MO Description of σ bonding in ML₄ tetrahedral

The tetrahedral geometry is electronically favored by d₈ or d⁹ metal complexes where the non-bonding orbitals are either 1/2 or entirely filled, respectively.

Organometallic Reaction Mechanisms

**Ligand association/disassociation**

CuBr + PBU₃ insoluble toluene (PBU₃)₃CuBr soluble

inactive catalyst

active catalyst for cross coupling

**Ligand Exchange:**

Associative - common for 16e- complexes

rate = k[py][Pt]

rate will depend on nature (sterics, electronics) of Nu and MLn

Disassociative - common for 18 e- complexes

Rate will depend on nature of leaving L, sometimes on new L'

-L slow:

Rate = k[ML]

+L' slow:

Rate = k'[ML][L']

Hydrogenation
Exchange rates vary over 20 orders of magnitude

Figure 1.26. Range of water exchange rate constants (log k_{rel}(s^{-1})) and mean residence times (t) for primary shell water molecules on aqua metal ions at 25 °C (the dotted line represents Tsche’s inelastic boundary [78]).

Oxidative Addition and Reductive Elimination

LnM(n) + X -> oxidative addition
LnM(n+2) -> reductive elimination

"O.A." and "R.E." give NO information on mechanism: can be concerted 3-centered, SN2-like or radical

Note cis product from concerted OA

Radical chain mech.

Stereochemical Issues

Vinyl and Aryl C-X much more reactive than allyl C-X despite more e-rich alkyl C-X

Why? precoordination

Precoordination with allylic substituted allows O.A. to moderately activated bonds:

Precoordination can even allow activation of C-H bonds in some cases:

Rhazinilam
Sames, JACS, 2002, 6900
Oxidative Addition: Thermodynamics

Bond strength is reflected in ease of O.A., with exceptions

<table>
<thead>
<tr>
<th>Rxn</th>
<th>BDE (kcal/mol) of Cleaved Bond</th>
<th>est ΔG for O.A.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir = Ir(t)</td>
<td>CH₃</td>
<td>56</td>
</tr>
<tr>
<td>L₅Ir(C₄H₉)₃L₅</td>
<td>H₂C</td>
<td>104</td>
</tr>
<tr>
<td>L₅Ir(C₄H₉)₃L₅</td>
<td>H-H</td>
<td>104</td>
</tr>
<tr>
<td>L₅Ir(C₄H₉)₃L₅</td>
<td>H₂CCH₃</td>
<td>88</td>
</tr>
</tbody>
</table>

M-H bonds are stronger than we might predict
O.A. to C-H and C-C remain very challenging, but could be valuable (more on this later in the course)

A picture of oxidative addition from calculations.

From CHNF, figure 5.2
Oxidative addition: reactivity trends

**Reaction rate increases with electron density on Pd**

\[ \text{OMe} \quad \bullet \quad \text{H} \quad \bullet \quad \text{CH}_3 \quad \bullet \quad \text{F} \quad \bullet \quad \text{Cl} \quad \bullet \quad \text{CF}_3 \]

\[ y = -2.8259x - 0.4246 \]

Amatore, *Organometallics*, 1995, 1818

**Reaction rate decreases with electron density on ArX**

\[ \text{OMe} \quad \bullet \quad \text{H} \quad \bullet \quad \text{Me} \quad \bullet \quad \text{tBu} \quad \bullet \quad \text{Cl} \quad \bullet \quad \text{CO}_2\text{Et} \quad \bullet \quad \text{CF}_3 \quad \bullet \quad \text{CN} \quad \bullet \quad \text{NO}_2 \]

\[ y = 2.547x + 0.078 \]

Jutand, *OM*, 1995, 1810
Oxidative addition: reactivity trends

With sp3 electrophiles, SN2 pathway dominates with Pd(0)
Rxns show other traits of SN2 (solvent effects, leaving group trends)

From Fu, *ACIEE, 2002*, 3910
See also Fu, *ACIEE, 2003*, 5749
Direct single electron OA:
\[ R-X + 2[\text{Co(CN)}_3]^3 \rightarrow R^+ + X-\text{Co}^{(CN)}_3^3 \rightarrow R-\text{Co}^{(CN)}_3^3 + X-\text{Co}^{(CN)}_3^3 \]

\( X = \text{halide} \)

Net single electron OA
\[ [\text{CpFe(CO)}_3]^2 + X_2 \rightarrow \text{CpFe}^t(X)\text{CO}_2 + \text{CpFe}^t(\text{CO}_3) \rightarrow 2 \text{CpFe}^t(X)\text{CO}_2 \]

