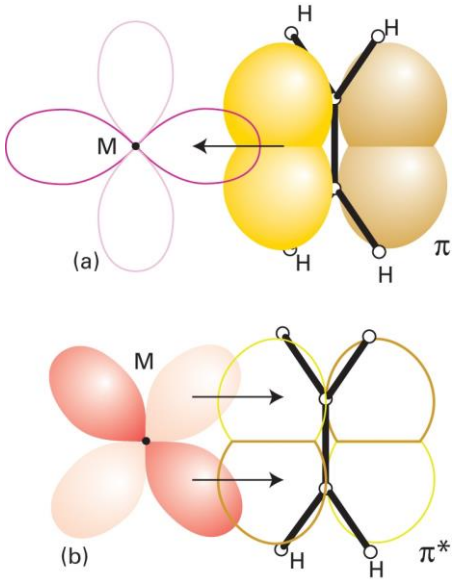
π (Olefin) Complexes and Metallocenes

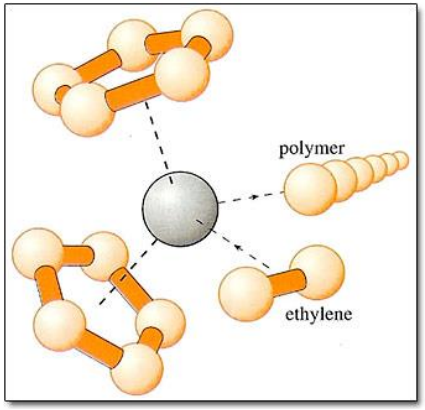
Lecture 4 and 6



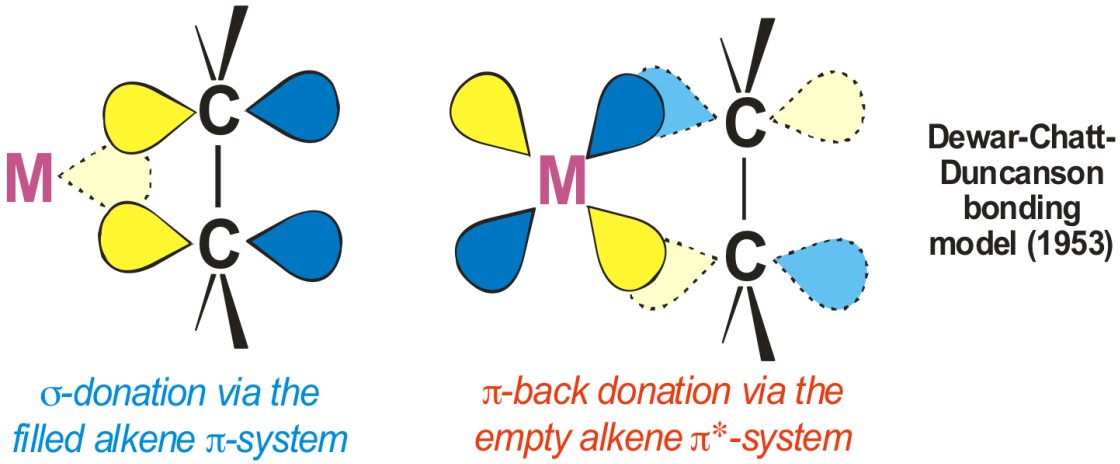
The Novel: Olefin Polymerization and Isomerization

The Characters:

- Olefin Complexes
- Metallocenes
- Bent Metallocenes
- Metal Hydrides and Alkyls
- Alkyl Insertion Reactions
- Beta-H Elimination Reactions
- Stereoregular Catalysis
- Asymmetric Catalysis



History: Olefin to Metal Binding

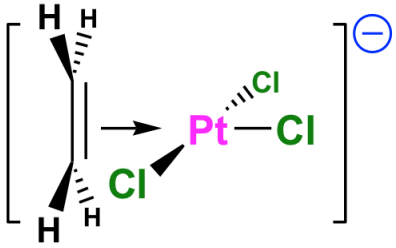


Dewar-Chatt-Duncanson bonding model (1953)

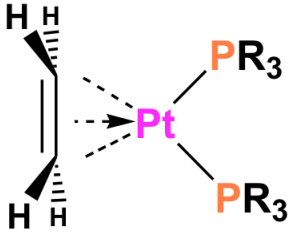
σ-donation via the filled alkene π-system

π-back donation via the empty alkene π-system*

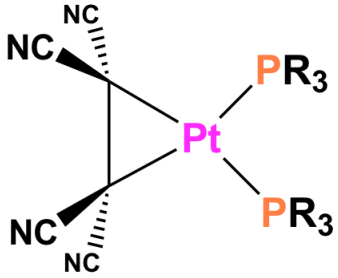
Influences of Metal Oxidation State and of Olefin on Bonding



Pt(2+)
C=C = 1.37Å
Zeiss's Salt



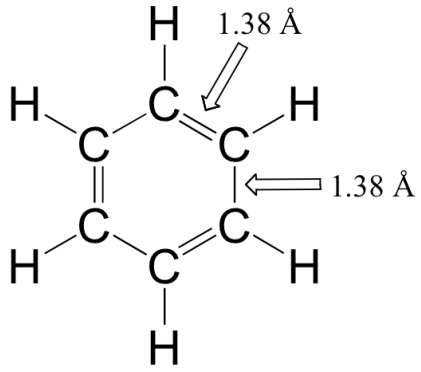
Pt(0)
C=C = 1.43Å



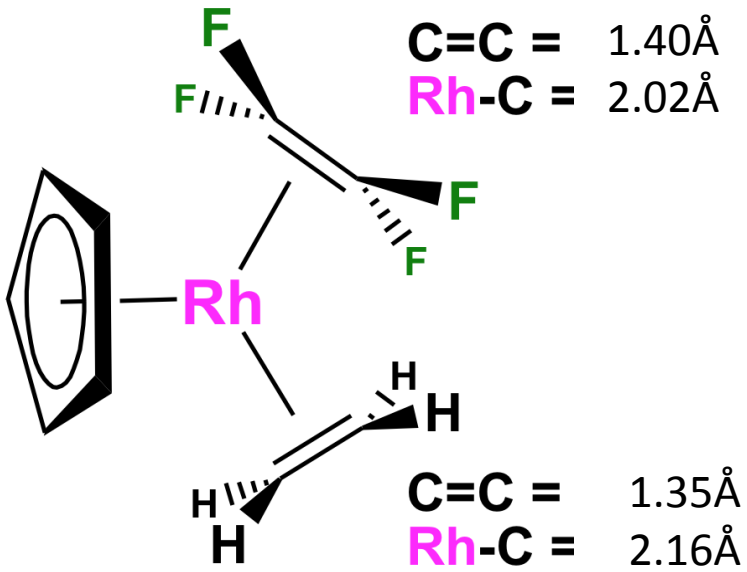
Pt(+2)
C--C = 1.49Å
metallocyclopropane

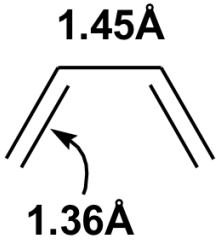
TABLE 8.5 Average Bond Lengths for Some Single, Double, and Triple Bonds

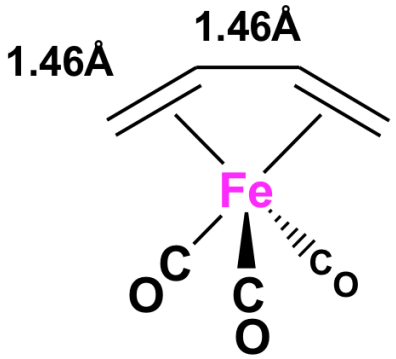
Bond	Bond Length (Å)	Bond	Bond Length (Å)
C—C	1.54	N—N	1.47
C=C	1.34	N=N	1.24
C≡C	1.20	N≡N	1.10
C—N	1.43	N—O	1.36
C=N	1.38	N=O	1.22
C≡N	1.16		
		O—O	1.48
C—O	1.43	O=O	1.21
C=O	1.23		
C≡O	1.13		

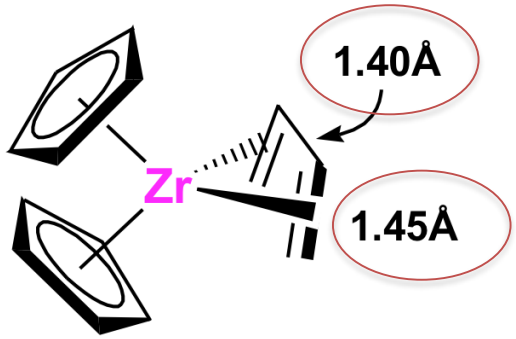


benzene


F
F
F
F
Rh
H
H
H
H
C=C = 1.40Å
Rh-C = 2.02Å
C=C = 1.35Å
Rh-C = 2.16Å


1.45Å
1.36Å


1.46Å
1.46Å
Fe
C
O
C
O
C
O

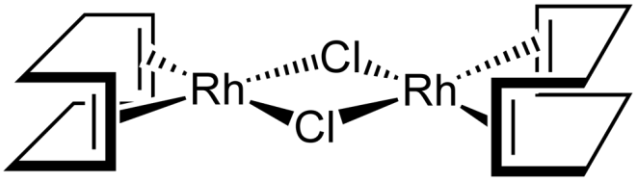

1.40Å
Zr
1.45Å

Ethylene Complex	νC=C (cm^{-1})
Free Ethylene	1623
$[Ag(H_2C{=}CH_2)_2]^+$	1584
$Fe(CO)_4(H_2C{=}CH_2)$	1551
$[Re(CO)_4(H_2C{=}CH_2)_2]^+$	1539
$[CpFe(CO)_2(H_2C{=}CH_2)]^+$	1527
$Pd_2Cl_4(H_2C{=}CH_2)_2$	1525
$[PtCl_3(H_2C{=}CH_2)]^-$	1516
$CpMn(CO)_2(H_2C{=}CH_2)$	1508
$Pt_2Cl_4(H_2C{=}CH_2)_2$	1506
$CpRh(H_2C{=}CH_2)_2$	1493

All are lower. Why?

