Metallocenes
and Related $\pi$ Complexes
Electronic structure and properties

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

- $4p_{a_2u, e_{1u}}$
- $4s_{a_{1g}}$
- $3d_{a_{1g}, e_{1g}, e_{2g}}$

- $e_{1u}$
- $e_{2g}$
- $e_{1g}$
- $a_{2u}$
- $a_{1g}$

18 Valence e-, Closed shell

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

TM 2Cp

VCp$_2$
CrCp$_2$
MnCp$_2$
FeCp$_2$
CoCp$_2$
NiCp$_2$
<table>
<thead>
<tr>
<th></th>
<th>(\text{Cp}_2\text{V})</th>
<th>(\text{Cp}_2\text{Cr})</th>
<th>(\text{Cp}_2\text{Mn})</th>
<th>(\text{Cp}_2\text{Fe})</th>
<th>(\text{Cp}_2\text{Co})</th>
<th>(\text{Cp}_2\text{Ni})</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 # unpaired</strong></td>
<td>15 3</td>
<td>16 2</td>
<td>17 5/1*</td>
<td>18 0</td>
<td>19 1</td>
<td>20 2</td>
</tr>
<tr>
<td><strong>M-C distance (Angstroms)</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

![Diagram of a molecule with Ti and Cp groups](image)
Ring Whizzing in Cp complexes—a part of the history
Or, is there an Fe analogue to the bent metallocene
i.e., What is the structure of \((C_5H_5)_2Fe(CO)_2\)?
Ring Slippage in Cp complexes

\[
\begin{align*}
\text{CpRe(CO)}_3 & \quad \xrightarrow{\text{PMe}_3} \quad \text{CpRe(CO)}_2(\text{PMe}_3) \\
\quad 11 & \quad 14 & \quad 13
\end{align*}
\]
Pyrazolyl borate: A Cp wannabee or Trofimenko’s scorpionate ligand
Structure and chemistry of bis(cyclopentadienyl)-MLn complexes
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 Metalocenes**

General form

16-electron

18-electron

18-electron

**Ansa Metalocenes**

\[ X \text{ML}_n \]

Coordination Chemistry Reviews

Volume 250, Issues 1–2,
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Metallocene Complexes as Catalysts for Olefin Polymerization
The \( \pi \)-allyl ligand. 3-electron donor as neutral ligand, 4-electron donor as anionic.

\[
\eta^3-\text{C}_3\text{H}_5: \quad \begin{array}{c}
\text{Ni} \\
\text{Ni}
\end{array}
\]

\[
\eta^1-\text{C}_3\text{H}_5: \quad \begin{array}{c}
\text{OC} \\
\text{OC}
\end{array}
\]

Bridging \( \text{C}_3\text{H}_5: \)

\[
[Mn(\text{CO})_5]^- + \text{C}_3\text{H}_5\text{Cl} \rightarrow (\eta^1-\text{C}_3\text{H}_5)\text{Mn(}\text{CO})_5 \\
+ \text{Cl}^- \rightarrow (\eta^3-\text{C}_3\text{H}_5)\text{Mn(}\text{CO})_4 \\
\Delta \text{ or } h\nu + \text{CO}
\]

Figure 5-2 Examples of Allyl Complexes
Just a little homework:

• Question 5-7
• A roadmap problem: Question 5.9
• A mistake in the problem: Question 5-14