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

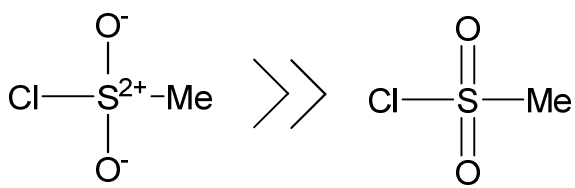
What is a bond?

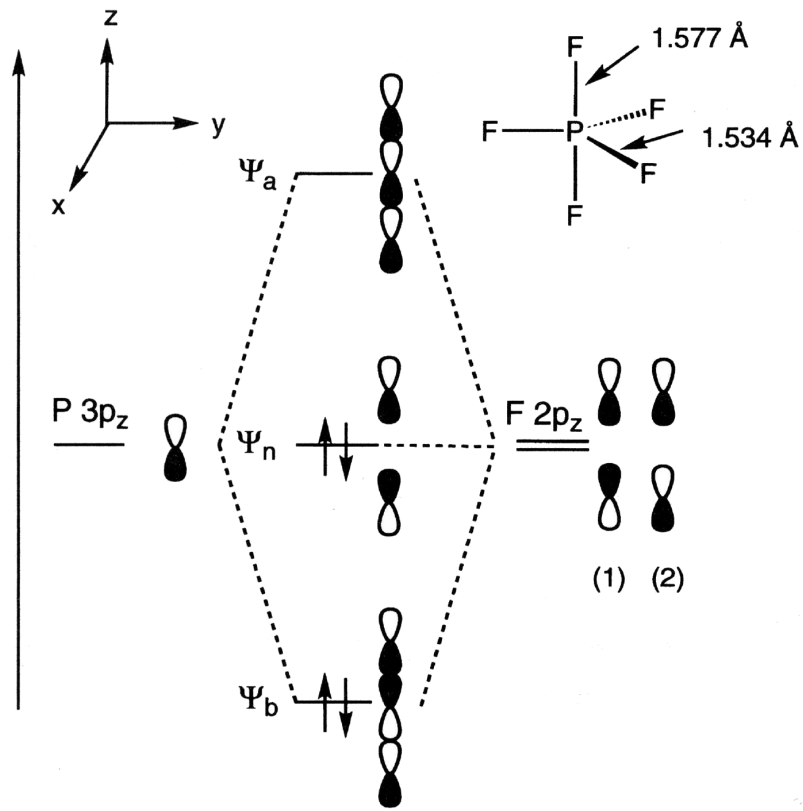
- **Chemical bond** - When forces acting between two atoms or groups of atoms lead to the formation of a stable independent molecular entity, a chemical bond is considered to exist between these atoms or groups. The principal characteristic of a bond in a molecule is the existence of a region between 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 reccomendation

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



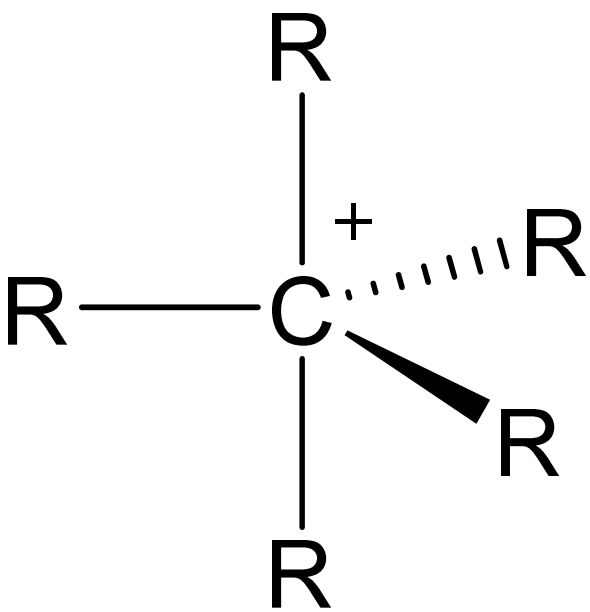


Akiba, Kin-ya. *Chemistry of Hypervalent Compounds*, **1999**, Chapter 2
Musher, J. I. *Angew. Chem. Internat. Edit.* **1969**, *8,* 54
Reed, A, E.; Schleyer, P. von R. *J. Am. Chem. Soc.* **1990,** *112,* 1434

Notation for hypervalent compounds

- # of valence e^- - Element - # of ligands

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



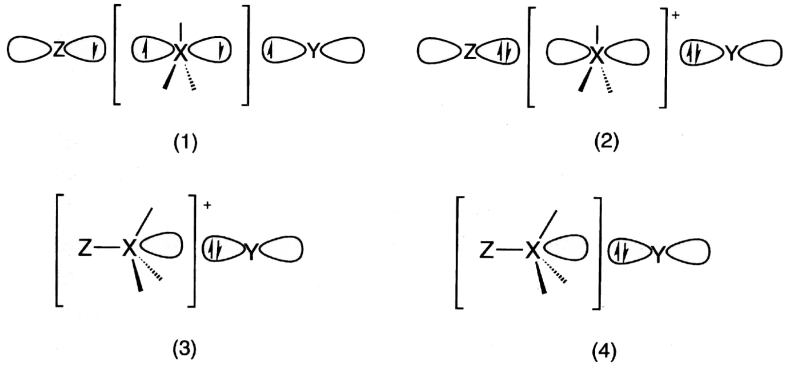
Akiba, Kin-ya. *Chemistry of Hypervalent Compounds*, 1999, Chapter 2

Bonding in hypervalent molecules

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

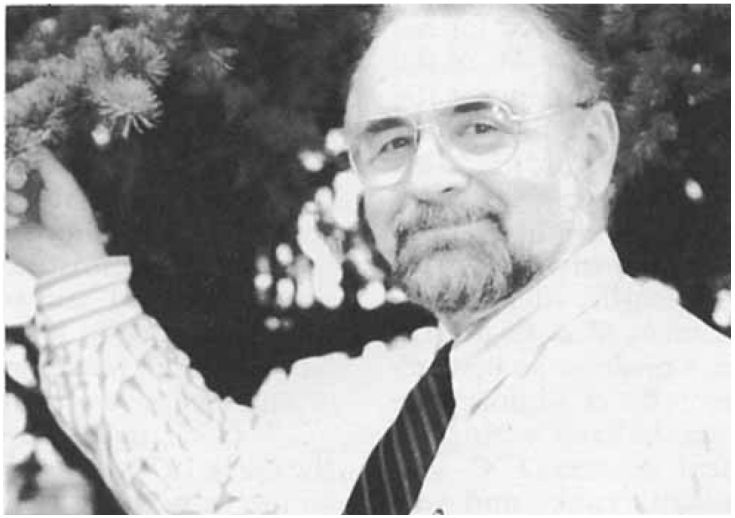
  This bond can be viewed in four ways

  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 σ* orbital of a cationic molecule
  4. Add a lone pair to the σ* orbital of a neutral molecule, “Frozen transition state”

