Isolobal Analogy

Roald Hoffmann
Organic Structures
• Systemization in organic chemistry
  - R is any alkyl group CH₃, C₂H₅, C₆H₅
  - Similarly H can be replaced by any R group.
  - =CH₂ can be replaced by any CR₂ group or oxygen!

• Transition metal Chemistry?

• Organometallic Chemistry?
Common fragments
Organic Fragments

- CH$_4$ saturated organic fragment.

- Remove hydrogens one by one
  \[ \text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH} \equiv \text{R} \cdot \]
Inorganic Fragments

- Start with \( \text{Cr(CO)}_6 \)
Relationship between the two?

Remove hydrogens one by one

- $\text{CH}_3.$
- $\text{CH}_2$
- $\text{CH}\equiv$
Evolution of metal Orbitals
Evolution of metal Orbitals

\[
\begin{align*}
n+1 & \quad p & \equiv & & \\
n+1 & \quad s & \equiv & & \\
\text{nd} & \equiv & & \\
\end{align*}
\]
s + 3p produced 4 hybrid orbitals
$sp^3$
Evolution of metal Orbitals

\[ n+1 \quad p \quad \equiv \quad n+1 \quad s \quad \equiv \quad nd \]

\[ \text{xyz, yz, xy, t}_{2g} \]
ML₆ orbitals

- t₂g
- bonding
- non-bonding
- anti-bonding

L → L → L → L
$ML_6$ orbitals

t_{2g}

{12} 

L L L L L
Basis of 18 electron rule
ML$_5$ orbitals

t$_{2g}$
Making the fragment

\[ t_{2g} \]
Mn(CO)$_5$ $d^7$

Not isostructural fragments
Not isoelectronic either...
A comparison of the frontier orbital...

They are isolobal!
Results of a computation!
What will a methyl radical do?
What will a methyl radical do?
Evolution of metal Orbitals

\[ \text{n+1} \quad \text{p} \quad \text{nd} \]
ML_4 fragment
ML$_4$ fragment

t$_{2g}$
Mendeleev’s Abacus

<table>
<thead>
<tr>
<th></th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td></td>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
<td>Fe</td>
<td>Co</td>
<td>Ni</td>
</tr>
<tr>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
<td>Rh</td>
<td>Pd</td>
<td></td>
</tr>
<tr>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
<td></td>
</tr>
</tbody>
</table>

\[ \text{Fe(CO)}_4 \rightarrow \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! \!  

\[ \text{CH}_2 \]
$\text{Fe(CO)}_4$
Carbene type reactivity

\[
\begin{align*}
\text{Ethylene} & : & \ce{C==C} \\
\text{Carbene-Fe(CO)}_4 & : & \ce{Fe==C} \\
\text{Fe}_2(\text{CO})_8 & : & \ce{Fe==Fe}
\end{align*}
\]

Unsaturated molecule like olefin but not stable at RT!
Understanding Complex Structures
\[ ML_3 \]

\[
\begin{align*}
\text{n+1 } p & \quad \equiv \\
\text{n+1 } s & \quad - \\
\text{nd} & \quad -
\end{align*}
\]
$\text{Co(CO)}_3$

Diagram:

- $t^2g$
- $a_1$
- Electron orbitals indicated with $e$
- Carbon atom labeled $c$
Co(CO)$_3$

d$^9$ML$_3$  $\rightleftharpoons$  CR
HOMO (36)  LUMO (37)  (38)  Co(CO)₃
Structures formed by units isolobal with C-H

```
\[ \begin{array}{ccc}
\text{RC} & \text{CR} & \text{RC} \\
\text{C} & \text{Co} & \text{C} \\
\text{R} & \text{CR} & \text{RC} \\
\end{array} \]
\[\text{(CO)}_3\text{Co} \quad \text{Co(CO)}_3\]
\[\text{R} \equiv \equiv \text{R} \quad \text{Co} \equiv \equiv \text{Co} \]
```

```
\[ \begin{array}{ccc}
\text{R} & \text{C} & \text{R} \\
\text{(CO)}_3\text{Co} & \text{Co(CO)}_3 \\
\text{(CO)}_3\text{Ir} & \text{Ir(CO)}_3 \\
\end{array} \]
```
Simple analogy...

