Organometallics: Hard to define usefully and completely at the same time, but generally: Compounds containing metal-carbon bond(s).

Catalysis further complicates the issue:

Buchwald, JACS, 1998, 9722

Zhang, JACS, 2003, 6370
Organometallics is dominated by d electrons and orbitals

Most commonly used in organometallic reactions

Transition metals (copper often included)

Usually d⁰

p e- dominate

Usually have e- configuration

Xd¹⁰(X+1)sⁿ

Note: for our purposes, t.m.’s will be s⁰
<table>
<thead>
<tr>
<th>Elements</th>
<th>Pauling Electronegativity (ε)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H        2.2</td>
<td></td>
</tr>
<tr>
<td>Li 1.0   Be 1.6</td>
<td></td>
</tr>
<tr>
<td>Na 0.9   Mg 1.3</td>
<td></td>
</tr>
<tr>
<td>K 0.8    Ca 1.0</td>
<td></td>
</tr>
<tr>
<td>Rb 0.8   Sr 1.0</td>
<td></td>
</tr>
<tr>
<td>Cs 0.8   Ba 0.9</td>
<td></td>
</tr>
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<tr>
<td>Consider M-C bonds: Strength ~ Orbital overlap</td>
<td></td>
</tr>
<tr>
<td>2.0   B 2.5   C 3.0   N 3.4   O 4.0   F 4.0   Ne</td>
<td>Al 1.6   Si 1.9   P 2.2   S 2.6   Cl 3.1   Ar</td>
</tr>
<tr>
<td>Ln 1.1   1.3  Ti 1.5   V 1.6   Cr 1.6   Mn 1.6   Fe 1.8   Co 1.9   Ni 1.9   Cu 1.9   Zn 1.7   Ga 1.8   Ge 2.0   As 2.2   S 2.5   Br 2.9   Kr</td>
<td></td>
</tr>
<tr>
<td>Ln 1.1   1.3  Y 1.2   Zr 1.3   Nb 1.6   Mo 2.1   Tc 1.9   Ru 2.2   Rh 2.3   Pd 2.2   Ag 1.9   Cd 1.7   In 1.6   Sn 1.8   Sb 2.0   Te 2.1   I 2.6   Xe</td>
<td></td>
</tr>
<tr>
<td>Ln 1.1   1.3  La 1.1   Hf 1.3   Ta 1.5   W 2.3   Re 1.9   Os 2.2   Ir 2.2   Pt 2.3   Au 2.5   Hg 2.0   Tl 1.6   Pb 1.9   Bi 2.0   Po 2.0   At 2.2   Rn</td>
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<td></td>
</tr>
</tbody>
</table>
Ready; Catalysis
Organometallics: bonding

(n+1) p orbitals

\[ \begin{align*}
  &p_z \\
  &p_x \\
  &p_y
\end{align*} \]

\( (n+1) \) s orbital

\[ \begin{align*}
  &s
\end{align*} \]

n d orbitals

\[ \begin{align*}
  &d_{xy} \\
  &d_{xz} \\
  &d_{yz} \\
  &d_{x^2-y^2} \\
  &d_{z^2}
\end{align*} \]

lobes between axes
- Centrosymmetric
- Lobes 90° apart

lobes on axes
- 9 orbitals, 9 bonds possible
- Hard to fit 9 ligands around most metals
- Usually up to 6 ligands, 3 non-bonding orbitals

Simple bonding:

- Can be covalent or dative (Lewis base)
- Same representation for both

\[ \begin{align*}
  &\text{L}_n\text{Zr} \quad \text{H} \\
  &\text{L}_n\text{Os} \\
  &\text{L}_n\text{Pd}
\end{align*} \]

Note: Ln used if we don't know (or don't care) about other ligands on the metal - analogous to "R" for organic chemists

\[ \begin{align*}
  &\pi \\
  &\text{Covalent: } \text{L}_n\text{Cr} \quad \text{OMe} \\
  &\text{Dative (metal can accept or donate e-)}
\end{align*} \]

\[ \begin{align*}
  &\text{Cl}_3\text{Ti} \equiv \text{Cl} \\
  &\text{Cl}_3\text{Ti} = \text{Cl}^+ \\
  &\text{(OC)}_4\text{Fe} \equiv \text{CO} \\
  &\text{(OC)}_4\text{Fe} = \text{CO}^+ \\
  &\text{L}_n\text{Pd} \\
  &\text{L}_n\text{Pd}^-
\end{align*} \]
**Ionic Bonding: Driven by electrostatics**