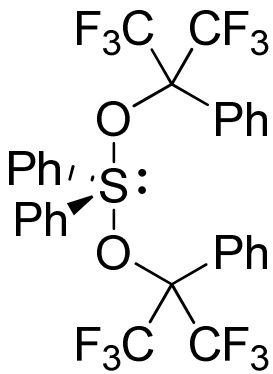


Akiba, Kin-ya. *Chemistry of Hypervalent Compounds*, 1999, Chapter 2

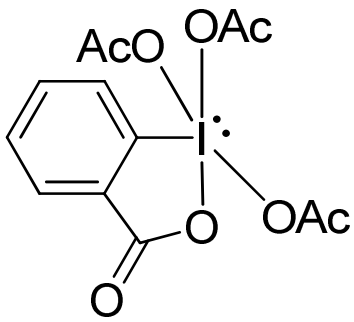
J.C Martin



- Extensive research on Hypervalent compounds
- Martin Sulfurane
- Dess-Martin Periodinane,
- Martin ligand



Martin Sulfurane



Dess-Martin Periodinane

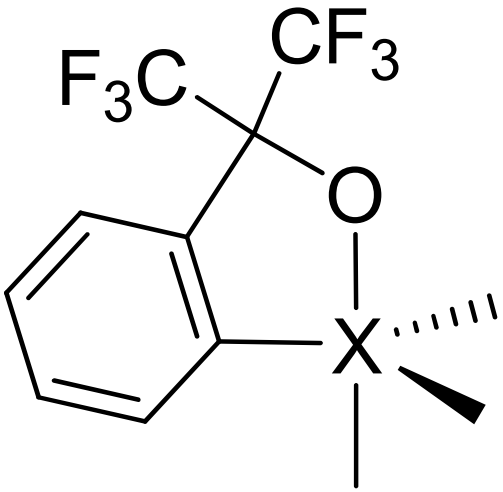
The Martin Ligand

Stabilizes Hypervalent Species

Gem-dimethyl effect

Electron withdrawing apical Ligand

Five membered ring effect



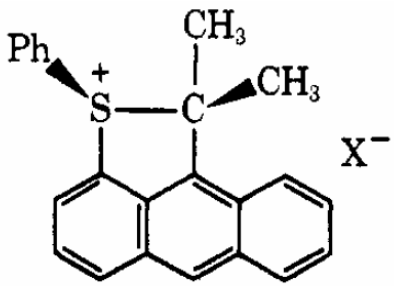
Perozzi, E. F.; Michalak, R.S.; Figuly, G.D.; Stevenson, W. H. III; Dess, D.B.; Ross, M. R.; Martin, J. C.; *J. Am. Chem. Soc.* **1981,** *46,*1049

Martin's First Attempts at Pentavalent Carbon

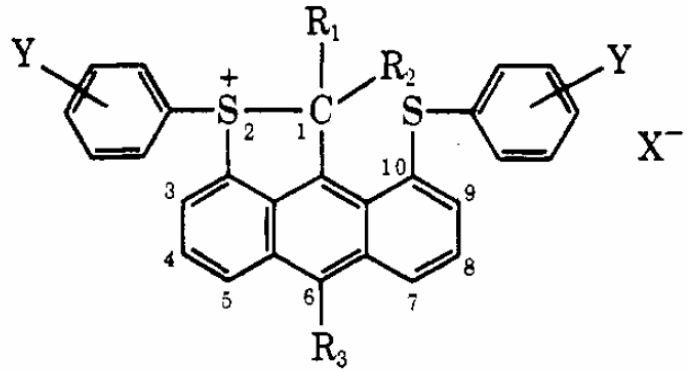
2 shows diastereotopic methyl signals by NMR

