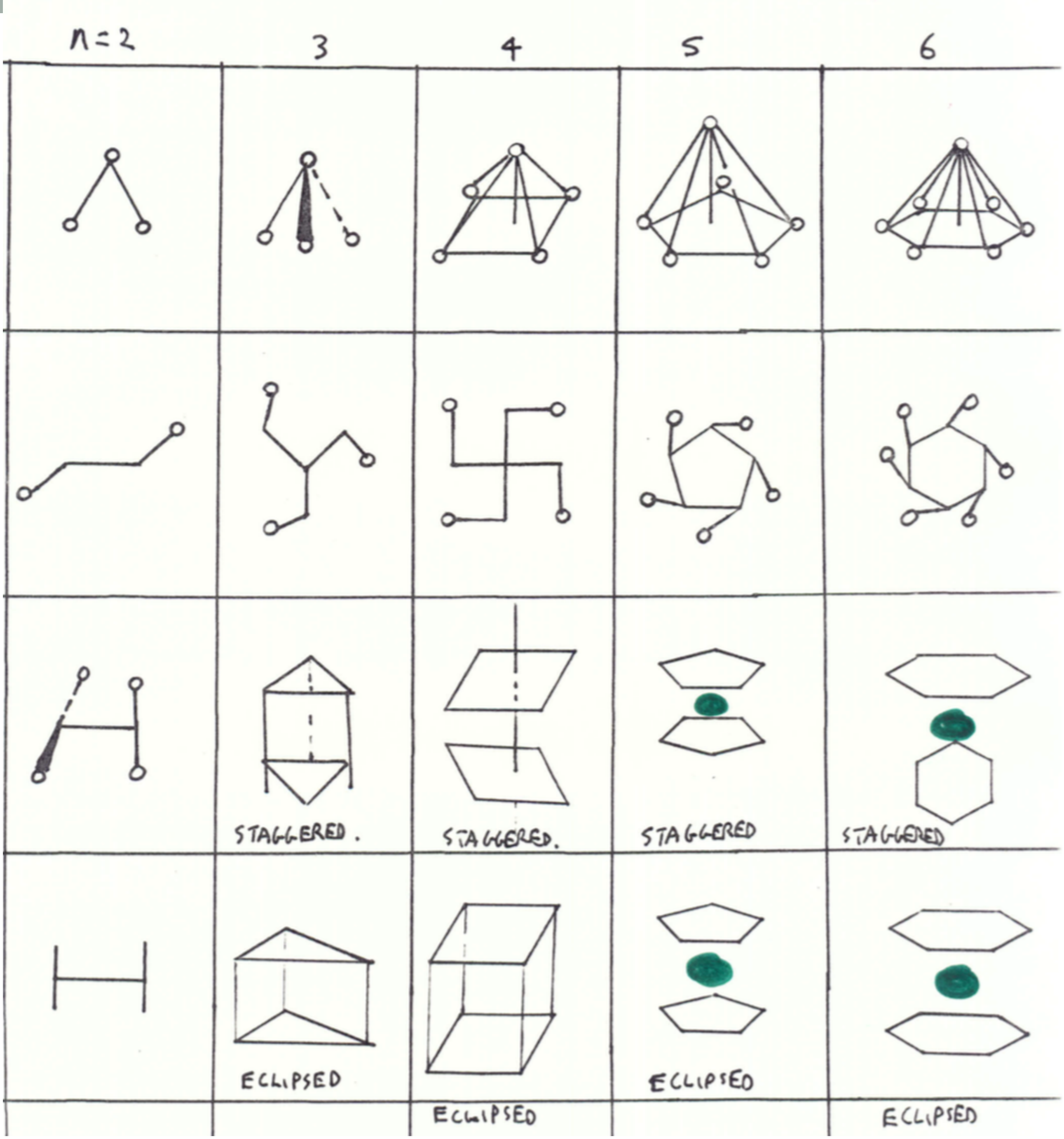
mirror plane
σ_v

mirror plane
σ_d

Point group flow chart



Point group short cuts

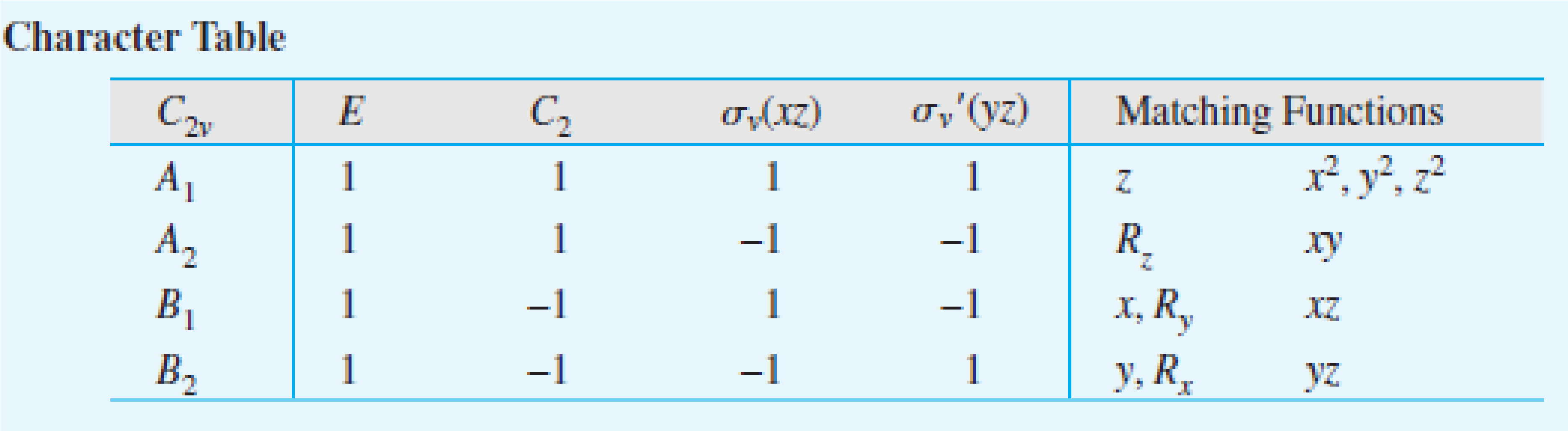


C_{nv}

C_{nh}

D_{nd}

D_{nh}



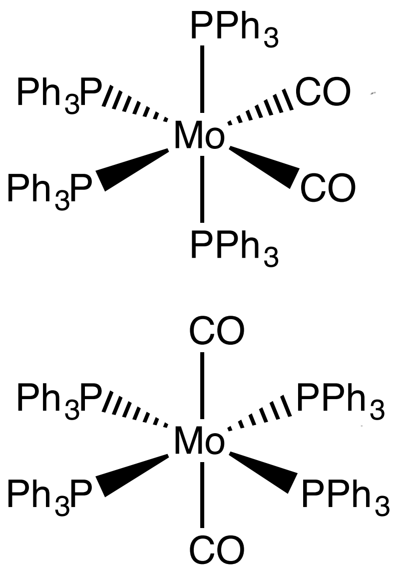
Character Table

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	Matching Functions	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	–1	–1	R_z	xy
B_1	1	–1	1	–1	x, R_y	xz
B_2	1	–1	–1	1	y, R_x	yz

Molecular Vibrations and Vibrational Spectroscopy

- Character tables are very useful for analyzing molecular vibrations and predicting peaks in Infrared and Raman spectra of a molecule