Single electron OA in catalysis

Fu, JACS, 2005, 10482

Reductive elimination: reactivity trends (substrate)

Hartwig, JACS, 2003, 16347
OM, 2003, 2775
Reductive elimination: reactivity trends (substrate + catalyst)

\[
\begin{align*}
&\text{MeO}_2\text{C}_\text{H}_3\text{Fe(CO)}_3^- + \text{Ph}_3\text{C}_\text{Cl} \\
&\xrightarrow{\text{Fe}^\text{II}} \xrightarrow{110^\circ \text{C}} \text{MeO}_2\text{C}_\text{H}_3\text{Fe}^\text{II} & \text{R} & \text{R} & \% \text{ Yield} \\
&\text{Hydrogen} & >90 & 95 & k_{\text{cr}}/k_{\text{cu}} \approx 2 \\
&\text{CF}_3 & 5-25 & & & \\
\end{align*}
\]

Oxidation-induced reductive elimination

\[
\begin{align*}
&\text{PF}_6^- + \text{MeO}_2\text{C}_\text{H}_3\text{Fe}^\text{III} \\
&\xrightarrow{\text{ClMg}} \text{MeO}_2\text{C}_\text{H}_3\text{Fe}^\text{II} \xrightarrow{\text{H}_3\text{C}} \xrightarrow{\text{MeO}_2\text{C}_\text{H}_3\text{Fe}^\text{III}} \text{MeO}_2\text{C}_\text{H}_3\text{Fe}^\text{II} \\
&\xrightarrow{\text{ox. at M}} \text{MeO}_2\text{C}_\text{H}_3\text{Fe}^\text{II} \xrightarrow{\text{ox. at L}} \text{MeO}_2\text{C}_\text{H}_3\text{Fe}^\text{II} \\
&\xrightarrow{\text{H}_2\text{O}_2} \text{MeO}_2\text{C}_\text{H}_3\text{Fe}^\text{II} \xrightarrow{\text{ox. at L}} \text{MeO}_2\text{C}_\text{H}_3\text{Fe}^\text{II} \xrightarrow{-\text{CO}_2, -\text{H}^+} \text{MeO}_2\text{C}_\text{H}_3\text{Fe}^\text{II} \xrightarrow{-\text{CO}_2, -\text{HO}^-} \text{MeO}_2\text{C}_\text{H}_3\text{Fe}^\text{II} \\
&\xrightarrow{-70\%} \text{MeO}_2\text{C}_\text{H}_3\text{Fe}^\text{II} \xrightarrow{\text{ox. at L}} \text{MeO}_2\text{C}_\text{H}_3\text{Fe}^\text{II} \xrightarrow{\text{ox. at L}} \text{MeO}_2\text{C}_\text{H}_3\text{Fe}^\text{II} \\
&\xrightarrow{-70\%} \text{MeO}_2\text{C}_\text{H}_3\text{Fe}^\text{II} \xrightarrow{\text{ox. at L}} \text{MeO}_2\text{C}_\text{H}_3\text{Fe}^\text{II} \xrightarrow{\text{ox. at L}} \text{MeO}_2\text{C}_\text{H}_3\text{Fe}^\text{II} \\
&\text{Donaldson, OL, 2005, 2047}
\end{align*}
\]
Oxidative addition: applications of Sn2-like OA and carbonylation

Note: 'CO insertion' is unfortunate name because alkyl group moves.

Rate increases with size and nucleophilicity of R
Rarely see double insertion (uphill by ~10 kca/mol - mostly b/c entropy decrease); exceptions: OL, 2009, 1321.

Rel rate: $k_{H} / k_{alkyl} = 10^7$ for Rh(III) and Co(III) even though insertion into M-R favored thermodynamically.

Spherical s orbital for H allows overlap with both olefin and M in transition state. Harder with directional orbital.

K > 1 for e- poor metals (e.g. Zr(IV), d^5)
K < 1 for e- rich metals (e.g. Pd(II), d^8)
Agostic interactions: stable intermediates on the way to α- or β-hydride elimination

- Stable interactions often found with electron-poor metals
- Especially common with d8 metals
- Computation with Ti(carbene) and W(carbyne) estimates BDE ≤ 10 kcal/mol (OM, 2006, 118)

**Schrock, et al**


**Figure 4.** A perspective view of the molecular structures of Ta(Cp*HCl)2BN3(Cp*HCl)PPh3 (L). Except for P(1) and the first
phosphorus-bound chloride, all hydrogen atoms have been omitted for clarity. The thermal ellipsoids do not represent the experimental values
(see Figure 3).