- Strongest bond when high opposite charges interact.
- Charge differences are reflected in electronegativity differences.
- Therefore large electronegativity differences give stronger bonds.

\[ E_i = f(-Q_M Q_L) = f(-\epsilon_M - \epsilon_L) \]

ML bonding for early M is substantially ionic

---

**Covalent Bonding: Driven by Overlap**

- Strongest covalent bond when orbitals of similar energy interact
- Strength of interaction directly proportional to orbital overlap (matching size)
- Strength of interaction inversely proportional to difference in electronegativity.

\[ E_c = f(\frac{\text{orbital overlap}}{\epsilon_M - \epsilon_L}) \]

ML bonding for late M is substantially covalent
### Hard nucleophiles (i.e. ligands): Low E HOMO, high charge density

### Hard electrophiles (i.e. metals): High E LUOM, high charge density

Hard-Hard interactions largely ionic (e.g. CsF)

### Soft nucleophiles: High E HOMO, low charge density

### Soft electrophiles: Low energy LUMO, low charge density

Soft-Soft interactions largely covalent (e.g. MeCu)
Hard/Soft effects on ligand binding

$\text{[M}_{\text{aq}}]^n \quad + \quad X^- \quad \xrightarrow{K_{\text{eq}}} \quad \text{[MX}_{\text{aq}}]^{n-1}$

$\text{Log}[K_{\text{eq}}]$

<table>
<thead>
<tr>
<th>$M^+$</th>
<th>$F^-$</th>
<th>$Cl^-$</th>
<th>$Br^-$</th>
<th>$I^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H^+$</td>
<td>3</td>
<td>-7</td>
<td>-9</td>
<td>-9.5</td>
</tr>
<tr>
<td>$\text{Zn}^{+2}$</td>
<td>0.7</td>
<td>-0.2</td>
<td>-0.6</td>
<td>-1.3</td>
</tr>
<tr>
<td>$\text{Cu}^{+2}$</td>
<td>1.2</td>
<td>0.05</td>
<td>0.03</td>
<td>-</td>
</tr>
<tr>
<td>$\text{Hg}^{+2}$</td>
<td>1.0</td>
<td>6.7</td>
<td>8.9</td>
<td>12.9</td>
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<tr>
<td>ligands</td>
<td>charge</td>
<td># e-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------------------</td>
<td>--------</td>
<td>------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>-1</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OR, NR&lt;sub&gt;2&lt;/sub&gt;, SR</td>
<td>-1</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F, Cl, Br, I</td>
<td>-1</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NR&lt;sub&gt;3&lt;/sub&gt;, PR&lt;sub&gt;3&lt;/sub&gt;, OR&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ketone</td>
<td>0</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>triplet (Schrock) carbene</td>
<td>-2</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>singlet (Fischer) carbene</td>
<td>0</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-Heterocyclic Carbenes (NHC)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ligands</th>
<th>charge</th>
<th># e-</th>
</tr>
</thead>
<tbody>
<tr>
<td>[\text{M} = \text{M}]</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>[\text{M} = \text{M}]</td>
<td>-1</td>
<td>4</td>
</tr>
<tr>
<td>[\text{M} = \text{C}=\text{O}] or [\text{M} = \text{C} = \text{M}]</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>[\text{M} = \text{O}]</td>
<td>-2</td>
<td>4</td>
</tr>
<tr>
<td>[\text{M} = \text{O}]</td>
<td>-1</td>
<td>2</td>
</tr>
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<td>[\text{M} = \text{O}]</td>
<td>-2</td>
<td>4</td>
</tr>
</tbody>
</table>

BF<sub>4</sub>, SbF<sub>6</sub>, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>, B[C<sub>6</sub>H<sub>3</sub>-(CF<sub>3</sub>)<sub>2</sub>]<sub>4</sub>, OTf
**Organometallics: phosphines**