3-**5** "Bell-Clapper" rearrangement

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



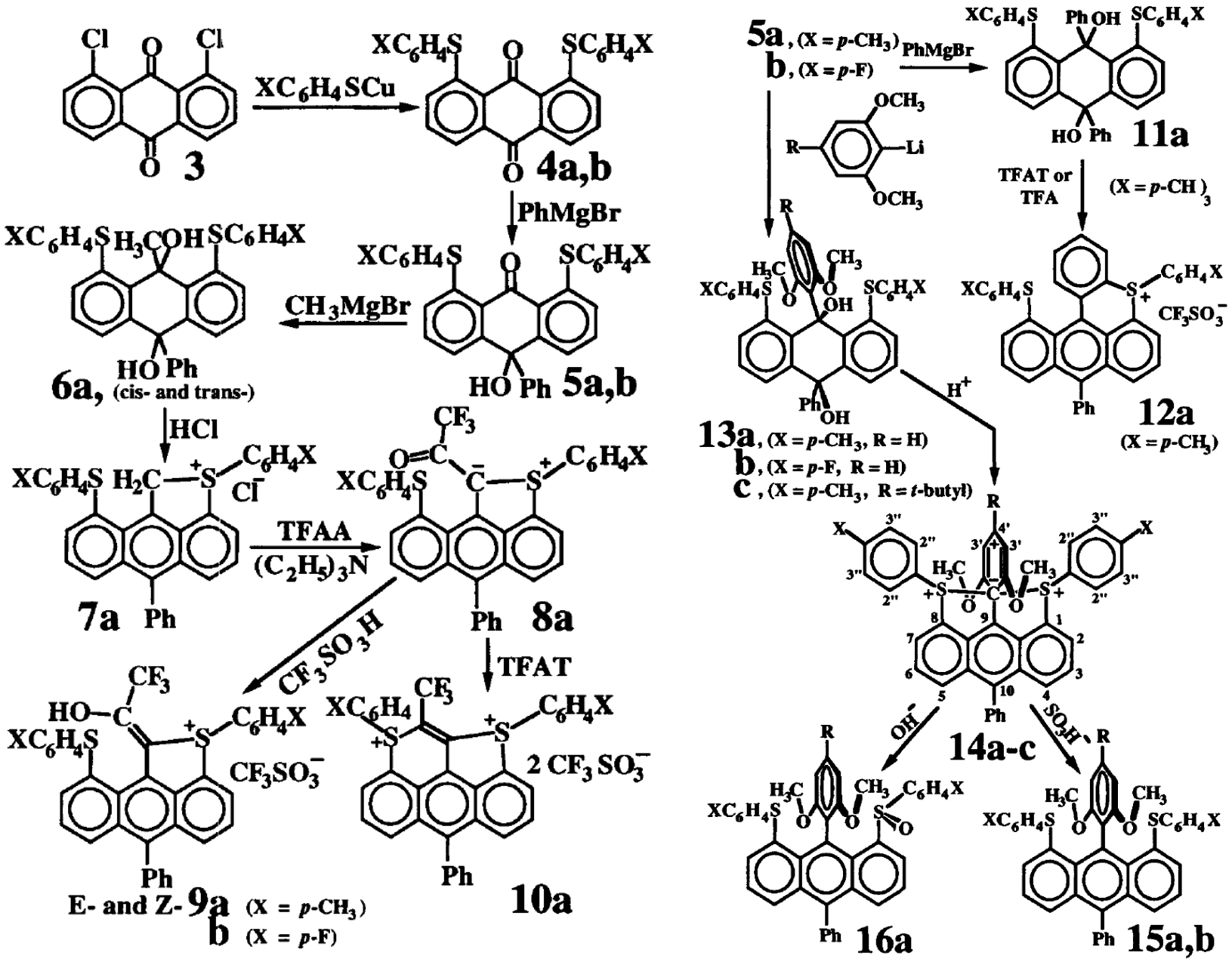
2



3, $R_1 = R_2 = CH_3$; $R_3 = H$
4, $R_1 = R_2 = H$; $R_3 = CH_3$
5, $R_1 = R_2 = H$; $R_3 = Ph$
a, Y = H
b, Y = 4-CH_3
c, Y = 3-CH_3
d, Y = 4-$C(CH_3)_3$
e, Y = 4-OCH_3

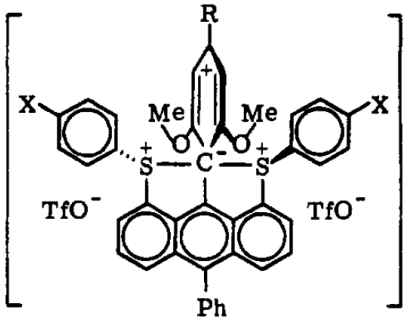
Martin, J.C., Basalay, Robert J.; *Journal of the American Chemical Society,* **1973**, *95*, 2572

Martin's Synthesis

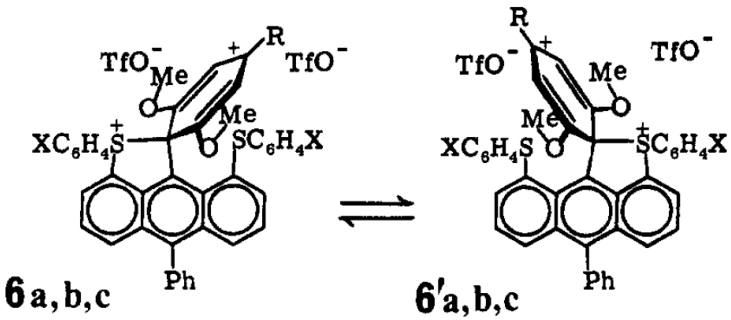


If at first you don't succeed…

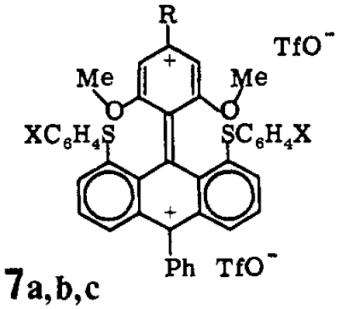
- single peak for para substituents and no sign of broadening as low as -100ºC,
- **2a** was ^{13}C labeled to measure ^{13}C-^{13}C couplings, in the range for directly bonded sp_2 carbons
- Structure 7a is argued against by analysis of the chemical shifts.
- Crystal structure could not be obtained.



2a (X = CH_3, R = H)
b (X = CH_3, R = t-Bu)
c (X = F, R = H)



6a,b,c **6'a,b,c**

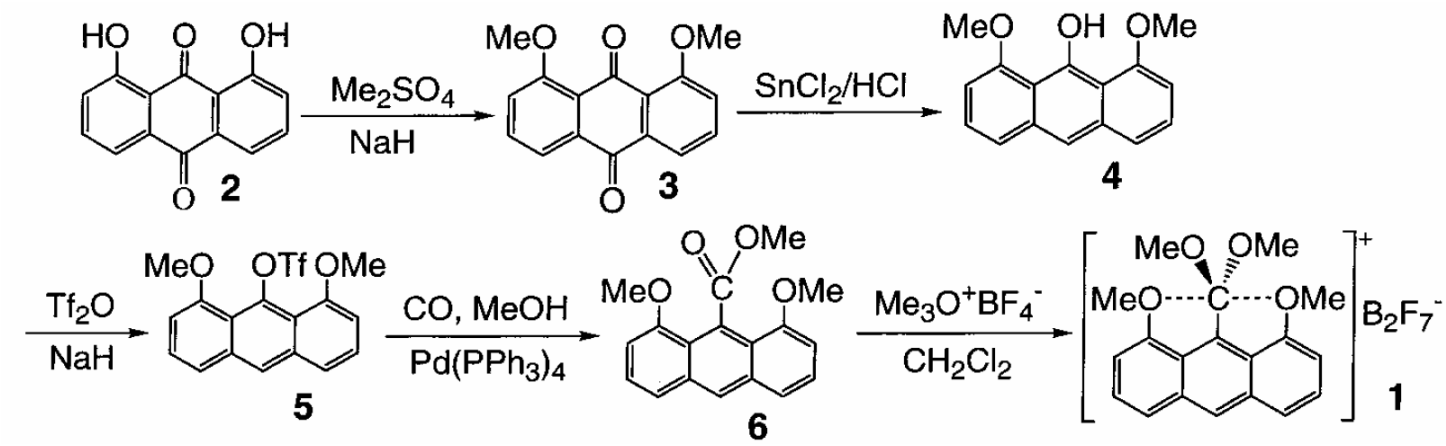


7a,b,c

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

Enter Akiba



Akiba, Kin-ya; Yamashita, Makoto; Yamamoto, Yohsuke; Nagase, Shigeru. *J. Am. Chem. Soc.* **1999,** *121,* 10644

Try...

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

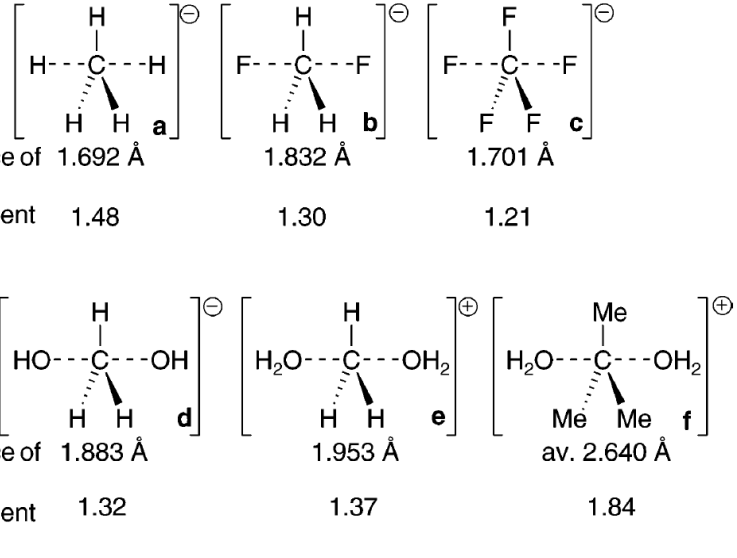


Figure 1. Calculated hypervalent pentacoordinate carbon structures for transition state of S_N2.

