

## Chapter 4 Covalent (X-Type) Ligands Bound Through Metal-Heteroatom Bonds

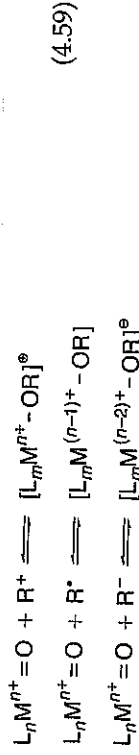
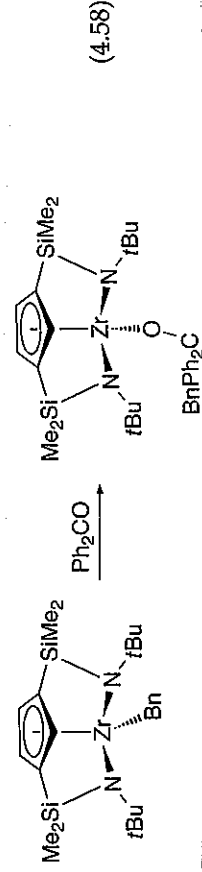
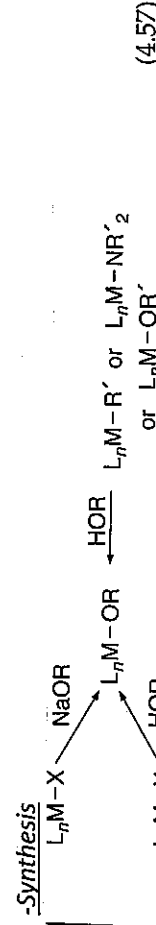
### 4.3 Metal-Oxygen

#### 4.3.1 Alkoxo Complexes

##### 4.3.1.2 Early Metal-Alkoxide

###### -Bonding

Hard-Hard (Ionic bond) } High hemolytic bond dissociation energy (ex. Cp\*<sub>2</sub>Zr(OH)Ph: 115kcal/mol)  
 π-donation (Lone pair of O → Metal *d*) } Lewis acidic metal

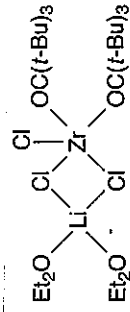


###### -Reactivity

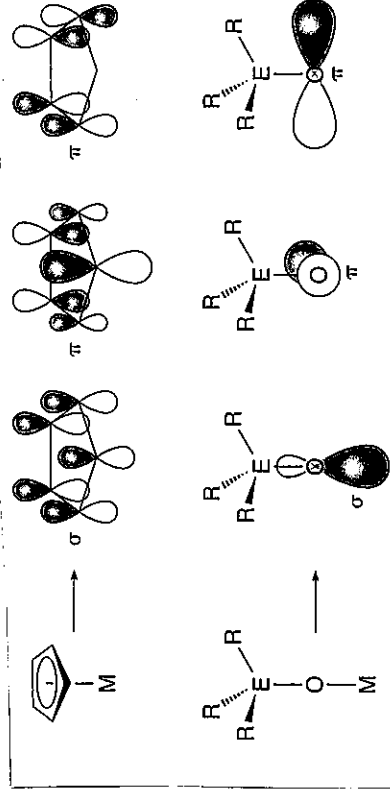
Not reactive for β-elimination, reductive elimination and migratory insertion.