**On Phosphines**

**Strong \(\sigma\)-donors**

\[
\begin{align*}
\text{M} & \quad \text{PR}_3 \\
\sigma\text{-donation} & \\
\text{PCl}_3 < \text{P(OR)}_3 < \text{PPh}_3 < \text{PR}_3
\end{align*}
\]

**Strong \(\pi\)-acceptors**

\[
\begin{align*}
d_M & \rightarrow d_P \\
d_M & \rightarrow \sigma^*_P-R
\end{align*}
\]

**Cone Angle**

\[
\begin{align*}
\text{ligand} & \quad \theta \\
\text{PF}_3 & \quad 104 \\
\text{P(OMe)}_3 & \quad 107 \\
\text{PMe}_3 & \quad 118 \\
\text{PPhMe}_2 & \quad 122 \\
\text{dppe} & \quad 125 \\
\text{PET}_3 & \quad 132 \\
\text{PPh}_3 & \quad 145 \\
\text{PCy}_3 & \quad 170 \\
\text{P(tBu)}_3 & \quad 182 \\
\text{H} & \quad 75 \\
\text{Me} & \quad 90 \\
\text{CO} & \quad 95 \\
\text{Cp} & \quad 136 \\
toleman \\
\text{Chem Rev. 1977, 313}
\end{align*}
\]

**Chiral and modular**

- **BINAP**
- **DuPhos**
- **DIPAMP**

*Orpen Chem. Com. 1985, 1310*
**N-Heterocyclic Carbenes (NHC's)**


**Characteristics:**
- Neutral, 2e- donor
- Strong σ-donor (similar to phosphine)
- Weak π acceptor
- Modular
- M(NHC) complexes:
  - Often air stable
  - Thermally and hydrolytically stable
  - E- rich

**Little backbonding - similar to olefin**

**Synthesis:** 3 common methods (see Herrman review)

- Formation of NHCs from ketones, amines, and other compounds.
Applications:

**Olefin metathesis**

Grubb’s 2nd generation catalyst

Optically active versions have been made

Almost all Pd-catalyst reactions work using NHCs. Heck, Suzuki, Stille, Buchwald-Hartwig, Sonagashira...

Ni, Fe and Ir chemistry also reported. Like with phosphines, best ligand is case-dependent.

Two most popular NHC precursors: (bulky NAr to prevent dimer formation)

For asymmetric hydrogenation

Burgess, JACS, 2001, 8878

Asymmetric metathesis

Grubbs, ACIEE, 2006, 7591;
JACS, 2006, 1840

Conjugate addition

Hoveyda, ACIEE, 2007, 1097
Conclusions:
M-C bond strength correlates with H-C bond strength
CH₃>1°>2°>3°
sp>sp²>sp³

Background:
Direct observation of C-H insertion
Bergman, JACS, 1982, 352

Determination of relative M-X bond strengths
Bergman, Polyhedron, 1988, 1429

Conclusions:
M-C bond strength correlates with H-C bond strength
CH₃>1°>2°>3°
sp>sp²>sp³
Bryndza, Bercaw et al. JACS, 1987, 1444

Observed experimentally:

\[ \text{L}_n\text{M}^{-} \text{X} + \text{H}^{-} \text{Y} \rightleftharpoons \text{ML}_n^{-} \text{Y} + \text{H}^{-} \text{X} \quad \text{K}_{eq} \approx 1 \]

\[ \text{Cp}^*\text{(PMe}_3)_3\text{RuOH} + \text{CH}_3\text{COCH}_3 \rightleftharpoons \text{Cp}^*\text{(PMe}_3)_3\text{RuCH}_2\text{COCH}_3 + \text{H}_2\text{O} \quad \text{K}_{eq} = 2.3 \]

Exceptions: M-H (5-15 kcal too strong)
M-OR too strong in d^0
M-S, M-Si too strong in late TM's. But:

\[ \text{Cp}^*\text{(PMe}_3)_3\text{RuSH} + \text{HSi(OEt)}_3 \rightleftharpoons \text{Cp}^*\text{(PMe}_3)_3\text{RuSi(OEt)}_3 + \text{H}_2\text{S} \quad \text{K}_{eq} = 0.75 \]
$^{13}$C resonance for different L's:

Representative 'common NHC' aka SiMes, found in Grubbs II, 178 ppm on this chart

Stronger L = more downfield

Huynh, *Organomet.* 2009, 5395
Same ligand, different metal = different reactivity

**olefin as nucleophile**

\[
\text{Bu} = \text{OEt} + \text{Ti(OiPr)}_4 \xrightarrow{c-C_6H_{11}MgCl} \text{Bu} \xrightarrow{\text{RO}} \text{Bu} \xrightarrow{\text{RO}} \text{Bu} \rightarrow \text{MeOH} \xrightarrow{\text{Bu}} 95\%
\]

see Chem Rev 2000, 2835

**olefin as electrophile**

\[
\text{C}_6H_{17} + \text{PdCl}_2 \xrightarrow{10\% \text{ CuCl}} \text{DMF/H}_2\text{O} \rightarrow \text{ClPd} \xrightarrow{\text{C}_6H_{17}} \text{OH} \xrightarrow{-\text{ClPdH}} \text{O} \xrightarrow{\text{Synthesis, 1984, 369}} \text{C}_6H_{17}
\]

Same metal, different ligand = different reactivity

**electrophilic Pd(allyl)**

\[
\text{Ph} = \text{OAc} + \text{E} \xrightarrow{\text{NaH, cat. Pd(PPh)}_3} \text{Ph} \xrightarrow{\text{E}} \text{E} \xrightarrow{\text{Chem Rev 1996, 395}} \text{Ph}
\]

**nucleophilic Pd(allyl)**

\[
\text{Ph} = \text{H} \xrightarrow{\text{cat. Pd(phenyl)}_3} \text{Ph} \xrightarrow{\text{Cl} \text{SnBu}_3} \text{OH} \xrightarrow{88\% \text{ ACIEE, 2003, 3656}} \text{Ph}
\]
Ready; Catalysis

Organometallics: Electronic effects

\[ \text{eq 1} \]

Kurosawa, JACS, 1980, 6996

\[ \text{eq 2} \]

Kurosawa, JACS, 1987, 6333

\[ \text{eq 3} \]

Stahl, JACS, 2004, 14832
Electron Counting and Oxidation State

1. Decide what charge a ligand has
2. Determine # e’s donated
3. Assume Metal has charge equal in magnitude, opposite in charge to sum of ligands
4. Oxidation state = charge on metal
5. d e- count = #e- for neutral element – charge
6. Total e- count = d e- + sum of ligand electrons
7. 18 e- is stable # of e- (noble gas configuration), 16 e- for square planar

Wilkinson’s catalyst

[Chemical structure image]

Noyori hydrogenation catalyst

[Chemical structure image]

Zeise’s salt
Crabtree's dehydrogenation catalyst

Total ligand charge = -3
Oxidation state = +3
Total metal e- = 6
Total ligand e- = 12
Total e- count = 18

Brintzinger's ligand

Total ligand charge = -4
Oxidation state = +4
Total metal e- = 0
Total ligand e- = 16
Total e- count = 16

JACS, 2003, 7900 propargylic alcohol substitution

Total ligand charge = -3
Oxidation state = +3
Total metal e- = 5
Ru-Ru bond = 1e-/Ru
Total ligand e- = 12
Total e- count = 18

Note: electron count same for each Ru b/c they are equivalent

COD: common for Ni and hydrogenation cat (why?)

Crabtree catalyst (homogeneous hydrogenation)

Total ligand charge = -1
Oxidation state = +1
Total metal e- = 8
PF6 contribution = 0
Total ligand e- = 8
Total e- count = 16
Geometries of transition metal complexes
Balance between steric (maximum ligand separation) and electronic (minimum filled antibonding, evenly distributed nb)
For MO treatment, see Albright, Tetrahedron, 1982, 1339.

