Hypervalence and the Search for Pentavalent Carbon

Matt Burk
SED Group Meeting 04-10-07
Why Make Pentavalent Carbon

- Model for Sn2 Transition State
- Intellectual curiosity
What is a bond?

- **Chemical bond** - When forces acting between two atoms or groups of atoms lead to the formation of a stable independent molecular entity, a chemical bond is considered to exist between these atoms or groups. The principal characteristic of a bond in a molecule is the existence of a region between the nuclei of constant potential contours that allows the potential energy to improve substantially by atomic contraction at the expense of only a small increase in kinetic energy. Not only directed covalent bonds characteristic of organic compounds, but also bonds such as those existing between sodium cations and chloride anions in a crystal of sodium chloride or the bonds binding aluminium to six molecules of water in its environment, and even weak bonds that link two molecules of O2 into O4, are to be attributed to chemical bonds. **Pauling** (1960); **Ruedenberg** (1962), **Sutcliffe** (1992). IUPAC 1999 recommendation
What is Hypervalence?

- Main group atoms with >8 valence electrons
- Not just >4 ligands
- HOMO of molecule is non-bonding
- d orbital involvement is not needed
- Bonding heavily ionic

[Chemical structure diagram]

Notation for hypervalent compounds

- # of valence e\textsuperscript{-} - Element - # of ligands

Ex. 10-C-5 10 valence electrons and 5 ligands attached to carbon

Bonding in hypervalent molecules

- Three-center-four-electron bond is the basic hypervalent bond. It is the apical bond in trigonal bipyramidal hypervalent molecules

This bond can be viewed in four ways

1. Add two radicals to a lone pair
2. Add two lone pairs to coordinate to an empty p orbital
3. Add a lone pair to the $\sigma^*$ orbital of a cationic molecule
4. Add a lone pair to the $\sigma^*$ orbital of a neutral molecule, "Frozen transition state"

Akiba, Kin-ya. Chemistry of Hypervalent Compounds, 1999, Chapter 2
• Extensive research on Hypervalent compounds
• Martin Sulfurane
• Dess-Martin Periodinane,
• Martin ligand
The Martin Ligand

Stabilizes Hypervalent Species

Gem-dimethyl effect

Electron withdrawing apical Ligand

Five membered ring effect

Martin’s First Attempts at Pentavalent Carbon

2 shows diastereotopic methyl signals by NMR

3-5 “Bell-Clapper” rearrangement

$\Delta H^\ddagger$ ranges from 9.8 to 19.9 kcal/mol

Martin, J.C., Basalay, Robert J.; Journal of the American Chemical Society, 1973, 95, 2572
If at first you don’t succeed…

- single peak for para substituents and no sign of broadening as low as -100ºC,

- $2a$ was $^{13}$C labeled to measure $^{13}$C-$^{13}$C couplings, in the range for directly bonded sp$_2$ carbons

- Structure 7a is argued against by analysis of the chemical shifts.

- Crystal structure could not be obtained.

Forbus, T.R., Martin, J.C.; *Journal of the American Chemical Society*, 1979, 101, 5057

Forbus, T.R., Martin, J.C.; *Heteroatom Chemistry*, 1993, 4, 113
Try...

- Crystal structure!
- C-O bonds angle inward, towards C19

![Figure 1. Crystal structure (30% thermal ellipsoids) of 1.](image)

**Table 1.** Comparison of the Distances between the Atoms at the 1,8,9-Positions ($a$ and $a'$) with Those between the Ipso Carbons ($b$ and $b'$) of Anthracene Derivatives

<table>
<thead>
<tr>
<th>compd</th>
<th>$a$</th>
<th>$a'$</th>
<th>$b$</th>
<th>$b'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7: X = Y = Br</td>
<td>3.2658</td>
<td>3.2738</td>
<td>2.564</td>
<td>2.567</td>
</tr>
<tr>
<td>5: X = OTf, Y = OMe</td>
<td>2.572</td>
<td>2.571</td>
<td>2.554</td>
<td>2.545</td>
</tr>
<tr>
<td>8: X = CN, Y = OMe</td>
<td>2.530</td>
<td>2.531</td>
<td>2.538</td>
<td>2.542</td>
</tr>
<tr>
<td>1: X = C+(OMe)$_2$ Y = OMe</td>
<td>2.45</td>
<td>2.43</td>
<td>2.49</td>
<td>2.52</td>
</tr>
</tbody>
</table>


Wait a minute…

Remove the cation, and O-O distance becomes shorter
C-O bonds still angle inwards!


