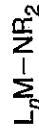
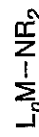


Chapter 4 Covalent (X-Type) Ligands Bound Through Metal-Heteroatom Bonds

4.2 Metal-Nitrogen

4.2.1 Amido Complexes

Early-metal-amido complexes Late-metal-amido complexes



- Stronger π -bonding
 - More ionic bonding
 - Hard-hard match
 - Stronger bonds
- π -Repulsion more common
 - Less ionic bonding
 - Hard-soft mismatch
 - Weaker bonds

4.2.1.1 Late-Metal-Amido

-Overview

Low-valent transition metal-Amido complex: **Unstable** (ex. β -Hydride elimination)

-Mismatch (Soft metal & Hard ligand)

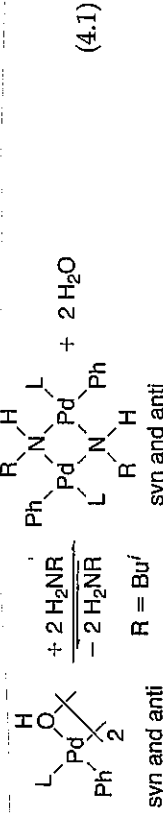
- π -Donation (Lone pair of N \rightarrow Saturated metal center)

\rightarrow Intermediates of catalytic processes

-Bonding

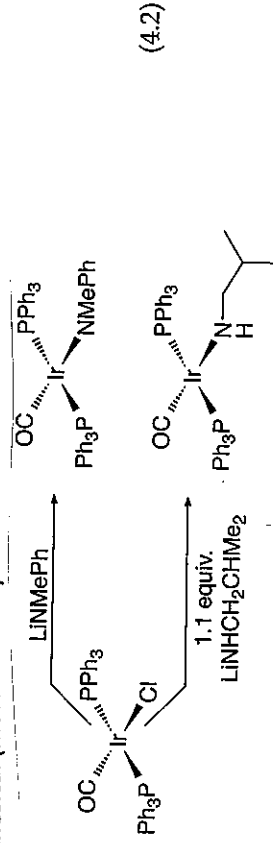
Soft metal & Hard ligand \rightarrow 1. Ionic bonding 2. π -repulsion (d -electron & lone pair) \rightarrow **Basic**

Strength: $M-C > M-N > M-O$

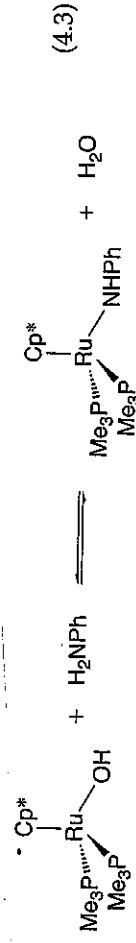


-Synthesis

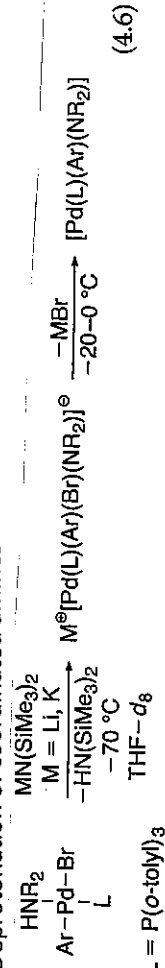
-Metathetical (most common)



- σ -Bonded ligand exchange



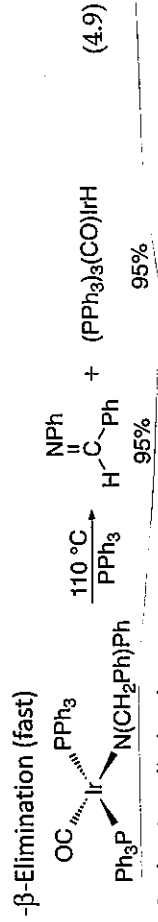
-Deprotonation of coordinated amines



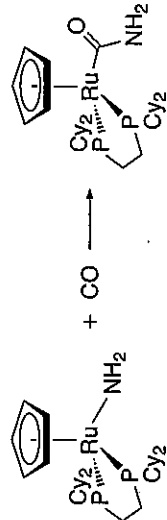
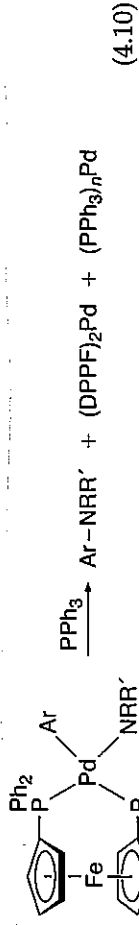
-Oxidative addition