**Octahedral**
most common geometry
for ML6; often 18e-, often for d6

```
O=C PR₃ CO
O=C PR₃ H
```

first eg of H₂ σ-complex
jacs 1984, 451

**Square Planar**
very common for d8 metals
16e- very stable (17th e- would be antibonding)

```
Ph₂ Pd Ph₂
PPh₃
```

intermediate in ketone arylation
Hartwig, Jacs, 2001, 5816

**Tetrahedral**
Common for d10, d4 and d0
sterically best way for ML4

```
Ph₃P Pd PPh₃
```

aka "tetrakis"
probably most common Pd source
Geometries of transition metal complexes, cont.

Some less common geometries

**Trigonal bipyramidal**

Note both are ML5, 18e-complexes of d8 metals

**Square pyramidal**

asymmetric aldol catalyst
evans, Jacs, 2003, 8706

**Bent**
giant phosphine precludes 4th ligand

Hartwig, Jacs, 2002, 9346

**Linear**
common for Cu, Ag and Au

Cl—Au—PPh3

For a list of geometry by metal and oxidations state, see
Jeffrey Moore's web site:
http://sulfur.scs.uiuc.edu/
Transition metals are such good catalysts because they can change oxidation states:

A useful reference, and fun for the whole family:
Web page for Jeffrey S. Moore (U. Illinois, chemistry)
http://sulfur.scs.uiuc.edu/
Under the ‘periodic table’ link
MO Description of σ bonding in ML₆

Metal Valence Orbitals

Linear Combinations of Ligand σ Donor Orbitals

18 e- Rule:
The octahedral geometry is strongly favored by d⁶ metals (e.g. Fe (II), Ru (II), Rh(III)). A stable electronic configuration is achieved at 18 e⁻, where all bonding (mostly L character) and non-bonding orbitals (mostly M d character) are filled.

Mulliken symbols: in an octahedral environment, the degenerate d orbitals split into orbitals of t₂g and e_g symmetries. Orbitals with different symbols have different symmetries and cannot interact.

Albright *Tetrahedron* 1982 (38) 1339.
**MO Description of σ bonding in ML₄ square planar**

**Metal Valence Orbitals**

- $a_{2u}$
- $e_u$
- $a_{1g}$
- $b_{1g}$
- $b_{2g}$
- $e_g$
- $d_{xy}$
- $d_{yz}$

**Linear Combinations of Ligand σ Donor Orbitals**

- HOMO
- LUMO

**16 e⁻ Rule:**
The square planar geometry is favored by d⁸ metals (e.g., Ni(II), Pd(II), Pt(II), Ir(I), Rh(I)). A stable electronic configuration is achieved at 16 e⁻, where all bonding and non-bonding orbitals are filled. Spin-paired compounds display diamagnetic behavior (i.e., weakly repelled by magnetic fields) and may be readily characterized by NMR.

In a square planar ligand field, the degenerate d orbitals split into orbitals of $a_{1g}$, $b_{1g}$, $e_g$, and $b_{2g}$ symmetries. The degenerate p orbitals split into orbitals of $e_u$ and $a_{2u}$ symmetries.

When combining orbitals, the resulting MO's must be symmetrically dispersed between bonding and antibonding. Thus, combining 3 orbitals (i.e., $a_{1g}$'s) requires one of the orbitals to be non-bonding.
MO Description of $\sigma$ bonding in ML$_4$ tetrahedral

The tetrahedral geometry is electronically favored by d$^4$ or d$^{10}$ metal complexes where the non-bonding orbitals are either 1/2 or entirely filled, respectively.
Organometallic Reaction Mechanisms

Ligand association/dissociation

CuBr + PBu₃ → (PBu₃)ₙCuBr
insoluble → soluble

NOTE: No ox. state change

Pd
 inactive catalyst
 active catalyst for cross coupling

Ligand Exchange:
Associative - common for 16e- complexes

rate = k[py][Pt]
rates will depend on nature (sterics, electronics) of Nu and MLn

Py + Et₃P/Pr/Cl → Et₃P/Pr/Cl
H     H
PEt₃ PEt₃

Dissociative - common for 18 e- complexes
Rate will depend on nature of leaving L, sometimes on new L'

-P-L slow:
Rate = k[ML]

+L' slow:
Rate = Kk₄[L][ML][L']