\[ d^7 \text{ ML}_5 \quad \leftrightarrow \quad \text{CH}_3 \]

\[ d^8 \text{ ML}_4 \quad \leftrightarrow \quad \text{CH}_2 \]

\[ d^9 \text{ ML}_3 \quad \leftrightarrow \quad \text{CH} \]
What would happen if you removed two *trans* ligands?

\[ \text{n+1 p} \quad \text{nd} \]

\[ \text{n+1 s} \]

\[ \text{pz} \]

\[ \text{d}_{xz} \]

\[ \text{d}_{yz} \]

\[ \text{t}_{2g} \]

\[ \text{xy} \]
\[ d^{10} \text{ML}_2 \]
BUILDING BRIDGES BETWEEN INORGANIC AND ORGANIC CHEMISTRY

ROALD HOFFMANN

Nobel lecture,

8 December 1981

Angewandte Chemie International Edition in English

Volume 21, Issue 10, pages 711–724, October 1982
• C-H $\rightarrow$ N

– As if the proton has been pushed into the nucleus of the C!

• BH$_2$ $\rightarrow$ C-H $\rightarrow$ N
Non-carbon Bread..

\[ C_5H_5 \equiv p_5 \]

1

2

\[ \text{Fe} \]

\[ \text{Ti} \]

\[ 2^- \]
\[ \text{TiCl}_4(\text{THF})_2 + 6 \left[ \text{K} \right] \rightarrow \text{THF, } -60^\circ \text{C} \]

\[ \frac{18\text{-Crown-6}}{\text{THF, } -60^\circ \text{C}} \rightarrow \frac{2.5\text{P}_4}{\text{THF, } -60^\circ \text{C}} \rightarrow (\text{K}(18\text{-C-6}))_2 \]
Selected bond distances (Å):
P1-P2, 2.1608(11); P1-Ti, 2.5617(8);
Fluxional Organometallic Molecules

Molecular Gymnastics
Molecular Gymnastics

• Static Crystal Structures

• Walk
  – Talk
    • Dance..
Classification of OM Reactions

A. Rearrangements, Isomerizations

\[ M - L \rightleftharpoons M - L' \]

B. Ligand Insertion Reactions

\[ X \]
\[ \quad \]
\[ M - L + X \rightarrow M - X - L \]

C. Oxidative Addition  Reductive Elimination

\[ M^{n+} + L \rightleftharpoons M^{(n+x)+} \quad \]

D. Reactivity changes on the Ligand

\[ M - L + Y \rightarrow M - L' + X \]

\[ X \]
Ligand Rearrangements

Isomerisation

Fluxional behaviour

5 H (s) on unsubstituted ring
Molecular Breathing

- Fe(CO)$_5$
Berry Pseudorotation

- Fe(CO)$_5$

anti-clockwise
Molecular Breathing

• Fe(CO)$_5$

anti-clockwise
Carbonyl Hopping
Carbonyl Hopping in Clusters
Metal Hopping
Cis Trans isomerism & CO Hopping
Simple Rotational Isomers
A molecular propeller!

At -25°C, Rotation stops, CD$_2$Cl$_2$.

- 2 distinct peaks for inner and outer protons
- $^2J_{\text{Rh-D}} = 1.8$ Hz
- $^2J_{\text{Rh-Ho}} = 2.5$ Hz

At RT spectrum shows only an $^2J_{\text{Rh-H}}$ average 2.1 Hz.