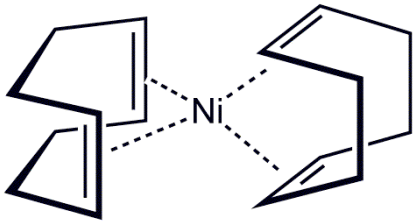
Propose a structure for the Rh complex.. And the others as well! . .

Chelating diolefins

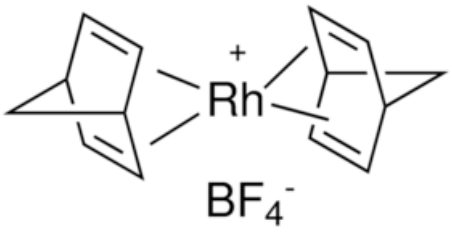


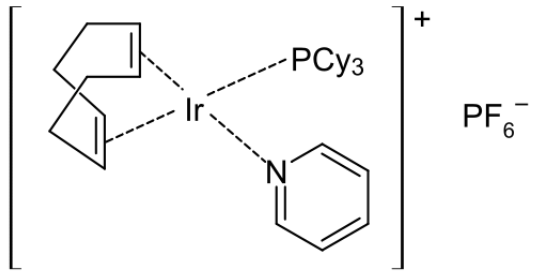
norbornadiene complex

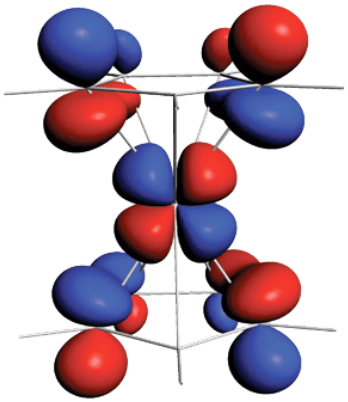
cyclooctadiene complex

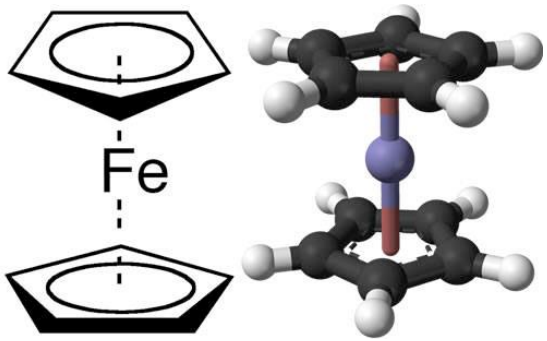


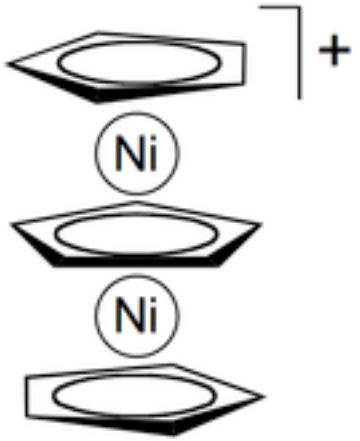
$Ni(COD)_2$

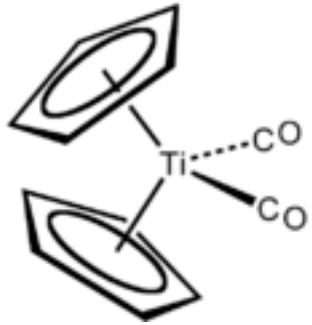


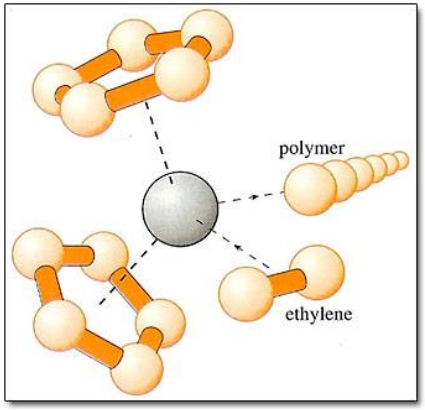


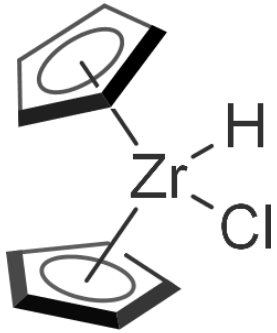




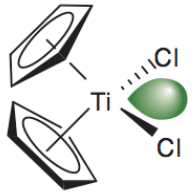




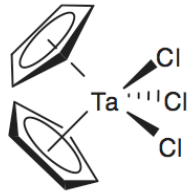