IR spectra (CO region) of *cis* vs *trans* $Mo(PPh_3)_4(CO)_2$



Inorganic Chemistry, Vol. 17, No. 9, 1978 **2681**

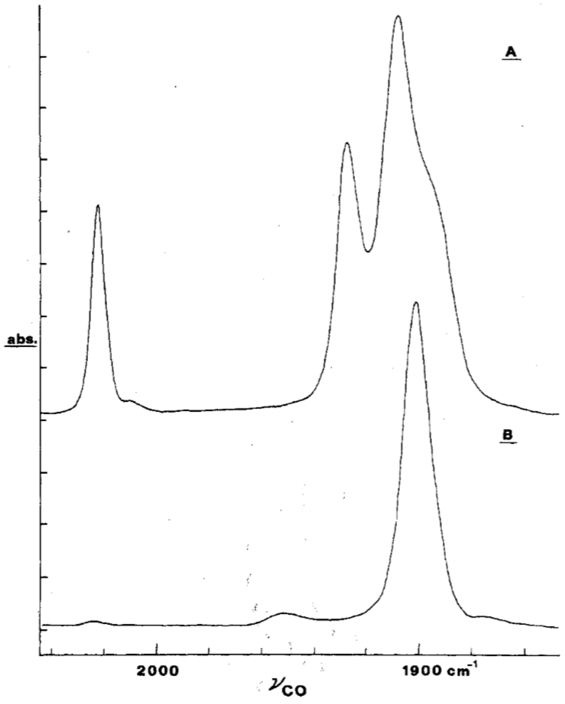
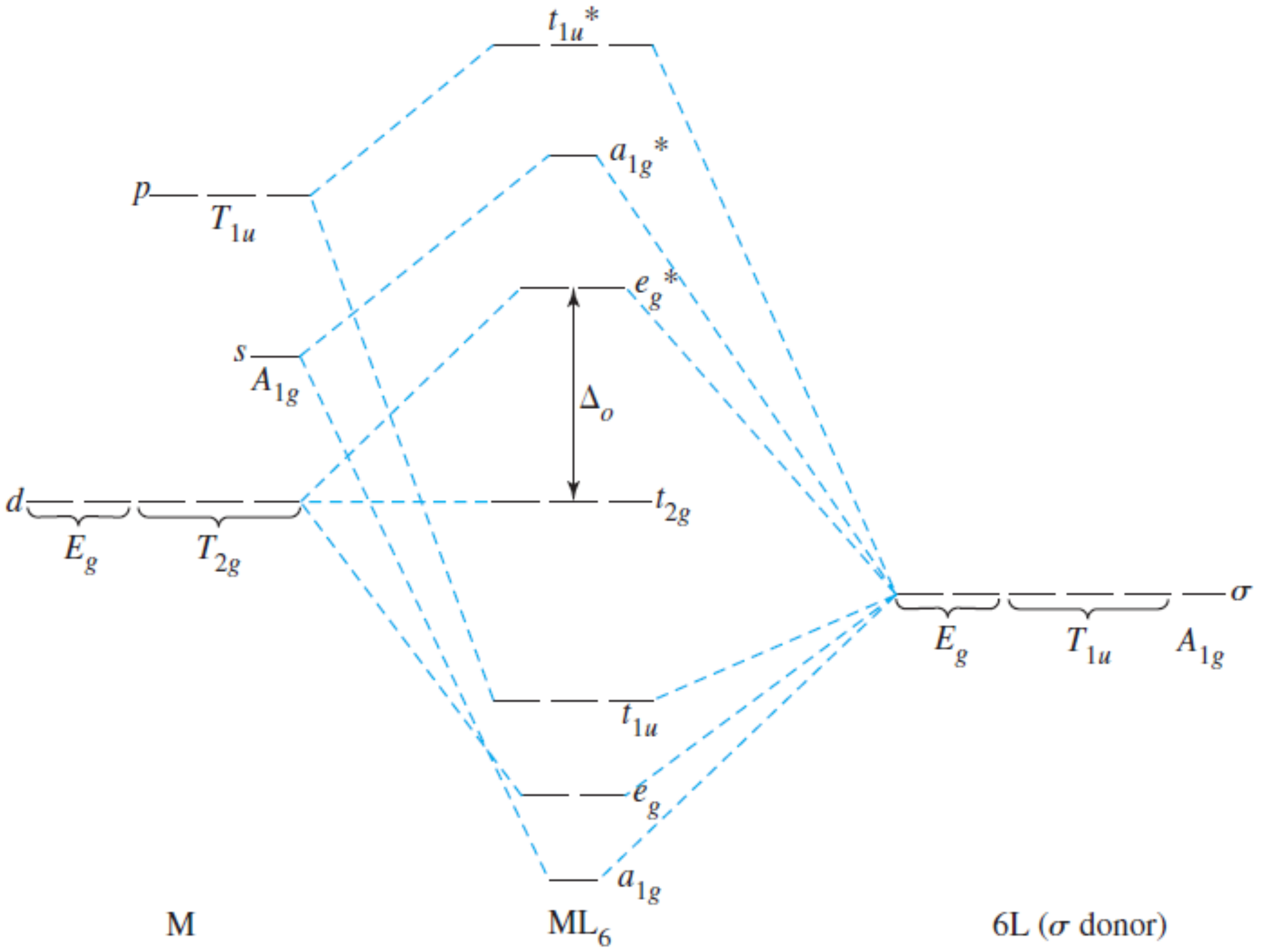


Figure 1. Infrared spectra in the CO stretching region in tetrachloroethylene of $Mo(CO)_4[PPh_3]_2$: A, *cis*-$Mo(CO)_4[PPh_3]_2$; B, *trans*-$Mo(CO)_4[PPh_3]_2$.

MO diagram of octahedral metal complex, sigma interactions only



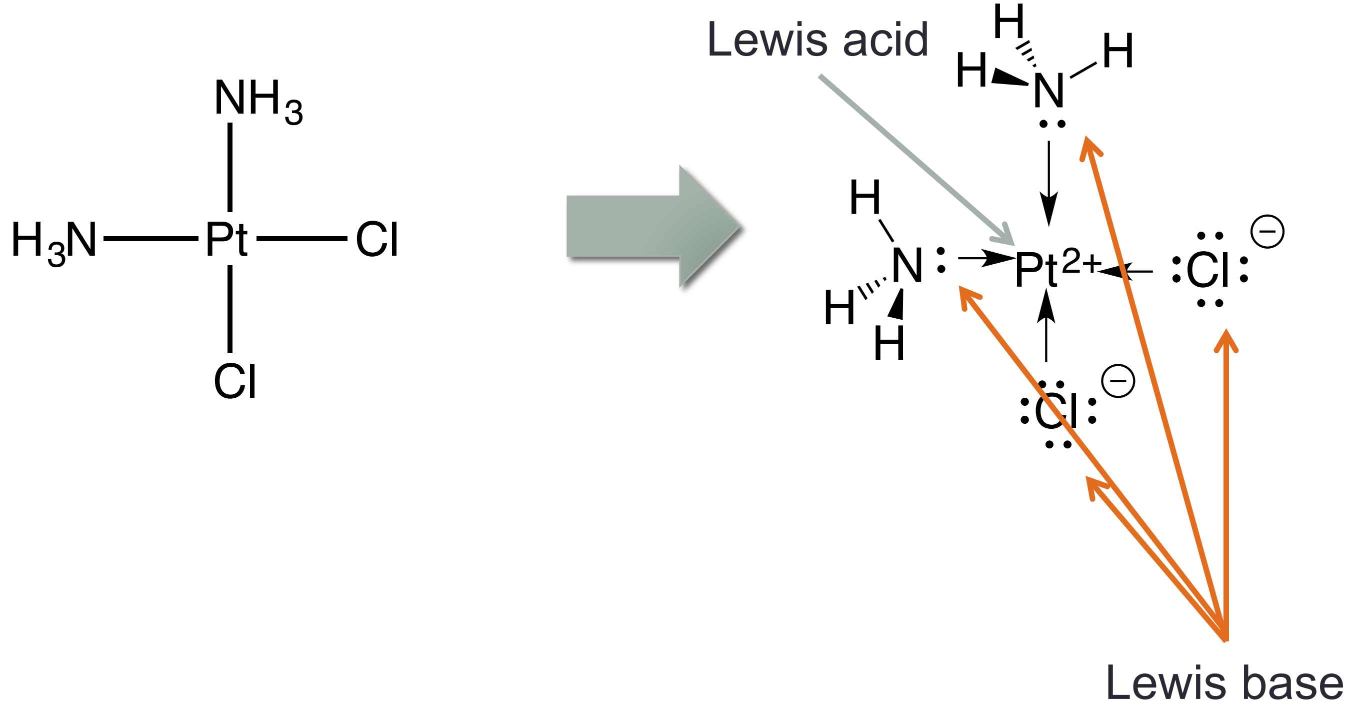
COORDINATION CHEMISTRY

see MFT Ch 6 for more details

Acid-Base Donor-Acceptor Chemistry

- In a coordination compound, the metal center (M^{n+}) acts as a **Lewis acid** and the ligand (L) acts as a **Lewis base**