Hydrogenation
Ready; Catalysis

Organometallics: ligand exchange

\[ \text{Nu} + \text{CH}_3\text{I} \rightarrow \text{Nu} \text{CH}_3 \] (Rxn 1)

\[ \begin{align*}
\text{Nu}^+ \text{MeI} &+ \text{Pt(Py)}_2\text{Cl}_2 \\
\text{MeOH} & \rightarrow 0.00 \\
\text{AcO}^- & \rightarrow 2.00 \\
\text{Et}_3\text{N} & \rightarrow 3.07 \\
\text{Cl}^- & \rightarrow 3.04 \\
\text{Py} & \rightarrow 3.19 \\
\text{I}^- & \rightarrow 5.46 \\
\text{PhS}^- & \rightarrow 7.23 \\
\text{Ph}_3\text{P} & \rightarrow 8.99
\end{align*} \]

\[ \begin{align*}
\text{log (krel)} &\quad \text{log (krel)} \\
\text{Nu}^+ \text{MeI} &+ \text{Pt(Py)}_2\text{Cl}_2 \\
\text{MeOH} & \rightarrow 0.00 \\
\text{AcO}^- & \rightarrow 2.00 \\
\text{Et}_3\text{N} & \rightarrow 3.07 \\
\text{Cl}^- & \rightarrow 3.04 \\
\text{Py} & \rightarrow 3.19 \\
\text{I}^- & \rightarrow 5.46 \\
\text{PhS}^- & \rightarrow 7.23 \\
\text{Ph}_3\text{P} & \rightarrow 8.99
\end{align*} \]

Graph:

- Reaction 1: Log krel vs. Log krel
- Reaction 2: Log krel vs. Log krel
Exchange rates vary over 20 orders of magnitude

Figure 1.26. Range of water exchange rate constants (log $k_{ex}$(s$^{-1}$)) and mean residence times (s) for primary shell water molecules on aqua metal ions at 25 °C (the dotted line represents Taube's inert/labile boundary [79])

Oxidative Addition and Reductive Elimination

\[ \text{LnM}(n) + X-Y \xrightarrow{\text{oxidative addition}} L_{n}M^{(n+2)} \xrightarrow{\text{reductive elimination}} \]

O.A. and R.E. involve 2e- change at M, increase # ligands by 2

"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

\[
\begin{align*}
R_1 & \quad \text{cis addition, olefin stereochemistry} \\
R_2 & \quad \text{is maintained} \\
R_3 & \quad X = I > Br \sim OTf \gg Cl \sim OTs 
\end{align*}
\]

Vinyl and Aryl C-X much more reactive than alkyl C-X despite more \textit{e}-rich alkyl C-X

Why? Precoordination

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

\[
\begin{align*}
\text{OR} & \rightarrow [ \text{C} \cdots \text{Pd} ] & \rightarrow \text{Backside (SN2-like) attack at C} \\
\text{OR} = OAc, OCO2R, OP(O)(OR)2, OTs, I, Br, Cl 
\end{align*}
\]

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

Rhazinilam
Sames, \textit{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(I)</td>
<td>56</td>
<td>-25</td>
</tr>
<tr>
<td></td>
<td>104</td>
<td>-6</td>
</tr>
<tr>
<td>88</td>
<td>+6</td>
<td></td>
</tr>
<tr>
<td>104</td>
<td>+8</td>
<td></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

Amatore, *Organometallics*, 1995, 1818
Oxidative addition: reactivity trends

Reaction rate decreases with electron density on ArX

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

\[ k_{\text{rel}} = \frac{k_{\text{obs, X}}}{k_{\text{obs, X=H}}} \]

\[ y = 2.547x + 0.078 \]

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

\[
\text{Ni(PPh}_3\text{)}_4 + \text{ArCl} \rightarrow \text{20 }^\circ\text{C} \rightarrow (\text{PPh}_3)_2\text{NiAr(X)}
\]

Kink indicates change in mechanism

![Graph showing relative rates of oxidative addition of substituted aryl halides with correlation line.](Image)