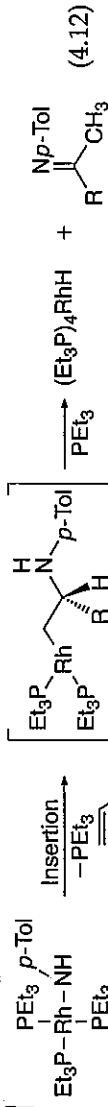
-Reactivity



-Reductive elimination



-Migratory insertion



4.2.1.2 Early-Metal-Amido

-Overview

Catalyst for olefin polymerization ("constrained geometry" catalysts (fig. 4.2. right))

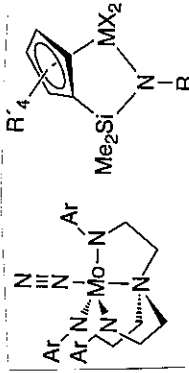


Figure 4.2.

Two types of early-metal complexes containing chelating amido ligands.

R = Alkyl, aryl
M = Ti, Zr
X = Cl, Me

-Bonding

Reactive toward protic acid: $[M]-NR_2 + H-X \rightarrow [M]-X + H-NR_2$ (X = alcohols, Cp, etc.)

Strength: $M-O > M-N > M-C$

+ p_N-d_M π -bonding

-Synthesis

$MCl_n + LiNR_2 \rightarrow M(NR_2)_n + nLiCl$

$MCl_n + HNR_2$ (excess) $\rightarrow M(NR_2)_n + nHNR_2 HCl$ (usually, mixed halo-amido complex)

4.2.2 Amidate and Amidinate Complexes

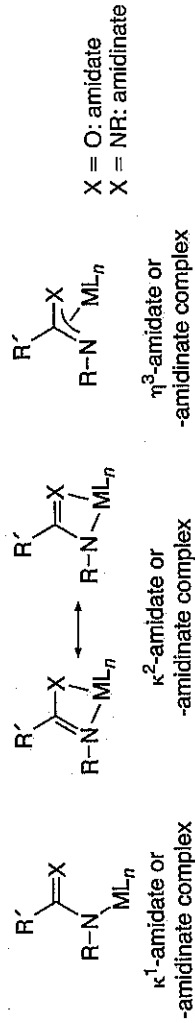
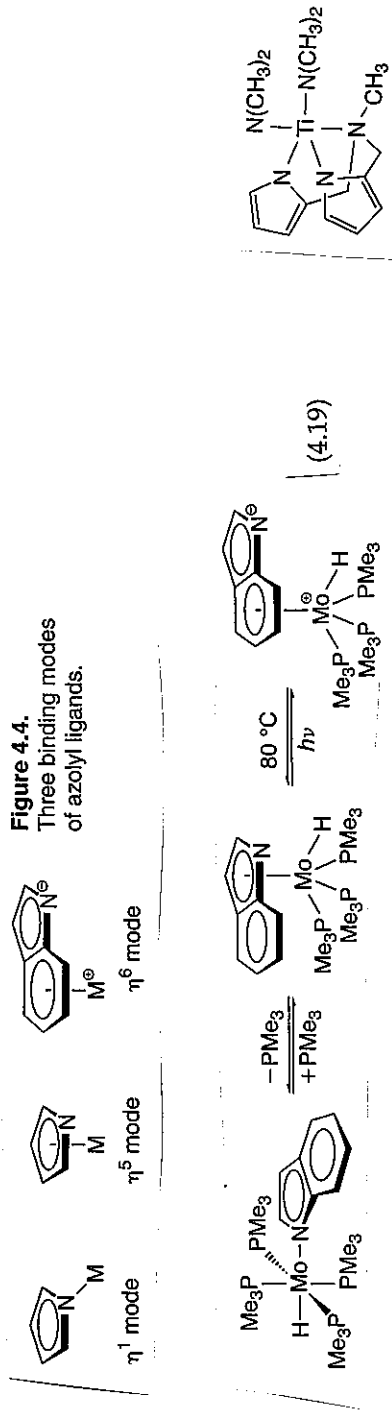


