

Chem 462 Lecture 2--2016



Classification of Ligands

Metal Oxidation States

Electron Counting

Overview of Transition Metal Complexes

1. The coordinate covalent or dative bond applies in $L:\rightarrow M$
2. Lewis bases are called LIGANDS—all serve as σ -donors
some are π -donors as well, and some are π -acceptors
3. Specific coordination number and geometries
depend on metal and number of d-electrons
4. HSAB theory useful $[ML_nX_m]^z$
 - a) Hard bases stabilize high oxidation states
 - b) Soft bases stabilize low oxidation states

Classification of Ligands: The L, X, Z Approach

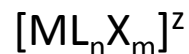
Malcolm Green : The CBC Method (or Covalent Bond Classification) used extensively in organometallic chemistry.

- L** ligands are derived from charge-neutral precursors: NH_3 , amines, N-heterocycles such as pyridine, PR_3 , CO, alkenes etc.
- X** ligands are derived from anionic precursors: halides, hydroxide, alkoxide alkyls—species that are one-electron neutral ligands, but two electron donors as anionic ligands. [EDTA](#)⁴⁻ is classified as an L_2X_4 ligand, features four anions and two neutral donor sites. C_5H_5 is classified an L_2X ligand.
- Z** ligands are RARE. They accept two electrons **from** the metal center. They donate none. The “ligand” is a Lewis Acid that accepts electrons rather than the Lewis Bases of the X and L ligands that donate electrons.

5. Oxidation State

Here, z = charge on the complex unit.

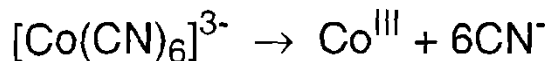
$$\text{ox. state} = z - \sum_N \text{L charge}$$



ligand removed from complex with closed shell configuration

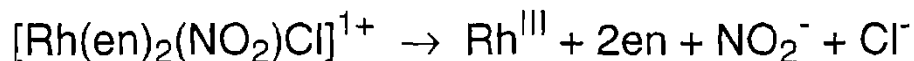
examples:

octahedral

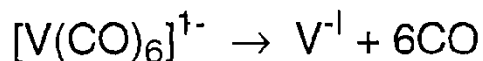
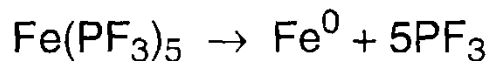


positive oxidation states usually written as Roman numerals

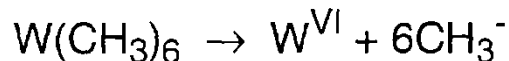
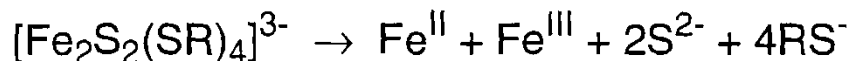
Square
pyramidal



Trigonal bi-
pyramidal



Tetrahedral



An oxidation state is a formalism which affords that d^n configuration consistent with molecular properties.

Range of Oxidation States in 3d Transition Metals

| element | ox. state range* (molecular compounds) | common (stable) ox. states** |
|---------|---|---------------------------------|
| Ti | 0 → 4+ | 3+, 4+ |
| V | 1- → 5+ | 3+, 4+, 5+ |
| Cr | 2- → 6+ | 2+, 3+, 6+ |
| Mn | 1- → 7+ | 2+, 3+, 4+, 7+ |
| Fe | 2- → 6+ | 0, 2+, 3+ |
| Co | 1- → 3+ | 2+, 3+ |
| Ni | 0 → 4+ | 1+, 2+, 3+ |
| Cu | 1+ → 3+ | 1+, 2+ |
| Zn | 2+ | 2+ |

*Relative oxidation state stabilities are highly ligand-dependent; very rare oxidation states are omitted. **Most frequently encountered oxidation states in boldface.

Summary:

Group 8

| d^3 | d^4 | d^5 | d^6 | d^7 | d^8 | d^9 | d^{10} | $d^{10}s^1$ |
|------------------------------|------------------------------|-----------------------------|-------------------------------|-------------------------------|------------------------------|----------------------------|------------------------------|---------------------------|
| 21 Sc Scandium | 22 Ti Titanium | 23 V Vanadium | 24 Cr Chromium | 25 Mn Manganese | 26 Fe Iron | 27 Co Cobalt | 28 Ni Nickel | 29 Cu Copper |
| 39 Y Yttrium | 40 Zr Zirconium | 41 Nb Niobium | 42 Mo Molybdenum | 43 Tc Technetium | 44 Ru Ruthenium | 45 Rh Rhodium | 46 Pd Palladium | 47 Ag Silver |
| 57 La Lanthanum | 72 Hf Hafnium | 73 Ta Tantalum | 74 W Tungsten | 75 Re Rhenium | 76 Os Osmium | 77 Ir Iridium | 78 Pt Platinum | 79 Au Gold |

Early Transition Metals

low electronegativities

higher oxidation states

“harder” metal centers

OXOPHILIC!!