- A: Average $^2J_{\text{Rh-H}}$
- B: Expect loss of Rh-H coupling

All protons equivalent at RT.
Isomerization of Diastereoisomeric Re-Styrene Complexes

Enantiotopic exchange without olefin dissociation
Possible Intermediates

‘Slipped' Carbocation  Alkylidene Intermediate

η²-arene intermediate
'Slipped' Carbocationic Intermediate

95°C

Halocarbon Solvent

Not Observed

Ruled Out
Isomerization can occur by a simple rotation of the $\equiv\text{CHR}$ terminus? No

\[
\begin{align*}
\text{ON} & \quad \text{Re} \quad \text{PPh}_3 \\
\text{H} & \quad \text{D} \\
\text{Ph} & \quad \text{(RRR, SSS)}
\end{align*}
\]

\[
\text{CD}_2\text{Cl}_2\text{CD}_2\text{Cl} \quad 95^\circ \text{C, 72h}
\]

\[
\begin{align*}
\text{ON} & \quad \text{Re} \quad \text{PPh}_3 \\
\text{Ph} & \quad \text{H} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{D}
\end{align*}
\]

\[
\text{not observed}
\]
Alkylidene Intermediate

Not Found ---- There is no 1,2-H shift taking place

Ruled Out
$\eta^2$-arene complex as an intermediate

Reactions of phenyl complexes – Replacement of benzene by solvent

\[ \text{Reactions:} \quad \begin{align*} \text{ON} & \quad \text{PPh}_3 \\ \text{CH}_2\text{Cl}_2 \text{ Solvent} & \quad -40 \, ^\circ\text{C} \\ \text{ON} & \quad \text{PPh}_3 \quad \text{ClCH}_2\text{Cl} \end{align*} \]
Carbon-Hydrogen $\sigma$ bond complex?

$k(H)/k(=\text{CHD}_E) = 1.6 \quad \text{Agostic interaction!!}!!!
Molecules are dynamic

• Watch Jason Gatson on parallel bars…
Allene Fluxionality
MOs of allene

0.02 eV

\( \sigma - \text{int} \)

\( \pi - \text{int weak} \)

-7.5 eV

HOMO
Ring Whizzing
Cyclopentadienyl Haptotropy
Importantly, the Cp is a ligand which can adjust the electron donation. By sliding the metal along the line shown by the arrow.
In $\text{SO}_2$ at $-70^\circ$ one obtains a typical $A_2B_2X$ pattern.
1,2 shifts

Single line at RT

In SO₂ at -70°C one obtains a typical A₂B₃X pattern

\[
\text{CuPE₃} \equiv \text{Cu} \quad \text{coded}
\]

Atm  Cu at 2  Cu at 1  Cu at 5

1. B ↔ A → B
2. A ↔ B → C
3. B ↔ C → C
4. C ↔ C → B
5. C → B → A

C and C will change only ½ the time
B,B will change all the time
A will change all the time
<table>
<thead>
<tr>
<th>Atm</th>
<th>Cu at 3</th>
<th>Cu at 1</th>
<th>Cu at 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C</td>
<td>A</td>
<td>C</td>
</tr>
<tr>
<td>2</td>
<td>B</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td>3</td>
<td>A</td>
<td>C</td>
<td>B</td>
</tr>
<tr>
<td>4</td>
<td>B</td>
<td>C</td>
<td>A</td>
</tr>
<tr>
<td>5</td>
<td>C</td>
<td>B</td>
<td>B</td>
</tr>
</tbody>
</table>

B and B will change only $\frac{1}{2}$ the time
C, C will change all the time
A will change all the time
Single line at RT

In SO₂ at -70°C one obtains a typical A₂B₂X pattern

1,2 Shifts

1,3 Shifts

1,3 Shifts
A Nuclear Magnetic Resonance Study of
v-Cyclopentadienyl ( triethylphosphine ) copper ( I)
George M. Whitesides and John S. Fleming
Journal of the American Chemical Society / 89:12, 1967 p 2855-2859
Ring whizzing

Cp  Cu  PEt₃

Single line at RT

In SO₂ at -70% one obtains a typical A₂B₂X pattern

CuPEt₃ ≡ Cu

1,3 Shifts

1,2 Shifts

color coded
Fluxional Behaviour of Allyls

Allyl/ Metal Flip through C3

Allyl / Metal Flip through C1
During Reactions

• Nucleophilic attacks at a Ru centre
$S_N2$ anti approach

Reactant Adduct (18e$^-$) 10 → Transition State 1 11 → Intermediate (16e$^-$) 12 → Product (18e$^-$) 13 → Product Adduct (18e$^-$) 14 → Transition state 2 15
Movie of TS2 in $S_{N2}$ anti approach of a complex
• Fluxional behaviour is associated with several structures having similar energy

• Energy of activation for going from one minima to the other is small.