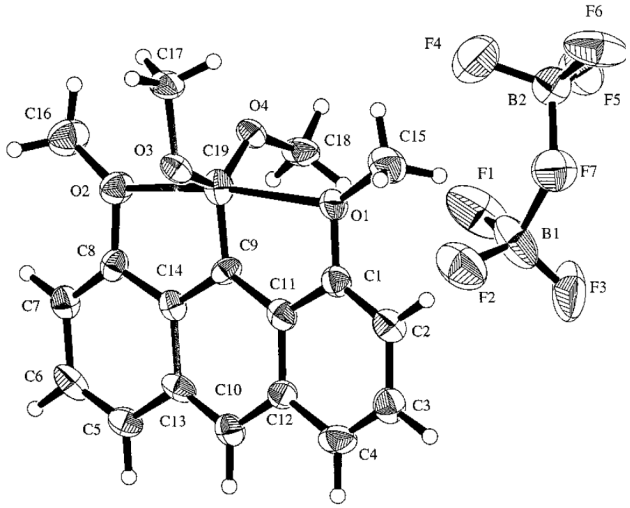
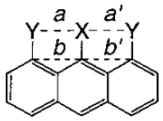


Figure 1. Crystal structure (30% thermal ellipsoids) of **1**.

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

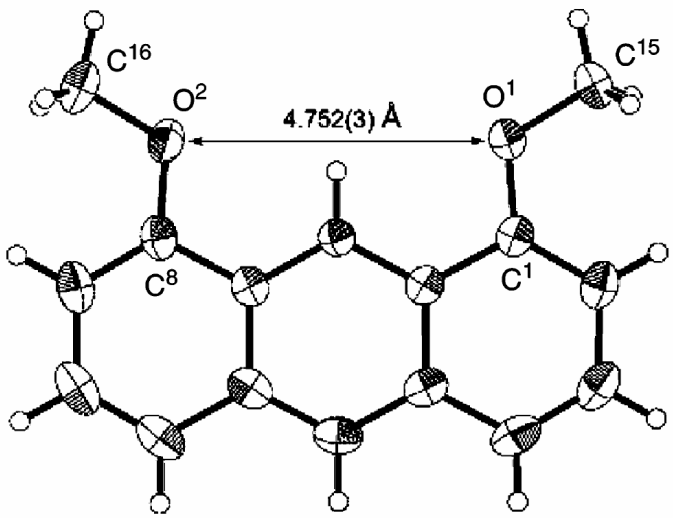


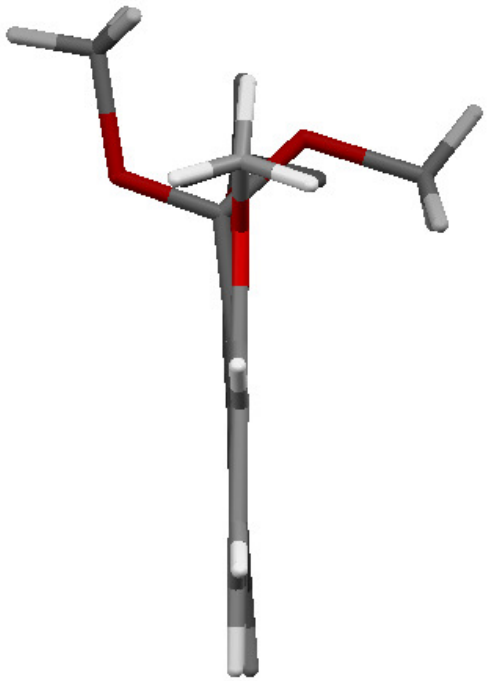
compd	*a*	*a′*	*b*	*b′*
7: X = Y = Br	3.2658(6)	3.2738(6)	2.564(6)	2.567(6)
5: X = OTf, Y = OMe	2.572(2)	2.571(2)	2.554(3)	2.545(3)
8: X = CN, Y = OMe	2.530(3)	2.531(3)	2.538(6)	2.542(4)
1: X = $C^+(OMe)_2$, Y = OMe	2.45(1)	2.43(1)	2.49(2)	2.52(2)

Akiba, Kin-ya; Yamashita, Makoto; Yamamoto, Yohsuke; Nagase, Shigeru. *J. Am. Chem. Soc.* **1999,** *121,* 10644

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

Wait a minute…





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

Levy, Jack B. *Chem. Eng. News,* **2000,** *78(7),* 13-14.

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

Try Again… In Parallel

New strategies:

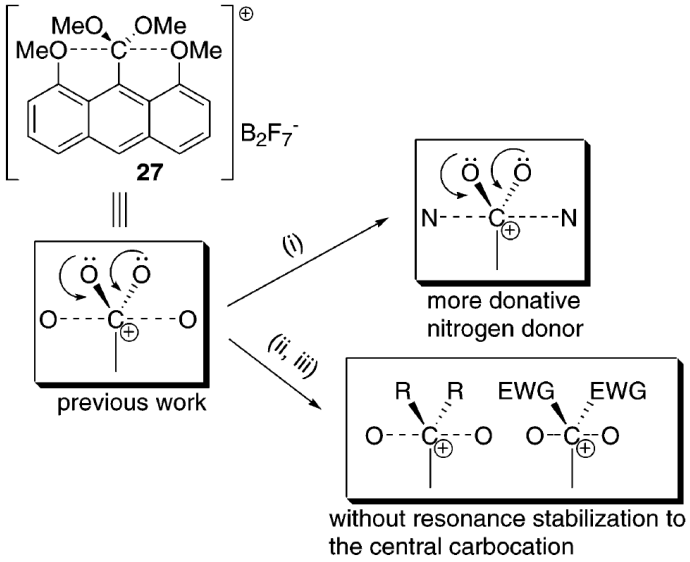
1) Use stronger donor atom

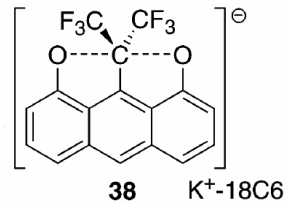
2) Destabilize carbocation

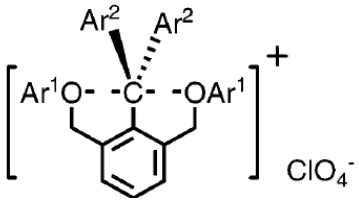
3) Switch to an anionic system, More Sn2 like