Late Transition Metals

higher electronegativities

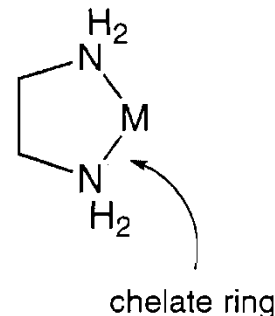
lower oxidation states

“softer” metal centers

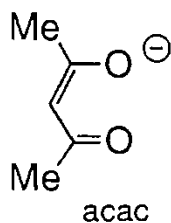
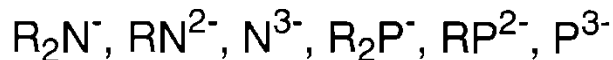
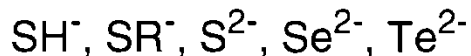
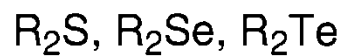
Classification of Ligands, II: type of donor orbitals involved: σ ; $\sigma + \pi$; $\sigma + \pi^*$; $\pi + \pi^*$

3. Ligands

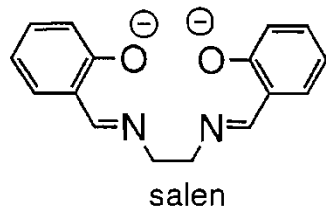
- σ : NH_3 , NR_3 , $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ (en), $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, ...
 σ -bonding only



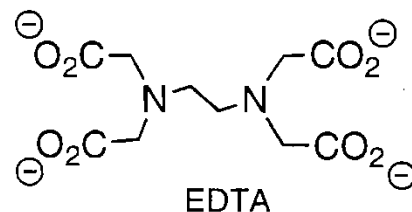
- $\sigma + \pi$ (lp): F^- , Cl^- , Br^- , I^- , NCO^- , NCS^- , N_3^- , ...
 π -donors



bidentate chelate

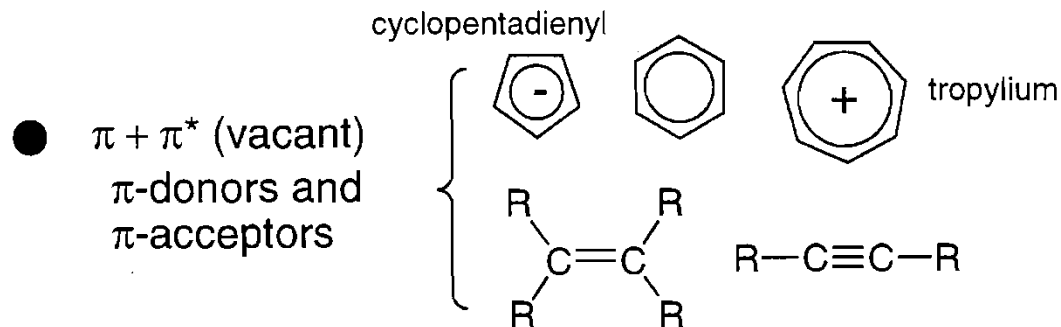
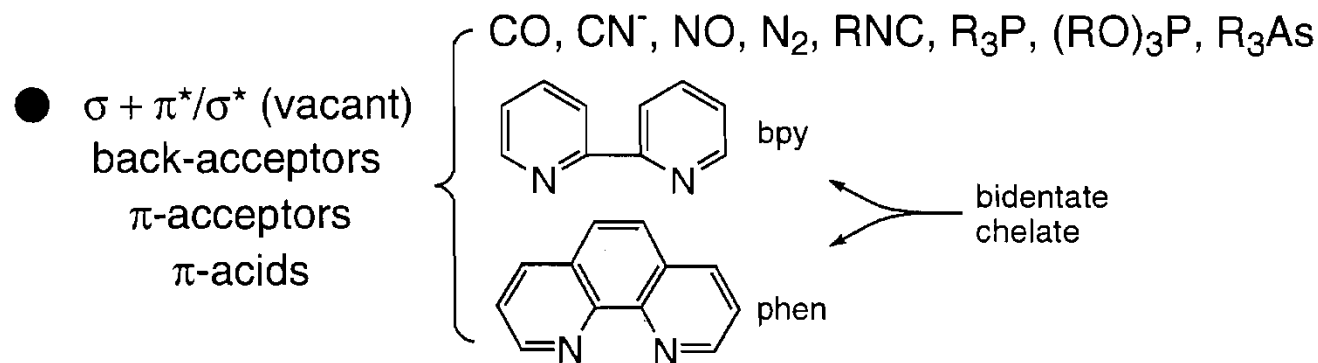


tetradentate chelate



hexadentate chelate

Ligands, Classification I, continued



These ligands form *organometallic* molecules.

Electron Counting and the famous Sidgwick epiphany

18 Electron "Rule"

Organic compounds, of course, follow the **8 electron rule**: there can only be a maximum of 8 valence electrons around a carbon center.

The vast majority of stable diamagnetic organometallic compounds have 16 or 18 valence electrons due to the presence of the five *d* orbitals which can hold 10 more electrons relative to C, O, N, etc.

Electron counting is the process of determining the number of valence electrons about a metal center in a given transition metal complex.

Two methods:

- 1) Neutral ligand (no ligand carries a charge—therefore X ligands are one electron donors, L ligands are 2 electron donors.)
- 2) Both L and X are 2-electron donor ligand (ionic method)

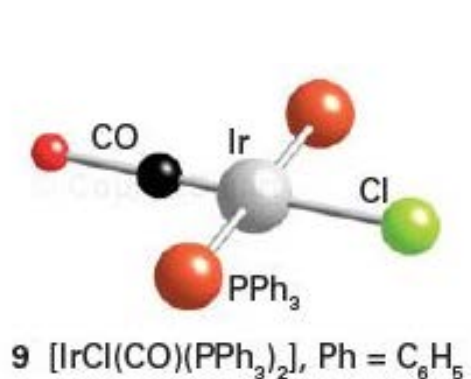
Applying the Ionic or 2-electron donor method:

To determine the electron count for a metal complex:

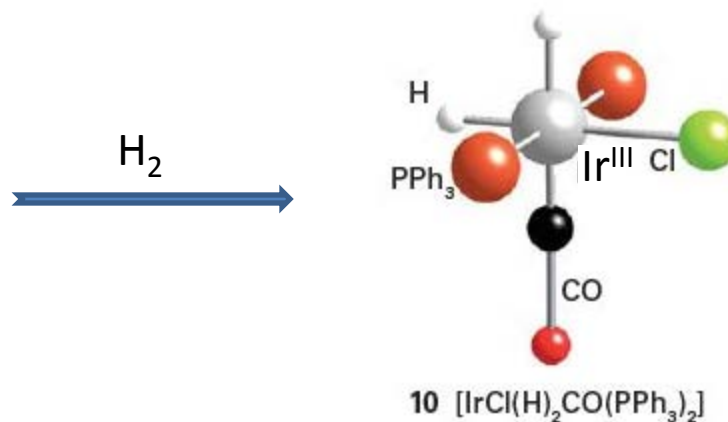
- 1) Determine the oxidation state of the transition metal center(s) and the metal centers resulting *d*-electron count. To do this one must:
 - a) note any overall charge on the metal complex
 - b) know the charges of the ligands bound to the metal center (ionic ligand method)
 - c) know the number of electrons being donated to the metal center from each ligand (ionic ligand method)
- 2) Add up the electron counts for the metal center and ligands

Complexes with 18 e- counts are referred to as saturated, because there are no empty low-lying orbitals to which another incoming ligand can coordinate. Complexes with counts lower than 18e- are called unsaturated and can electronically bind additional ligands if they are sterically allowed.

Oxidative addition of H_2 to chloro carbonyl bis triphenylphosphine Iridium(I) yields Chloro-dihydrido-carbonyl bis-triphenylphosphine Iridium(III). Note the neutral precursor, H_2 , becomes two X^- ligands once added to Ir.



An ML_3X complex



An ML_3X_3 complex

Electron count: 16 e

$\text{Ir}(\text{I}) \text{d}^8 = 8 \text{ e}$

L ligands: $2 \times (2) + 2 = 6$

X- ligand: 2

—

18e

$\text{Ir}(\text{III}) \text{d}^6 = 6 \text{ e}$

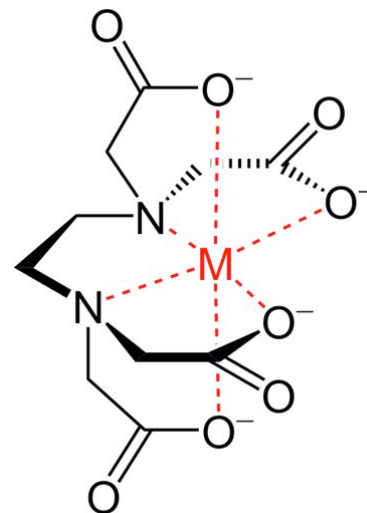
3 L ligands: $3 \times 2 = 6$

3 X^- ligands: $3 \times 2 = 6$

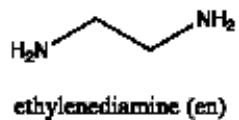
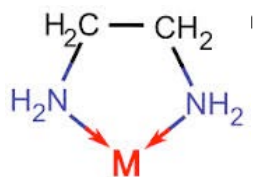
Classification of Ligands: II

A description of properties

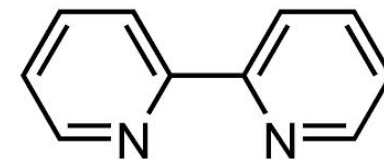
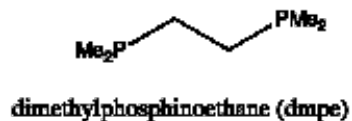
- ❑ Strong Field/Weak Field Ligands
- ❑ Chelating Ligands and Denticity
 - ❖ Polydentate: bi-, tri-, tetra, penta-
 - ❖ Hexadentate, etc.
- ❑ Bridging Ligands
 - ❖ 4-electron bridge; 3 center, 4 electrons
 - ❖ 2-electron bridge; 3-center, 2 electrons
- ❑ Ambidentate Ligands
- ❑ Bulky Ligands
- ❑ Chiral Ligands
- ❑ Hemi-labile Ligands
- ❑ Non-innocent Ligands
- ❑ Spectator Ligands



Chelating Ligands/Polydentate Ligands--examples

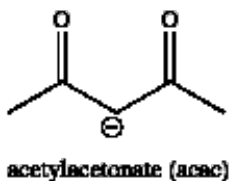


b)

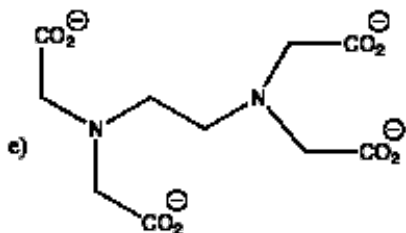
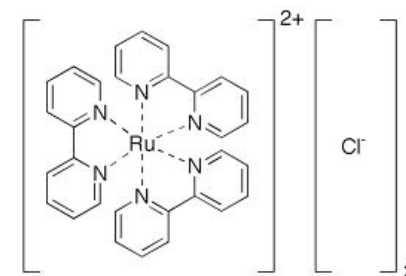
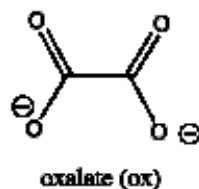


4,4'-bipyridine

c)

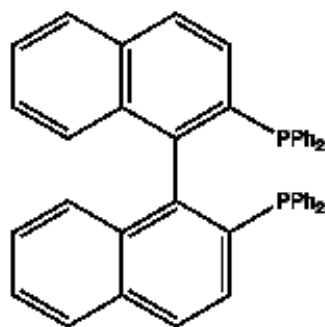


d)

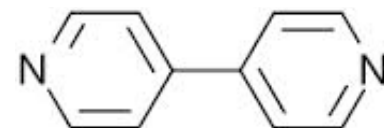


ethylenediamine tetraacetate (edta)

f)