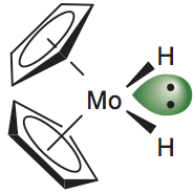
General form



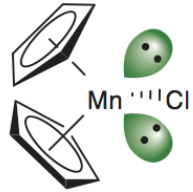
16-electron



18-electron

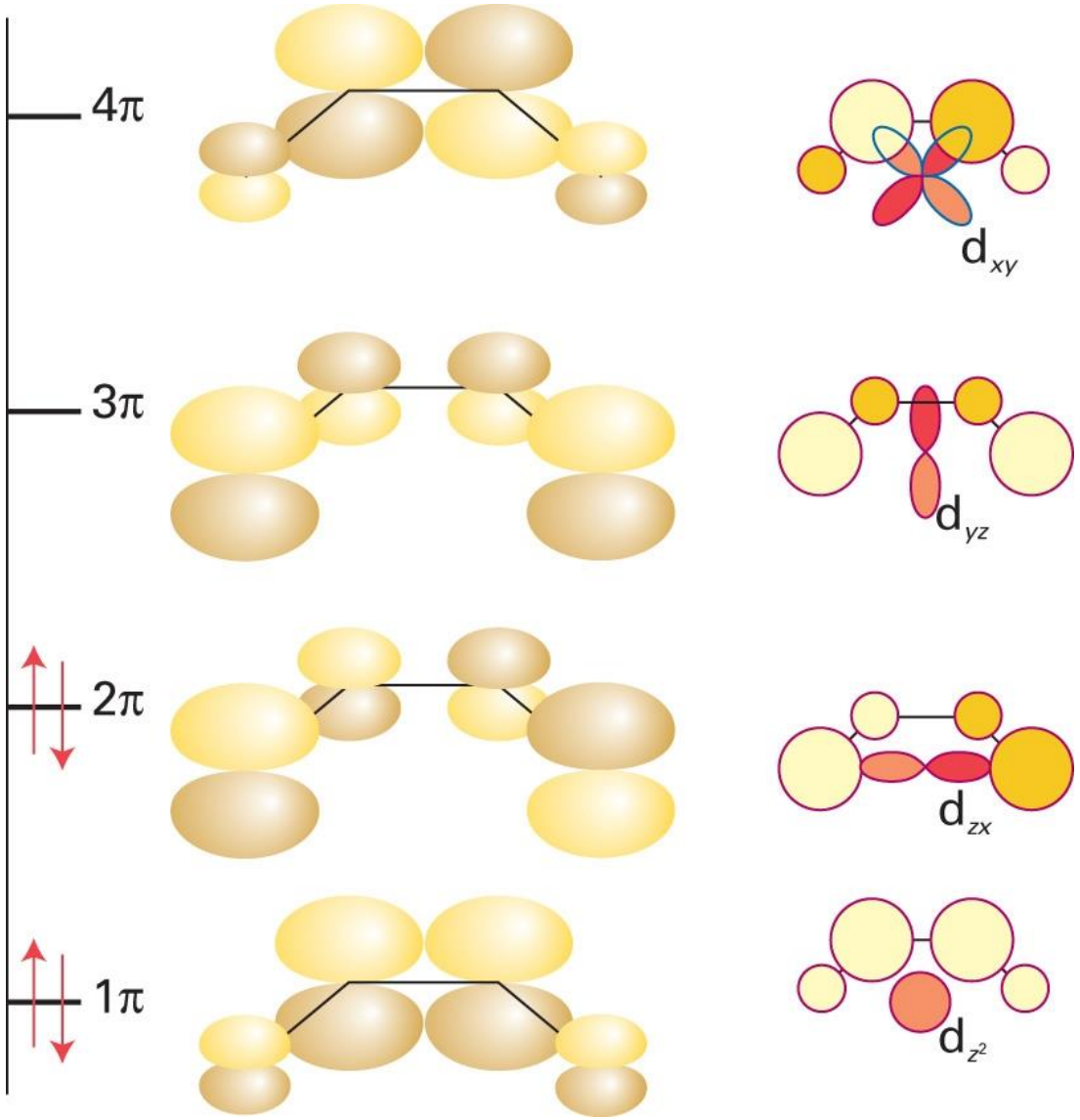


18-electron



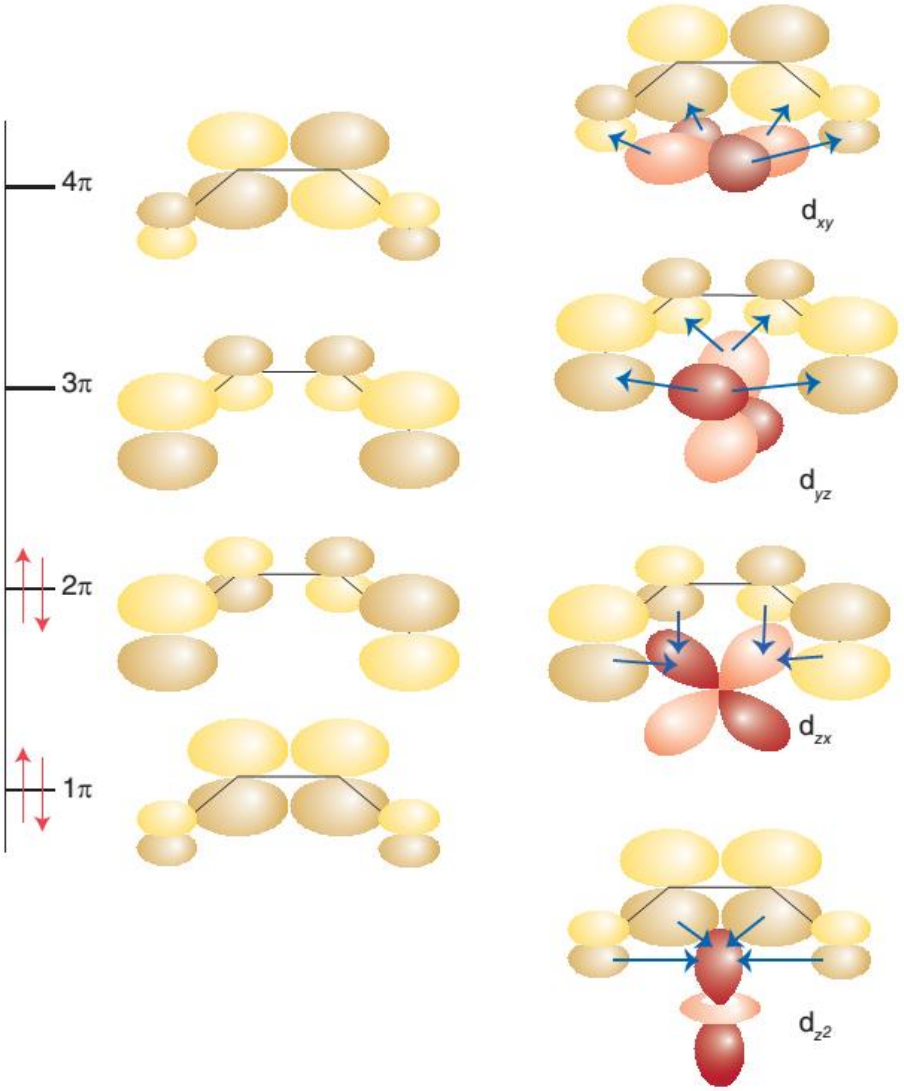
18-electron

Butadiene and its interactions with d orbitals



Shriver, Weller, etc. 6th ed.

Butadiene and its interactions with d orbitals



Shriver, Weller, etc. 6th ed.

cyclobutadiene and its interactions with d orbitals

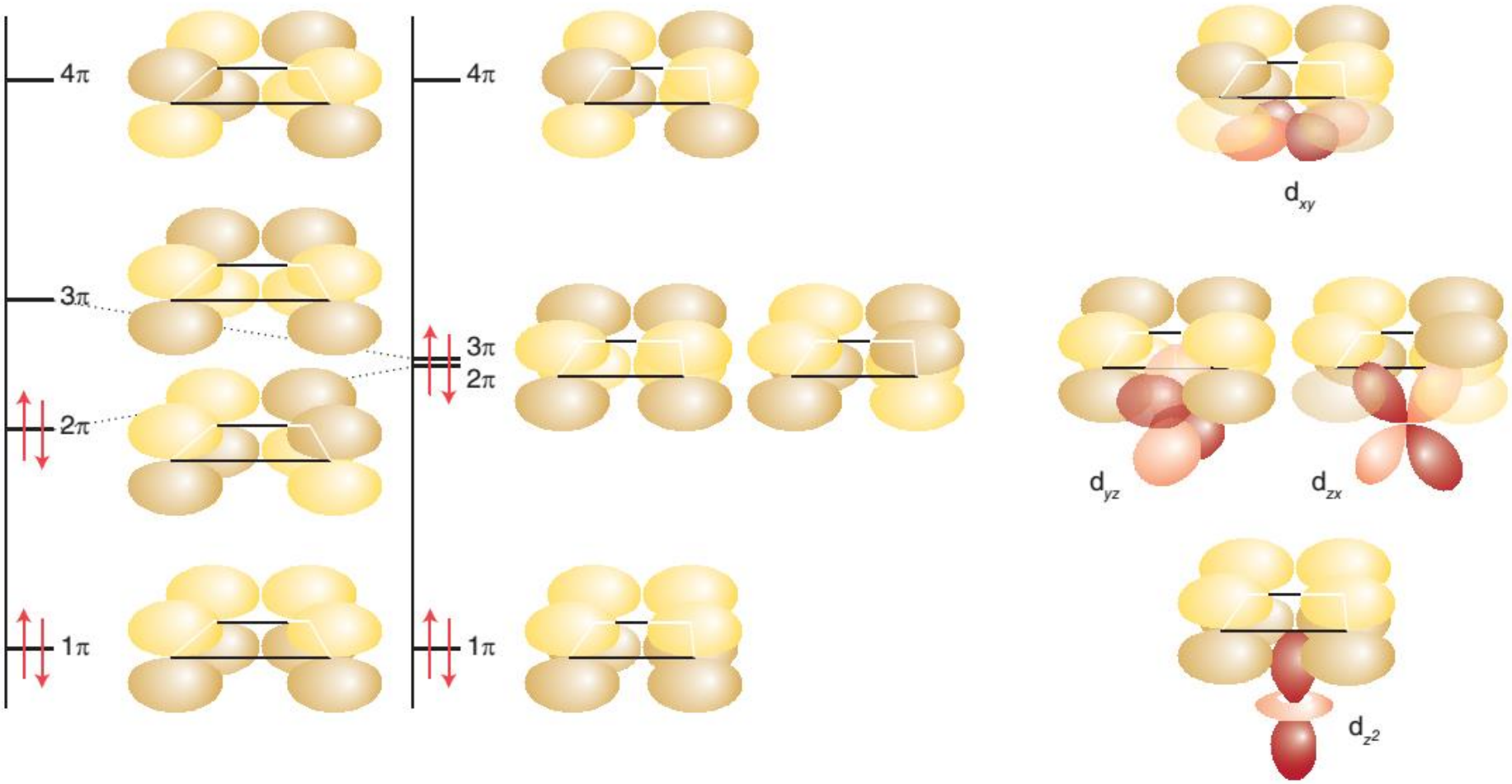
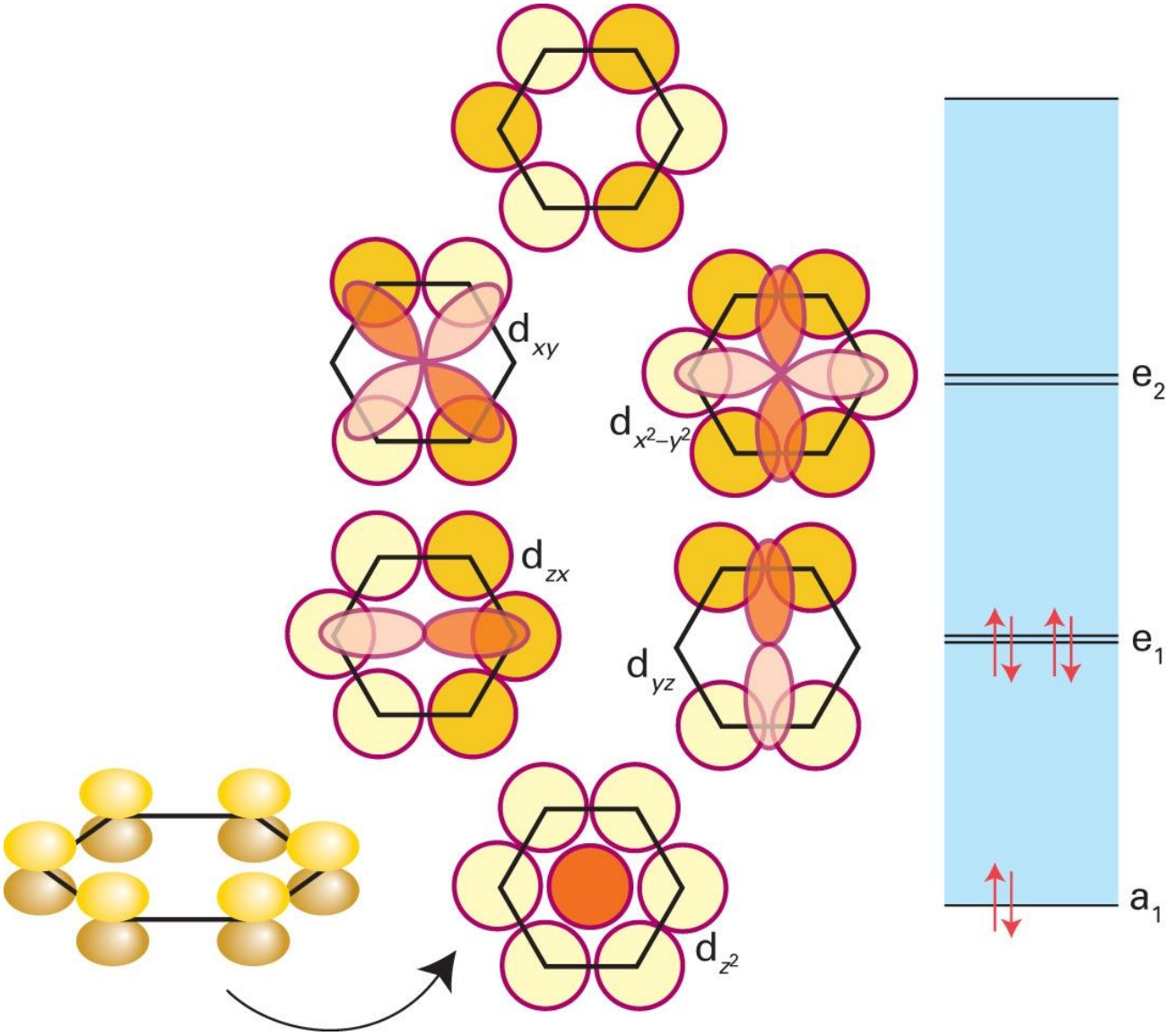
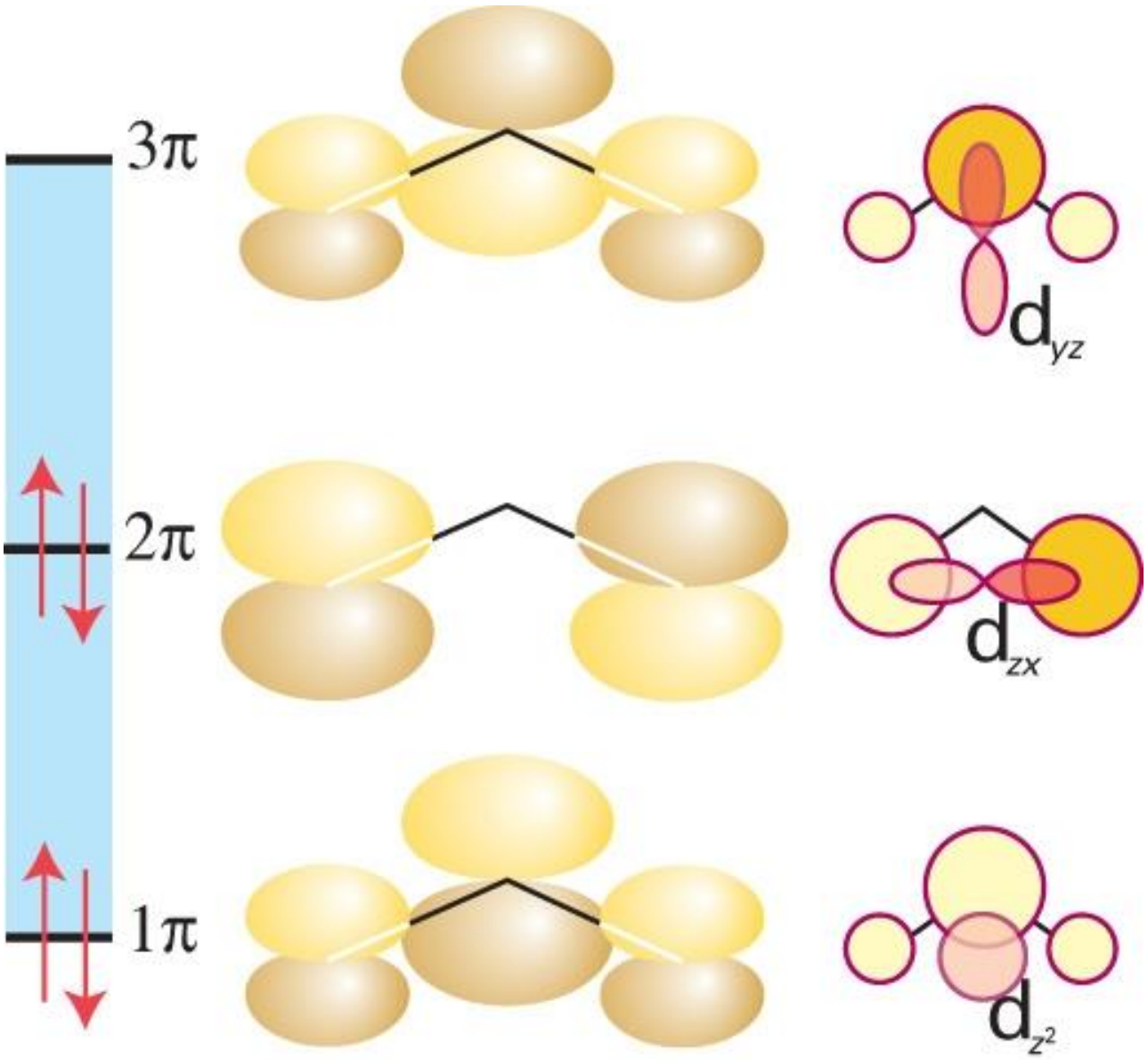