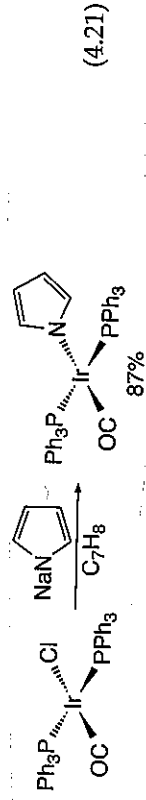
Figure 4.3. Generic structures of κ^1 , κ^2 , and η^3 -amidate and -amidinate complexes.

4.2.3 Azolyl Complexes

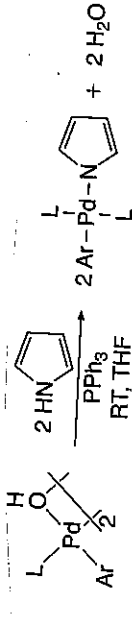


-Synthesis

-Displacement of halides



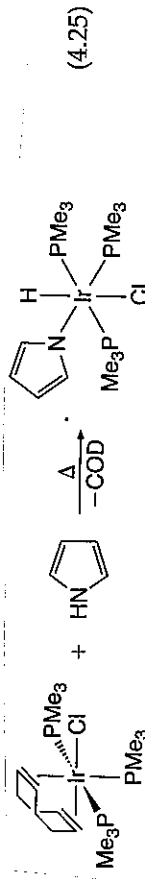
-Proton transfer



syn and anti

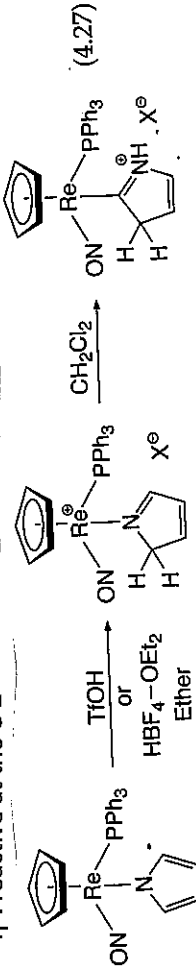
L = PPh₃

-N-H Activation

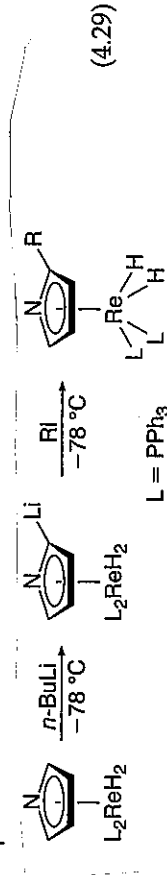


-Reactivity

$-\eta^1$: reactive at the C-2



$-\eta^5$



4.2.4 Nitrosyl Complexes

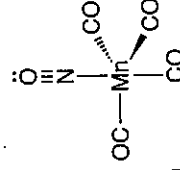
Properties of NO

MO diagram: similar to CO or N₂

CO or N₂ + one electron in a π*-orbital

→ Bond order: 2.5; NO⁺ is stable

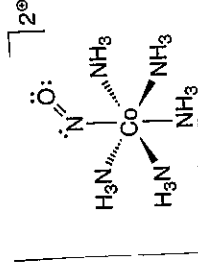
Two Structures



Linear (160-180°)

Considered as NO⁺ (3-electron donor)

Poorer σ-donor, better π-acceptor vs. CO



Bent (120-140°)

Considered as NO⁻ (1-electron donor)

EXAMPLE

Mn(NO)(CO)₄ containing a linear metal-nitrosyl group (∠Mn-N-O = 180°)

Covalent electron-counting method:

Mn = 7 e⁻

One linear NO ligand = 3 e⁻

Four CO ligands = 8 e⁻

Total = 18 e⁻

Ionic electron-counting method:

Mn⁺ = 8 d e⁻

Linear NO ⇒ NO⁺ ligand = 2 e⁻

Four CO ligands = 8 e⁻

Total = 18 e⁻

EXAMPLE

[Co(NO)(NH₃)₅]J²⁺ containing a bent metal-nitrosyl group (∠Co-N-O = 119°)