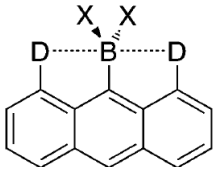
4) Mount a parallel effort using a different ligand framework

5) Change the objective, switch to boron







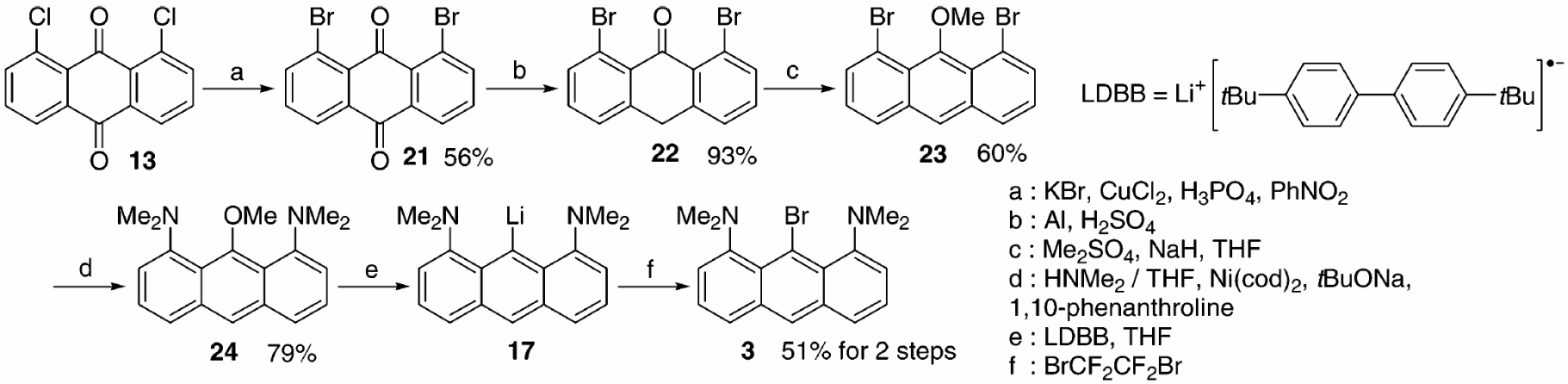


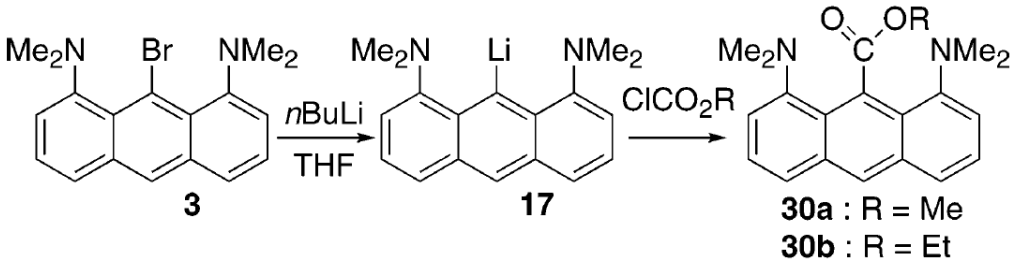
Yamashita, Makato; Yamamoto, Yohsuke; Akiba, Kin-ya; Hashizume, Daisuke; Iwasaki, Fujiko; Takagi, Nozumi; Nagase, Shigeru. *J. Am. Chem. Soc.* **2005**, *127,* 4354

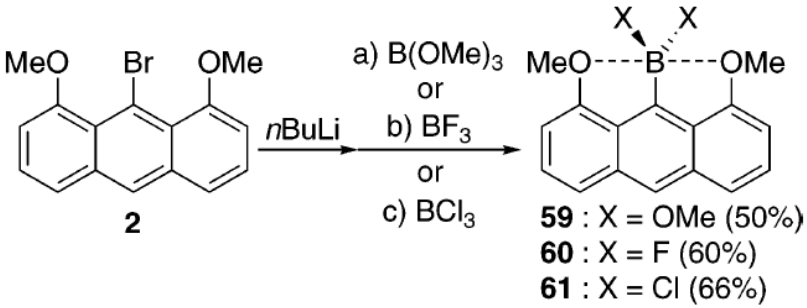
Akiba, Kin-ya; Moriyama, Yuji; Mizozoe, Mitsuhiro; Inohara, Hideki; Nishii, Takako; Yamamoto, Yohsuke; Minoura, Mao; Hashizume, Daisuke; Iwasaki, Fujiko; Takagi, Nozumi; Ishimura, Kazuya; Nagase, Shigeru. *J. Am. Chem. Soc.* **2005**, *127,* 5893

Synthesis

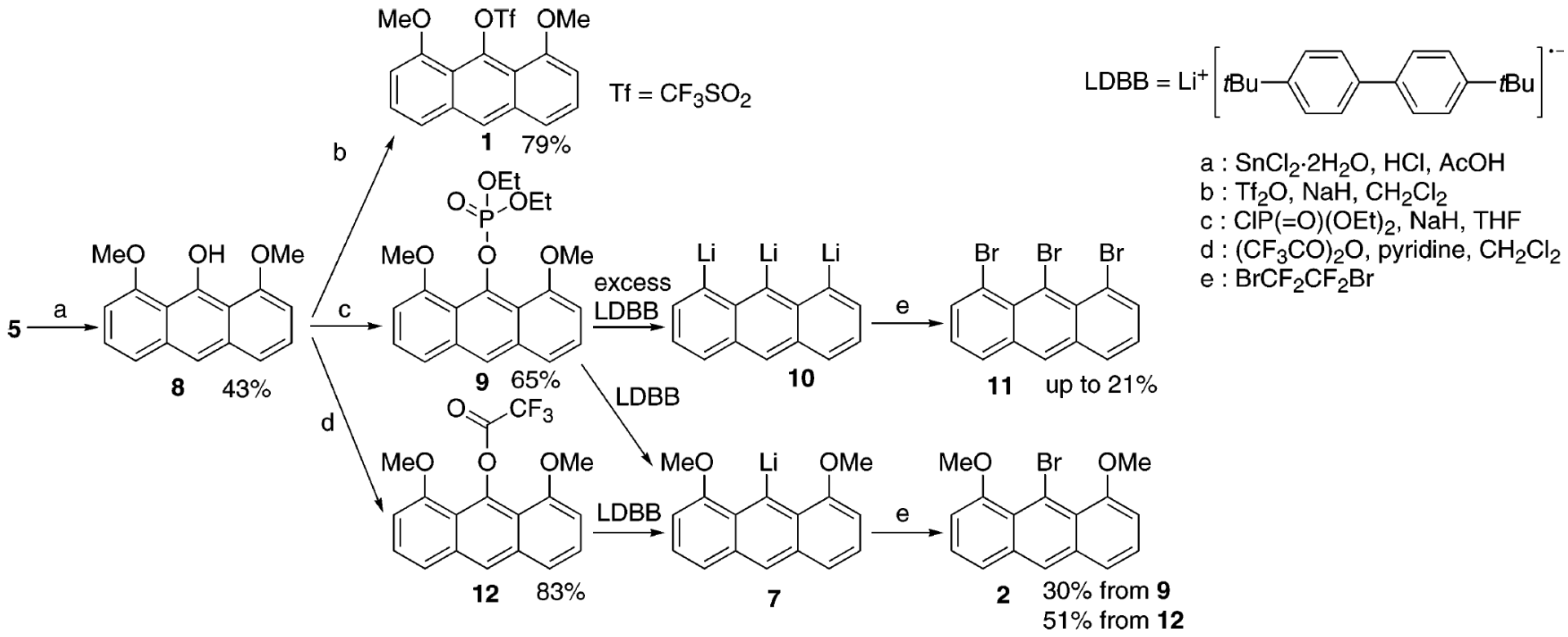
Scheme 5. Synthesis of 9-Bromo-1,8-bis(dimethylamino)anthracence **3**