**Figure 1** Correlation of relative rates of oxidative addition of substituted aryl halides with $\sigma$ (D. M. McDaniel and H. C. Brown, *J. Org. Chem.*, 1988, 23, 420) at 0.02M-PPh$_3$
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:

\[ R \text{-} X + 2 [\text{Co(CN)}_5]^{-3} \rightarrow \left\{ R \cdot + X\text{-}\text{Co(CN)}_5^{-3} \right\} \rightarrow R\text{-}\text{Co(CN)}_5^{-3} + X\text{-}\text{Co(CN)}_5^{-3} \]

\( X = \text{halide} \)

Net single electron OA

\[ [\text{CpFe(CO)}_2]_2 + X_2 \rightarrow \left\{ \text{CpFe}^{\text{III}}X_2\text{(CO)}_2 + \text{CpFe}^{\text{I}}(\text{CO})_2 \right\} \rightarrow 2 \text{CpFe}^{\text{II}}X\text{(CO)}_2 \]

Single electron OA in catalysis

\[
\begin{align*}
\text{(±)} & \quad \text{Br} \\
\text{Hex} \quad \text{ZnBr} & \quad \text{NiBr}_2 \cdot \text{diglyme (10 mol\%)} & \quad \text{13 mol\%} \\
\text{achiral} & \quad \text{NiLn} & \quad \text{nC}_6\text{H}_{13} \\
\text{L}_n\text{Ni(0)} & \quad \text{Br} & \quad \text{NiLn} \\
\end{align*}
\]

Fu, JACS, 2005, 10482
Reductive elimination: reactivity trends (substrate)

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

\[
\begin{align*}
\text{R} & \quad \% \text{ Yield} \\
H & \quad >90 \\
CF_3 & \quad 95 \quad k_{CF_3}/k_H \approx 2
\end{align*}
\]

\[
\begin{align*}
\text{R' R} & \quad \% \text{ Yield} \\
H & \quad 2\text{-Me} \quad 5\text{-}25 \\
Ph_5 & \quad 2\text{-Me} \quad 66 \\
Ph_5 & \quad 4\text{-Me} \quad 0
\end{align*}
\]

\[
\begin{align*}
110 \degree C & \\
110 \degree C
\end{align*}
\]
Oxidation-induced reductive elimination

\[
\begin{align*}
&\text{PF}_6^- \\
&\text{ClMg} \\
\text{MeO}_2\text{C}\text{Fe(CO)}_3^+ &\xrightarrow{\text{ox. at M}} \text{MeO}_2\text{C}\text{Fe(CO)}_3^{18-} \\
&\text{Ce(NH}_4)_2\text{(NO}_3)_6 \\
\text{MeO}_2\text{C}\text{Fe(CO)}_3^{17-} &\xrightarrow{69\%} \text{CO}_2\text{Me}
\end{align*}
\]

\[
\begin{align*}
&\text{H}_3\text{C} \text{CH}_3 \\
&\text{ox. at L} \\
\text{MeO}_2\text{C}\text{Fe(CO)}_3^{18-} &\xrightarrow{\text{H}_2\text{O}_2} \text{MeO}_2\text{C}\text{Fe(CO)}_3^{18-} \\
&-\text{CO}_2, -\text{HO}^- \\
\text{MeO}_2\text{C}\text{Fe(CO)}_2^{16-} &\xrightarrow{\sim 70\%} \text{CO}_2\text{Me}
\end{align*}
\]

Donaldson, OL, 2005, 2047
Note: 'CO insertion' is an unfortunate name because alkyl group moves.

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

Rel rate: $k_H / k_{alkyl} \sim 10^7$ 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 [eg Zr(IV), $d^0$]
$K < 1$ for $e^-$ rich metals [eg, Pd(II), $d^8$]
Oxidative addition: applications of Sn2-like OA and carbylation

Coates, JACS, 2007, 4948
agostic interactions: stable intermediates on the way to $\alpha$- or $\beta$-hydride elimination

• Stable interactions often found with electron-poor metals
• Especially common with $d^0$ metals
• Computation with Ti(carbene) and W(carbyne) estimates BDE $\leq$ 10 kcal/mol (OM, 2006, 118)

Schrock, et al

![Molecular structure diagram](image)