$$M^{n+} \longleftarrow :L$$

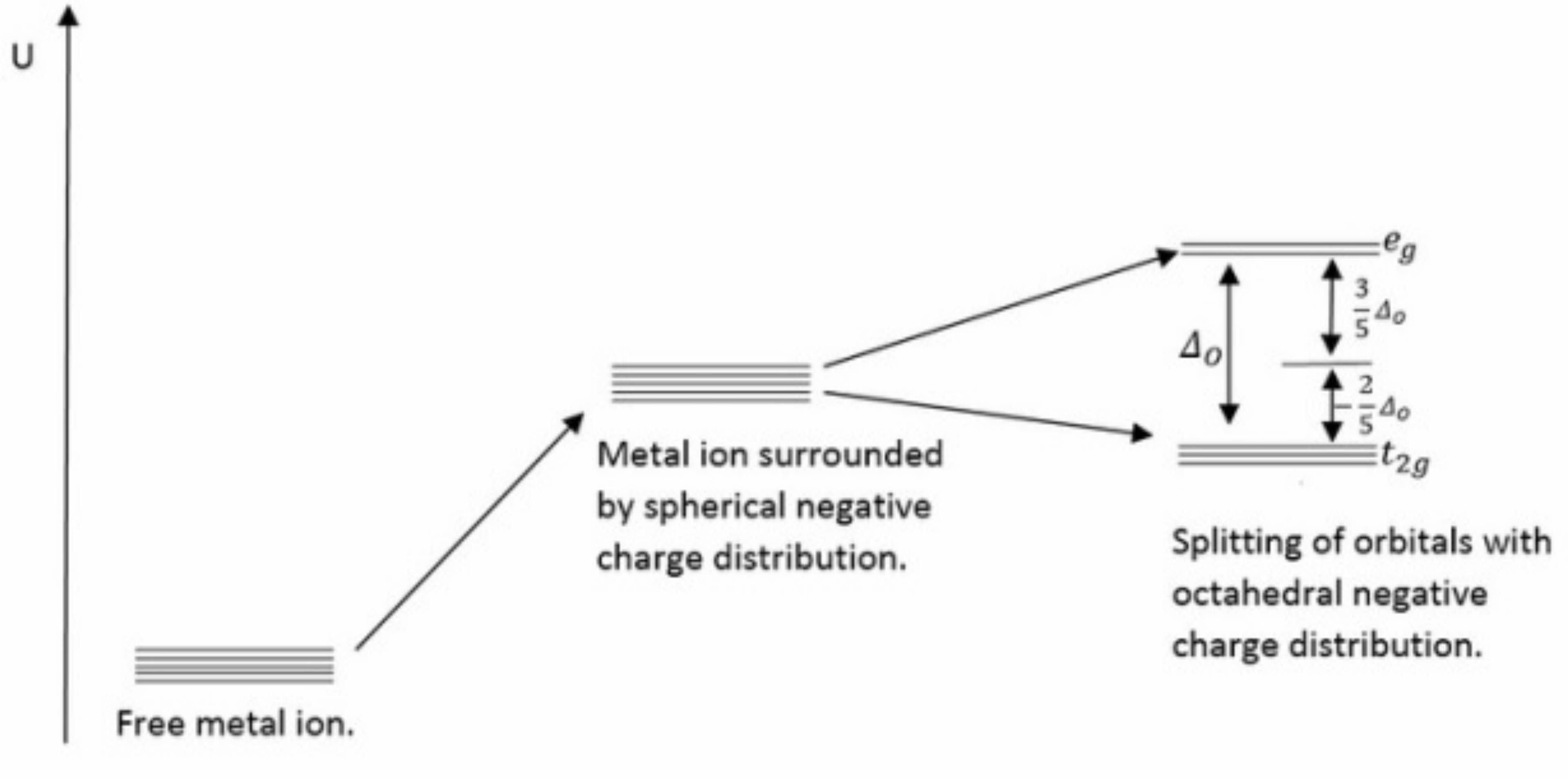


Description of hard and soft acids and bases, section 6.6.1 MFT, Tables 6.14 and 6.15

Hard Soft Acid Base Theory

- Metal-ligand bonds are a result of the interaction between a Lewis acid and a Lewis base
- These acids and bases can be described as either *hard* or *soft*
- Hard acid or base: small, compact, non-polarizable
    - Hard acids: typically cations with large postive charge (3+ or larger), cations whose d electrons aren't available for π bonding (e.g. alkali and alkaline earth cations)
    - Hard bases: smaller anions, like F^-
- Soft acid or base: larger, less compact, more polarizable
    - Soft acids: typically cations with d electrons are available for π bonding, neutral metals, 1+ cations, 2+ cations that are heavier
    - Soft bases: larger anions, like I^-

Octahedral crystal field splitting



Free metal ion.

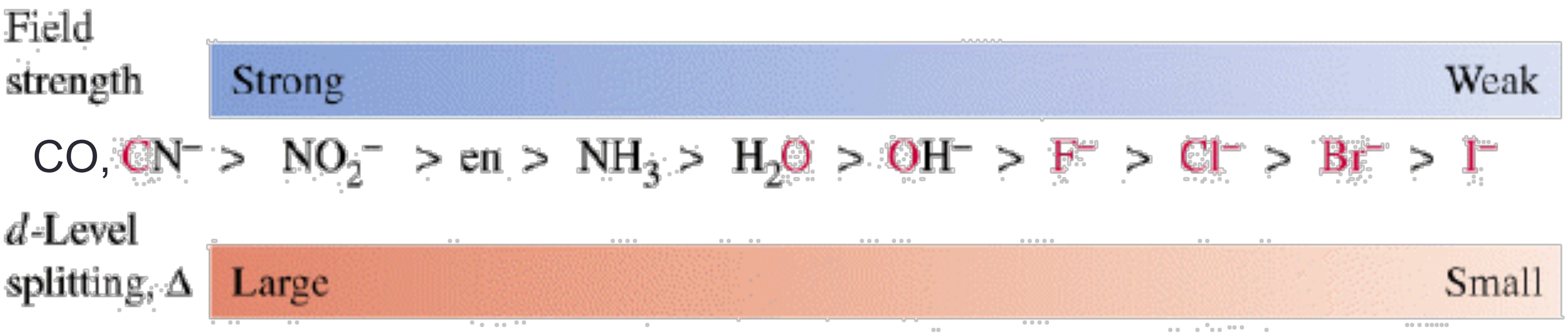
Metal ion surrounded by spherical negative charge distribution.

Splitting of orbitals with octahedral negative charge distribution.

The spectrochemical series

Next week’s lab will explore this!

- The spectrochemical series ranks ligands in the order of their ‘field strength’



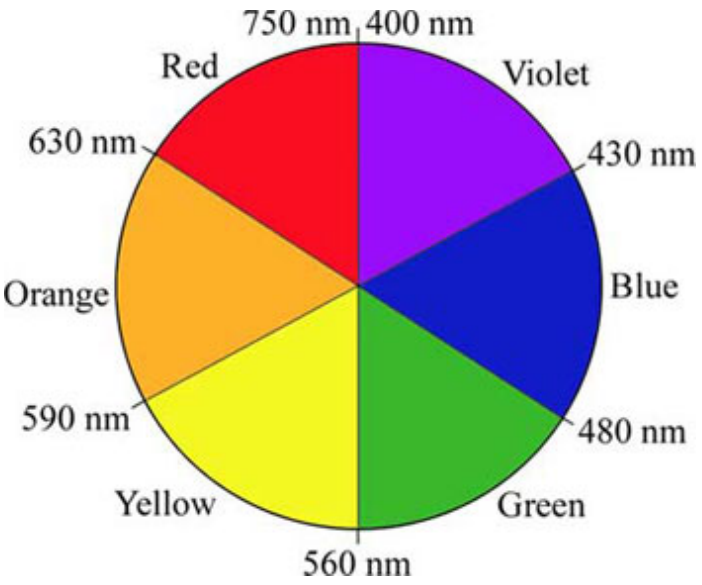
CO, CN^- > NO_2^- > en > NH_3 > H_2O > OH^- > F^- > Cl^- > Br^- > I^-

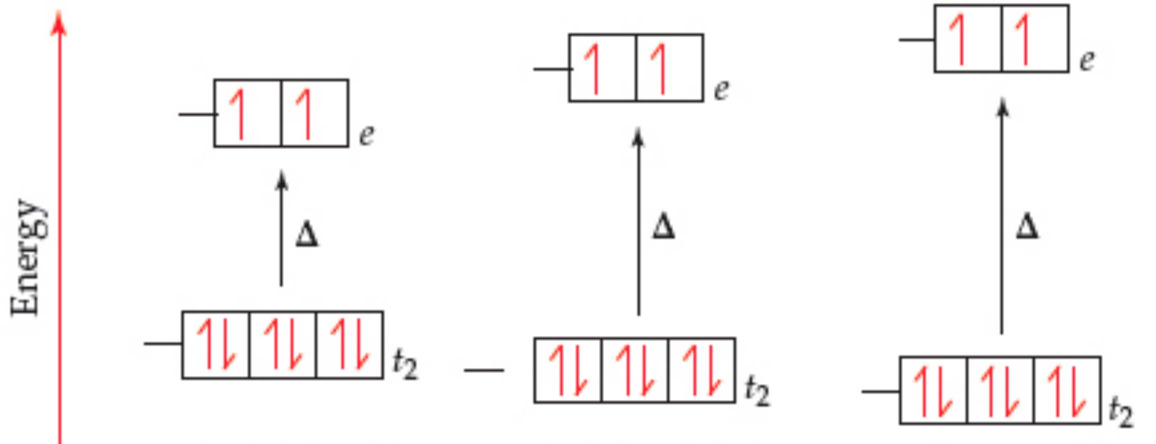
- Strong field ligands produce complexes with a large Δ_o
- Weak field ligands produce complexes with a small Δ_o

- Strong field ligands are pi acceptors, weak field ligands are pi donors

Electronic spectra: UV-vis

- Remember: color of light absorbed by the compound is complementary to the color it is (see color wheel)





$[Ni(H_2O)_6]^{2+}$
Max absorption in visible = 720 nm

$[Ni(NH_3)_6]^{2+}$
Max absorption in visible = 570 nm

$[Ni(en)_3]^{2+}$
Max absorption in visible = 545 nm

Spin only magnetic moment

$\mu_S = g\sqrt{[S(S+1)]}$

You must know this equation!