• 18 ve. To 16 ve to 14 v.e is easy..
Steric and Electronic Effects of Supporting Ligands
In which ligands are steric effects important?

- CO
- NO\(^+\), CN\(^-\)
- PR\(_3\)
- Carbene complexes and NHC
- Isocyanides R-NC
- H\(^-\)
Concepts

• Steric influence exerted by the ligand.
  – A radius? Or just an angle? Is it a volume?
    These are nebulous parameters in chemistry.

• Tolman’s cone angle
• Nolan’s Buried Volume

• van der Waals radius, covalent radius, ionic radius
• Non-spherical distributions of the electron cloud!
Tolman’s Cone Angle
Phosphines: Key Features

- A versalite $\pi$ acceptor PR$_3$ –
- Electronic properties of PR$_3$ can be tuned by varying R.
- Although not as good as CO, it has a variable steric influence.

  - The STERIC influence of R groups in PR$_3$ gives us an advantage
Approximated the volume occupied by a ligand - to an angle! "2 dimensional" projection of the space occupied would result in a flat area. From this an angle $\theta$ can be taken as the steric parameter!

Rational: Some ligands have flat phenyl groups and a 3 dimensional volume is difficult to estimate.
Problem: The angle at M depends on the M-L distance!

SOLUTION: FIX it at an average distance 2.28 Å
Quantifying Steric Effects

- Cone angle measured by Tolman is the simplest / fastest measure of the steric requirement.
- Using space filling models, he constructed physical models and measured the angle using a protractor.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Angle</th>
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</thead>
<tbody>
<tr>
<td>PH₃</td>
<td>87</td>
</tr>
<tr>
<td>PF₃</td>
<td>104</td>
</tr>
<tr>
<td>PMe₃</td>
<td>118</td>
</tr>
<tr>
<td>PPh₃</td>
<td>145</td>
</tr>
<tr>
<td>P(ᵗBu)₃</td>
<td>182</td>
</tr>
</tbody>
</table>
Does it matter?

<table>
<thead>
<tr>
<th>COMPLEX</th>
<th>$\theta$</th>
<th>$K_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P(O\text{Et})_3$</td>
<td>109</td>
<td>$10^{-10}$</td>
</tr>
<tr>
<td>$P(O\text{iPr})_3$</td>
<td>114</td>
<td>$2.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>$P(O-p\text{Tol})_3$</td>
<td>121</td>
<td>$6 \times 10^{-10}$</td>
</tr>
<tr>
<td>$PMe_3$</td>
<td>118</td>
<td>$10^{-9}$</td>
</tr>
<tr>
<td>$P(Et)_3$</td>
<td>132</td>
<td>$1.2 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

(0)$

$NiL_4 \rightleftharpoons K_d \quad NiL_3 + L$
Importance of Steric Effects

As you put more and more bulky groups, the complexes on the left side become less and less stable. The equilibrium shifts to the right.
Steric forces of the ligand changes the structure!!

• Extreme example is [CoL_4]^+
  – Here L is P(O^iPr)_3

  – d^8 complexes prefer square planar structures and not octahedral or tetrahedral. Why?
    • Difference in energy required for O_h d^2sp^3 and SqP dsp^2 suggests that the latter is better when M-L bonds are weak! (not strong enough to compensate for mixing in p_z)

    • A choice between Td and SqP complexes depends on LFSE differences (π bonding is poorer in Td, no. of d electrons) and steric pressure favor Td!

  – The Co complex is tetrahedral showing importance of steric effects!
Tolman’s angle is not just steric!

It **is** stereoelectronic!

<table>
<thead>
<tr>
<th>R</th>
<th>cone angle in PR$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>87</td>
</tr>
<tr>
<td>OMe</td>
<td>107</td>
</tr>
<tr>
<td>Me</td>
<td>118</td>
</tr>
<tr>
<td>Et</td>
<td>132</td>
</tr>
<tr>
<td>Ph</td>
<td>145</td>
</tr>
<tr>
<td>F</td>
<td>104</td>
</tr>
<tr>
<td>tBu</td>
<td>182</td>
</tr>
<tr>
<td>Mesityl</td>
<td>212</td>
</tr>
</tbody>
</table>

Two ways in which it is electronic!