Covalent electron-counting method:

Co = 9 e⁻

One bent NO ligand = 1 e⁻

Five NH₃ ligands = 10 e⁻

2+ total charge = -2 e⁻

Total = 18 e⁻

Ionic electron counting-method:

Co³⁺ = 6 e⁻

Bent NO ⇒ NO⁻ ligand = 2 e⁻

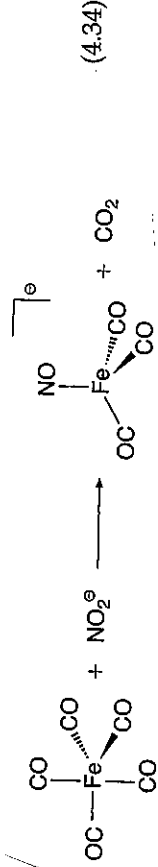
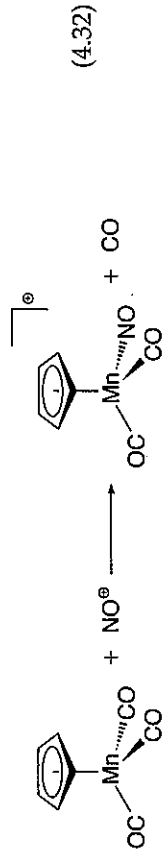
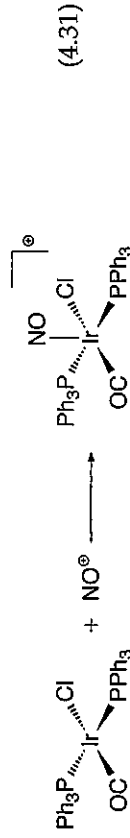
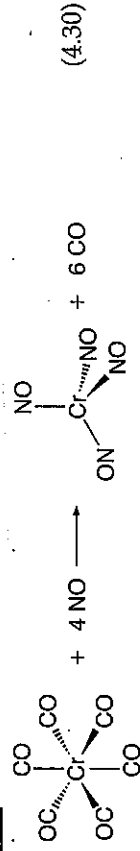
Five NH₃ ligands = 10 e⁻

Total = 18 e⁻

-Comparison with CO

Stronger π -accepting ability \rightarrow Stronger M-N bond, Weaker N-O bond

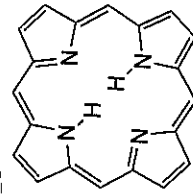
-Synthesis



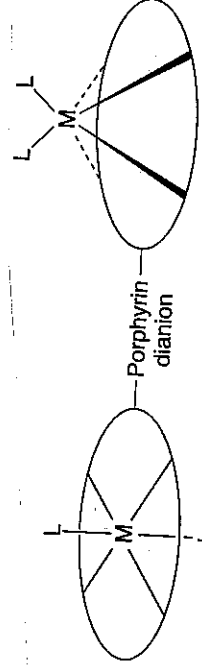
4.2.5 Polydentate N Donor Ligands

4.2.5.1 Porphyrin Complexes

-Structure



The core ring system of a porphyrin

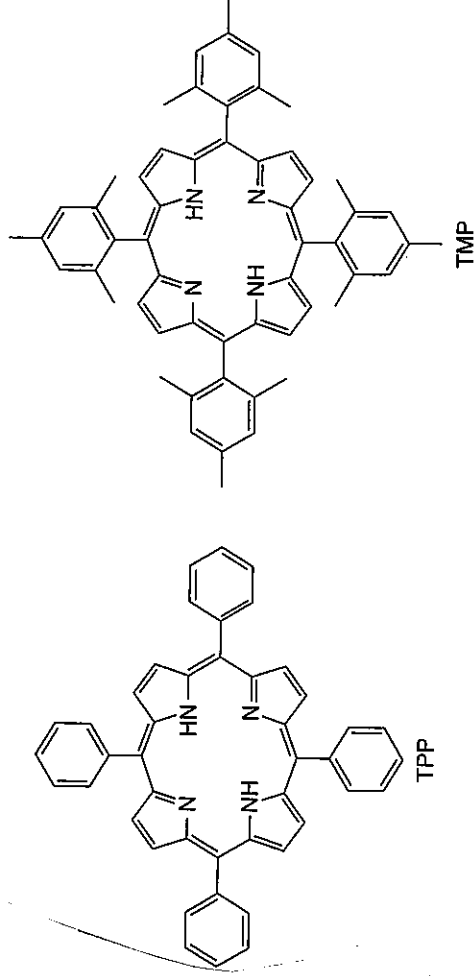
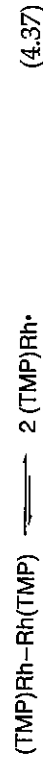
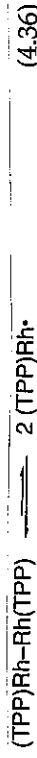