Figure 22.7* The molecular orbitals of the π system in cyclobutadiene; also shown are metal d orbitals of appropriate symmetry to form bonding interactions.

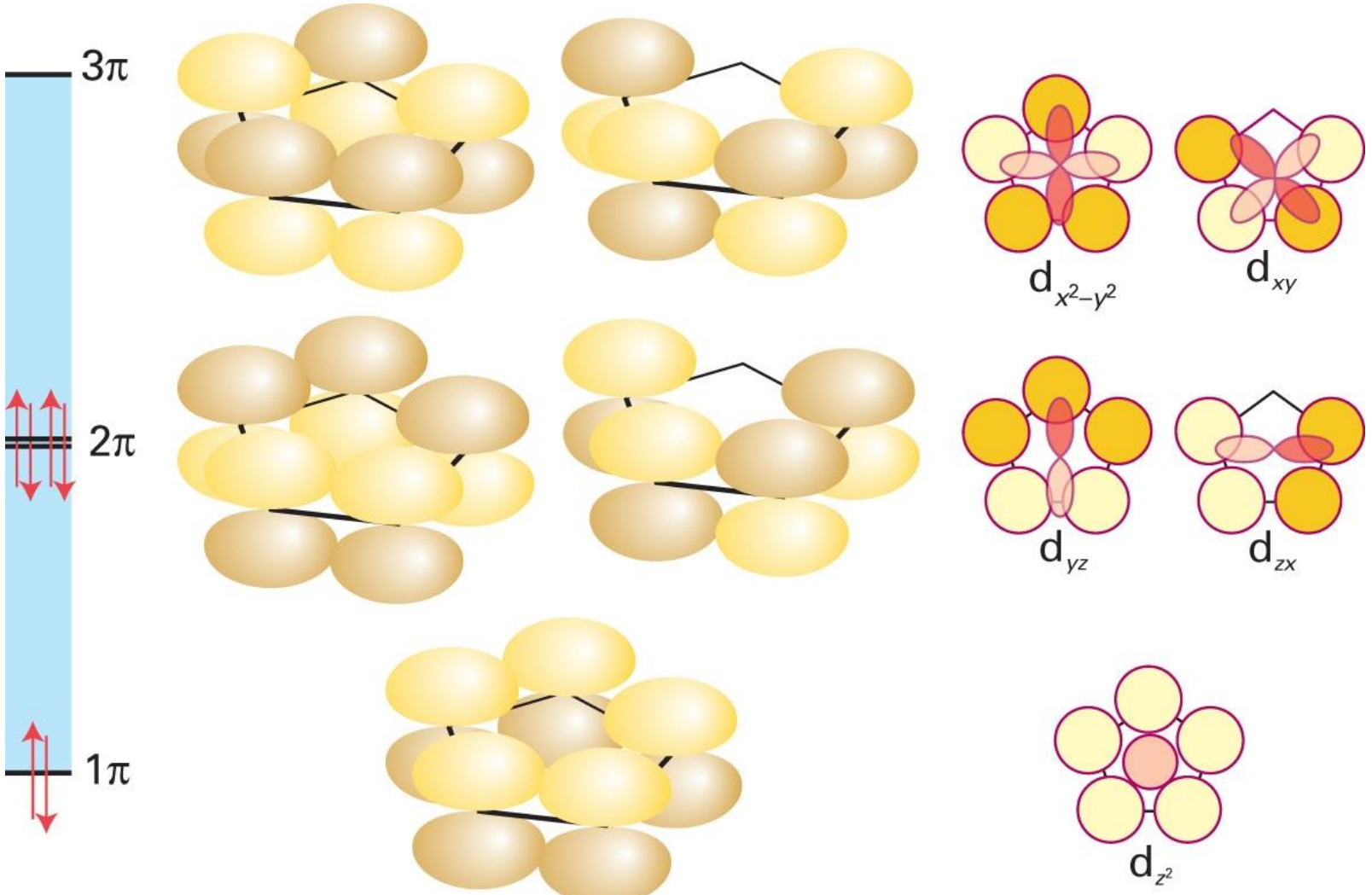
Shriver, Weller, etc. 6th ed.

Benzene and d-orbital interactions (as in bis-benzene Chromium(0)