**Figure 4.** A perspective view of the molecular structure of $\text{Ta}(\sigma^2$-$\text{C}_2\text{Me}_3)(\text{CHMe}_3)(\sigma^2$-$\text{C}_2\text{H}_4)(\text{PMe}_3)$ (2). Except for H(1) and the four ethylene hydrogen atoms, 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 ($d^2$)
- Small Ta-C-H angle (78°)
- Long C-H bond (1.14Å, average here is 1.085Å)
  - i.e. weakening of C-H bond
- Big Ta-C-C angle (170°)
- Unrelated to agostic interactions:
  - Ethylene C’s out of plane (average 0.33Å out of 4H plane)
  - Long ethylene C-C distance (1.48 v. 1.34 when free)
Agostic interactions are likely unobserved intermediates in normal transition metal-catalyzed reactions:

**Heck Rxn:**

\[
\text{I} \quad + \quad \text{Cyclohexene} \quad \xrightarrow{\text{Pd}(0)} \quad \text{L}\text{Pd(H)}\text{I} \quad + \quad \text{PhC}_{\text{Ph}}
\]

**Generation of Pd(0)**

\[
\text{PdCl}_2 \quad \xrightarrow{\text{Et}_2\text{Zn}} \quad \text{transmetalation} \quad \xrightarrow{-\text{CH}_2\text{CH}_2} \quad \text{Pd}^{\text{II}} \quad \xrightarrow{\beta\text{-Hydride elim}} \quad \text{Pd}^{\text{III}} - \text{H} \quad \xrightarrow{\text{red. elim.}} \quad \text{L}_n\text{Pd}(0)
\]

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

\[
\text{Cp}_2\text{ZrCl}_2 \quad \xrightarrow{\text{lewis acid}} \quad \text{catalyst for ethylene polymerization cation stabilized by agostic interaction}
\]

likely intermediate in α-elimination:

\[
\text{Cp}^*\text{TaClBn}_3 \quad \xrightarrow{-\text{PhCH}_3} \quad \text{Ta}_{\text{Ph}}_{\text{Cl}}_{\text{Cp}^*_{\text{Bn}}}
\]

Schrock, Accts, 1979, 98
Agostic interaction can be dynamic

Nolan, ACIEE, 2005, 2512

'cyclometalated' Ir(III)bis(NHC)
A C-H complex observed crystallographically:

Reversible deprotonation with Et3N to form Ar-Rh bond

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

\[
\begin{align*}
\text{RCH} &= \text{RCH}_2\text{CHO} + \text{RCH}_2\text{CHO} \\
\text{cat. Rh(I)} &\quad \text{H}_2/\text{CO (syn gas)} \\
\end{align*}
\]

\[
\begin{align*}
\text{HRh(CO)}_2\text{L}_2 &\quad \text{HRh(CO)}\text{L}_2 \\
\text{H}_2 &\quad \text{R} \\
\text{RCH}_2\text{Rh(CO)}\text{L}_2 &\quad \text{RCH}_2\text{Rh(CO)}_2\text{L}_2 \\
\text{CO} &\quad \text{RCH}_2\text{Rh(CO)}\text{L}_2 \rightarrow \text{RCHO} \\
\end{align*}
\]
4-centered reactions:

\[
\begin{align*}
2+2 & \quad R_NH_2 + R' \equiv \equiv R' \\
\text{cat. } & \quad \text{cat. } C_pZr(NHR)_2 \\
& \quad \text{NR} \\
& \quad ZrC_p \\
\begin{bmatrix}
R & N & \equiv \\
& Zr & \equiv \\
C_p & C_p & C_p \\
& R' & R'
\end{bmatrix} & \quad \rightarrow & \quad \rightarrow & \quad \rightarrow
\end{align*}
\]

see Eur. JOC, 2003, 935

\(\sigma\)-bond metathesis

Tilley, Jacs, 2003, 7971
Transmetallation:

\[ R-M + M'-X \rightarrow R-M' + M-X \]

Stoichiometric Use:
Great way to make Grinards, alkyl zincs, cuprates, stannanes etc. Esp useful on small scale where O.A. to R-X not possible

In catalytic cycle:

- 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