μ = magnetic moment

g = gyromagnetic ratio (= 2.00023 μ_B/Bohr magnetons)

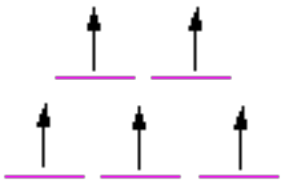
S = spin quantum number

Orbital contribution (L) is more important in molecules containing larger orbitals (metals from 4d, 5d, 4f…)

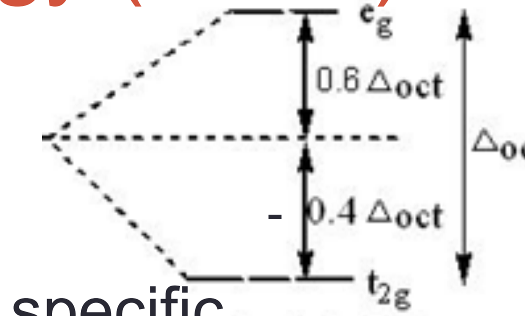
Ligand Field Stabilization Energy (LFSE)

Low spin

d^5



High spin



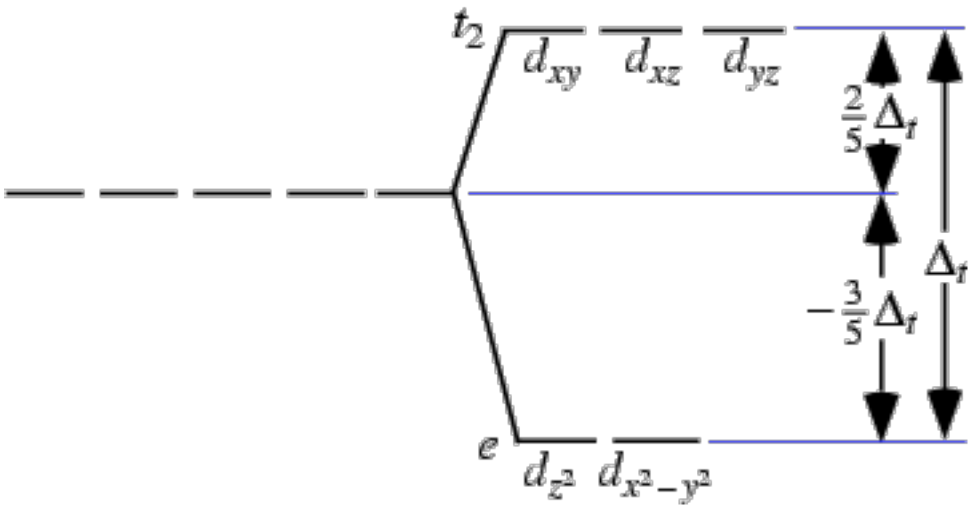
- LFSE: stabilization energy associated with a specific electronic configuration

This is for octahedral geometry! Other geometries will have similar types of calculations but numbers are different

- LFSE = $(-2/5\Delta_o)$ x (# of t_2g electrons) + $(3/5\Delta_o)$ x (# of e_g electrons)
- LFSE for low spin d^5: $(-2/5\Delta_o)*5 = -2\Delta_o$
- LFSE for high spin d^5: $(-2/5\Delta_o)*3 + (3/5\Delta_o)*2 = 0$
- More negative values are more stable, (however if Δ_o is small, so is the LFSE, so h.s. complexes are observed!)

d orbital splitting in Tetrahedral geometry

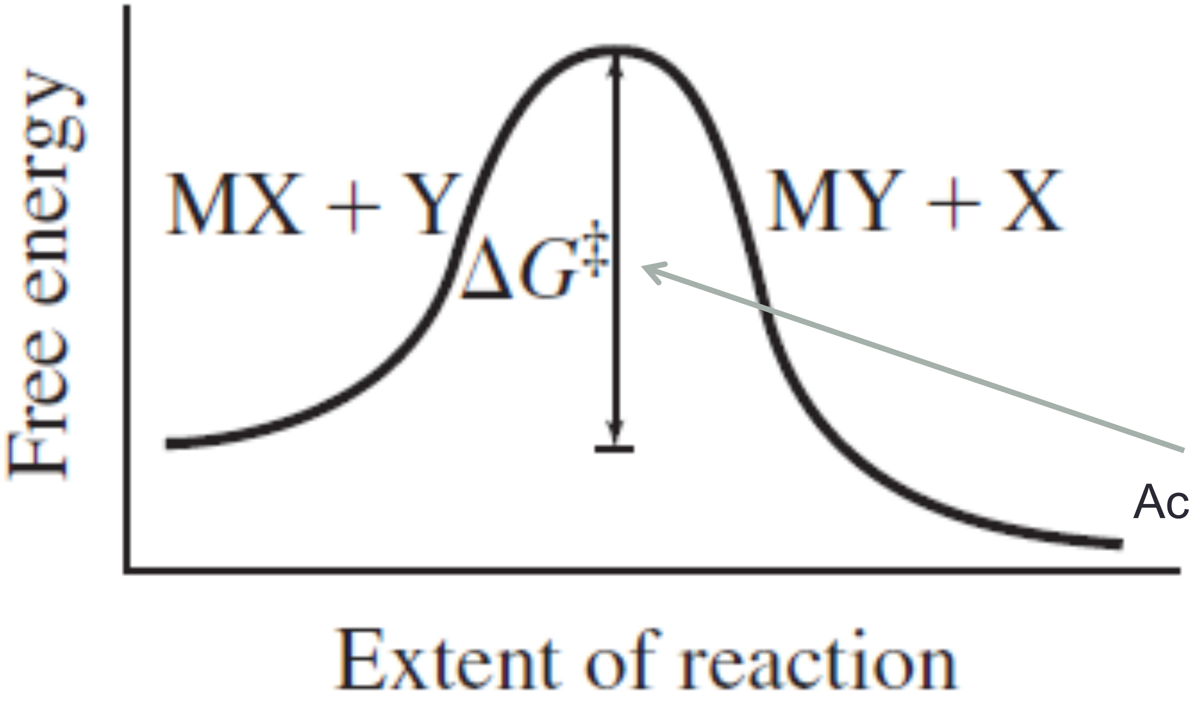
- Tetrahedral splitting, Δ_t, is not as large as Δ_o because only 4 ligands in tetrahedral vs. 6 ligands in octahedral
- $\Delta_t \approx 4/9\Delta_o$
- As a result of this smaller splitting, in practice tetrahedral complexes are high spin



LFSE can be calculated in tetrahedral just as in octahedral, except using the coefficients shown here

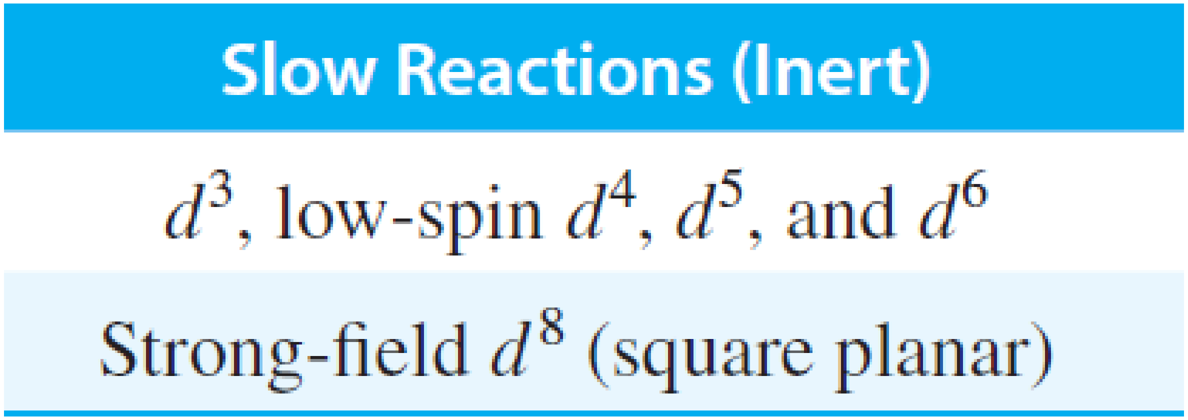
Note: coefficients used for LFSE calculations will give a LFSE = 0 d^{10} and high spin d^5 complexes

Reaction coordinate for ligand substitution

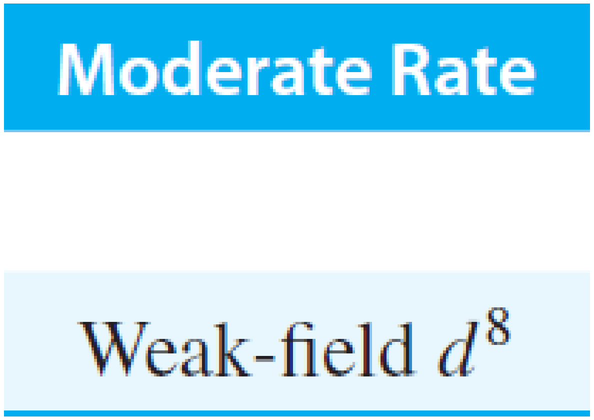


Activation energy

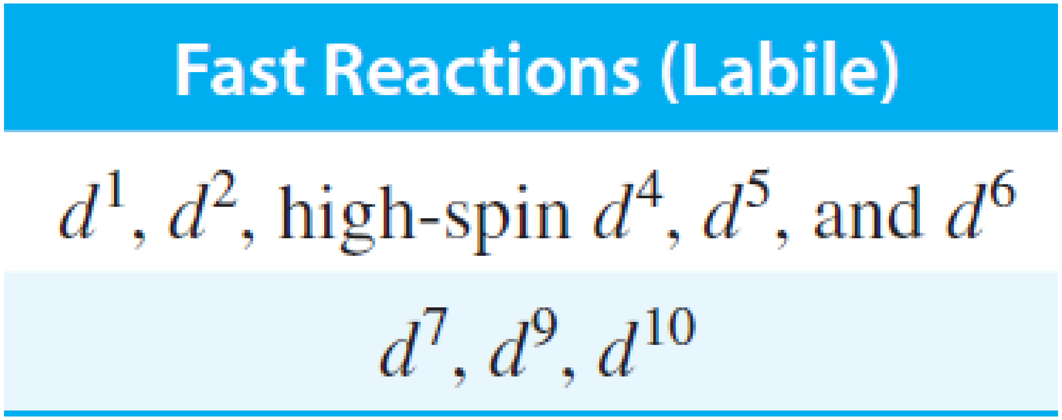
Labile and inert electronic configurations