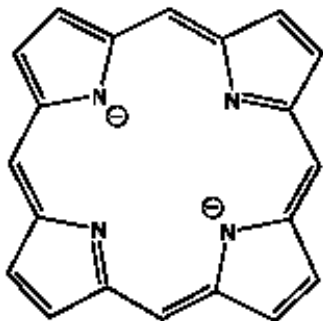


BINAP



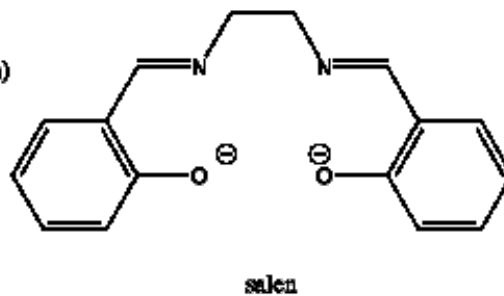
4,4'-bipyridine

g)



porphine (from porphyrin family)

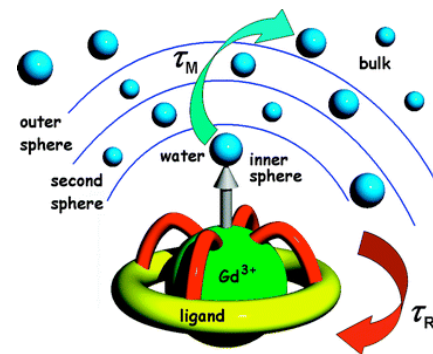
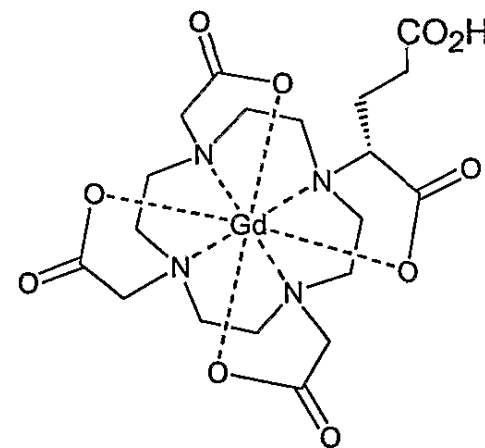
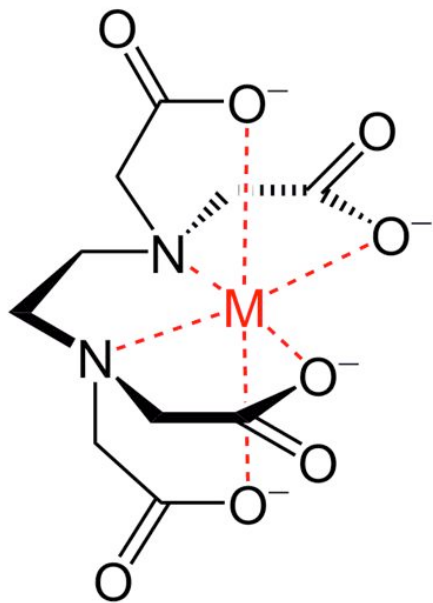
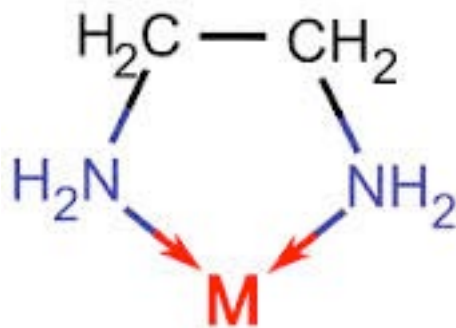
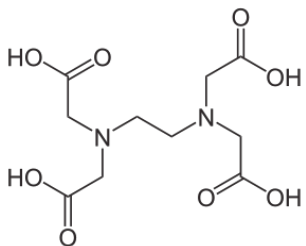
h)



salen

Chelating Ligands/Polydentate Ligands

Ethylenediamine: An L_2 bidentate ligand



Ethylenediaminetetraacetate:
An L_2X_4 hexadentate ligand, an exceptional chelating agent with many uses. In medicine, for lead and mercury poisoning; also for thalassaemia (iron overload).

So, how do we mix these ligands and metals with their various oxidation states to get stable molecules?

1. Hard/Soft Acid Base Approach to stability
2. Knowledge of preferred coordination numbers and geometries

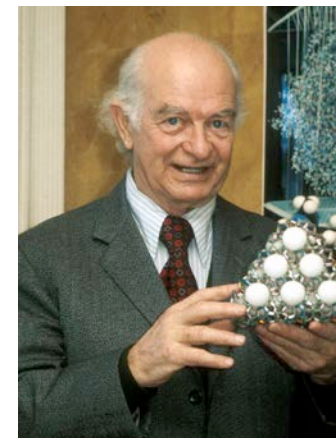
- high oxidation states stabilized by anionic π -donor ligands of electronegative atoms
- low oxidation states stabilized by neutral π -acceptor ligands

examples:

| | "high" | "low" |
|----|---|---|
| Ti | $[\text{TiF}_6]^{2-}$, TiO_2 | $\text{Ti}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2\text{Cl}_2$ |
| V | $[\text{VF}_6]^{2-}$, $[\text{VOCl}_4]^{1-}$, $[\text{VO}_2\text{Cl}_2]^{1-}$ | $[\text{V}(\text{CO})_6]^{0,1-}$ |
| Cr | $[\text{CrO}_4]^{2-}$, $[\text{CrOCl}_4]^{1-}$, $[\text{CrF}_6]^{2-}$ | $[\text{Cr}(\text{CNR})_6]^{1+}$, $\text{Cr}(\text{CO})_6$, $[\text{Cr}(\text{CO})_5]^{2-}$ |
| Mn | $[\text{MnO}_4]^{1-,2-}$, $[\text{MnCl}_6]^{2-}$ | $\text{Mn}(\text{CO})_5\text{Cl}$, $\text{Mn}_2(\text{CO})_{10}$, $[\text{Mn}(\text{CO})_5]^{1-}$ |
| Fe | $[\text{FeO}_4]^{2-}$, $[\text{FeCl}_4]^{1-}$ | $\text{Fe}(\text{CO})_5$, $\text{Fe}(\text{PF}_3)_5$, $[\text{Fe}(\text{CO})_4]^{2-}$ |
| Co | $[\text{CoF}_6]^{3-}$, $[\text{Cr}(\text{en})_3]^{3+}$ | $[\text{Co}(\text{CO})_4]^{1-}$, $\text{Co}(\text{CO})_3\text{NO}$, $\text{Co}_2(\text{CO})_8$, $\text{Co}(\text{PR}_3)_3\text{Br}$ |
| Ni | $[\text{NiF}_6]^{2-}$, $[\text{Ni}(\text{diars})_2\text{Cl}_2]^{1+}$ | $\text{Ni}(\text{CO})_4$, $\text{Ni}(\text{PF}_3)_4$, $\text{Ni}(\text{PR}_3)_3\text{Br}$, $[\text{Ni}_2(\text{CN})_6]^{4-}$ |
| Cu | $[\text{CuF}_6]^{3-}$ | $[\text{Cu}(\text{CN})_2]^{1-}$, $[\text{CuCl}_2]^{1-}$ |

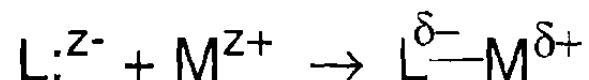
At parity of ligand and coordination number, higher oxidation states become increasingly stable down a vertical group.

Linus Pauling



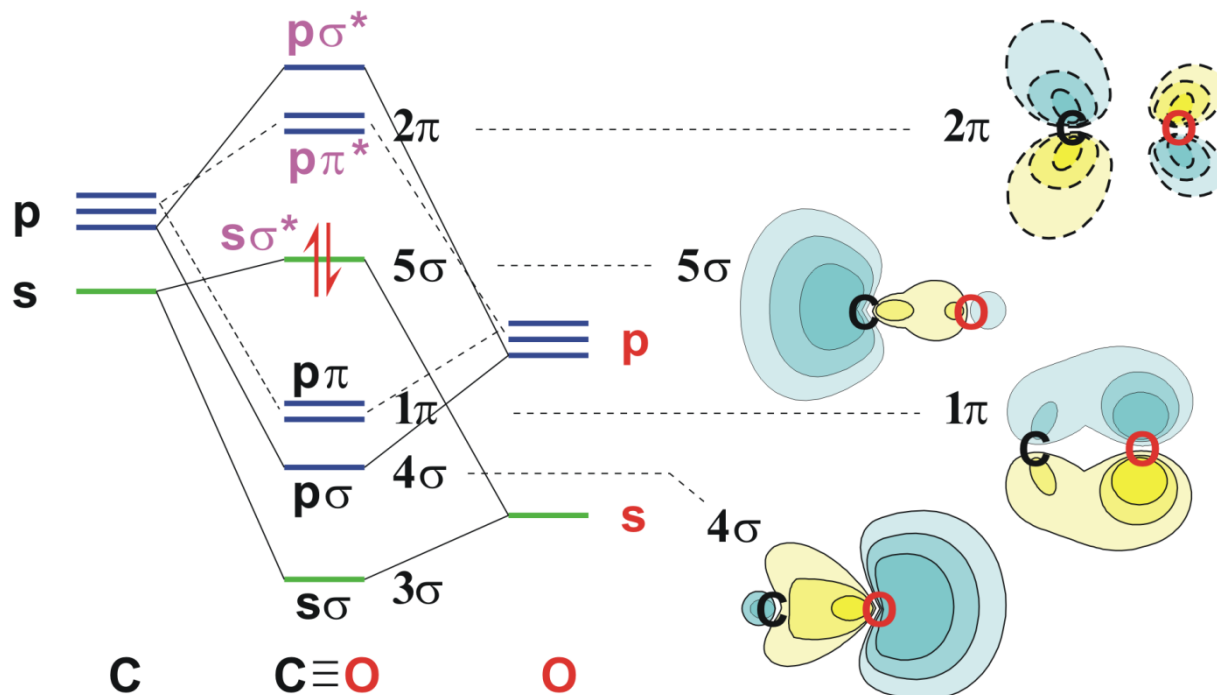
6. Electroneutrality Principle:

In any molecule, bonding electrons are distributed in such a way that individual atoms are as close to electroneutrality as possible.

