π (Olefin) Complexes and Metalloccenes

Lecture 7
The Novel: Olefin Polymerization and Isomerization

The Characters:

• Olefin Complexes
• Metalloccenes
• Bent Metalloccenes
• Metal Hydrides and Alkyls
• Alkyl Insertion Reactions
• Beta-H Elimination Reactions
• Stereoregular Catalysis
• Asymmetric Catalysis
Olefin to Metal Binding

\[ \sigma\text{-donation via the filled alkene } \pi\text{-system} \]
\[ \pi\text{-back donation via the empty alkene } \pi^*\text{-system} \]

Influences of Metal Oxidation State and of Olefin on Bonding

\[ \text{Pt}(2+) \quad \text{C} = \text{C} = 1.37\text{Å} \quad \text{Zeiss's Salt} \]
\[ \text{Pt}(0) \quad \text{C} = \text{C} = 1.43\text{Å} \]
\[ \text{Pt}(+2) \quad \text{C}--\text{C} = 1.49\text{Å} \quad \text{metalallocyclopropane} \]
<table>
<thead>
<tr>
<th>Ethylene Complex</th>
<th>$\nu$C=CN (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free Ethylene</td>
<td>1623</td>
</tr>
<tr>
<td>$[\text{Ag}(\text{H}_2\text{C}=\text{CH}_2)_2]^+$</td>
<td>1584</td>
</tr>
<tr>
<td>$\text{Fe(CO)}_4(\text{H}_2\text{C}=\text{CH}_2)$</td>
<td>1551</td>
</tr>
<tr>
<td>$[\text{Re(CO)}_4(\text{H}_2\text{C}=\text{CH}_2)_2]^+$</td>
<td>1539</td>
</tr>
<tr>
<td>$[\text{CpFe(CO)}_2(\text{H}_2\text{C}=\text{CH}_2)]^+$</td>
<td>1527</td>
</tr>
<tr>
<td>$\text{Pd}_2\text{Cl}_4(\text{H}_2\text{C}=\text{CH}_2)_2$</td>
<td>1525</td>
</tr>
<tr>
<td>$[\text{PtCl}_3(\text{H}_2\text{C}=\text{CH}_2)]^-$</td>
<td>1516</td>
</tr>
<tr>
<td>$\text{CpMn(CO)}_2(\text{H}_2\text{C}=\text{CH}_2)$</td>
<td>1508</td>
</tr>
<tr>
<td>$\text{Pt}_2\text{Cl}_4(\text{H}_2\text{C}=\text{CH}_2)_2$</td>
<td>1506</td>
</tr>
<tr>
<td>$\text{CpRh(H}_2\text{C}=\text{CH}_2)_2$</td>
<td>1493</td>
</tr>
</tbody>
</table>

All are lower. Why?

Propose a structure for the Rh complex. And the others as well! . . .
Problem: To which of the following (each with a single open coordination site) will trifluoroethylene bond to the most strongly? Why?

a) [Diagram of a coordination complex with a question mark]

b) [Diagram of a coordination complex with a question mark]

c) [Diagram of a coordination complex with a question mark]

---

R\_C≡C\_R

M

R\_C≡C\_R

M\_M
Chelating diolefins

norbomadiene complex

cyclooctadiene complex

\[
\text{Ni} \quad \text{BF}_4^- \\
\text{Ir} \quad \text{PCy}_3 \quad \text{PF}_6^-
\]
**Problem:** The \( \text{Cp}_2\text{Rh}_2[\mu-(\text{CF}_3\text{C}≡\text{CCF}_3)](\text{CO})(\text{CNR}) \) complex shown above has a Rh-Rh bond distance of 2.67 Å, strongly indicating a covalent bond between the rhodium atoms. How would you electron count this complex to accommodate a Rh-Rh covalent bond?
Electronic structure and properties

TM

4p
a₂u, e₁u

4s
a₁g

3d
a₁g, e₁g, e₂g

2Cp

e₁u

a₁g

e₂g

a₂u

e₂u

e₂g, e₂u

VCp₂

CrCp₂

MnCp₂

FeCp₂

CoCp₂

NiCp₂

18 Valence e⁻, Closed shell

Diamagnetic
Thermally and air stable
Reversible Fe²⁺/Fe³⁺ potential

http://www.ilpi.com/organomet/cp.html
<table>
<thead>
<tr>
<th></th>
<th>Cp₂V</th>
<th>Cp₂Cr</th>
<th>Cp₂Mn</th>
<th>Cp₂Fe</th>
<th>Cp₂Co</th>
<th>Cp₂Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Color</strong></td>
<td>purple</td>
<td>red</td>
<td>amber</td>
<td>orange</td>
<td>purple</td>
<td>green</td>
</tr>
<tr>
<td><strong>m.p.</strong></td>
<td>162</td>
<td>172</td>
<td>193</td>
<td>173</td>
<td>173</td>
<td>173</td>
</tr>
<tr>
<td><strong>d count</strong></td>
<td>15</td>
<td>16</td>
<td>17</td>
<td>18</td>
<td>19</td>
<td>20</td>
</tr>
<tr>
<td><strong># unpaired</strong></td>
<td>3</td>
<td>2</td>
<td>5/1*</td>
<td>0</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td><strong>M-C distance</strong></td>
<td>2.28</td>
<td>2.17</td>
<td>2.38</td>
<td>2.06</td>
<td>2.12</td>
<td>2.20</td>
</tr>
</tbody>
</table>

*Exists in both high and low spin states in thermal equilibrium
Derivatization of Ferrocene:

苯 \xrightarrow{RCOCl \text{ or } (RCO)_2O, \text{AlCl}_3 \text{ catalyst, reflux, anhydrous conditions}} \text{RCO}_R

苯：

\begin{align*}
\text{RCO}_R & \xrightarrow{\text{AlCl}_3} \text{RCOCl}_R \\
\text{RCO}_R & \xrightarrow{\text{AlCl}_3} \text{RCO}_R
\end{align*}

\text{Fe} + [\text{CH}_3\text{CO}]^+ \xrightarrow{\text{H}^+} \text{Fe}

\text{Fe} + [\text{CH}_3\text{CO}]^+ \xrightarrow{\text{H}^+} \text{Fe}
Lithiation of ferrocene:

"Ferrocene" Pauson, 1951

1-lithio-ferrocene

1,1'-dilithio-ferrocene
Pyrazolyl borate: A Cp wannabee or Trofimenko’s scorpionate ligand
Structure and chemistry of bis(cyclopentadienyl)-MLn complexes

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

**Figure 2.** Cp$_2$M orbitals as a function of the bending angle $\theta$. Bending is from an eclipsed $D_{5d}$ form, but the labels at left are given for both $D_{5d}$ and $D_{5h}$ geometries.
Figure 3. Contour diagram, in the $yz$ plane, of the three important $\text{Cp}_2\text{M}$ orbitals, computed at $\theta = 136^\circ$. 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 Metalloccenes

General form
16-electron
18-electron

18-electron
18-electron

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

Ansa Metalloccenes

ML_n

Metalloccene Complexes as Catalysts for Olefin Polymerization
*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 C₂H₄ using the homogenous catalyst Cp₂ZrCl₂/MAO.
Metallacycles from Bent Metalloccenes
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

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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
Ring Slippage in Cp complexes

\[ \text{CpRe(CO)}_3 \xrightarrow{\text{PMe}_3} \text{CpRe(CO)}_2(\text{PMe}_3) \]