1. Smaller ligands can come closer while larger ligands bump into one another and stay far from the metal! Poor bonding...

2. If the ligand is more π bonding, it will come closer to the metal and cone angle would increase!

Unfortunately it was initially done with models.
Tolman’s cone angle from crystallographic data.

“Determination of Tolman’s cone angle from crystallographic..... Data Base”
Muller T. E. and Mingos D.M.P.
Complications with $\text{P(OR)}_3$

- “Steric parameters of ....Environments”
  - Smith J.M. and Coville N.J.
  - Organometallics 2001, 20, 1210-1215.
A tale of two ligands

• Special Ligand no. 1: N-heterocyclic carbenes
• Special Ligand no. 2: The hydride
NHC are super heroes

A comparison between nickel and palladium precatalysts of 1,2,4-triazole based N-heterocyclic carbenes in hydroamination of activated olefins
Chandrakanta Dash, Mobin M. Shaikh, Ray J. Butcher and
Prasenjit Ghosh
*Dalton Trans.*, 2010, 39, 2515-2524

Beyond catalysis: *N*-heterocyclic carbene complexes as components for medicinal, luminescent, and functional materials applications
Laszlo Mercs and Martin Albrecht

**N-Heterocyclic Carbenes in Late Transition Metal Catalysis**

Silvia Díaz-Gonzlez, Nicolas Marion and Steven P. Nolan
*Chemical Reviews* 2009 109 (8), 3612-3676
Steric properties of “NHC”

- A neutral ligand with $\pi$ acceptor capability
- Very good sigma donation
- Tunable electronic and **steric property**
- Ligand is easily synthesized *in situ*
- **NHC are super heroes!**
Steric Features

Will rotation around the M=C bond change the cone angle?
Nolan’s buried volume

M-C bond length 2.0 Angstroms

3.5 angstroms

imaginary
Percent buried volume for phosphine and N-heterocyclic carbene ligands: steric properties in organometallic chemistry
Clavier, Herve; Nolan, Steven P.

A portion of this volume in this imaginary sphere of 3.5 Å radius is occupied by each ligand.

% used by the ligand is called the buried volume.
WIRE FRAME MODEL

“ADUVOL” from the CSD

trans-bis(1,3-bis(2,4,6-Trimethylphenyl)imidazolidin-2-ylidene)-dichloro-nickel(II)
SPACE FILLING MODEL
ADUVOL

\( trans\)-bis(1,3-bis(2,4,6-Trimethylphenyl)imidazolidin-2-ylidene)-dichloro-nickel(ii)
Metal ion dependence

<table>
<thead>
<tr>
<th>No.</th>
<th>R</th>
<th>% buried volume (M=Cu)</th>
<th>% buried volume (M=Ag)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>cyclohexyl</td>
<td>29</td>
<td>28</td>
</tr>
<tr>
<td>2</td>
<td>Mesityl</td>
<td>36</td>
<td>36</td>
</tr>
<tr>
<td>3</td>
<td>Adamantyl</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>tButyl</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Di -sopropyl phenyl</td>
<td>48</td>
<td>46</td>
</tr>
</tbody>
</table>
BDE in Kcal / mol

I-Mesityl 41
SL-Mes 40 (S stands for saturated I ring)
I-Adam 20
I-tButyl 24

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<tr>
<td>5</td>
<td>Di-isopropyl phenyl</td>
<td>48</td>
</tr>
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</table>
Steric Effects

• Approximations are required to quantify steric effects!
  (a) Angle subtended at the metal using a fixed M-L distance.
  (b) The % volume occupied by the solid cone in an imaginary sphere around the metal and a fixed M-L distance.

• Ignore M-L bond distance effects.