###### -Use

+Low coordination number



+Mimic Cp



**Figure 4.12.**  
 Examples of sterically hindered  
 early-metal-alkoxo complexes.

**Figure 4.13.** Orbital analogy between a Cp and an alkoxo ligand.  
 +Metathesis Catalyst, Chiral Catalyst

### 4.3.1.3 Late Metal-Alkoxide

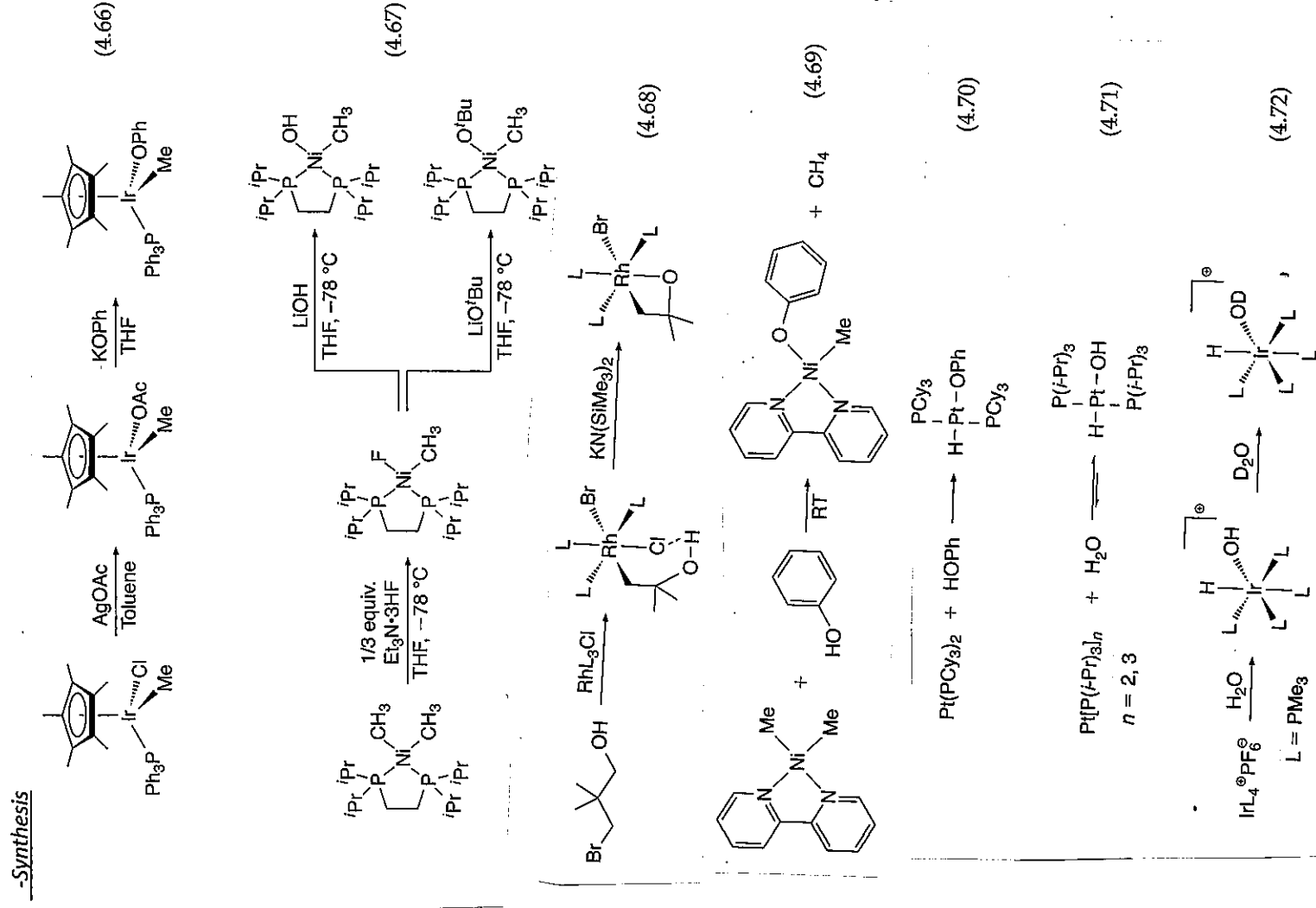
#### -Bonding

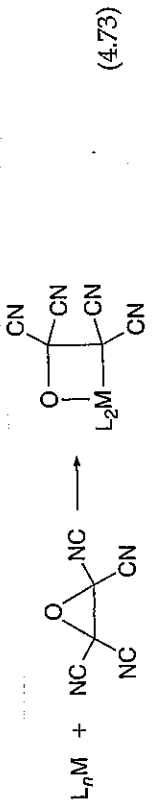
Strength:  $M-C(sp^3) \approx M-O > M-N$

Electron donating ability

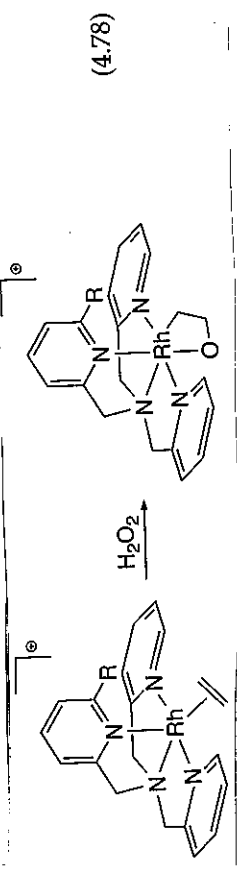
$OEt > OCPh_3 > OSiMe_3 > OSiMe_2Ph > OSiPh_3 >$   
 $F \approx OCH_2CF_3 > OH \approx OB(Mesityl)_2 >$   
 $NHPh \approx OPh > SPh \approx Cl > C_2Ph \approx Br > I$