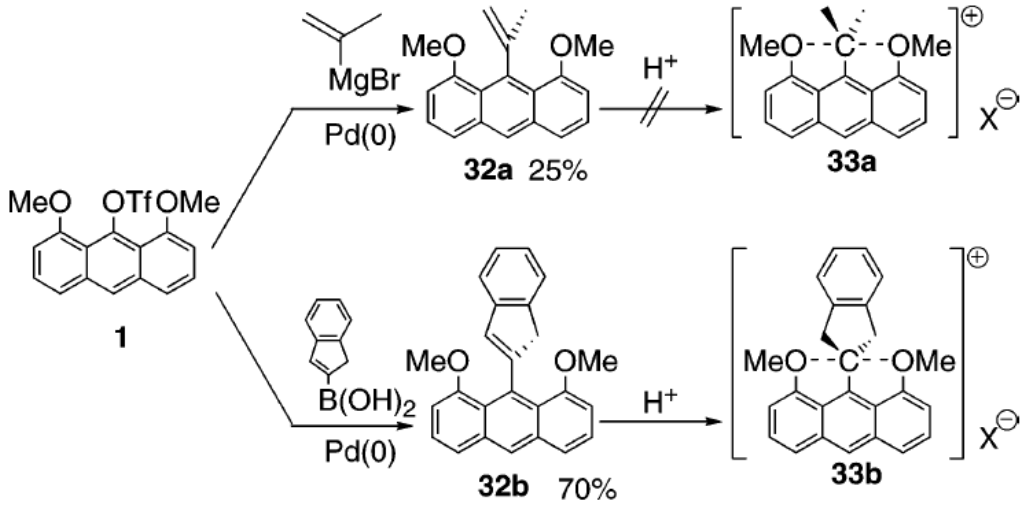




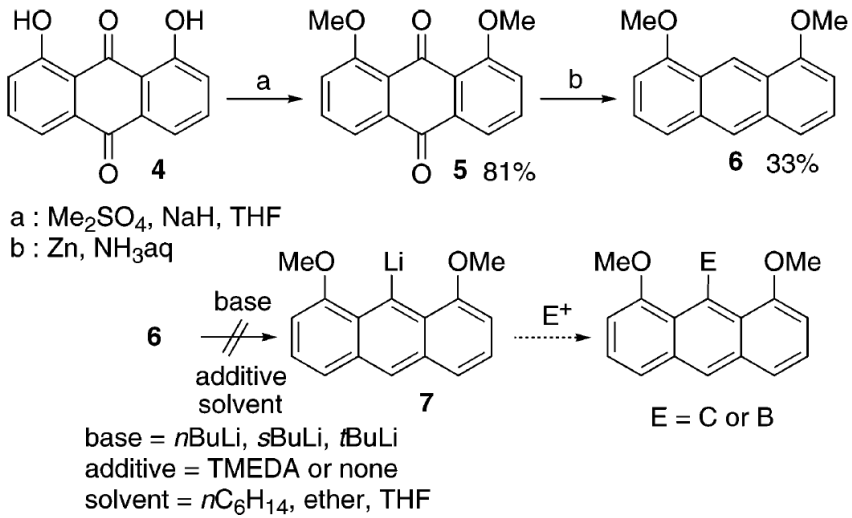


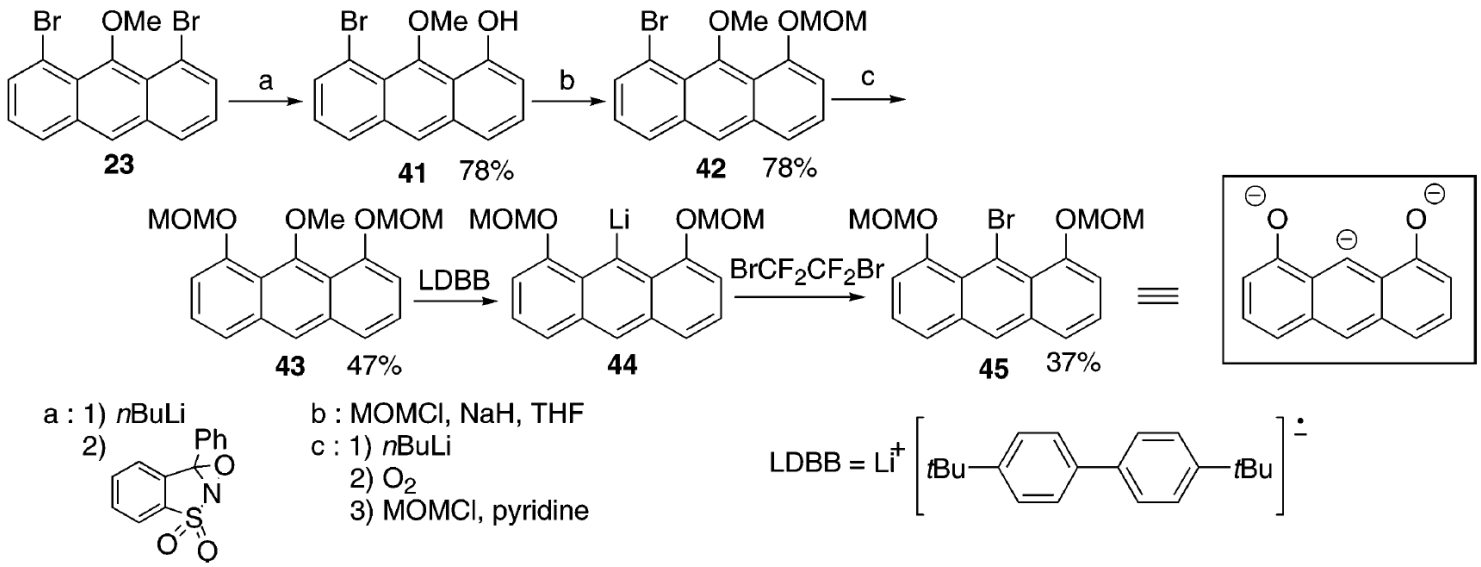
Yamashita, Makato; Yamamoto, Yohsuke; Akiba, Kin-ya; Hashizume, Daisuke; Iwasaki, Fujiko; Takagi, Nozumi; Nagase, Shigeru. *J. Am. Chem. Soc.* **2005**, *127,* 4354