Slow Reactions (Inert)
d^3, low-spin d^4, d^5, and d^6
Strong-field d^8 (square planar)



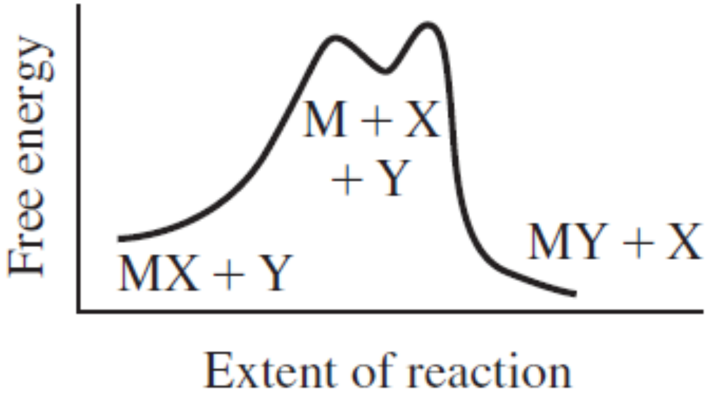
Moderate Rate
Weak-field d^8



Fast Reactions (Labile)
d^1, d^2, high-spin d^4, d^5, and d^6
d^7, d^9, d^{10}

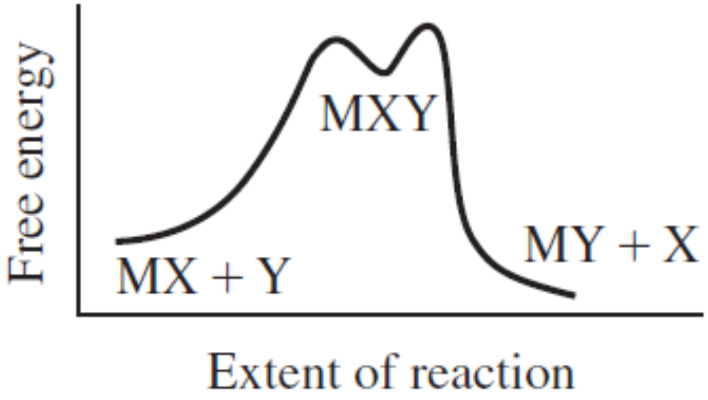
Reaction coordinates

Dissociative mechanism



(a)

Associative mechanism



(b)

Substitution reactions in square-planar complexes

- In square planar complexes, substitution reactions tend to follow an associative-type mechanism
- Evidence for this comes from the large effect the incoming ligand has on reaction rates (Table 12.12)

$$ML_2TX + Y \rightarrow ML_2TXY \rightarrow ML_2TY$$

For example, if M is Pt(II): the identity of Y affect rate of reaction:

$$Cl^- < Br^- < I^- < SCN^- < PR_3$$

Trend follows HSAB (Pt(II) is soft)

The *trans* effect

- Final ligand ranking a result of both pi and sigma effects

Ligand ranking for trans effect

$CN^- \sim CO \sim C_2H_4 > PH_3 \sim SH_2 > NO_2^- > I^- > Cl^- > NH_3 \sim py > OH^- > H_2O$

Large trans effect **Small trans effect**

Strong pi acceptor → strong sigma donor → neither strong sigma donor or pi acceptor

Redox

- **Redox**: refers to oxidation/reduction chemistry

- **Reduction**: gain of electrons
- **Oxidation**: loss of electrons

  Pneumonic: OIL RIG (oxidation is loss, reduction is gain)

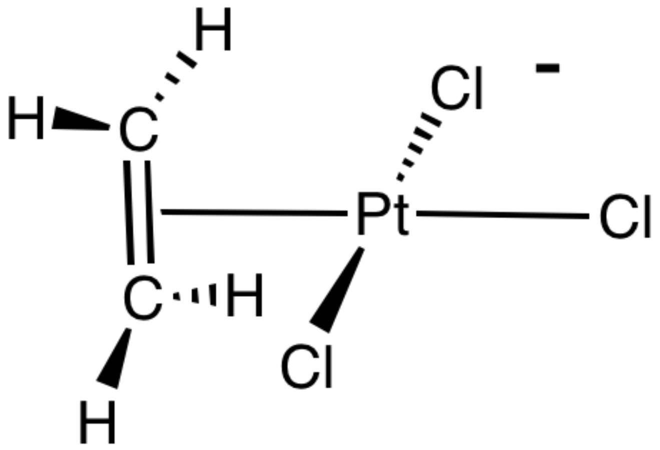
- **Oxidizing agent**: a substance that oxidizes a substrate by being reduced
- **Reducing agent**: a substance that reduces a substrate by being oxidized

https://ch302.cm.utexas.edu/echem/index.php#redox/intro-redox.html

ORGANOMETALLIC CHEMISTRY

History of organometallic chemistry: Zeise' salt

- The first reported organometallic compound: Zeise's salt (1827), structure was not verified until 1868



- This was the first compound identified in which an organic molecule was attached to a metal center through it's pi electrons
- →What do you think the orbital interactions look like in the alkene-metal bond?

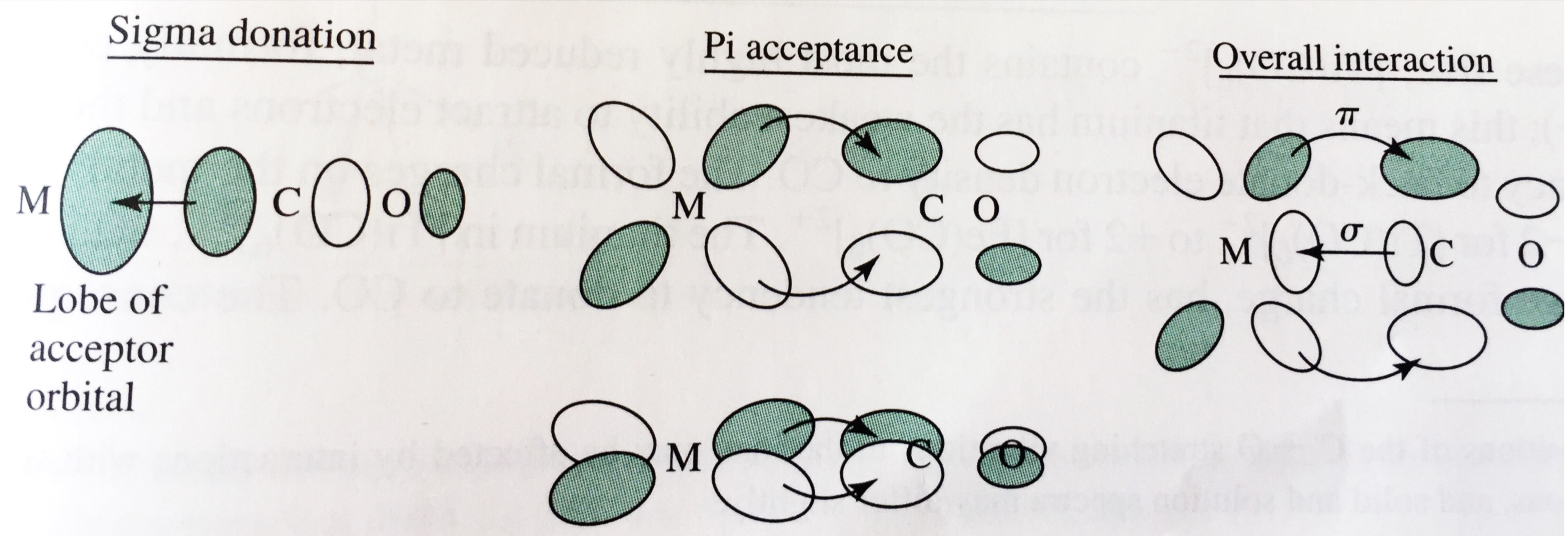
The 18 electron rule

- In main group chemistry, we have the octet rule, namely compounds tend to have 8 electrons surrounding each atom to fill their valence shell

- For metal complexes, the valence shell consists of s, p, and d electrons, which gives us 18 total spots for electrons in the valence shell

- Organometallic complexes often follow the 18 electron rule, though just like the octet rule, there are exceptions

CO interactions with a metal center



Covered previously with crystal field theory and spectrochemical series

Experimental evidence for differences in M-CO interactions

- Sigma bond between CO and M takes electron density away from CO bond
- π backbonding donates electron density into π* anti-bonding orbitals of CO