**Figure 4.17.**  
Relative electron-donating ability of various ligands bound through M-X bonds.





$L_nM$ :  $M = \text{Pt}$ ;  $L = \text{PPPh}_3, \text{P}(p\text{-tolyl})_3, \text{AsPh}_3$ ;  $n = 4$   
*trans*-( $\text{PPh}_3$ )<sub>2</sub>(CO)MX;  $M = \text{Rh, Ir}$ ;  $X = \text{Cl, Br}$



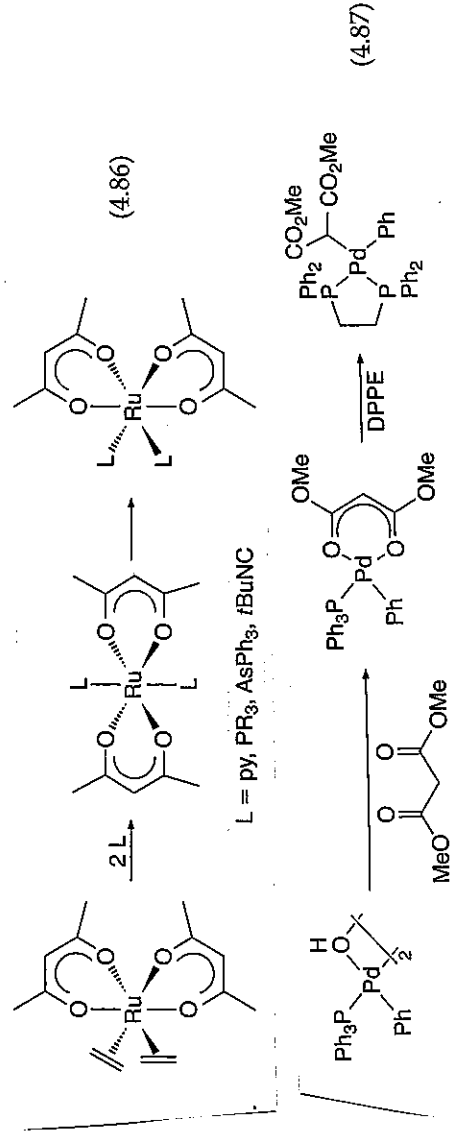
**-Reactivity**

Reductive elimination, insertion of CO and olefin,  $\beta$ -elimination

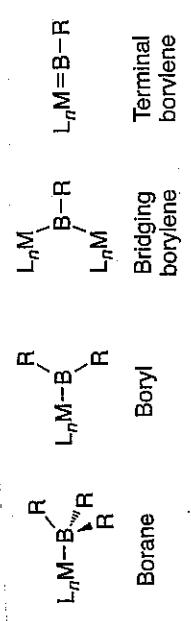
**4.3.2  $\beta$ -Diketionate Complexes**

+Stable

+M(acac)<sub>3</sub>: octahedral, monomer; M(acac)<sub>2</sub>: oligomer

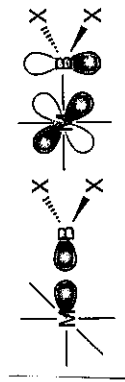


**4.4 Metal-Boryl**



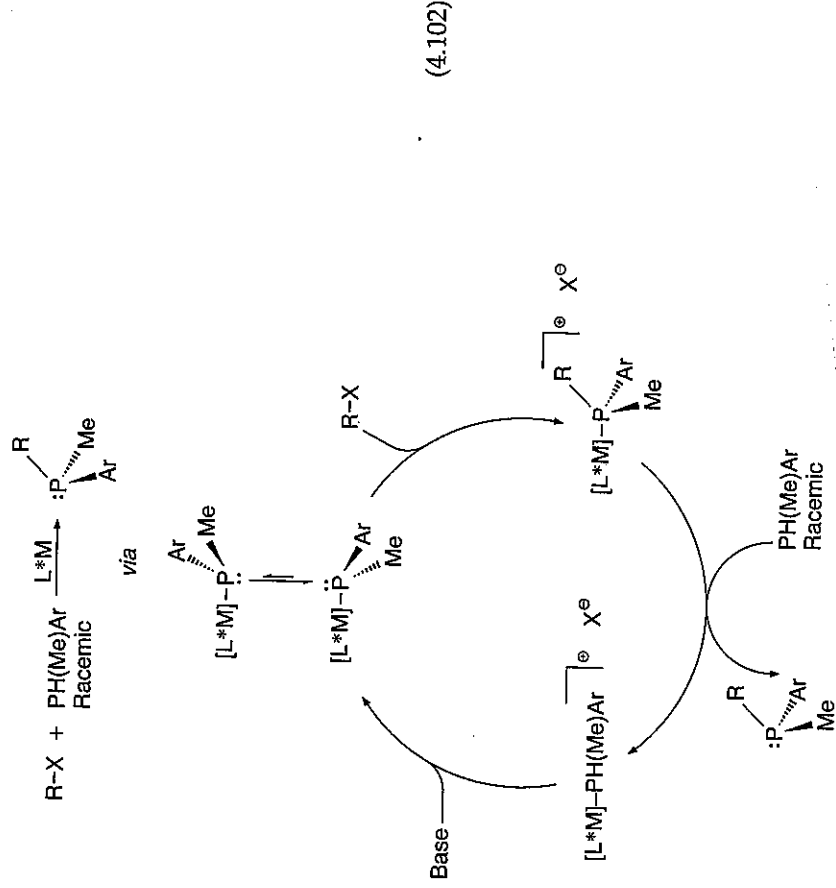
**Figure 4.20.**  
 Classification system for boron ligands containing a single boron atom.