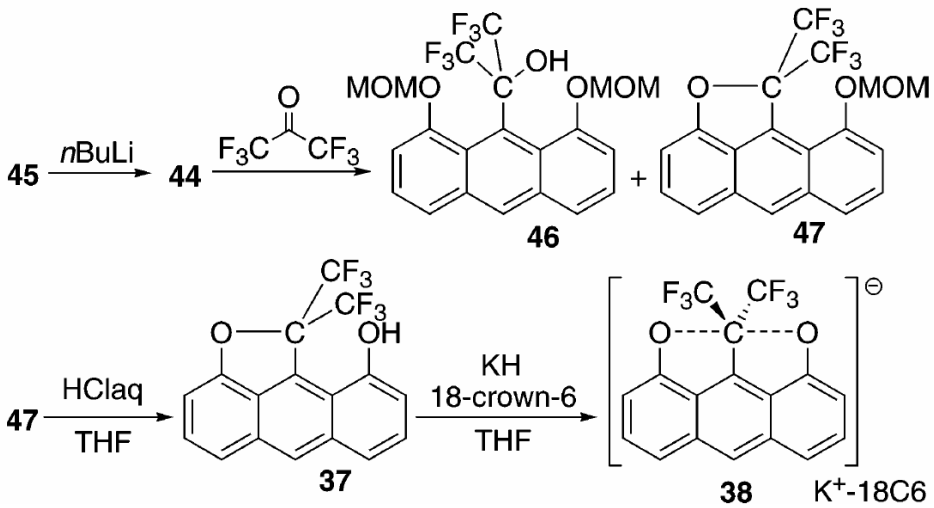

MeO OTf OMe
Tf = CF3SO2
1 79%
b
OEt
O P OEt
MeO OH OMe
MeO O OMe
5
a
c
excess
LDBB
Li Li Li
Br Br Br
e
8 43%
9 65%
10
11 up to 21%
LDBB
d
O CF3
MeO O OMe
MeO Li OMe
MeO Br OMe
LDBB
e
12 83%
7
2 30% from 9
51% from 12
LDBB = Li+ [tBu tBu]•−
a : SnCl2·2H2O, HCl, AcOH
b : Tf2O, NaH, CH2Cl2
c : ClP(=O)(OEt)2, NaH, THF
d : (CF3CO)2O, pyridine, CH2Cl2
e : BrCF2CF2Br



Scheme 1. Attempted *peri*-Lithiation of 1,8-Dimethoxyanthracene **6**

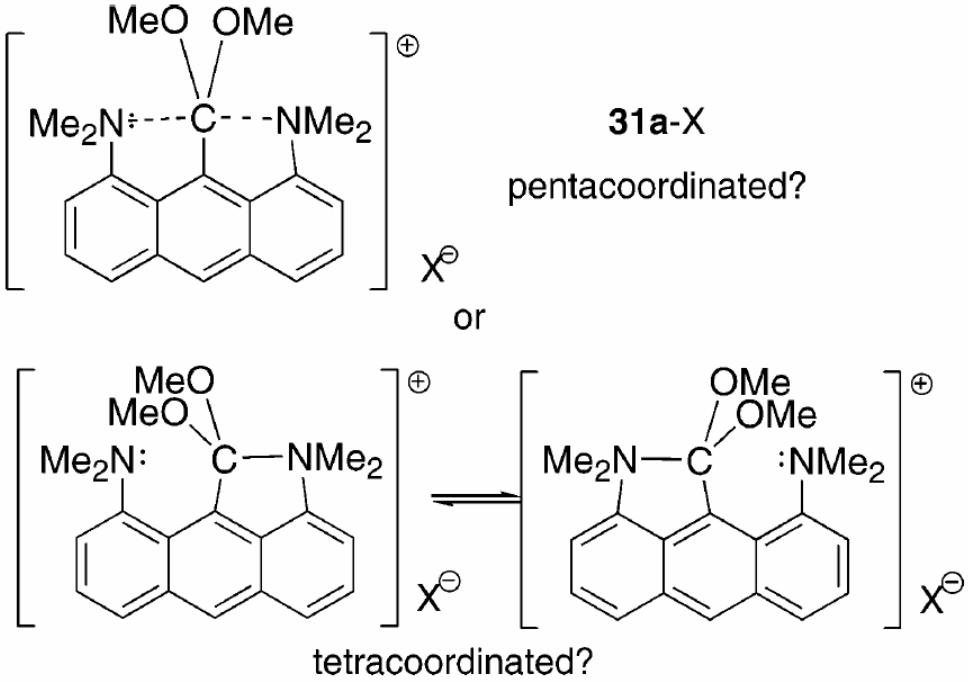



Br OMe Br
23
a
Br OMe OH
41 78%
b
Br OMe OMOM
42 78%
c
MOMO OMe OMOM
43 47%
LDBB
MOMO Li OMOM
44
BrCF2CF2Br
MOMO Br OMOM
45 37%
a : 1) nBuLi
2)
Ph
O
N
S
O O
b : MOMCl, NaH, THF
c : 1) nBuLi
2) O2
3) MOMCl, pyridine
LDBB = Li+
tBu
tBu


45
nBuLi
44
F3C CF3
O
F3C
F3C
OH
MOMO
C
OMOM
46
+
CF3
CF3
O
C
OMOM
47
47
HClaq
THF
CF3
CF3
O
C
OH
37
KH
18-crown-6
THF
F3C CF3
O
C
O
38
K+-18C6