• Use crystallography to make it more realistic: corrects for the errors mentioned above!
Caveats in using “steric effects”

- Size of the balloon depends on how much you squeeze the balloon with the Vernier calipers you are using to measure the balloon with! \( P(OR_3)_3 \)

- Estimating the solid angle or the cone angle can be computed using a computational model:

  **SambVca: A Web Application for the Calculation of the Buried Volume of N-Heterocyclic Carbene Ligands**

  Poater A., Cosenza B., Correa A., Giudice S., Ragone F., Scarano V. and Cavallo L.


**Improved Algorithm for Accurate Computation of Molecular Solid Angles**

A brief comment on the Hydride..

• Smallest ligand known in chemistry.
  – What is its size?
Hydrogen occupies a coordination site on the metal.
Structures of metal hydrides!
Flexible steric effects!

\[(\text{HRh(CO)(PPh}_3)_3 \leftarrow \text{HRh(PPh}_3)_4\]
RhHCO(PPh$_3$)$_3$

P-Rh-P angle is 120°
RhH(PPh$_3$)$_4$

P-Rh-P angle is $\sim 109^\circ$
$\text{RhH(PPh}_3\text{)}_4$
Electronic Effects

• Quantification of electron donation:
  – Tolman’s Electronic Parameter TEP
    • (See the video lecture on substitutes for CO and the lecture on N-heterocyclic carbenes)
Quantifying Electronic Effects

- Better to look at a series of complexes.

- Tolman did this with \([\text{Ni(CO)}_3(L)]\) where the L is a NHC. He quantified the symmetric stretch of the 3 CO ligands as a function of L

- \(L = \text{CO} \quad \text{TEP is 2060}\)

- The average CO stretch is called the Tolman electronic parameter. (TEP)
Electronic Character of NHC

• $^{13}$C chemical shift in a Pd(II) complex is used as a probe. Chemical shift increases with NCN angle.

Usually on complexation, the chemical shift goes upfield by 30 ppm. 180 ppm.
Quantitative Analysis of the Ligand’s Electronic Effects

- ECW Model of R.S. Drago
  - Property = EaEb + CaCb + W
  - Does not model the steric effects of ligands
Quantitative Analysis of Ligand Effects

• QALE method Developed by Giering and Prock
  • Property = aχ + bθ + c (θ - θ_st) + dE_ar + e
    //a, b, c, d, e is determined for each property//
    – χ is the electronic parameter and θ the cone angle (Ar is no. aromatic rings)

Comments on Coupling Graphical and Regression Analyses of Ligand Effect Data
• Organometallics 1996, 15, 295-301
An Example of QALE

Kinetics of the dissociation
Plotted against cone angle

The break at 160° indicates a threshold for the steric parameter!

\[ \theta = 160° \]
QALE and thermodynamics

\[
\text{BDAFe(CO)_3 + 2L} \rightarrow \text{Fe(CO)_3L}_2 + \text{BDA} + \text{Benzylidene acetone}
\]

\[
-\Delta H = -0.73(\chi) \pm 0.10 \theta - 0.461(\theta - 135)\lambda \pm 0.026 - 1.68E_{ar} \pm 0.34 + 46.3 \pm 0.8
\]

\[r^2 = 0.964 \quad n = 16\]

Negative coefficient indicates that heat of reaction increase as the phosphines become better donors.

For this reaction, there is no steric effect till the Tolman angle reaches 135.

Data from PR_3 and PAr_3 fall on two different lines when \(\chi\) is plotted against \(\Delta H\).

If there is no aromatic ring effect the lines cross at \(\chi = 4.8\).
QALE

• Properties can be: Thermodynamic data (pKₐ values, E° values, heats of reaction, equilibrium constants), bond lengths, and NMR, IR, UV/vis, photoelectron, and Mossbauer spectroscopic data

• Recent example: “Quantitation of the ligand effect in oxo-transfer Reactions of dioxo-Mo(VI) trispyrazolyl borate Complexes”
Partha Basu, Brian W. Kail, Andrew K. Adamsa and Victor N. Nemykinb
Dalton Trans., 2013, 42, 3071–3081
Quantifying S&E Effects!

- It is possible to quantify steric effects from crystallographic data! Use with caution!
- Electronic effects from spectroscopic data!

- To have predictive value, one needs to include both steric and electronic effects!