**-Bonding**



**Figure 4.21.**  
 Bonding in metal-boryl complexes.





#### 4.6 Metal-Thiolate

-Bonding

Stable

-Softness

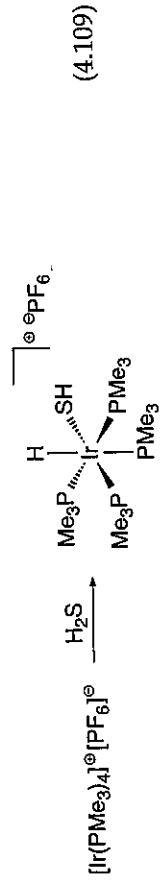
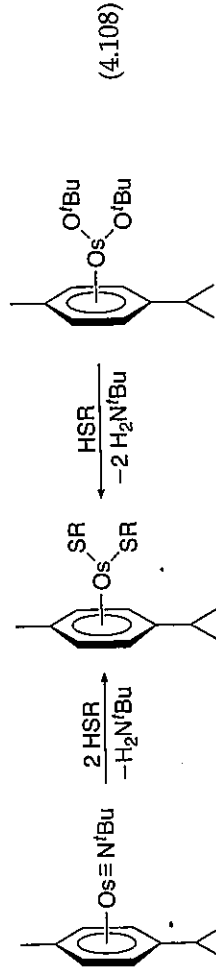
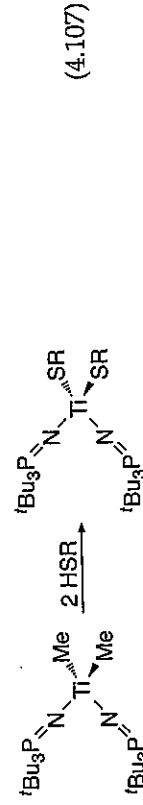
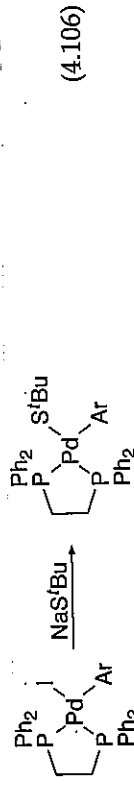
-Weakness of C=S bond (unfavorable  $\beta$ -elimination)

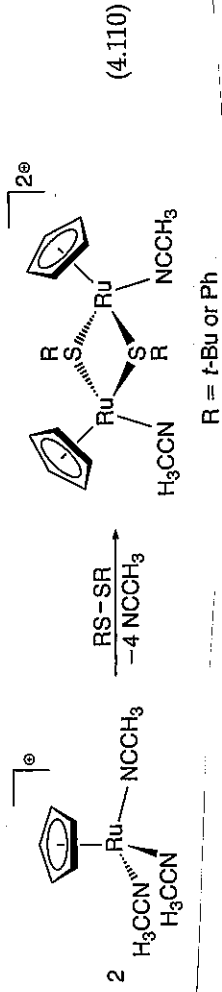
-M-S  $\pi$ -bonding



Figure 4.26.  
A qualitative description of the bonding in a metal-thiolate complex.