→Both interactions will weaken the CO bond: this results in lower IR stretching energy and longer CO bond

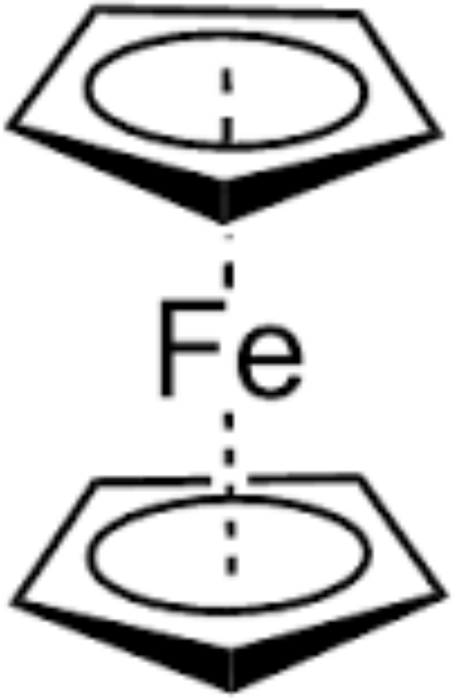
- Example: free CO vs. $Cr(CO)_6$

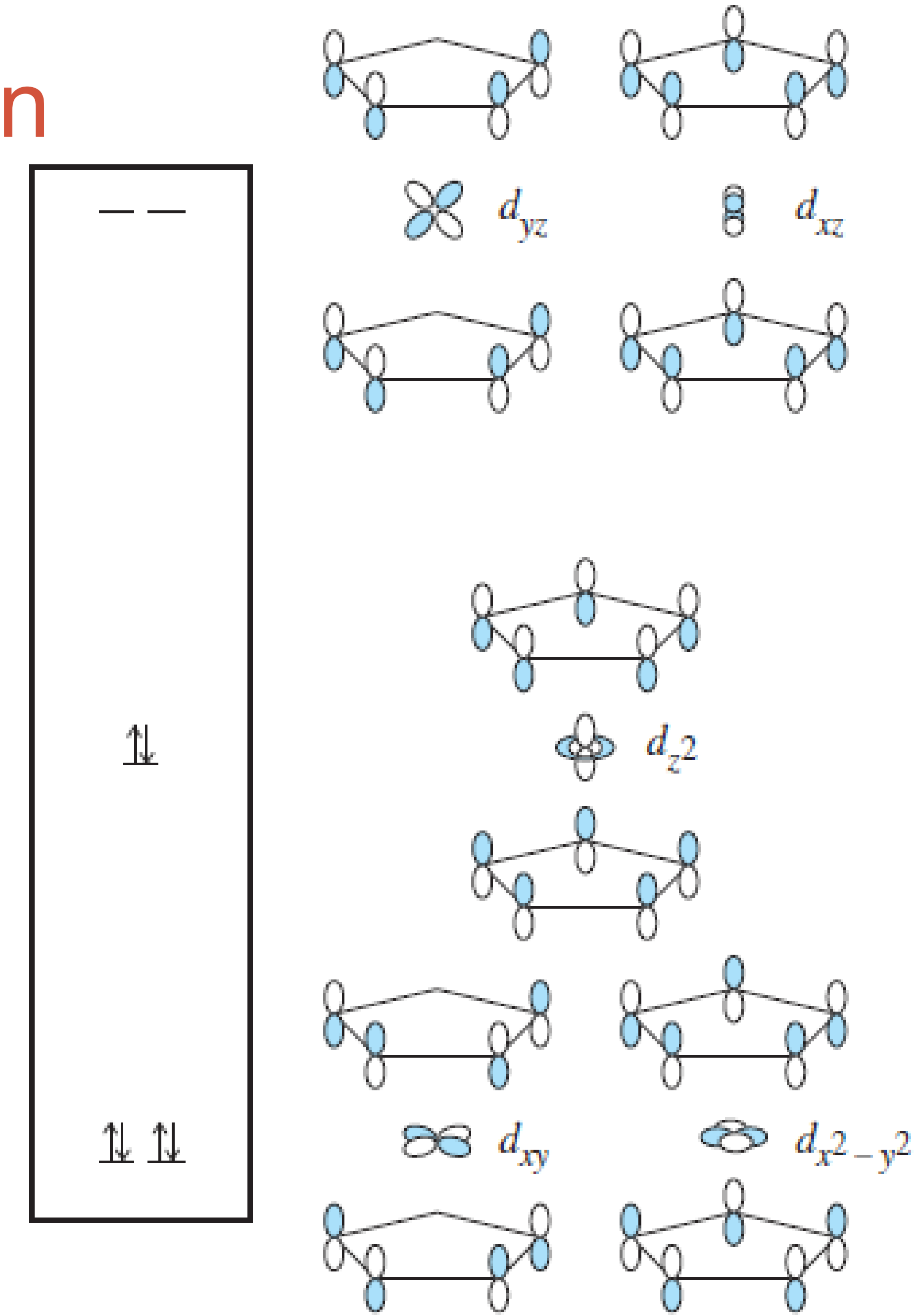
	CO stretching frequency (IR)	C-O bond distance
Free CO	2143 cm^{-1}	112.8 pm
$Cr(CO)_6$	2000 cm^{-1}	~115 pm

→Smaller cm^{-1} = lower energy = weaker bond

→Longer bond = lower bond order = weaker bond

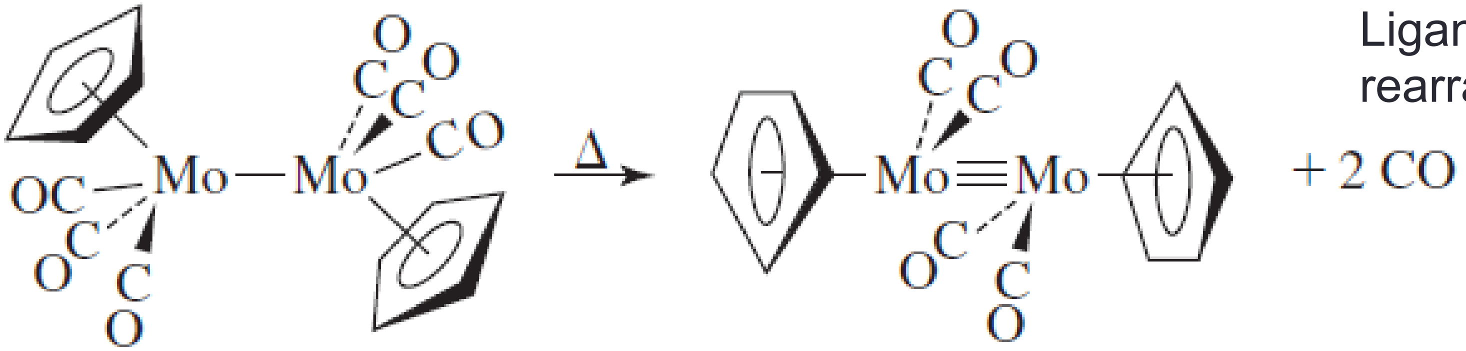
Orbital interactions in ferrocene: $FeCp_2$





Ligand dissociation: CO dissociation

- CO can be lost from a metal complex either thermally (with heat) or photochemically (with light)
- The reaction will either cause the metal complex to rearrange or for CO to be replaced by another ligand



Ligand dissociation, rearrangement

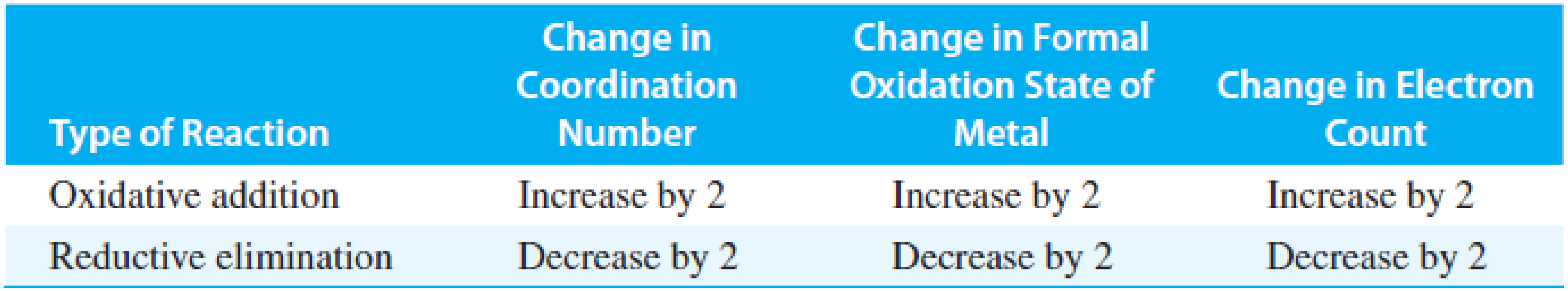
$$Fe(CO)_5 + P(CH_3)_3 \xrightarrow{\Delta} Fe(CO)_4(P(CH_3)_3) + CO$$

ligand substitution

Oxidative addition and reductive elimination

- **Oxidative addition (OA)** involves both *oxidation* of the metal center and *addition* of ligands to the metal coordination sphere
- The reverse reaction is called **reductive elimination (RE)** which involves both *reduction* of the metal center *elimination* of ligands from the metal coordination sphere