Try Again… In Parallel

New strategies:
1) Use stronger donor atom
2) Destabilize carbocation
3) Switch to an anionic system, More Sn2 like
4) Mount a parallel effort using a different ligand framework
5) Change the objective, switch to boron


Akiba, Kin-ya; Moriyama, Yuji; Mizozoe, Mitsuhiro; Inohara, Hideki; Nishii, Takako; Yamamoto, Yohsuke; Minoura, Mao; Hashizume, Daisuke; Iwasaki, Fujiko; Takagi, Nozumi; Ishimura, Kazuya; Nagase, Shigeru. *J. Am. Chem. Soc.* **2005**, *127*, 5893
Synthesis

Scheme 5. Synthesis of 9-Bromo-1,8-bis(dimethylamino)anthracence 3

Yamashita, Makato; Yamamoto, Yohsuke; Akiba, Kin-ya; Hashizume, Daisuke; Iwasaki, Fujiko; Takagi, Nozumi; Nagase, Shigeru. J. Am. Chem. Soc. 2005, 127, 4354
Rearrangement of 5 to 8 (43% yield):  

5 \[\rightarrow\] 8 (43%)

Reagents and Conditions:  

5: SnCl₂·2H₂O, HCl, AcOH  
6: Tf₂O, NaH, CH₂Cl₂  
7: Cl(O=O)OEt₂, NaH, THF  
8: (CF₃CO)₂O, pyridine, CH₂Cl₂  
9: BrCF₂CF₂Br

Chemical Structures:  

- 1: OMe, OTf, OMe \[Tf = CF₃SO₂\]  
- 2: MeO, Br, OMe  
- 3: MeO, OH, OMe  
- 4: MeO, Et, POEt₂  
- 5:  
- 6:  
- 7: Li, Li, Li  
- 8: MeO, OH, OMe  
- 9: OMe, OMe, CF₃  
- 10: Li, Li, Li  
- 11: Br, Br, Br  
- 12: MeO, OMe, MeO  
- LDBB = Li⁺[Bu−C₆H₄−C₆H₄−Bu−]⁻
Scheme 1. Attempted peri-Lithiation of 1,8-Dimethoxyanthracene

Reagents:
- a: Me₄SO₄, NaH, THF
- b: Zn, NH₃aq

Base:
- nBuLi, sBuLi, tBuLi

Additive:
- TMEDA or none

Solvent:
- nC₆H₁₄, ether, THF
Nitrogen donor

- NMR consistent with symmetrical structure
- Does not crystallize

Reduced stabilization

- NMR inconsistent with **33a**
- **33b** doesn’t crystallize

Anionic model

loose pentacoordinate

![Chemical structures and distances](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>O-B(or C)-O distances (av.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>56</td>
<td>4.82</td>
</tr>
<tr>
<td>57</td>
<td>4.81</td>
</tr>
<tr>
<td>58</td>
<td>4.87</td>
</tr>
<tr>
<td>59</td>
<td>4.88</td>
</tr>
<tr>
<td>27</td>
<td>4.88</td>
</tr>
</tbody>
</table>

tight pentacoordinate

![Chemical structures and distances](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>O-B-O distances (av.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>4.59</td>
</tr>
</tbody>
</table>

tetracoordinate

![Chemical structures and distances](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>O-B(or C)-O distances (av.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>61</td>
<td>4.48</td>
</tr>
<tr>
<td>52</td>
<td>4.79</td>
</tr>
<tr>
<td>51</td>
<td>4.86</td>
</tr>
<tr>
<td>50</td>
<td>4.75</td>
</tr>
<tr>
<td>38</td>
<td>4.46</td>
</tr>
</tbody>
</table>
Synthesis of a New Ligand System

Scheme 4. Attempted Synthesis of a Cation (10) Bearing 2,6-Bismethoxymethylbenzene

Scheme 5. Synthesis of Cations (15a–c and 16a–d) Bearing 2,6-Bis(p-substituted phenyloxymethyl)benzene

13a(alcohol), 15a(cation): Ar¹=p-Tol, Ar²=Ph  
13b(alcohol), 15b(cation): Ar¹=p-Tol, Ar²=p-FC₆H₄  
13c(alcohol), 15c(cation): Ar¹=p-Tol, Ar²=p-CIC₆H₄  
13d(alcohol): Ar¹=p-Tol, Ar²=p-CH₃OC₆H₄  
14a(alcohol), 16a(cation): Ar¹=p-CH₃OC₆H₄, Ar²=Ph  
14b(alcohol), 16b(cation): Ar¹=p-CH₃OC₆H₄, Ar²=p-FC₆H₄  
14c(alcohol), 16c(cation): Ar¹=p-CH₃OC₆H₄, Ar²=p-CIC₆H₄  
14d(alcohol), 16d(cation): Ar¹=p-CH₃OC₆H₄, Ar²=p-CH₃OC₆H₄

