

Chapter 1: Structure and Bonding

1.1 General Properties of the Ligands1.1.1. Classification of Ligands**Covalent ligands**

1e⁻ from ligand
1e⁻ from metal

Dative ligands

2e⁻ from ligand
(e.g. BF₃-NH₃)

Two systems for classification of ligands

(1) ligand

||

neutral (dative) **or**
charged (covalent)

(2) ligand = neutral

2e⁻ donor: **L-type** ligands
1e⁻ donor: **X-type** ligands
LX, L₂, L₂X... etc.

1.1.2. Classification by Number of Electrons Donated to the Metal1.1.3. π-Bonded Ligands1.1.4. Combinations of σ- and π-Donors1.1.5. Cationic Ligands (nitrosyl)1.2 Properties of the Ligands1.2.1. Oxidation State

oxidation state: far from the true charge on the metal

e.g. **[Fe(CO)₄]²⁻** : Fe(- II), iron atom bears little if any negative charge1.2.2. The Relationship Between Oxidation State and the Number of d-electrons1.2.3 Trends in the Properties of Transition Metals1.2.3.1 Trends in Ionization Potentials**Ionization Potential** (figure 1.9)

increases from left to right
(electronegativity, effective nuclear charge)

e.g.)

Zr(II)

more easily oxidized
more basic
more electron-rich

than Pd (II)

For **middle to late transition metals**:

accessibility of
oxidation state
higher than +3

first
row

<

second
row

<

third
rowe.g. Pt(IV) vs Ni(IV),
Os(VIII) vs Fe (VIII)

basicity of
metal complexes

first
row

<

second
row

<

third
rowOs(CO)₄(H)₂
is less acidic than
Ru(CO)₄(H)₂

Chapter 3

1.2.3.2 Trends in Size

size
(figure 1.10)

first row < second row ~ third row ← lanthanoid contraction

for **low-spin metal complexes 4~7 groups**
with same charge and oxidation state

size
decreases from left to right

1.2.3.3 Trends in Bond Strength

Strength of M-L bond first row < second row < third row
greater orbital overlap
smaller ΔE of **M** and **L** orbitals

1.3 Metal-Ligand Complexes

1.3.1. Electron Counting

1.3.2. The 18-Electron Rule

1.3.3. Metal-Metal Bonding and Electron Counting in Polynuclear Complexes

$$\text{Number of M-M bonds} = \frac{1}{2} (18M - N)$$

M: number of metals
N: total number of valence electrons

e.g.) figure 1.12

1.3.4. Geometries of Transition Metal Complexes

coordination number = the number of atoms directly linked to the metal (IUPAC)
= the number of **electron pairs** donated to the metal (**conventionally**)

electronic effects often > **steric effects**

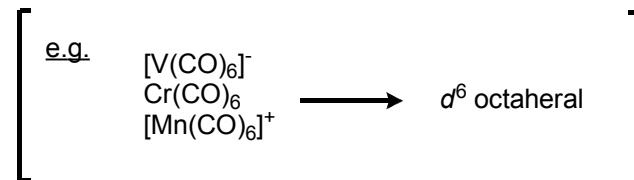
figures of several geometries => figure 1.13

<p>four-coordinate d^8 complexes of second and third row</p> <p>however in the first row complexes.</p>	→	square planar	extremely high $d_{x^2-y^2}$ in square planar
	→	tetrahedral e.g. $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$	(cf. square planar $\text{Ni}(\text{PPh}_3)_2\text{Me}_2$ strong donation => strong electronic preference)
<p>five-coordinate d^8</p>	→	trigonal bipyramidal	
<p>five-coordinate d^6</p>	→	square-based pyramidal	

