Catalysis further complicates the issue:

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

Organometallics is dominated by d electrons and orbitals

Pauling Electronegativity (\(\epsilon\))

<table>
<thead>
<tr>
<th>H</th>
<th>Be</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
<th>Ne</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>1.0</td>
<td>2.0</td>
<td>2.5</td>
<td>3.0</td>
<td>3.5</td>
<td>4.0</td>
<td>4.5</td>
</tr>
<tr>
<td>Na</td>
<td>0.9</td>
<td>1.3</td>
<td>1.8</td>
<td>2.3</td>
<td>2.8</td>
<td>3.3</td>
<td>3.8</td>
</tr>
<tr>
<td>K</td>
<td>0.8</td>
<td>1.2</td>
<td>1.7</td>
<td>2.2</td>
<td>2.7</td>
<td>3.2</td>
<td>3.7</td>
</tr>
<tr>
<td>Rb</td>
<td>0.8</td>
<td>1.2</td>
<td>1.7</td>
<td>2.2</td>
<td>2.7</td>
<td>3.2</td>
<td>3.7</td>
</tr>
<tr>
<td>Cs</td>
<td>0.8</td>
<td>1.2</td>
<td>1.7</td>
<td>2.2</td>
<td>2.7</td>
<td>3.2</td>
<td>3.7</td>
</tr>
</tbody>
</table>

Lanthanides and Actinoids: 1.1 – 1.3

Alkali and main group, electronegativity decreases down the column
Transition metals: electronegativity increases down the column

Consider M-C bonds: Strength ~ Orbital overlap

T.M.-Carbon bond covalent, strong (note C-Pd less polarized than C-Si)
Alkali metal-Carbon bond largely ionic
Soft-Soft interactions largely covalent (e.g. MeCu)

Hard nucleophiles (i.e. ligands): Low E HOMO, high charge density
Hard electrophiles (i.e. metals): High E LUMO, high charge density
Hard-Hard interactions largely ionic (e.g. CuF)

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

\[ \text{[M]}_{\text{lig}} + X \overset{K_{eq}}{\rightleftharpoons} \text{[M]X} \]

\[ \log(K_{eq}) \]

<table>
<thead>
<tr>
<th>M⁺</th>
<th>Ligand</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>
<td></td>
</tr>
<tr>
<td>Zn⁺</td>
<td>0.7</td>
<td>-0.2</td>
<td>-0.6</td>
<td>-1.3</td>
<td></td>
</tr>
<tr>
<td>Cu⁺</td>
<td>1.2</td>
<td>0.05</td>
<td>0.03</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Hg⁺</td>
<td>1.0</td>
<td>6.7</td>
<td>8.9</td>
<td>12.9</td>
<td></td>
</tr>
</tbody>
</table>

Organometallic: hard/soft

- [M]⁺ + X ⇌ [MX]⁻¹

Log(K_{eq})

**Ligands**

- H
- OR, NR₂, BR
- F, Cl, Br, I
- NR₂, PH₃, OR₂

**Carbon**

- Triplet (Schrock) carbon
- Singlet (Pfaender) carbon
- N-Heterocyclic carbene (NHC)

**Organo:halide**

- PH₃
- P(DMMA)₃
- PMe₃
- PPh₃
- dppz
- dppp
- Ph₃P
- Ph₂P
- Me
- CO
- Cp

**Cone Angle**

- PF₃
- P(DMMA)₃
- PMe₃
- PPh₃
- dppz
- dppp
- Ph₃P
- Ph₂P
- Me
- CO
- Cp

**Organometallic: phosphine**

- BINA Phos
- DuPhos
- DIPAMP
**Ready: Catalysts**

**Organometallics: NHC’s**

[Hoveyda Conjugate addition](#)

**Characteristics**
- Novel: 2nd generation
- Strong electron donor similar to phosphines
- [NHC]-based catalyst
- NHC containing: 
  - atm or stable, however, non-stoichiometrically stable

**Synthesis**
- 3 common methods (see Chemical reviews)

- potential for optically active ligands

**Applications**
- Optically active ligands have been made

- For asymmetric substitution: Burgess, JACS, 2012, 1038

- For conjugate addition: Hoveyda, JACS, 2006, 1940

**Ligand Identity Can Dictate Reaction Efficiency**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>Eyring [kcal/mol]</th>
<th>Endo [mol%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>L1</td>
<td>-1</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>L2</td>
<td>-2</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>L3</td>
<td>-3</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>L4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>L5</td>
<td>1</td>
<td>80</td>
</tr>
<tr>
<td>6</td>
<td>L6</td>
<td>2</td>
<td>20</td>
</tr>
</tbody>
</table>

- A typical case: Buchwald, ACS, 2012, 11110
- An extreme case: Sowers, JACS, 2012, 12924
**Conclusions:**

M-C bond strength correlates with H-C bond strength:

\[
\begin{align*}
\text{CH}_3 &> 1^\circ & > 2^\circ & > 3^\circ \\
\text{sp}^2 & > \text{sp}^3
\end{align*}
\]

Exceptions:

- M-H (5-15 kcal too strong)
- M-OR too strong in d
- M-S, M-Si too strong in late TM

But:

\[
\text{Cp^* (PMMe_3)_3 RuSH + HS(OEt)_3 = 0.75}
\]
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 if d e- (noble gas configuration), 16 e- for square planar
Ready; Catalysis

Organometallics

Geometries of transition metal complexes

Note: between deoxy (maximum ligand separation) and edenanto (minimum bonding).

For MO treatment, see Albrecht, T. "[Year]."

**Chelates**
- Most common geometry for ML₆, often 18e, often for d⁸

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

**Tetradeptals**
- Common for d⁸, d⁹, and d₁₀
- Eschenmoser's salt for ML₆

Note: "trivak" probably most common Pt source

Geometries of transition metal complexes, cont.

Some less common geometries

**Tetrahedral**
- Note both are ML₆, 18e-complexes of d⁸ metals

**Square Pyramidal**
- Asymmetric axial catalyst

**Linear**
- Common for Cu, Ag, and Au

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

[Periodic table with 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, these diagrams:

1. I stole the next 3 slides!!!
MO Description of bonding in ML₄ square planar

Electronic Configuration of Ligand or donor orbitals

Note: The electronic configuration is shown for ML₄ in a square planar geometry. The orbitals are labeled as σ, π, and σ'. The bonding and antibonding orbitals are indicated with dashed and dotted lines, respectively.