In-plane, trans coordination

Out-of-plane, cis coordination

Figure 4.8.

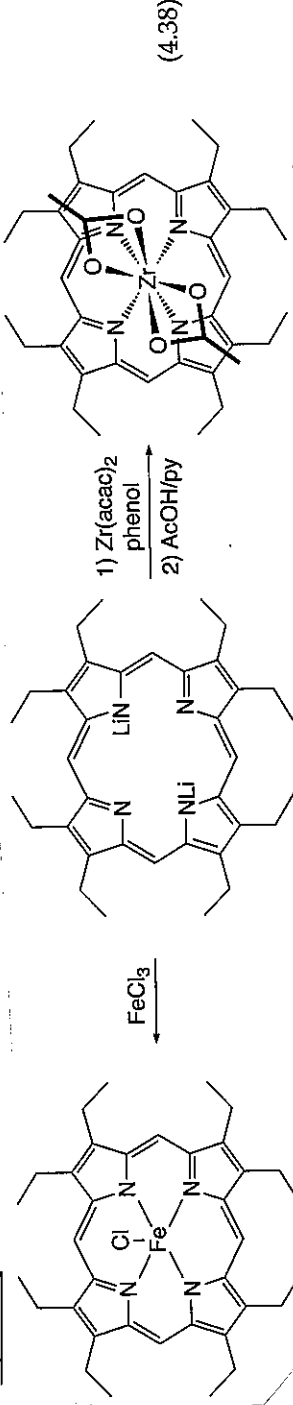
Effect of metal size on coordination mode and disposition of the ancillary ligands.



TPP

TMP

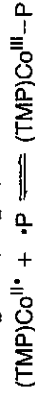
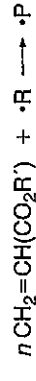
Synthesis



Reactivity

-Late-metal-porphyrin: Radical reactions (No *cis* ligands)

Ex. Polymerization, C-H Activation



P = polymer

Scheme 4.1.

Mechanism of atom-transfer radical-radical polymerization.