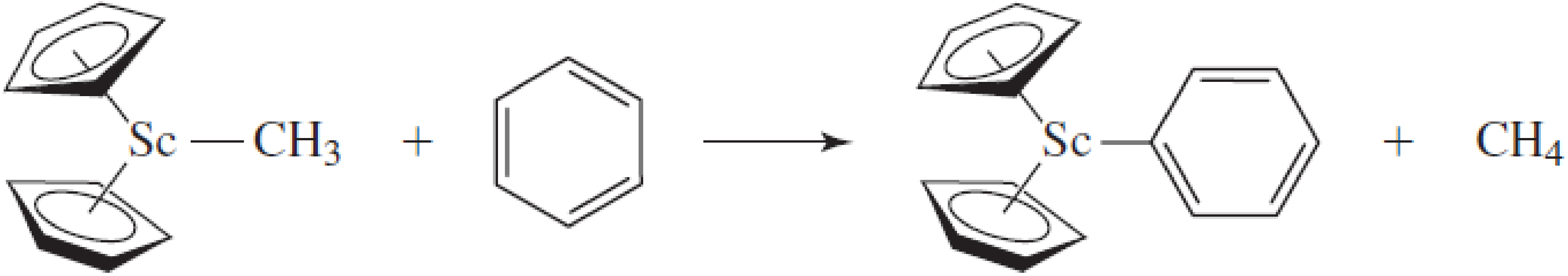
$$L_nM + X{-}Y \underset{\text{RE}}{\overset{\text{OA}}{\rightleftharpoons}} L_nM\begin{matrix} X \\ Y \end{matrix}$$



Type of Reaction	Change in Coordination Number	Change in Formal Oxidation State of Metal	Change in Electron Count
Oxidative addition	Increase by 2	Increase by 2	Increase by 2
Reductive elimination	Decrease by 2	Decrease by 2	Decrease by 2

Sigma bond metathesis

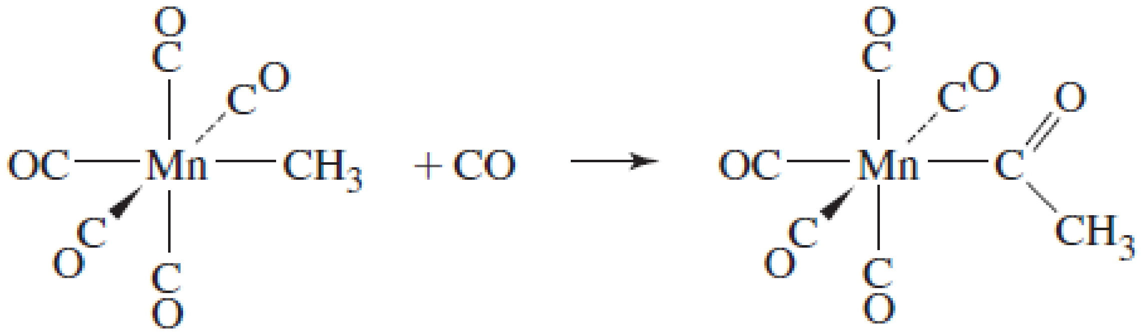
- In this type of reaction, two sigma bonded ligands are exchanged on a metal center without a change in metal oxidation state



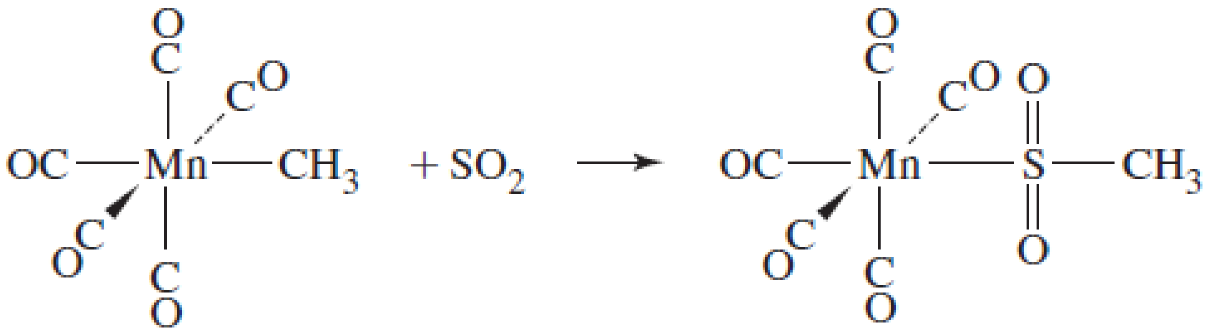
  - In this reaction, C-H bond of methane is made and C-H bond of benzene is cleaved