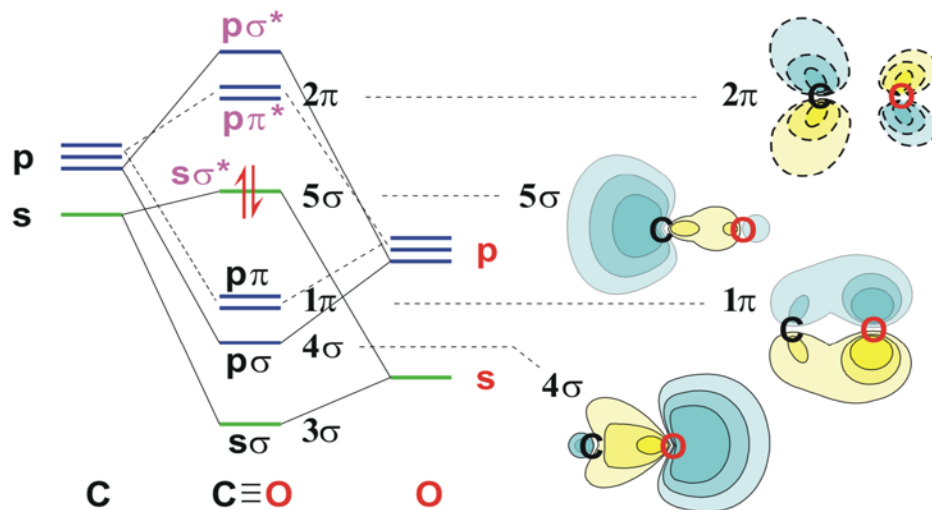


Metal-ligand bond formation tends to reduce +ve charge on M (and -ve charge on L^{z-}), with the result that the *actual* charge on M is much below that corresponding to its oxidation state. The oxidation state conveys the d^n configuration of the coordinated metal.

Carbon Monoxide or Carbonyl: MO description



How do we know?



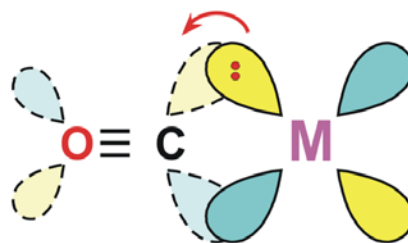
Experimental Data Supporting Nature of MO's in CO

| Species | Config | C-O Å | ν_{CO} cm ⁻¹ | Comment |
|-----------------|-------------------------------------|--------|------------------------------------|-------------------------------|
| CO | (5σ) ² | 1.13 | 2143 | |
| CO ⁺ | (5σ) ¹ | 1.11 | 2184 | 5σ MO is weakly antibonding |
| CO* | (5σ) ¹ (2π) ¹ | S 1.24 | 1489 | 2π MO is strongly antibonding |
| | | T 1.21 | 1715 | |

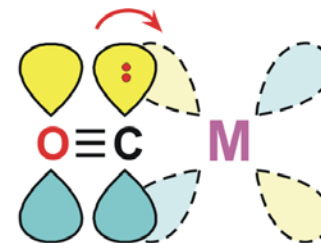
The M-C bond in Metal Carbonyls



CO-M sigma bond



M to CO pi backbonding



CO to M pi bonding
(rare)

M-C bond: increases
C-O bond: increases
 ν_{CO} freq: increases

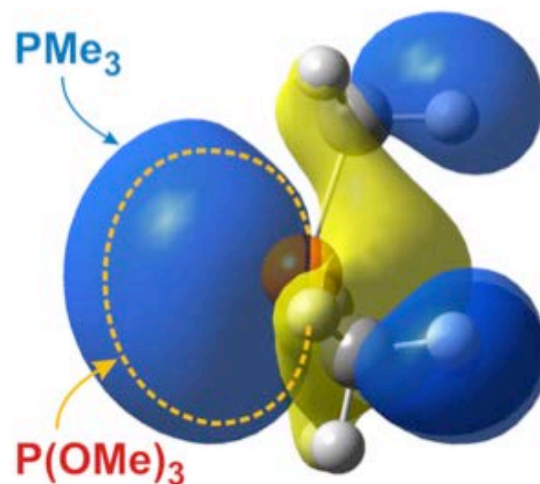
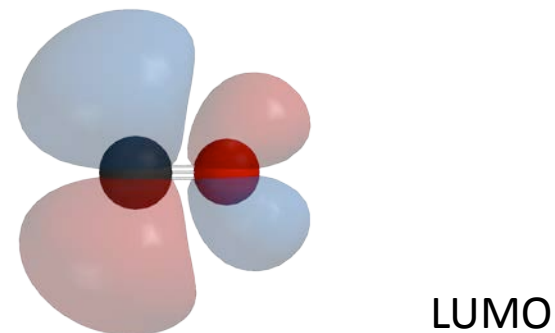
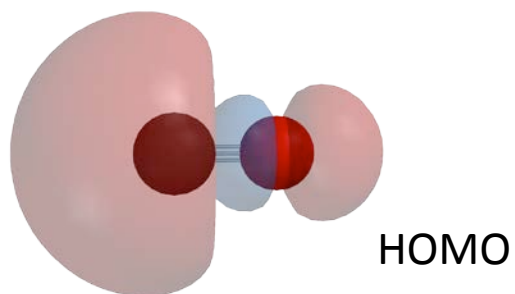
increases
decreases
decreases

increases
decreases
decreases

Carbonyl IR Stretching Frequencies

- The **position** of the carbonyl bands in the IR depends mainly on the **bonding mode** of the CO (terminal, bridging) and the **amount of electron density on the metal being π -backbonded to the CO**.
- The **number** (and intensity) of the carbonyl bands one observes depends on the **number of CO ligands present** and the **symmetry** of the metal complex. There are also secondary effects such as Fermi resonance and overtone interactions that can complicate carbonyl IR spectra.

Ligands of Organometallic Chemistry. Homoleptic complexes from CO and PR_3 .