1.3.5. Isoelectronic and Isolobal Analogies

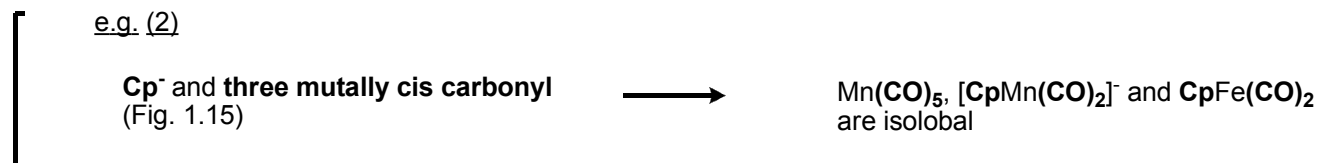
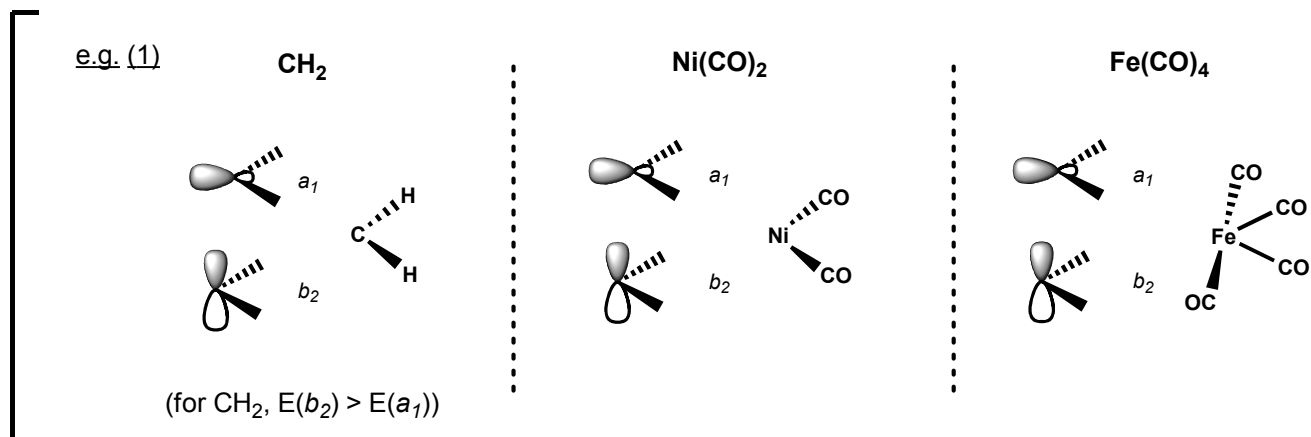
• **isoelectronic:**

group of metal fragments that have **same structure** and **number of electrons**



• **isolobal:** (by Hoffmann)

group of molecules with **similar frontier orbital** (number, symmetry, approx. energy, and shape)



• **isolobal analogy:** e.g.) **Me radical** and $\text{Mn}(\text{CO})_5$

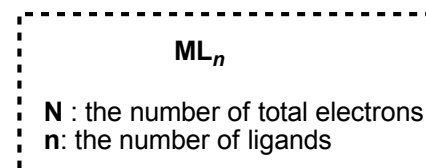
Me radical dimerizes to form ethane \longrightarrow

bonding between **Me** group and $\text{Mn}(\text{CO})_5$
 \parallel
 orbital interaction like C-C bond in ethane

1.3.6. Molecular Orbitals for Transition Metal Complexes

• **SALCs** = symmetry-adapted linear combinations \Rightarrow Figure 1.16

• **Valence bond theory** (Ref. *JACS* **1998**, 120, 12650)



• hybrid orbitals are constructed from **s-** and **d-orbitals** (p-orbitals: not used)

• $\mathbf{N} \leq 12$; when there are n metal-ligand bonds \Rightarrow hybrid orbitals are generated from **s-** and $(n-1)$ **d-orbitals**

• $\mathbf{N} > 12$: **some M-L bonds** are considered as **delocalized 3c-4e bonding**

• lone electron pairs of metal occupy **purely d-orbitals**

$N \leq 12$

- hybridization of each M-L bonds: sd^{n-1}
- remaining electrons occupy other pure d orbitals to make metal lone pairs

e.g.) WMe_6 ($N = 12$, $n = 6$)
 sd^5 (optimal 63° and 117° L-M-L angle)
 (Figure 1.17, Table 1-3)