1,1 insertions

- Both new bonds formed are to the same atom



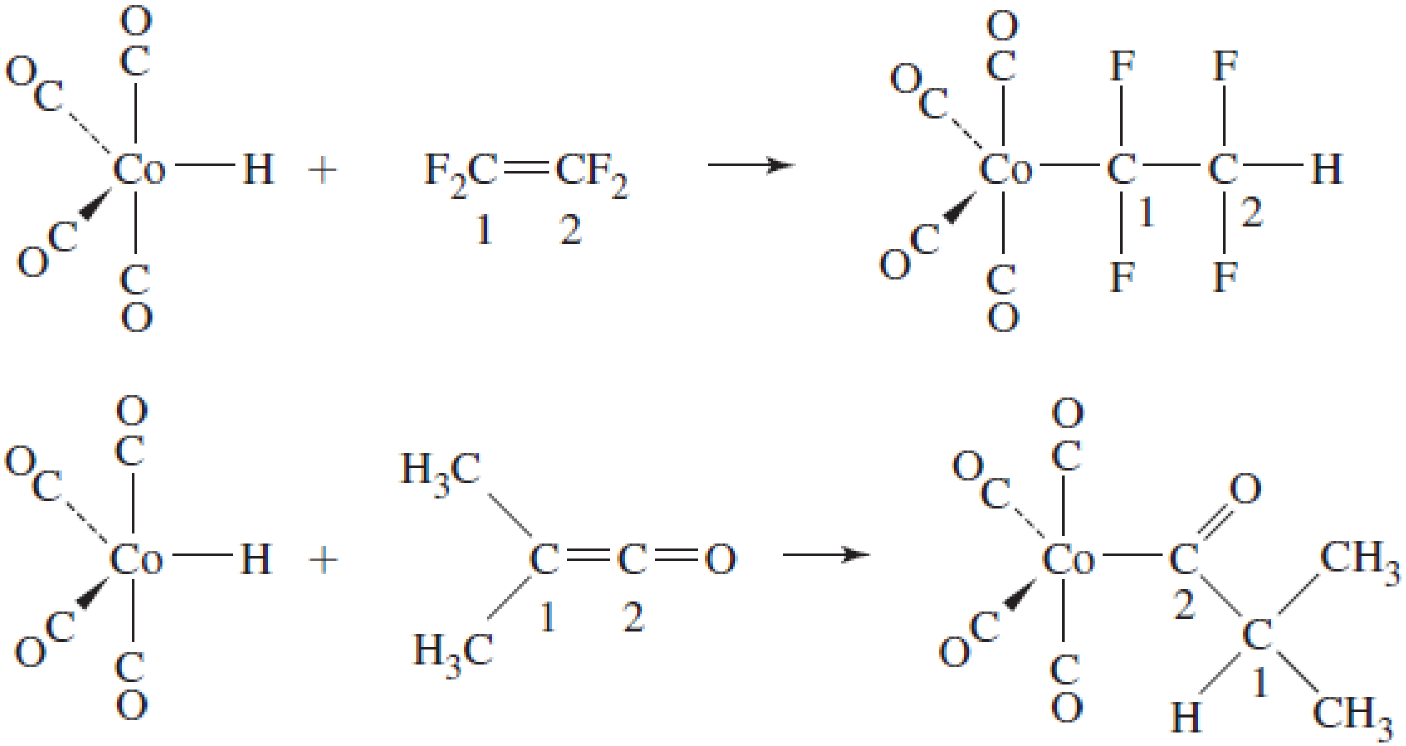
CO insertion into metal-alkyl bond



SO_2 insertion into a metal-alkyl bond

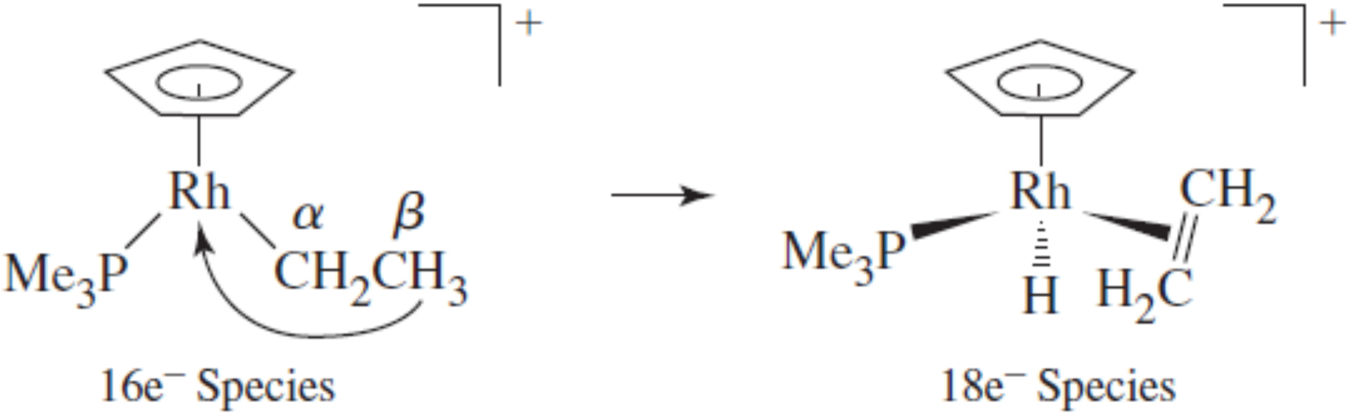
1,2 insertions

- New bonds are made to adjacent (1,2) atoms



Hydride elimination

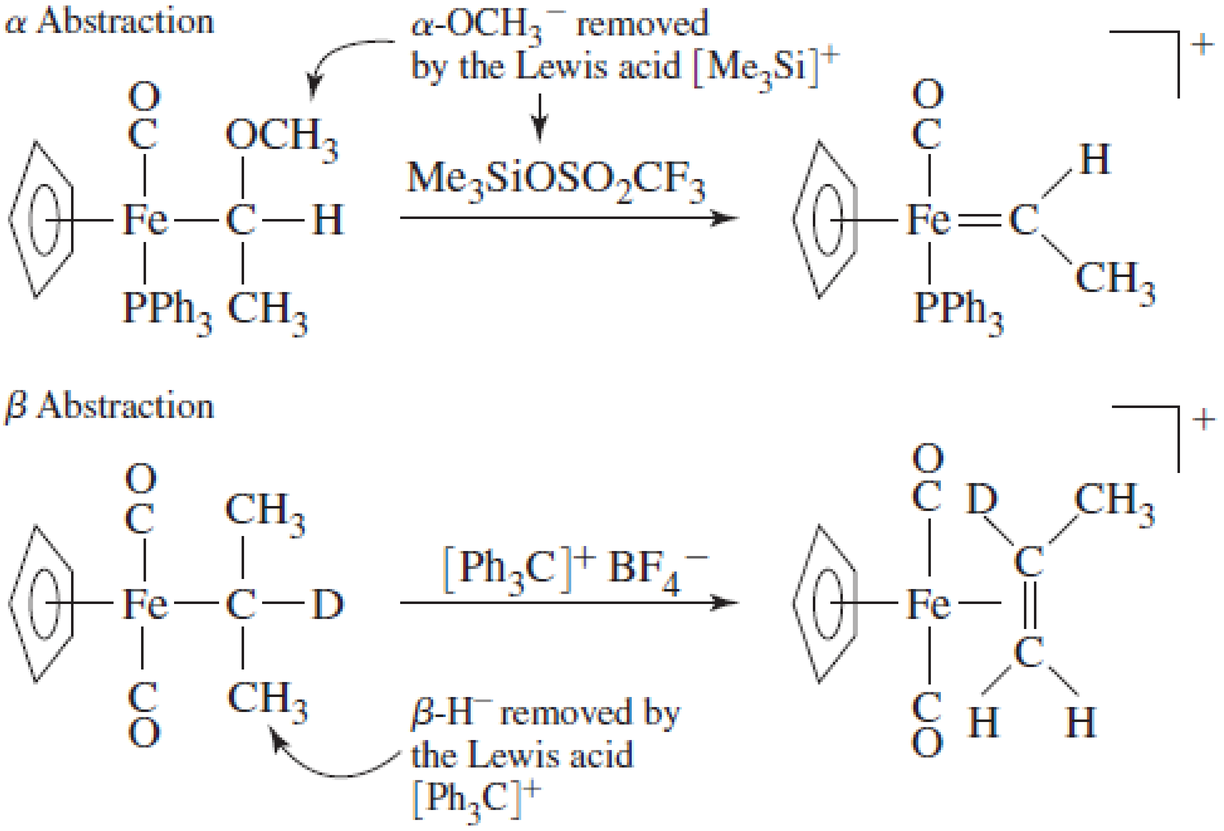
- In hydride eliminations, a hydrogen atom is transferred from a ligand to a metal
- The most common is **Beta hydride elimination**



  - Metal-alkyl complexes without beta hydrogens are more stable because they cannot undergo beta hydride elimination
- Alpha, gamma, and other hydride eliminations are also possible

Abstraction reactions

- These are elimination reactions in which the coordination number of the metal does not change
- Mediated by an external reagent like a Lewis acid



α Abstraction

α-OCH_3^- removed by the Lewis acid $[Me_3Si]^+$

$Me_3SiOSO_2CF_3$

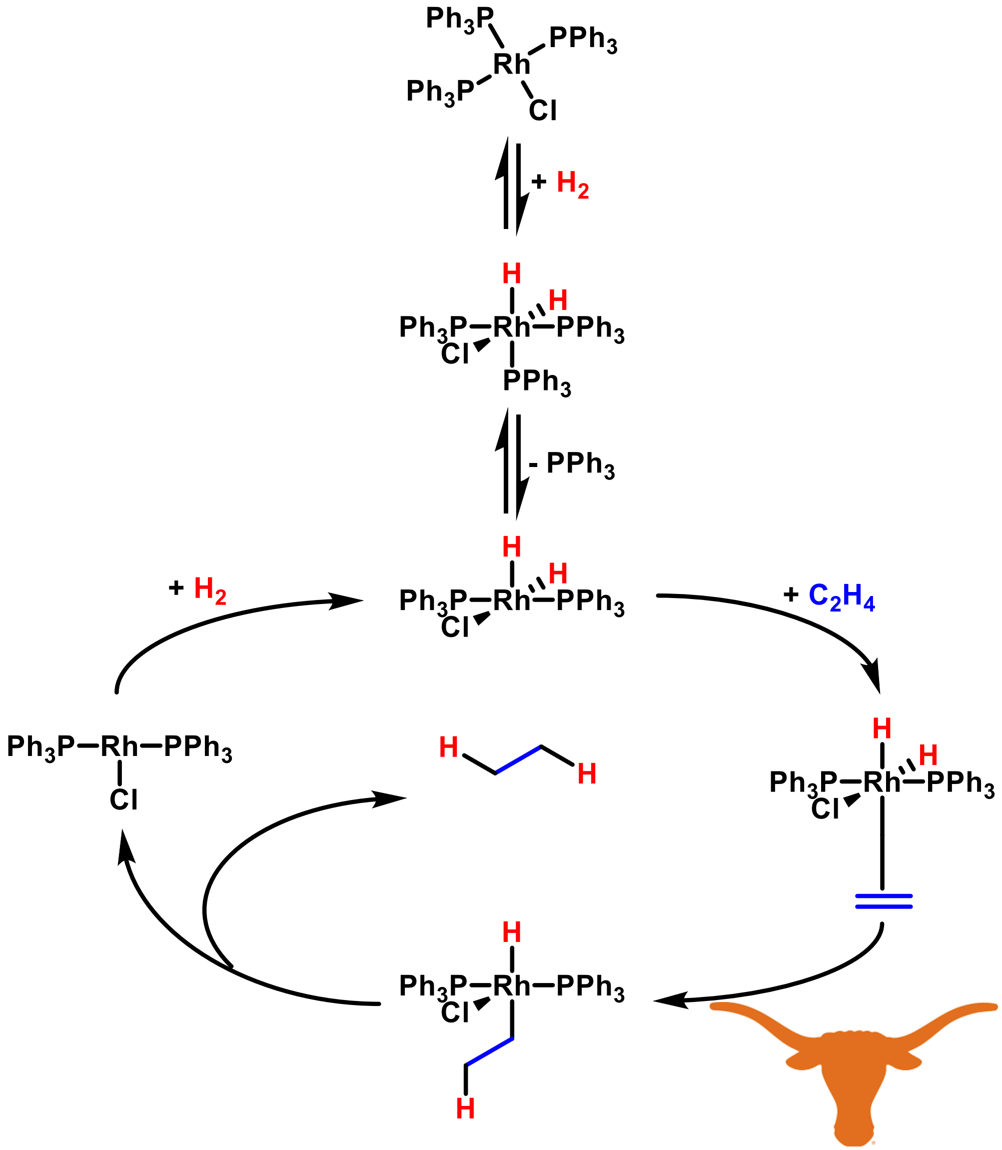
β Abstraction

$[Ph_3C]^+ BF_4^-$

β-H^- removed by the Lewis acid $[Ph_3C]^+$

Hydrogenation: Wilkinson's Catalyst

- First known homogeneous hydrogenation catalyst (1966)
- The choice of ligand plays an important role in selectivity of the catalyst
- The bulky PPh_3 ligands (cone angle) make the catalyst selective for unhindered positions on alkenes



Final

- Old Material (~50%)
- New Material (~50%)
- One question on final projects: short answer, will be asked to broadly describe the uses/functions of molecules people presented on for final projects-you do not need the fine details! Just a broad 1-2 sentence description of why the molecule is interesting in the real world.