-Synthesis





#### 4.7 Metal-Silyl

##### -Structure

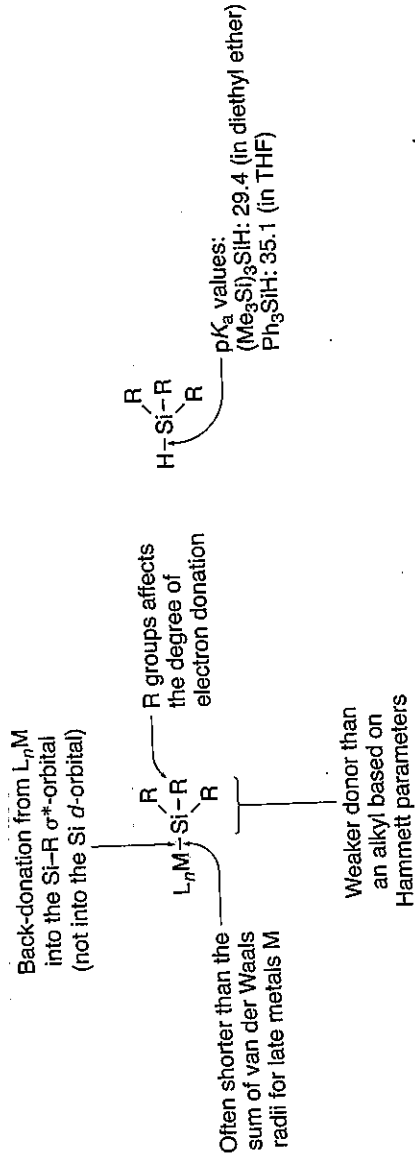
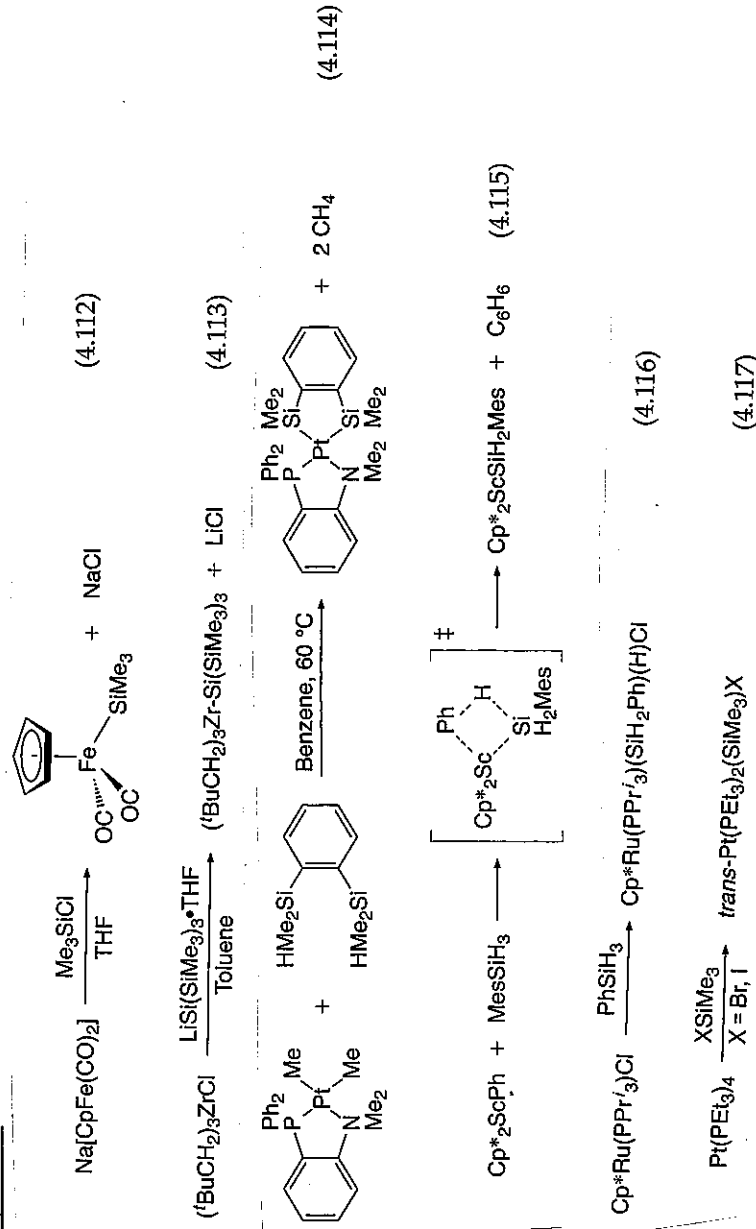


Figure 4.29. Summary of several of the electronic properties of silyl ligands and silyl complexes.

##### -Synthesis



##### Reactivity

Analogous to alkyl compounds

Differences

- Weakness of C=Si bond (unfavorable  $\beta$ -elimination)

- Disfavor homolysis