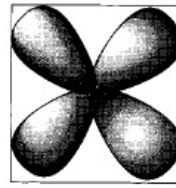
$N > 12$

- considered as hypervalent
- give rise to delocalized $3c-4e^-$ bonding (3 center-4-electrons)
- every pair of electrons greater than 12 requires one $3c-4e^-$ bonding interaction

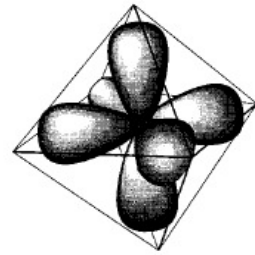
$m = 1/2 * (N-12)$
 • $m \times (3c-4e^- \text{ bond}) \Rightarrow sd^{m-1}$ hybridization

e.g.) $[PtH_6]^{2-}$ ($N = 18$, $n = 6$)
 • three $3c-4e^-$ bonds, sd^2 hybridization
 • remaining $6e^-$ are in metal's d-orbital

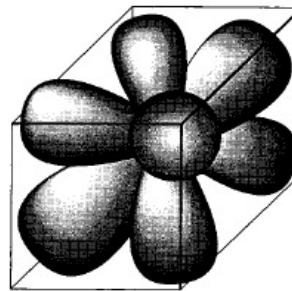
N : the number of total electrons
 n : the number of ligands



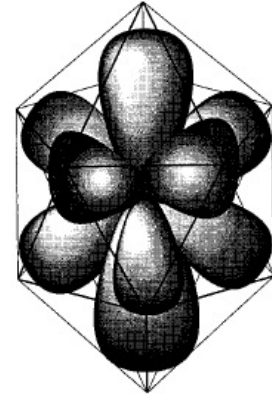
sd^1 hybridization



sd^2 hybridization



sd^3 hybridization



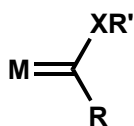
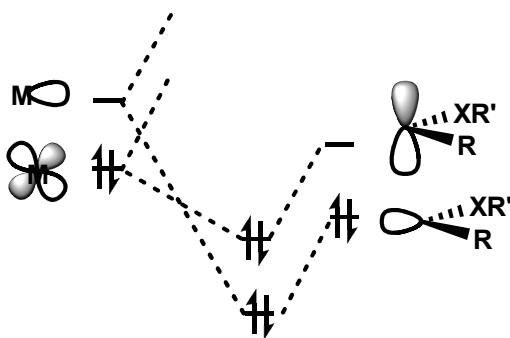
sd^5 hybridization

1.3.7. π -Bonding in Organotransition Metal Complexes

1.3.7.1. π -Bonding in CO and Its Analogs

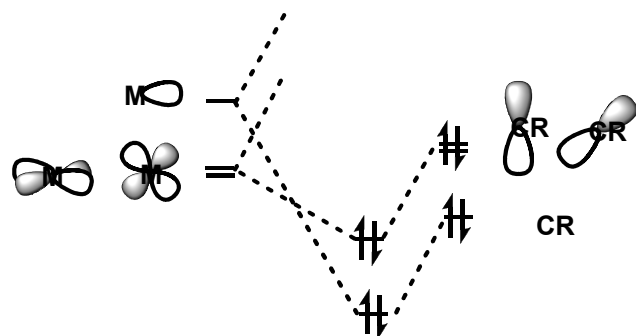
MO, π -backdonation

1.3.7.2. π -Bonding in Carbene and Carbyne Complexes



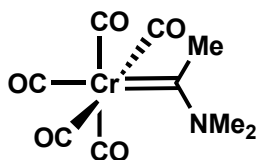
carbene (Fischer type)

- one σ -orbital and one π -orbital
- L: σ -donor and π -acceptor

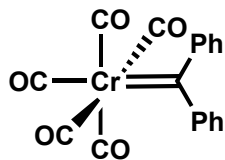


carbyne

- one σ -orbital and two π -orbital
- two d_M interact with two p_L
- carbyne ligand is often assigned as trianionic
- L: σ -donor and two π -donor



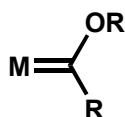
Cr(0)