-Early-metal-porphyrin: Migratory insertion, Reductive elimination

4.2.5.2 Bis-Sulfonamide Complexes

Structure

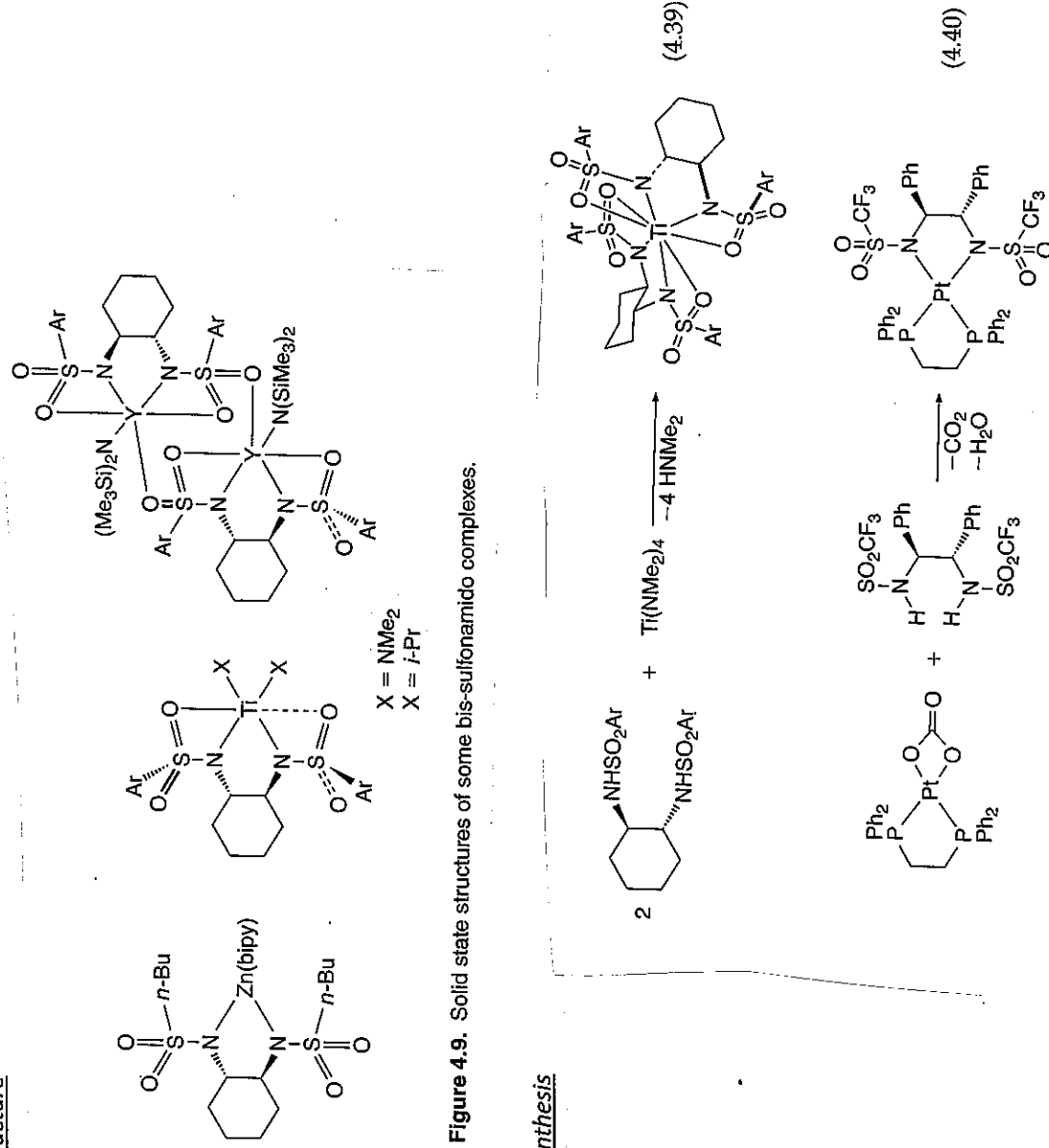
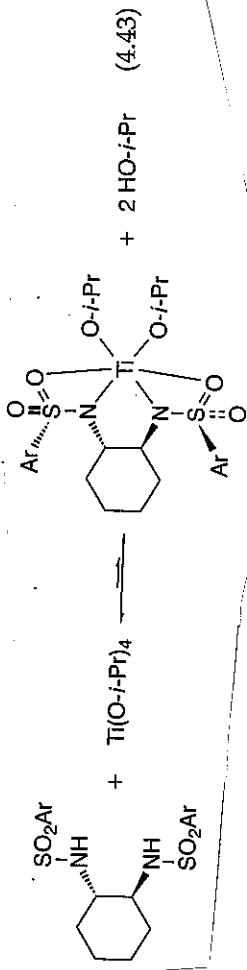


Figure 4.9. Solid state structures of some bis-sulfonamido complexes.

Synthesis



4.2.5.3 Pyrazolylborate Complexes

-Bonding

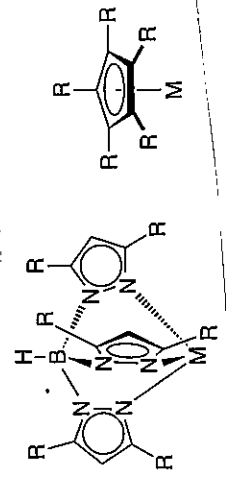
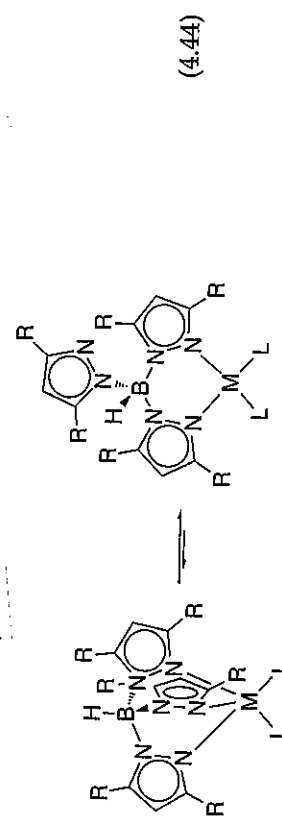


Figure 4.10.
A comparison of the orientation of substituents in Tp and Cp derivatives. This figure is adapted from reference 227.