3π
2π
1π
d_{yz}
d_{zx}
d_{z^2}

Orbital overlaps in cyclopentadienide



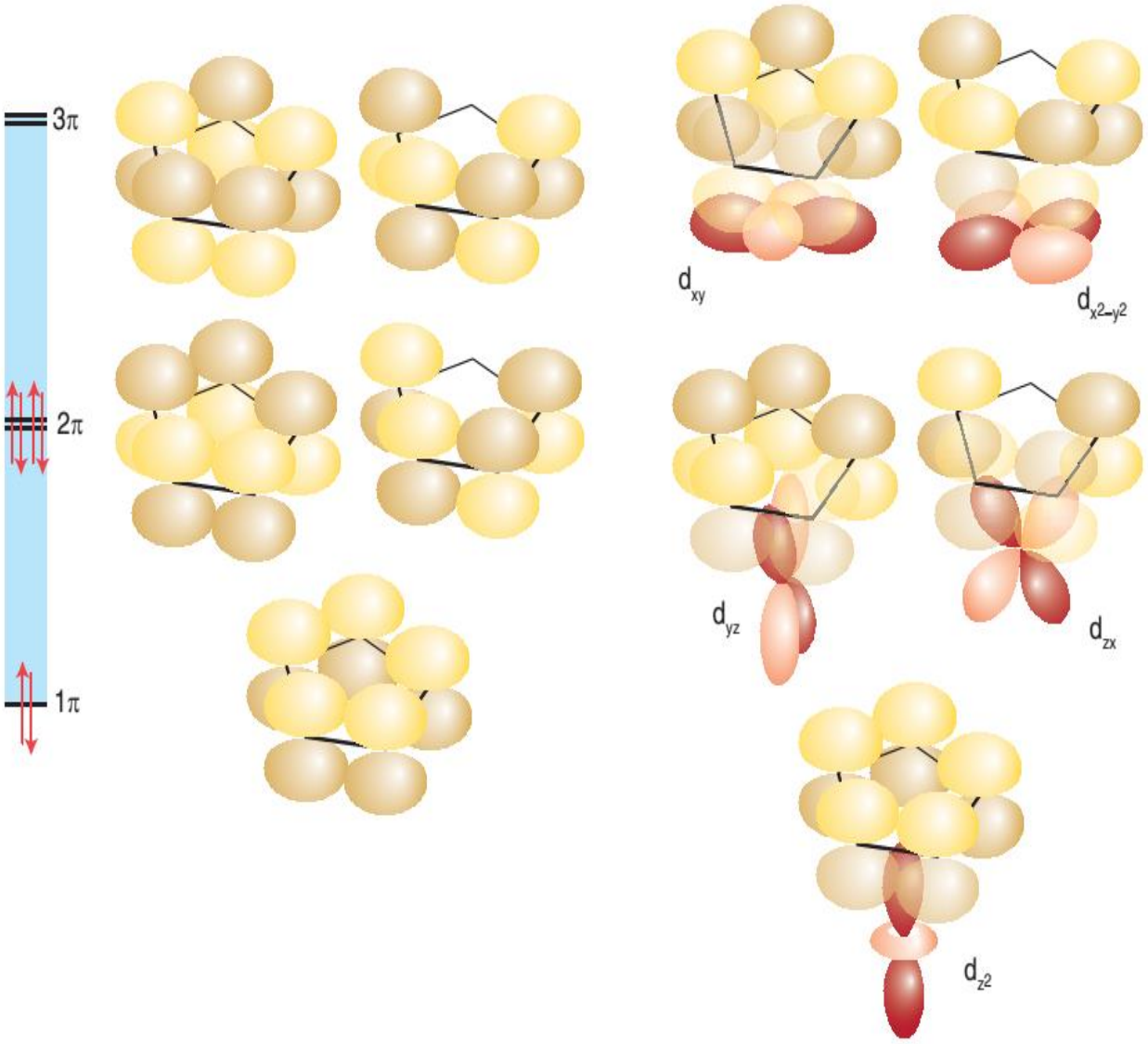
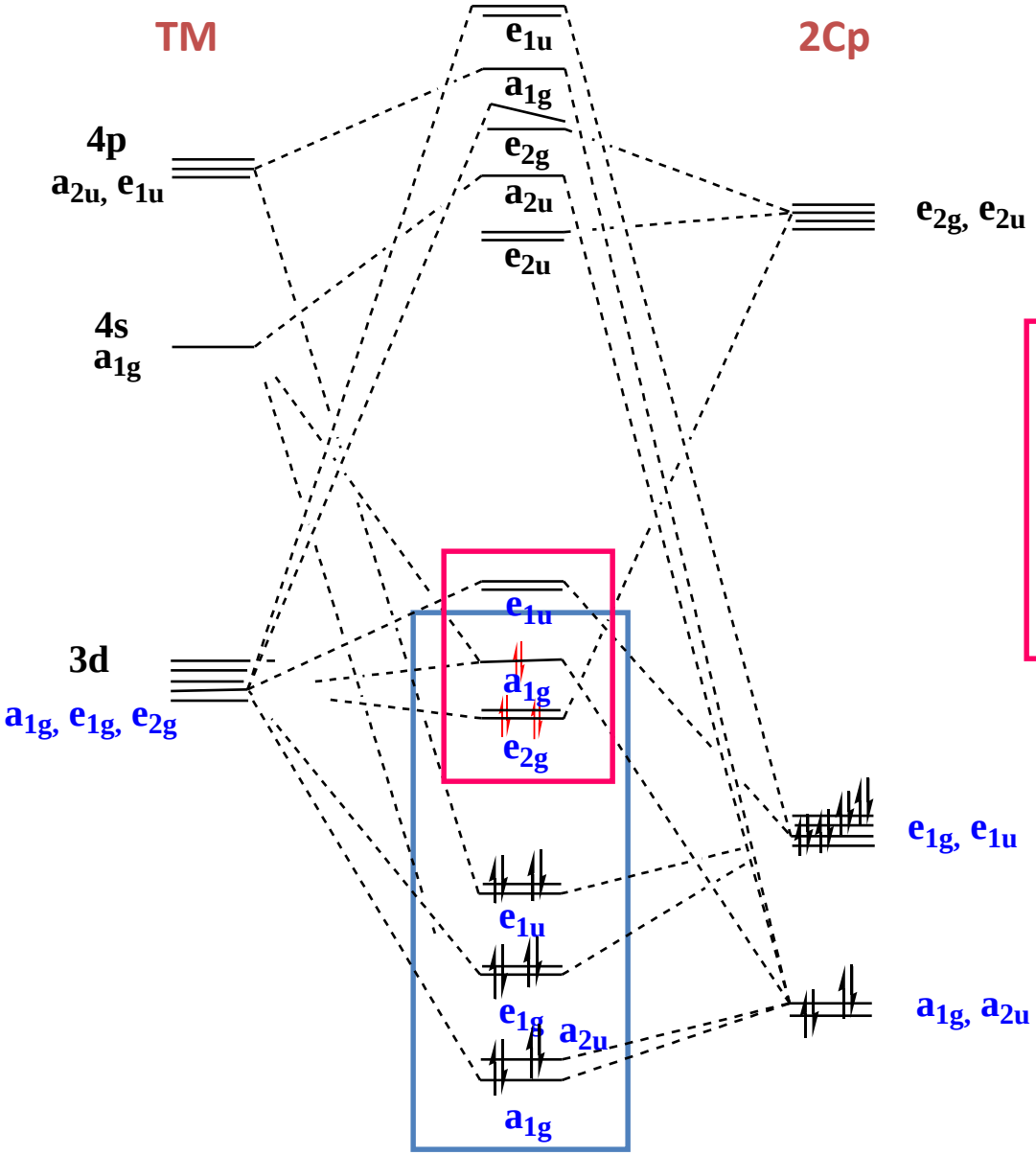
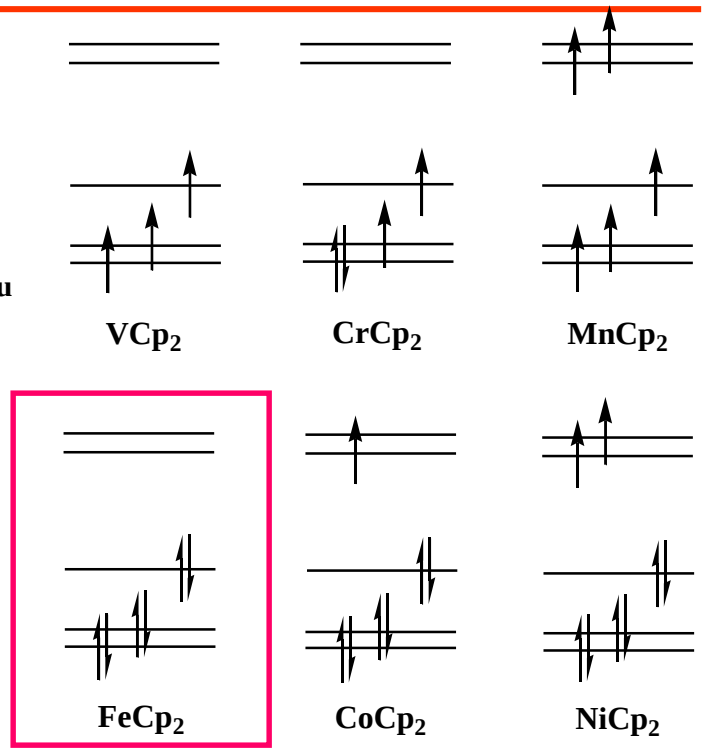


Figure 22.10* The molecular orbitals for the π systems of the cyclopentadienyl$^-$ group; also shown are metal d orbitals of appropriate symmetry to form bonding interactions.

Electronic structure and properties of the Cp_2M^n





18 Valence e^-, Closed shell

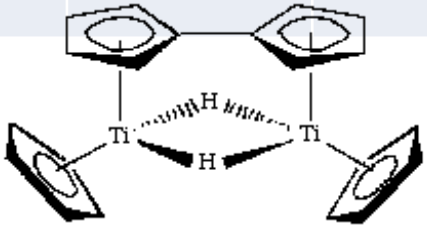
Diamagnetic
Thermally and air stable
Reversible Fe^{2+}/Fe^{3+} potential

http://www.ilpi.com/organomet/cp.html

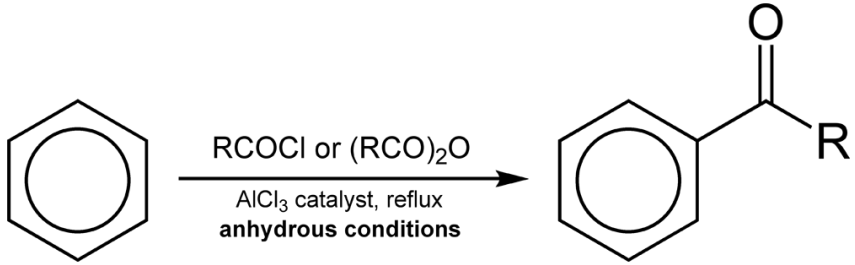
Metallocenes across the periodic table

	Cp_2V	Cp_2Cr	Cp_2Mn	Cp_2Fe	Cp_2Co	Cp_2Ni
Color	purple	red	amber	orange	purple	green
m.p.	162	172	193	173	173	173
d count **# unpaired**	15 3	16 2	17 5/1*	18 0	19 1	20 2
M-C distance (Angstroms)	2.28	2.17	2.38	2.06	2.12	2.20

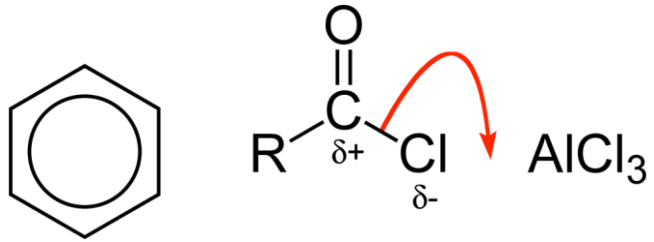
*Exists in both high and low spin states in thermal equilibrium