PMe_3

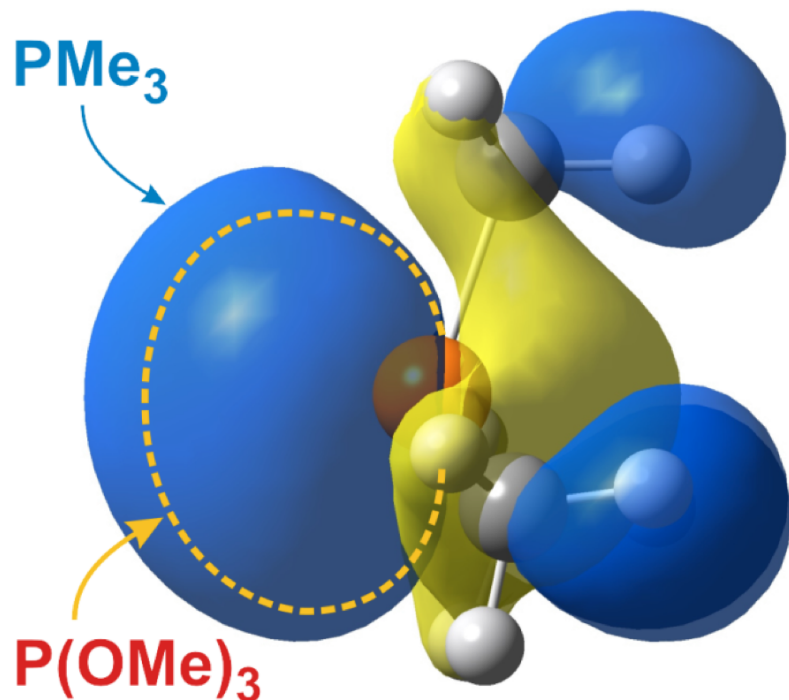
HOMO = -5.03 eV
Charge on P = $+0.22$

P(OMe)_3

HOMO = -7.40 eV
Charge on P = $+0.75$

MO plot of the lone pair orbital (HOMO) for PMe_3 . Dashed outline indicates the spatial extent of the lone pair for P(OMe)_3 .

Donor Ability of Phosphines vs. Phosphites:



PMe₃

HOMO = -5.03 eV

Charge on P = $+0.22$

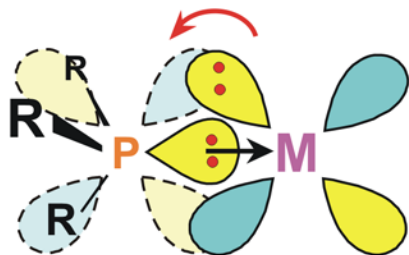
P(OMe)₃

HOMO = -7.40 eV

Charge on P = $+0.75$

MO plot of the lone pair orbital (HOMO) for PMe₃. Dashed outline indicates the spatial extent of the lone pair for P(OMe)₃.

*empty d orbitals on phosphine
can act as π -acceptor orbitals* } not very important unless R-groups are electron-withdrawing



Phosphine ligands

*excellent soft-donor ligands
with a wide variety of easily adjusted
steric and electronic factors*

neutral $2e^-$ donor

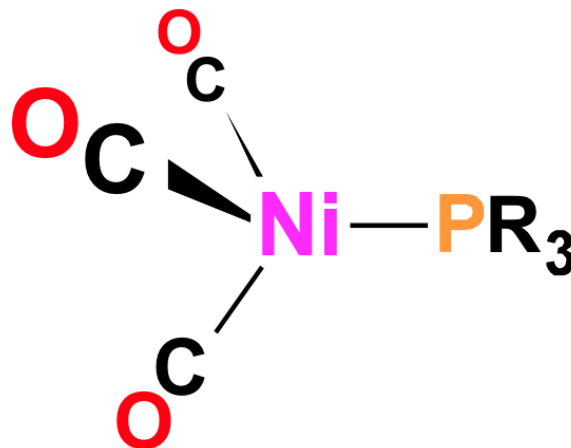
R = carbon groups { **phosphine (US)**
phosphane (Germany/Europe)

R = OR groups \longrightarrow **phosphite**

Tolman Electronic Parameter for Ligand Donor Ability

Lowest CO stretching frequency:

most donating phosphine



Highest CO stretching frequency:

least donating phosphine

(best π -acceptor)

Tolman electronic parameter

2) Strong π acceptor ligands will compete with CO for the electron back donation and C-O stretch frequency will remain high

Weak back donation \rightarrow High C – O stretch

The IR frequencies represent a reliable yardstick for the electronic properties of a series of P ligands toward a particular metal, M.

$\text{CrL}(\text{CO})_5$ or $\text{NiL}(\text{CO})_3$ as examples; L = $\text{P}(\text{t-Bu})_3$ as reference

The electronic parameter, χ (chi) for other ligands is simply defined as the difference in the IR frequencies of the symmetric stretch of the two complexes

| <u>Ligand, PR_3, R=</u> | <u>χ (chi)</u> | <u>IR Freq (A_1) of $\text{NiL}(\text{CO})_3$ in cm^{-1}</u> |
|---|--------------------------------|--|
| T-Bu | 0 | 2056 |
| N-Bu | 4 | 2060 |
| 4- $\text{C}_6\text{H}_4\text{NMe}_3$ | 5 | 2061 |
| Ph | 13 | 2069 |
| 4- $\text{C}_6\text{H}_4\text{F}$ | 16 | 2072 |
| | | |
| CH_3O | 20 | 2076 |
| PhO | 29 | 2085 |
| $\text{CF}_3\text{CH}_2\text{O}$ | 39 | 2095 |
| Cl | 41 | 2097 |
| $(\text{CF}_3)_2\text{CHO}$ | 54 | 2110 |
| F | 55 | 2111 |
| CF_3 | 59 | 2115 |

Tolman steric parameter

B. Steric Effects

1) Cone angle (Tolman's parameter, θ) (Monodentate ligands)

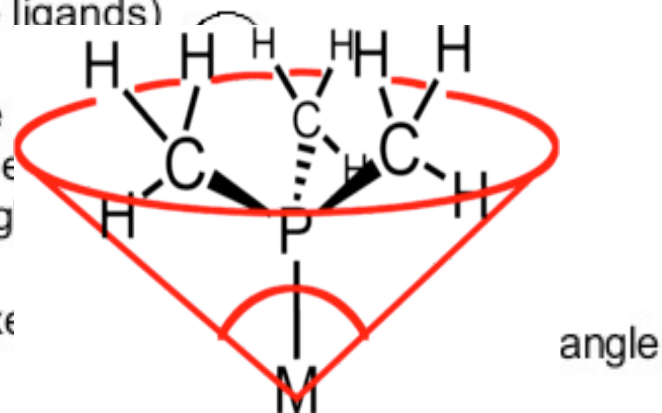
From the metal center, located at a distance of 2.28 Å from the phosphorus atom in the appropriate direction, a cone is constructed which embraces all the atoms of the substituents on the P atom, even though ligands never form a perfect cone.