Akiba, Kin-ya; Moriyama, Yuji; Mizozoe, Mitsuhiro; Inohara, Hideki; Nishii, Takako; Yamamoto, Yohsuke; Minoura, Mao; Hashizume, Daisuke; Iwasaki, Fujiko; Takagi, Nozumi; Ishimura, Kazuya; Nagase, Shigeru. J. Am. Chem. Soc. 2005, 127, 5893
Benzene skeleton

Table 2. Distances of the Central Carbon Atom (C') and the Donating Oxygen Atoms (O' and O") and the O'–C'–O" Angles Revealed by X-ray Analysis of 15b-ClO₄, 15c-ClO₄, 15e-ClO₄, 15f-ClO₄, 16a-ClO₄, 16b-PF₆, and 16d-PF₆

<table>
<thead>
<tr>
<th></th>
<th>15c-ClO₄ (X = Cl)</th>
<th>15b-ClO₄ (X = F)</th>
<th>16a-ClO₄ (X = H)</th>
<th>16b-PF₆ (X = F)</th>
<th>16b-PF₆ (X = OCH₃)</th>
<th>15e-ClO₄ (Z = S)</th>
<th>15f-ClO₄ (Z = O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C'–O'</td>
<td>2.671(4)</td>
<td>2.690(4)</td>
<td>2.705(2)</td>
<td>2.718(5)</td>
<td>2.77(1)</td>
<td>2.776(4)</td>
<td>3.026(4)</td>
</tr>
<tr>
<td>C'–O&quot;</td>
<td>2.682(4)</td>
<td>2.690(4)</td>
<td>2.705(2)</td>
<td>2.718(5)</td>
<td>2.78(1)</td>
<td>2.855(5)</td>
<td>4.23</td>
</tr>
<tr>
<td>O'–C'–O&quot;</td>
<td>161.9(1)</td>
<td>162.3(1)</td>
<td>158.9(2)</td>
<td>160.4(4)</td>
<td>159.1(4)</td>
<td>155.7(2)</td>
<td>165.0(2)</td>
</tr>
</tbody>
</table>
Benzene skeleton cont.

“both oxygens (O¹ and O²) are sp²; that is, the sum of the angles (C⁵-O¹-C⁶, C¹-O¹-C⁶, C¹-O¹-C⁵) around O¹ is 360.0°”

116.33+126.09+84.99=327.41°

Compare with

Yamashita, Makato; Yamamoto, Yohsuke; Akiba, Kin-ya; Hashizume, Daisuke; Iwasaki, Fujiko; Takagi, Nozumi; Nagase, Shigeru. J. Am. Chem. Soc. 2005, 127, 4354

Akiba, Kin-ya; Moriyama, Yuji; Mizozoe, Mitsuhiro; Inohara, Hideki; Nishii, Takako; Yamamoto, Yohsuke; Minoura, Mao; Hashizume, Daisuke; Iwasaki, Fujiko; Takagi, Nozumi; Ishimura, Kazuya; Nagase, Shigeru. J. Am. Chem. Soc. 2005, 127, 5893
Background on Atoms in Molecules Theory

Proposed By R. F. W. Bader

Topological analysis of electron density

Proposes that bonds are defined by the existence of bond paths, ridge lines of charge stretching between bonded atoms.

Whether this is a sufficient condition for the existence of a bond, has been disputed.

Bond paths can be found in systems where conventional analysis would suggest the existence of a repulsive interaction. e.g. H-H interaction in planar conformer of biphenyl.

Bond Paths and Experimental Electron Density

Figure 9. Static model map of 15b-CIO₄ based on the accurate X-ray analysis. Positive and negative regions are shown as blue and red lines, respectively, and zero contours are omitted.

Figure 10. Bond paths of 15b-CIO₄ between the central carbon and the oxygen of the arm based on the accurate X-ray analysis.

Figure 18. Bond paths of the B¹-O¹ and B¹-O² bonds of 56 obtained by the accurate X-ray analysis. Bond paths are shown as red lines.

Akiba, Kin-ya; Moriyama, Yuji; Mizozoe, Mitsuhiro; Inohara, Hideki; Nishii, Takako; Yamamoto, Yohsuke; Minoura, Mao; Hashizume, Daisuke; Iwasaki, Fujiko; Takagi, Nozumi; Ishimura, Kazuya; Nagase, Shigeru. J. Am. Chem. Soc. 2005, 127, 5893
Conclusion?

- Pentavalent boron has been made.
- Pentavalent carbon may have been made.