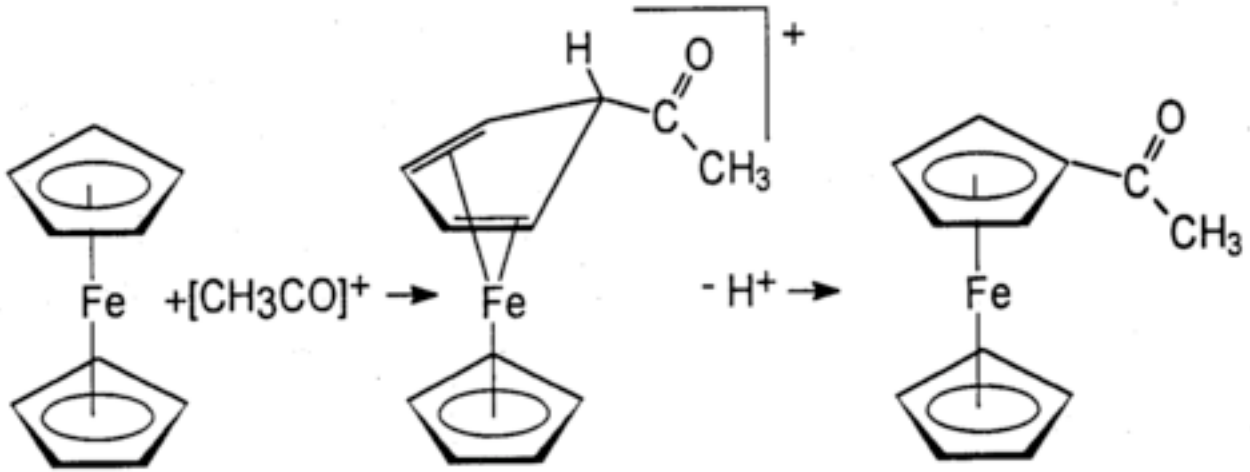


Ferrocene is a very useful molecule:

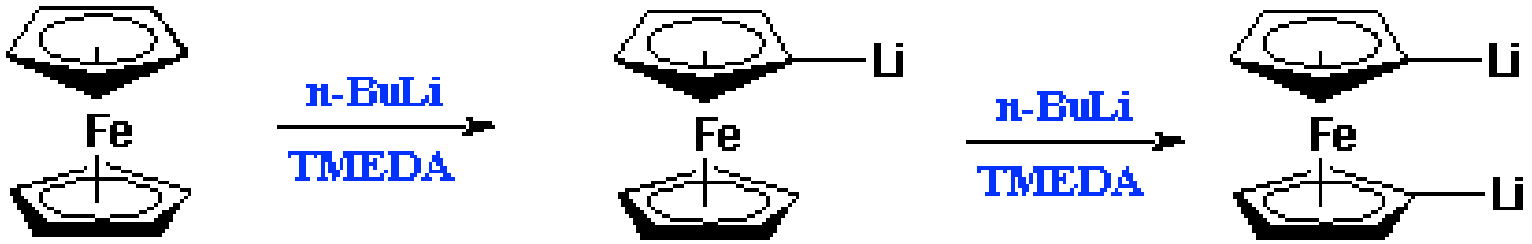


Friedel-Crafts Acylation





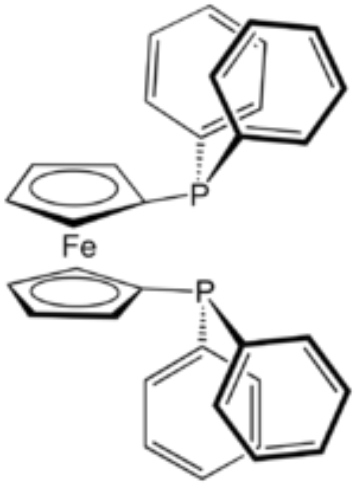
Lithiation of ferrocene:

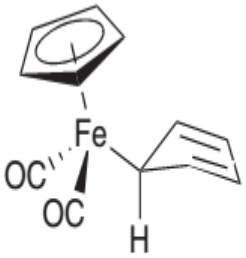


" Ferrocene "
Pauson, 1951

1-lithio-ferrocene

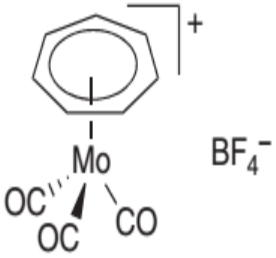
1,1'-dilithio-ferrocene





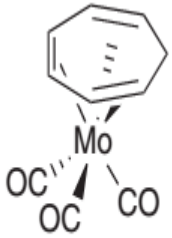
50

53 Cycloheptatriene

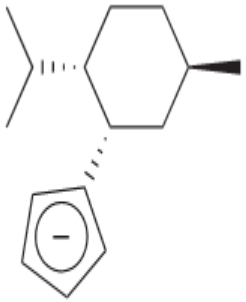


56

51



54



52 *neo*-Menthylcyclopentadienyl

55

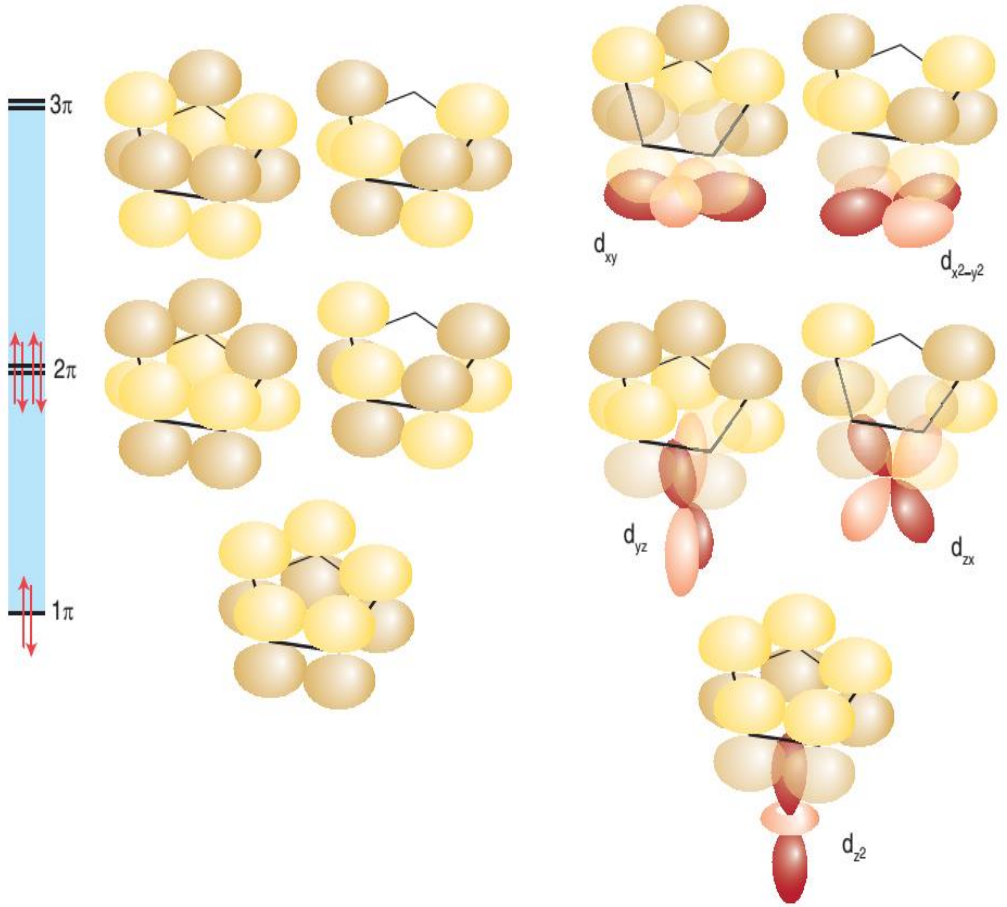
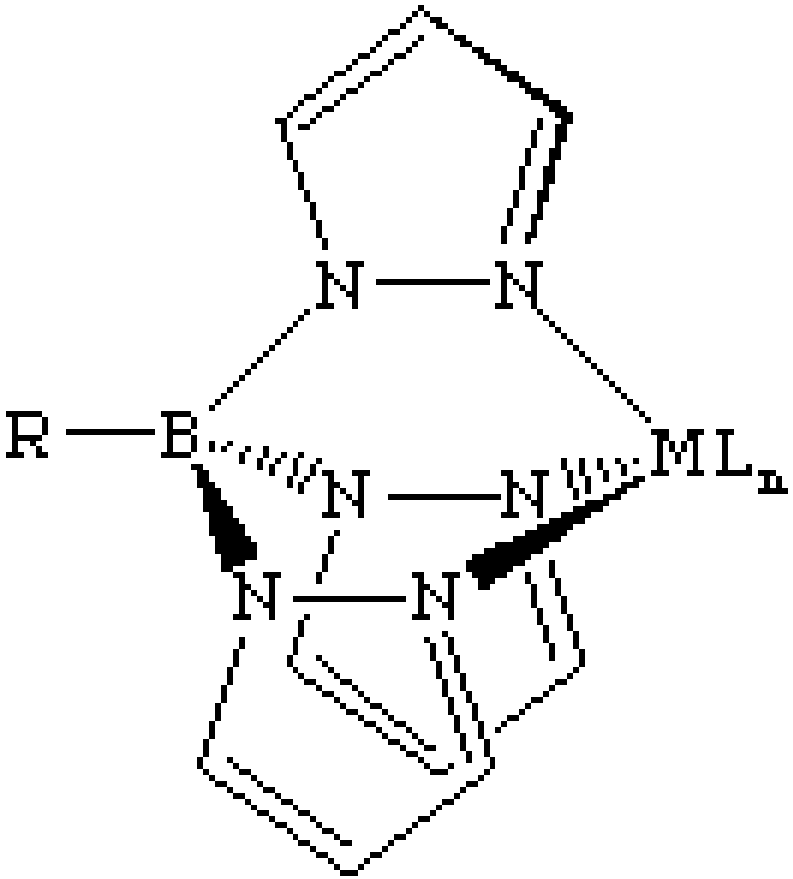


Figure 22.10* The molecular orbitals for the π systems of the cyclopentadienyl⁻ group; also shown are metal d orbitals of appropriate symmetry to form bonding interactions.