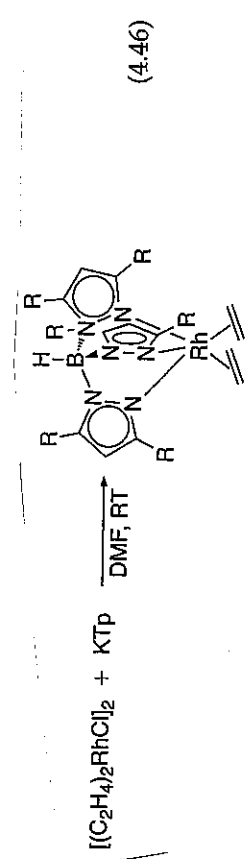
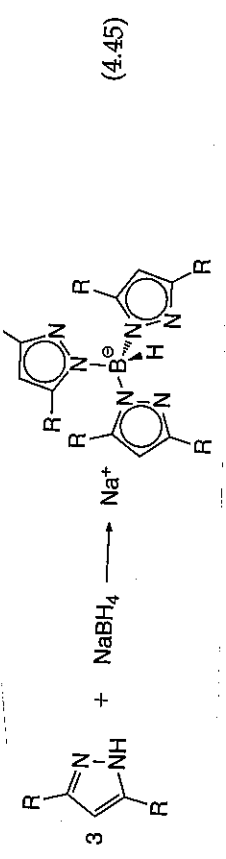
“tetrahedral enforcers”
Bun in the case of d^8 complexes...



κ^3 - Tp ligand
M = Rh (I), Ir (I) d^8

κ^2 - Tp ligand
M = Rh (I), Ir (I) d^8

-Synthesis



-Use

Study of C-H activation & paramagnetic organometallic species

(Dissociation of one N → Coordination site & Electronic changes in redox processes)

4.2.5.4 β -Diketiminato (NacNac) Complexes

-Structure

κ^2 (major) & κ^1 & η^5

Substituents on N → Sterically demanding → Unsaturated complexes

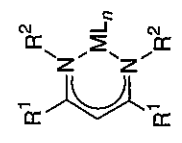
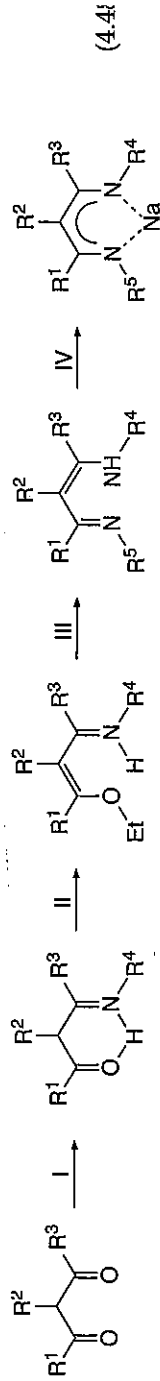
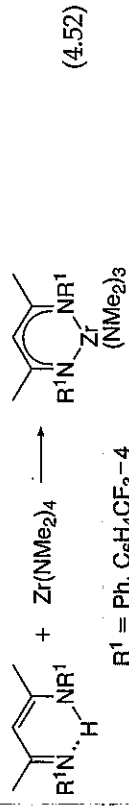
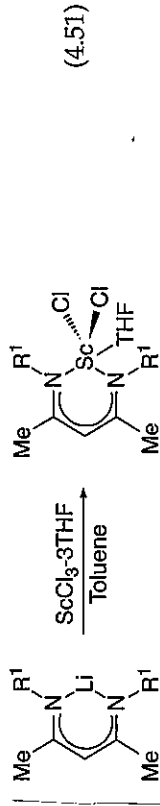
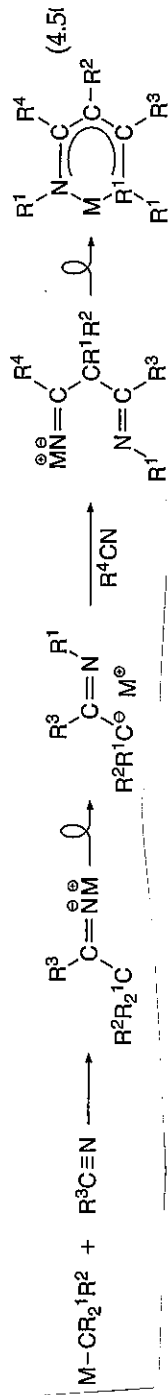