Sterically, more bulky ligands give less stable complexes. Crystal structure determination, angles smaller than θ values would suggest.

Thermochemistry: heat of formation of metal-phosphine adducts.

When electronic effects are small, the heats measured are a measure of the steric hindrance in the complexes.

Heats of formation decrease with increasing steric bulk of the ligand.

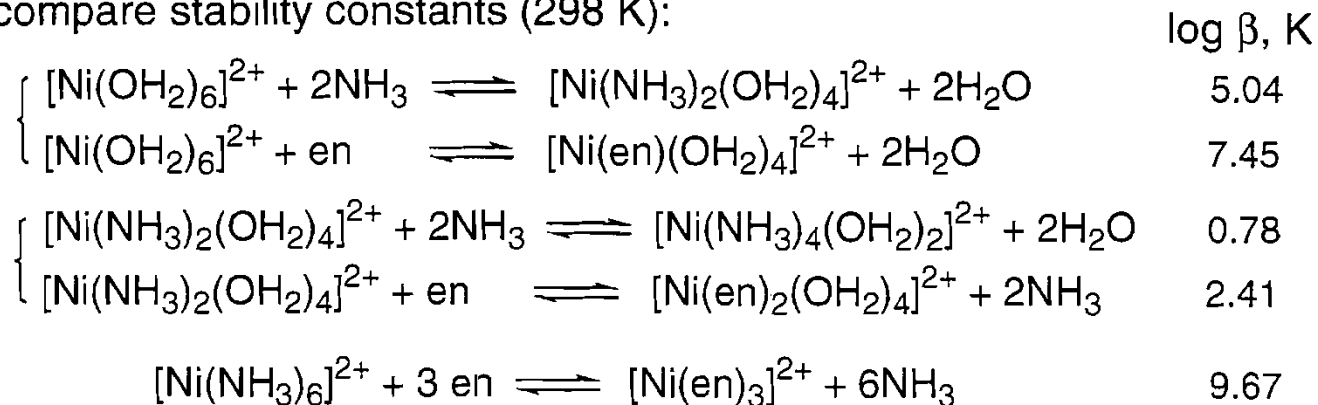


| Ligand, PR_3 ; R = | | θ value = | |
|----------------------|--|------------------|--|
| H | | 87 | |
| CH_3O | | 107 | |
| n-Bu | | 132 | |
| PhO | | 128 | |
| Ph | | 145 | |
| i-Pr | | 160 | |
| C_6H_{11} | | 170 | |
| t-Bu | | 182 | |

Famous Principles: The Chelate Effect

● Chelate effect

compare stability constants (298 K):



$$\Delta H = -2.89 \text{ kcal/mol} \quad \text{small favorable contribution}$$

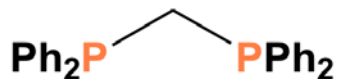
$$\Delta H_{SE} = -2.75 \text{ kcal/mol}$$

$$T\Delta S = 13.2 \text{ kcal/mol}$$

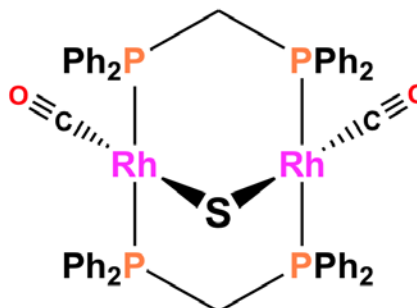
entropy increase (4→7 particles) dominates reaction

(even though NH_3 more strongly solvated than en)

Commonly Used Polydentate Phosphines:



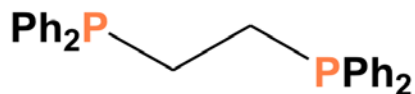
dppm (121°)
 diphenylphosphinomethane
 bis(diphenyl)phosphinomethane
bridging ligand



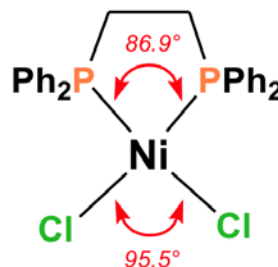
A-Frame bimetallic



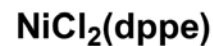
Kubiak & Eisenberg
 JACS, 1977, 99, 6129



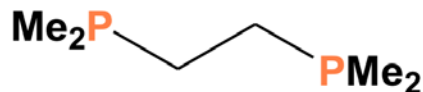
dppe (125°)
 diphenylphosphinoethane
 bis(diphenyl)phosphinoethane
chelating ligand



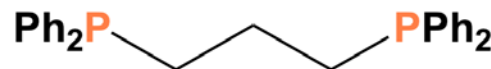
*typical P-M-P angle for a
 5-membered chelate ring
 82-87°*



van Koten, et al
 Acta Crys. C, 1987, 43, 1878



dmpe (107°)
 dimethylphosphinoethane
 bis(dimethyl)phosphinoethane
chelating ligand
electron-rich, strong donor



dppp (127°)
 diphenylphosphinopropane
 bis(diphenyl)phosphinopropane
chelating ligand
forms 6-membered rings

*typical P-M-P
 angle for a
 6-membered
 chelate ring
 88-92°*