Pyrazolyl borate: A Cp wannabee or Trofimenko's scorpionate ligand



Transitioning to bent metallocenes

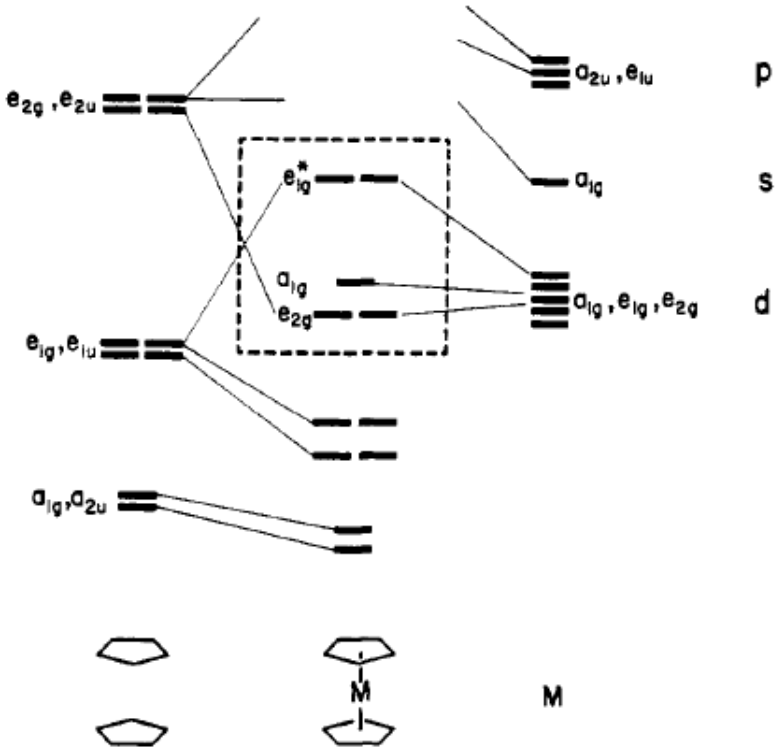


Figure 1. Interaction diagram for a D_{5d} metallocene. The frontier orbitals are in the box.

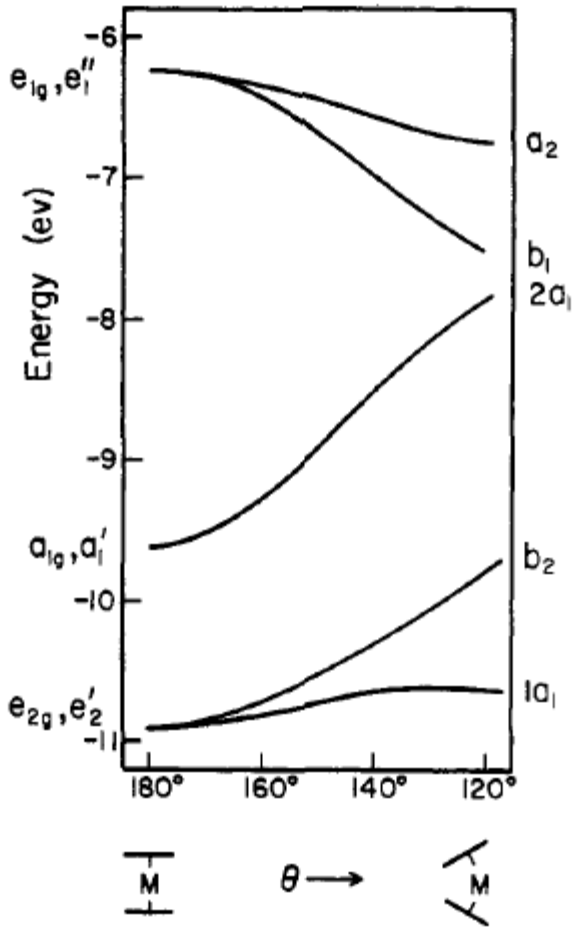
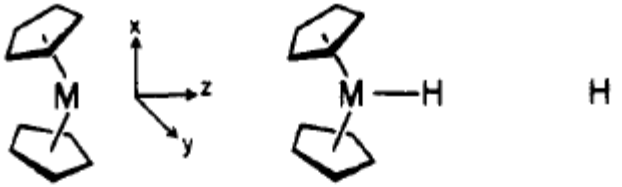


Figure 2. Cp_2M orbitals as a function of the bending angle θ. Bending is from an eclipsed D_{5d} form, but the labels at left are given for both D_{5d} and D_{5h} geometries.

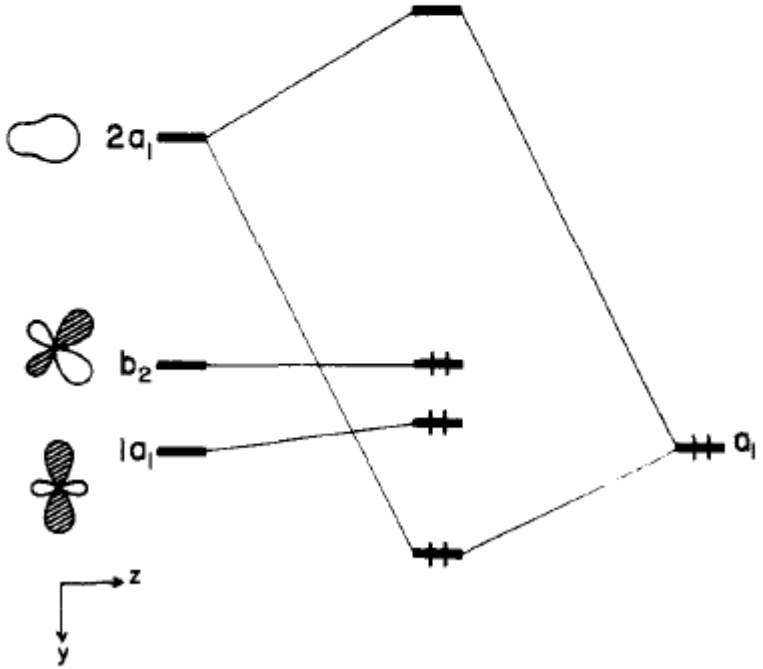
Walsh Diagram/Correlation Diagram

Structure and chemistry of bis(cyclopentadienyl)-MLn complexes

Lauher, J. W.; Hoffmann, R. , *J. Am. Chem. Soc.*, **1976**, 98, pp 1729–1742



4



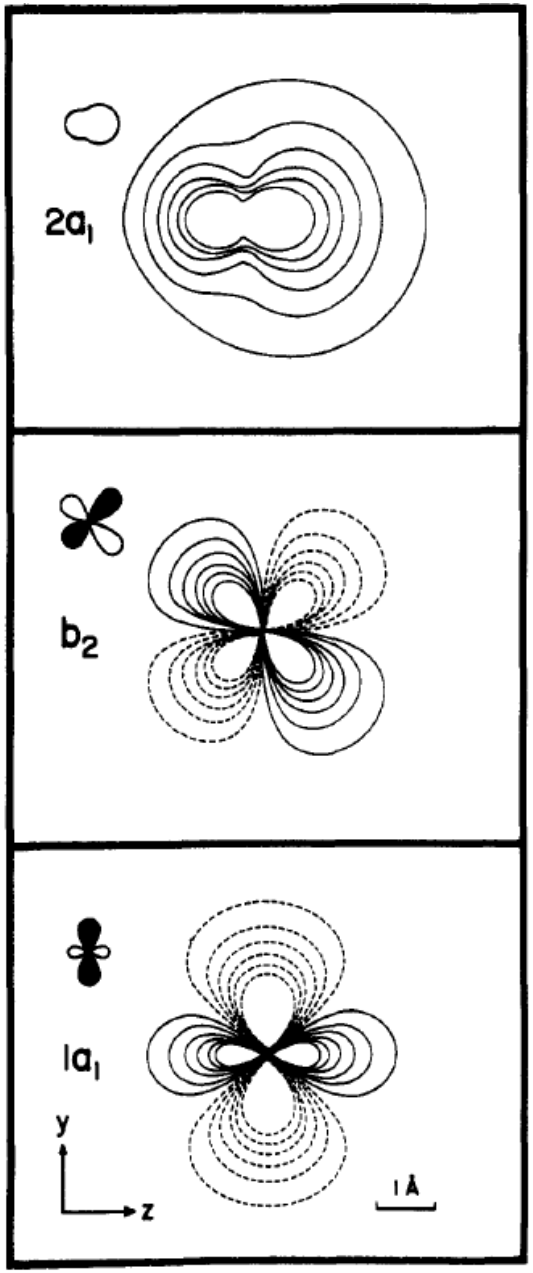
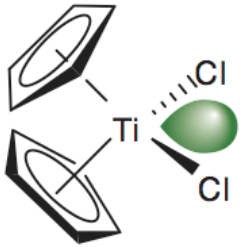


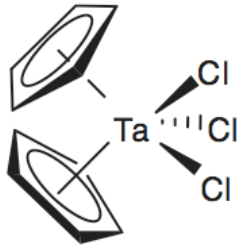
Figure 3. Contour diagram, in the *yz* plane, of the three important Cp_2M orbitals, computed at $\theta = 136°$. From top to bottom: $2a_1$, b_2, $1a_1$. Solid line = positive and dashed line = negative contour of the wave function. The contours are at intervals of 0.02.