**Things to note**

- Ta(III) carbene (d2)
- Small Ta-C-H angle (78°)
- Long C-H bond (1.14 Å, average here is 1.085 Å)
- i.e. weakening of C-H bond
- Big Ta-C-C angle (170°)
- Unrelated to agostic interactions:
  - Ethylene C' s out of plane (average 0.33 Å out of 4H plane)
  - Long ethylene C-C distance (1.48 v. 1.34 when free)

Ready; Catalysis Organometallics

Agostic interactions are likely unobserved intermediates in normal transition metal-catalyzed reactions:

**Heck Rxn:**

\[
\begin{align*}
\text{Cp}_{2}ZrCl_2 & \xrightarrow{\text{catalyst for ethylene polymerization}} \text{cation stabilized by agostic interaction} \\
\text{Cp}_2ZrCl_2 & \xrightarrow{\text{lewis acid}} \text{catalyst for ethylene polymerization cation stabilized by agostic interaction} \\
\text{PdCl}_2 & \xrightarrow{\text{transmetalation}} \text{Generation of Pd(0)} \\
\text{PdCl}_2 & \xrightarrow{\text{Et}_2\text{Zn}} \text{Generation of Pd(0)} \\
\text{H}_2\text{C} & \xrightarrow{\text{-CH}_2\text{CH}_2} \text{β-Hydride elim.} \\
\text{H}_2\text{C} & \xrightarrow{\text{-CH}_3\text{CH}_3} \text{β-Hydride elim.} \\
\end{align*}
\]

**α-agostic interactions can happen, too**

**Likely intermediate in α-elimination:**

\[
\begin{align*}
\text{Cp*TaClBn}_3 & \xrightarrow{\text{Schrock, Accts, 1979, 98}} \text{Likely intermediate in α-elimination:} \\
\text{L}_2\text{TaClBn}_3 & \xrightarrow{\text{PhCH}_3} \text{Ph} \\
\end{align*}
\]
Agostic interaction can be dynamic

Nolan, ACIEE, 2005, 2512

'Recyclometalated' Ir(III)bis(NHC)

Reversible deprotonation with Et3N to form Ar-Rh bond

Milstein, JACS, 1998, 12539
Hydroformylation (7 bil Kg/yr)

\[ R\text{H} \xrightarrow{\text{cat. Rh(I)}} R\text{H}_2\text{CO (syn gas)} \xrightarrow{\text{linear}} \text{RCHO} \]

4-centered reactions:

\[ 2\times2 \quad \text{R NH}_2 + \text{R'} \xrightarrow{\text{cat. Cp}_2\text{Zr(NHR)}_2} \text{see Eur. JOC, 2003, 935} \]

σ-bond metathesis

\[ \text{-HCMe}_3 \xrightarrow{\text{Cp}^+\text{Sc-CH}_3} \text{Cp}^+\text{Sc-CH}_3 \xrightarrow{\text{Cp}^+\text{Sc-CH}_2} \text{Cp}^+\text{Sc-CH}_2 \xrightarrow{\text{Cp}^+\text{Sc-CH}_3} \text{Tilley, Jacs, 2003, 7971} \]
**Stoichiometric Use:**
Great way to make Grinards, alkyl zinics, cuprates, stannanes etc. Esp useful on small scale where O.A. to R-X not possible

\[
\text{Transmetallation: } R-M + M'-X \rightarrow R-M' + M-X
\]

\[
\begin{align*}
&\text{NC} \quad \text{BuLi} \quad \text{Li} \\
&\text{TMS} \quad \text{MgBr}_2 \quad -100^\circ \text{C}, 5\text{min}
\end{align*}
\]

Tet, 1996, 7201

**In catalytic cycle:**

\[
\text{Cl} \quad + \quad \text{TMS} \quad \text{MgBr}
\]

\[
\text{via} \quad \text{Ni} \quad \text{Cl} \quad \text{MgBrCl} \quad \text{Ln} \quad \text{TMS}
\]

-T.M. usually from more electropositive M to more electronegative M
-Endothermic T.M.'s can be part of catalytic cycle if R-M' subsequently reacts
-Likely by associative mech for coordinatively unsaturated M
-Likely metathesis for coordinatively saturated