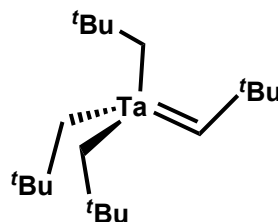
Cr(0)

"Fischer" carbene

- carbene ligands bearing at least one **hetero atom** or other substituents **capable of π -interaction**



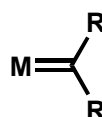
Formal charge: 0
Electrons donated: 2



Ta(V)

"Schrock" carbene (alkylidenes)

- carbene ligands containing **alkyl groups** or **hydrogens**
- considered to be **dianionic** (chapter 3)



Formal charge: -2
Electrons donated: 4

1.3.7.3. π -Bonding in Olefin Complexes

electron rich: more π -back donation

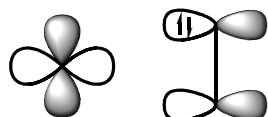
1.3.7.4. π -Bonding with Other Unsaturated Ligands

alkyne,
ketone, imine
(softer metal capable of backbonding)

1.3.8. π -Donor Ligands

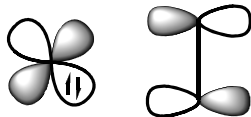
MO of arene, metallocene

- π -donation in some alkyne complex



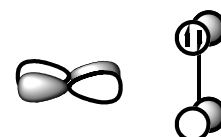
M alkyne

σ -Bonding



M alkyne

π -Backbonding

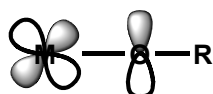


M alkyne

π -Donation

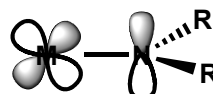
- π -donation in alkoxide and amide (Chapter 4)

alkoxide



M-O-C angle $\sim 180^\circ$
sp hybridization at O

amide



planar at nitrogen
sp² hybridization at N

other π -donors:
halides oxide, nitride ligands

Chapter 2: Dative Ligands

2.1 Introduction

Chapters 2-4: presents illustrative summary of the types of complexes
Chapter 2: steric and electronic properties of neutral ligands
(Chapters 3&4: formally anionic ligands)

2.2 Carbon Monoxide and Related Ligands

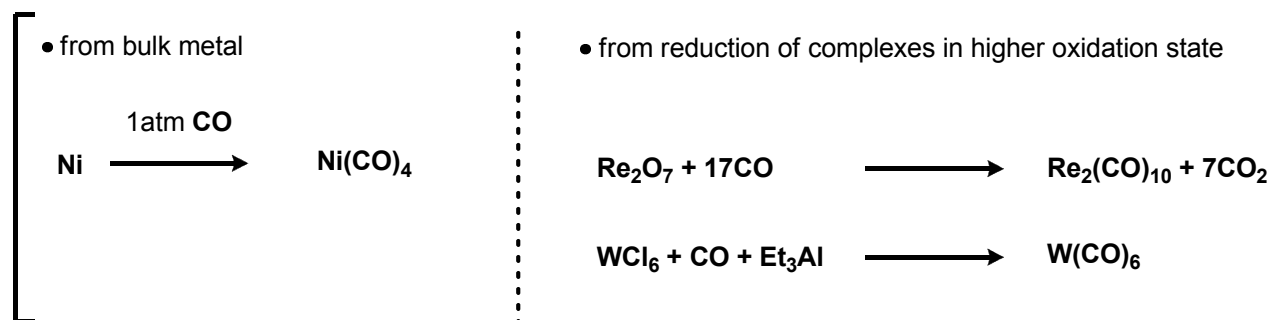
2.2.1. Properties of Free Carbon Monoxide