Figure 4.11.
A generic structure of a β -diketiminato complex.

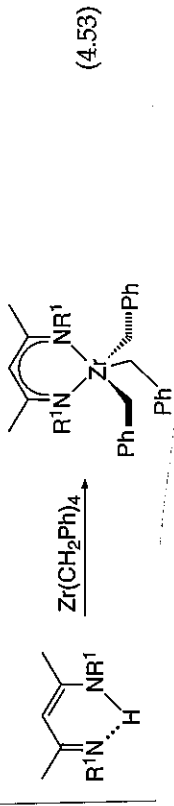
Synthesis



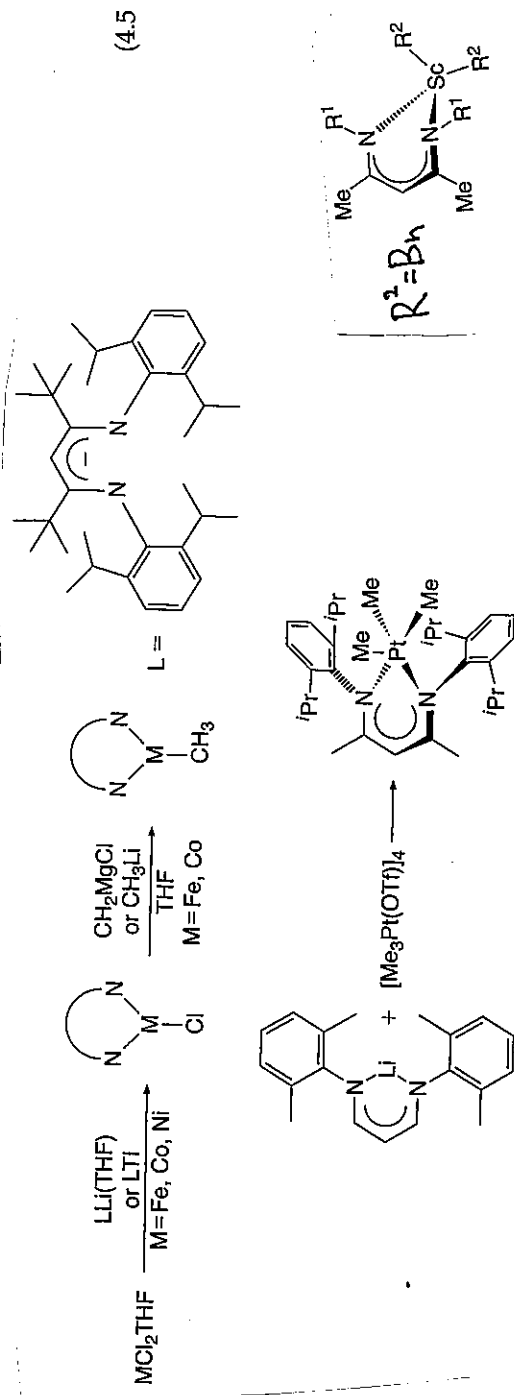
(I) NH_2R^4 , C_6H_6 , azeotropic distillation; (II) $[\text{Et}_3\text{O}][\text{BF}_4]$, Et_2O , 278°C ; (III) NH_2R^5 , Et_3O^+ ; (IV) NaOMe , MeOH .



$\text{R}^1 = \text{Ph}, \text{C}_6\text{H}_4\text{CF}_3-4$



Examples



$\text{R}^2 = \text{Bn}$