Bent Metallocenes

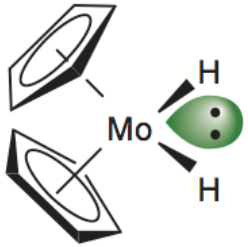
General form



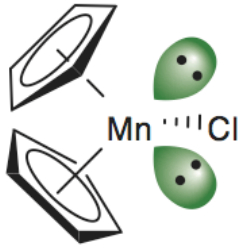
16-electron



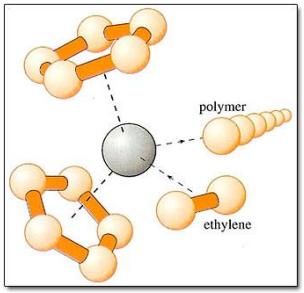
18-electron

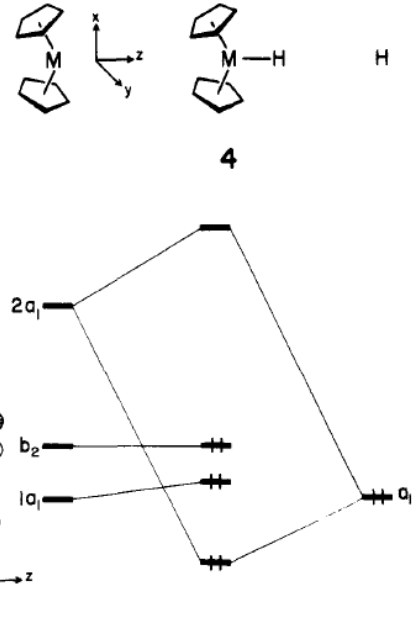


18-electron



18-electron



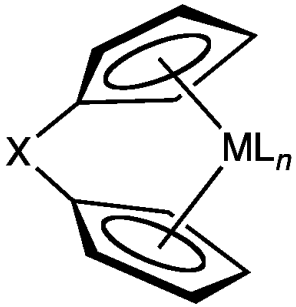


Coordination Chemistry Reviews

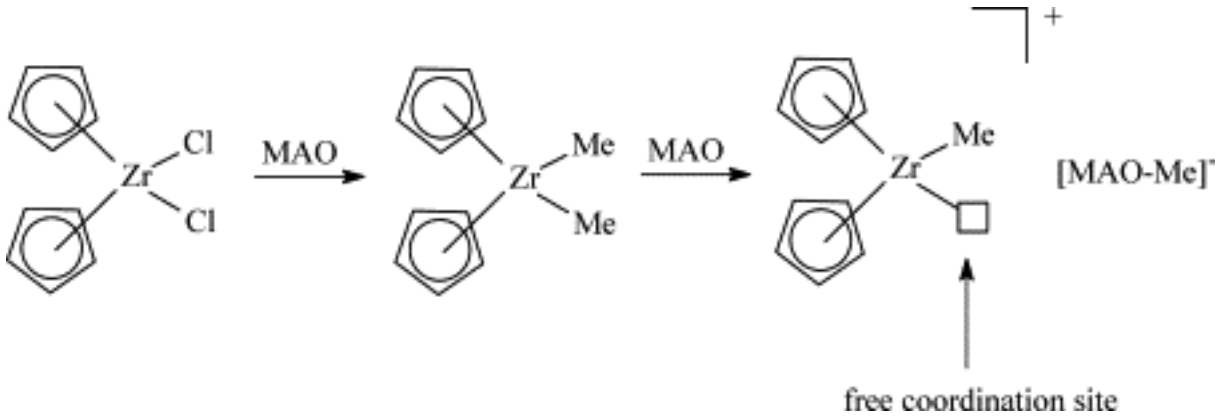
Volume 250, Issues 1–2, January 2006, Pages 242–258

Metallocene Complexes as Catalysts for Olefin Polymerization

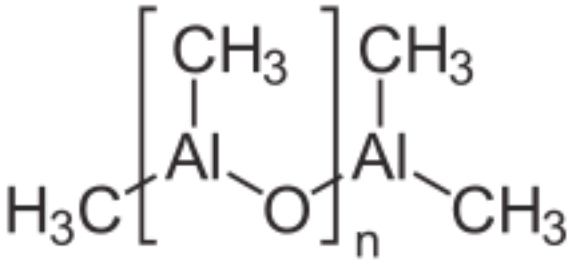
Ansa Metallocenes



Bent Metallocenes as Pro-Catalyst for Olefin Polymerization



What is MAO?



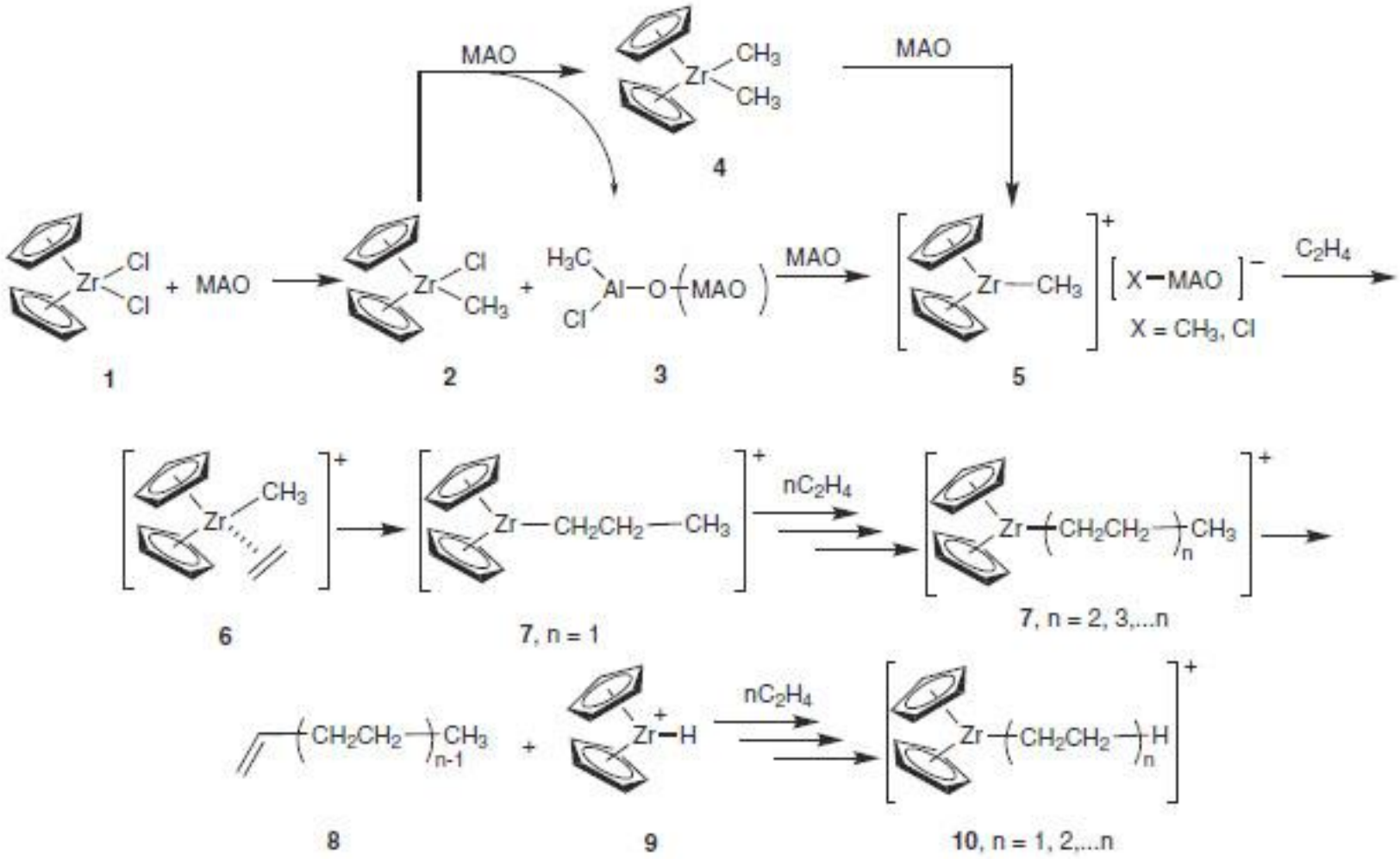
Helmut G. Alt, Erik H. Licht, Andrea I. Licht, Katharina J. Schneider

Metallacyclic metallocene complexes as catalysts for olefin polymerization

Coordination Chemistry Reviews, Volume 250, Issues 1–2, 2006, 2–17

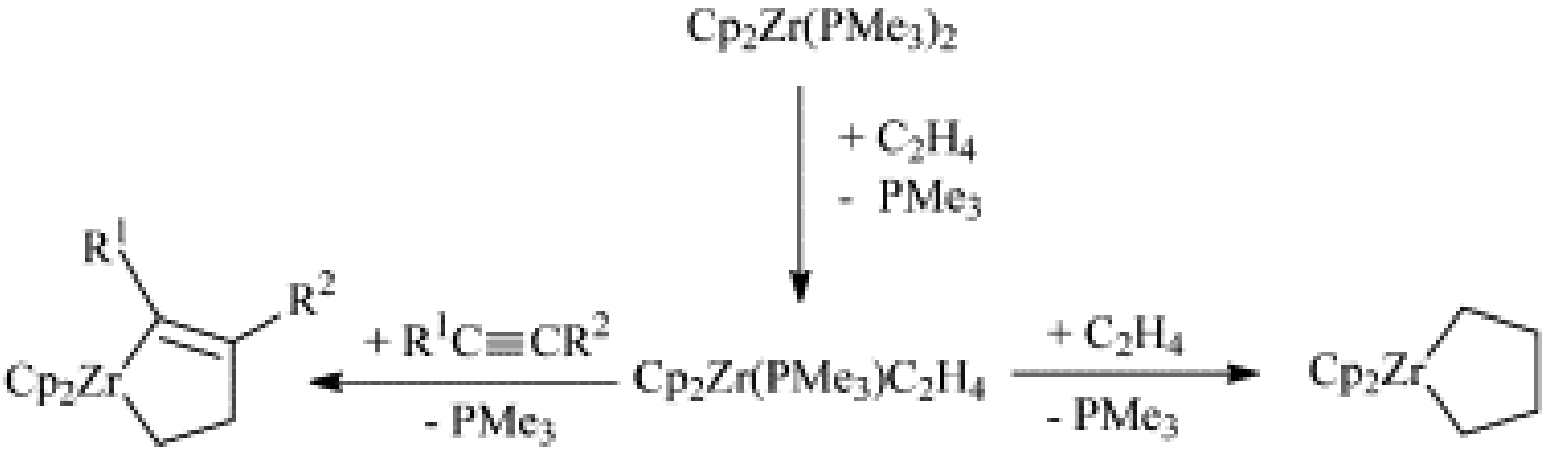
http://dx.doi.org/10.1016/j.ccr.2005.01.016

Mechanism of Olefin Polymerization???



Scheme 13. Proposed mechanism of Ziegler-Natta polymerization of C_2H_4 using the homogenous catalyst Cp_2ZrCl_2/MAO.

Metallacycles from Bent Metallocenes



R = alkyl, aryl

Helmut G. Alt, Erik H. Licht, Andrea I. Licht, Katharina J. Schneider

Metallacyclic metallocene complexes as catalysts for olefin polymerization

Coordination Chemistry Reviews, Volume 250, Issues 1–2, 2006, 2–17

http://dx.doi.org/10.1016/j.ccr.2005.01.016

What is the structure of $(C_5H_5)_2Fe(CO)_2$?
Is there an Fe analogue to the bent metallocene? No.
Ring Whizzing in Cp complexes—a part of the history of F. Albert Cotton