CO

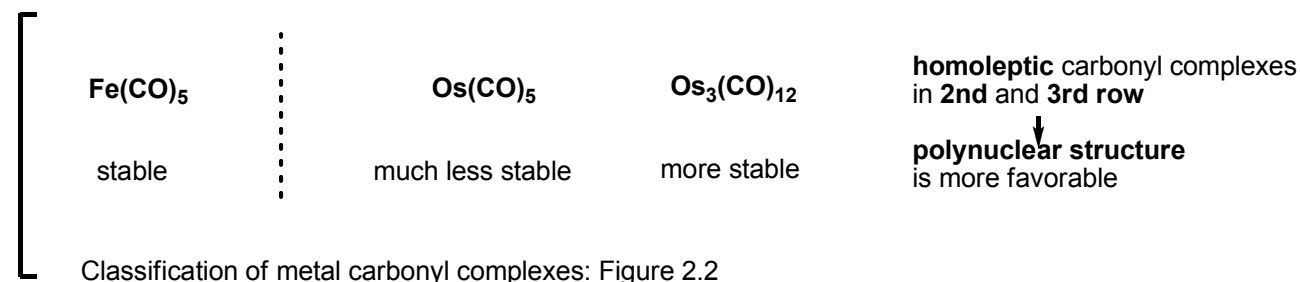
- small dipole moment with negative end located on carbon
- strong vibration in IR at 2143 cm^{-1}
- neutral ligand, commonly binds to metal C's lone pair electrons
- normally binds to one metal, but bridging coordination is possible (M-C-M angle is much less than 120°)

2.2.2. Types of Metal Carbonyl Complexes

• Preparation of metal-carbonyl complexes



• polynuclear carbonyl complexes



2.2.3. Models for CO Binding: Introduction of Backbonding

- CO binds strongly to **electron-rich, low valent** metals (backbonding, soft metal and soft ligand)

2.2.4. Evidence for Backbonding in Terminal Carbonyl

IR, C-O length

2.2.5. Infrared and X-ray Diffraction Data for Complexes with Bridging Carbonyls

2.2.6. Thermodynamics of the M-CO Bonds

dissociation of CO ligands: key step in many reactions

Table 2.3

- $\text{Cr}(\text{CO})_6 < \text{Mo}(\text{CO})_6 < \text{W}(\text{CO})_6$
- $\text{Ni}(\text{CO})_4 < \text{Cr}(\text{CO})_6$
- $\text{Ir}(\text{P}^i\text{Pr}_3)_2\text{Cl}(\text{CO})$ (particularly strong)

higher energy of orbitals, backdonation
third row, electron-rich alkylphosphine

2.2.7. Isoelectronic Analogs of CO: Isocyanides and Thiocarbonyls



- stronger σ -donor, weaker π -acceptor than CO
- weaker C-X π -bond than CO

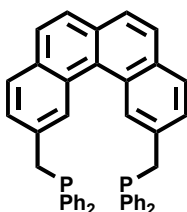
2.3 Dative Phosphorous Ligands and Heavier Congeners

2.3.1 Tertiary Phosphines and Related Ligands

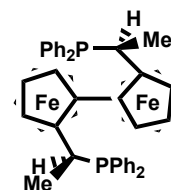
2.3.2 Chelating Phosphines

bidentate, asymmetric bisphosphine, P-M-P angle

trans coordination

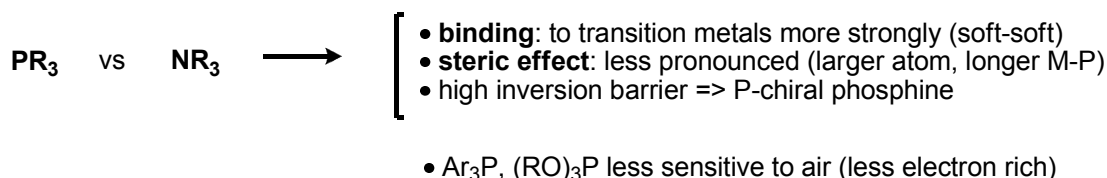


Transphos



Ph-Trap

2.3.3 Properties of Free Phosphines



2.3.4 Properties of Phosphine Complexes

2.3.4.1 Bonding and Electronic Properties

- **Electron-donating ability:** $\text{R}_3\text{P} > \text{Ar}_3\text{P} > (\text{RO})_3\text{P}$

greater s-character of sp^2 -hybridized orbital of aryl
 \Rightarrow weaker electron donor than alkyl

electron-donation: alkyl > alkoxy

- **π -acceptor orbital:** hybrid of P-X σ^* -orbital and phosphorus d -orbital (Figure 2.9)

- **π -acceptor ability:**