Nitrogen donor

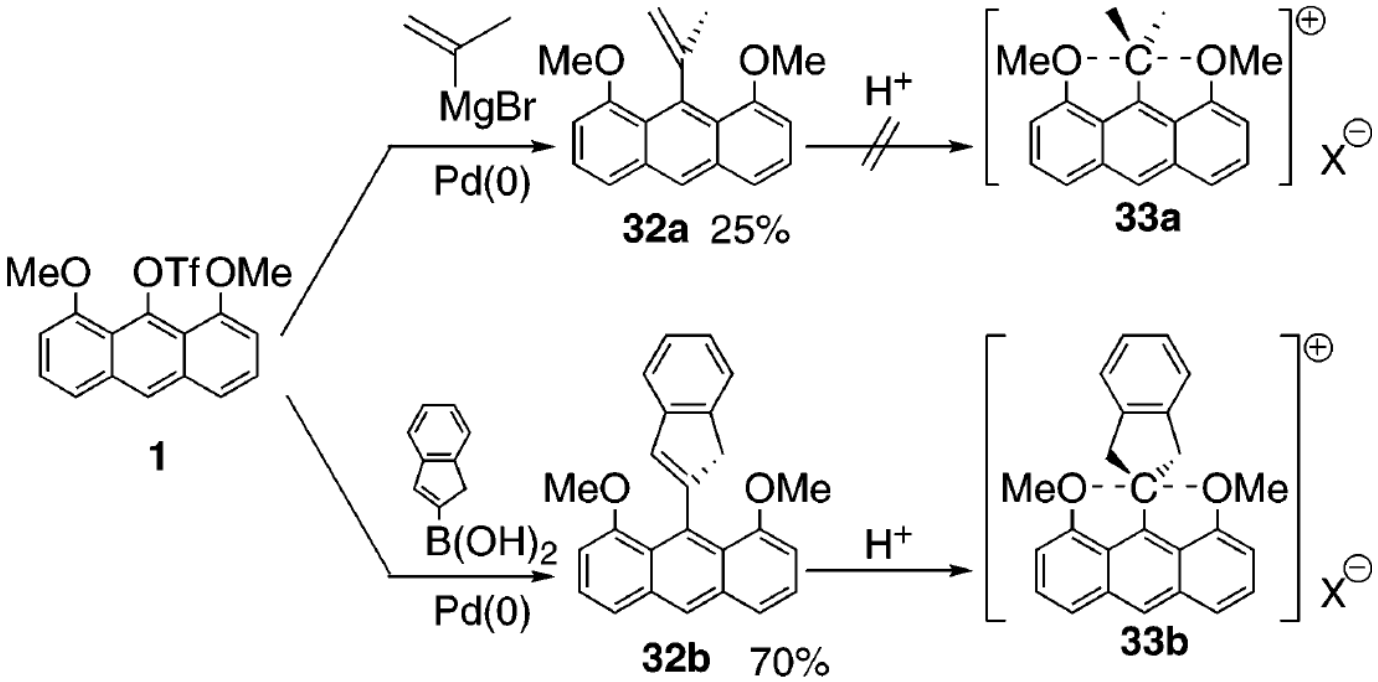
- NMR consistent with symmetrical structure
- Does not crystallize



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

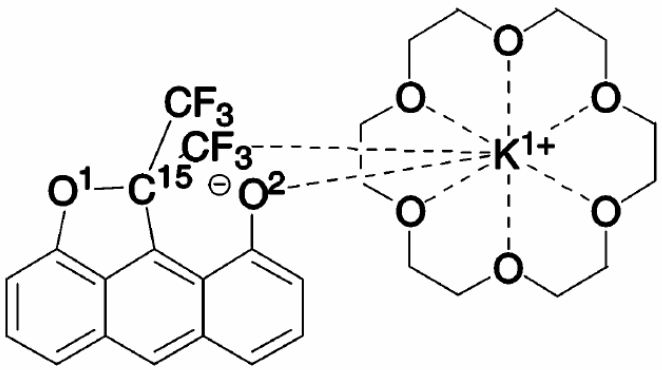
Reduced stabilization

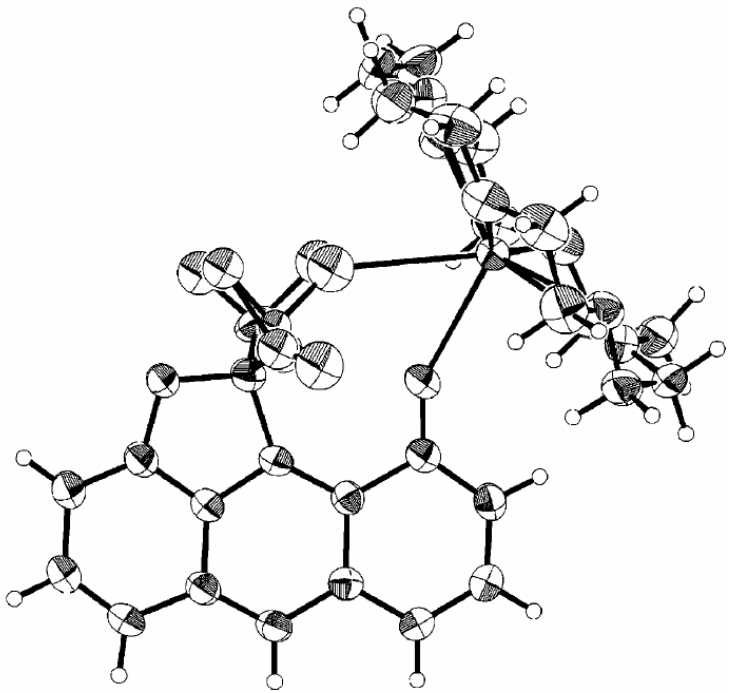
- NMR inconsistent with **33a**
- **33b** doesn't crystallize



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

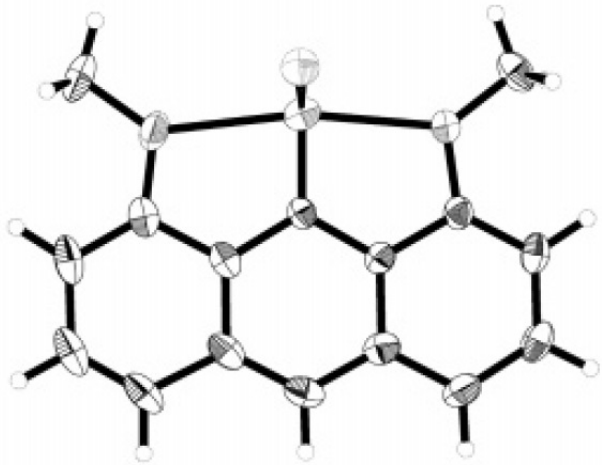
Anionic model



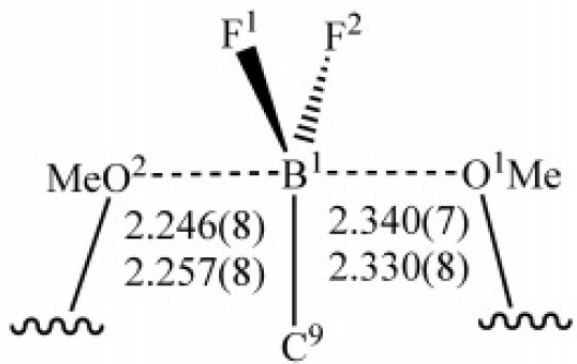


Yamashita, Makato; Yamamoto, Yohsuke; Akiba, Kin-ya; Hashizume, Daisuke; Iwasaki, Fujiko; Takagi, Nozumi; Nagase, Shigeru. *J. Am. Chem. Soc.* **2005**, *127,* 4354

Boron



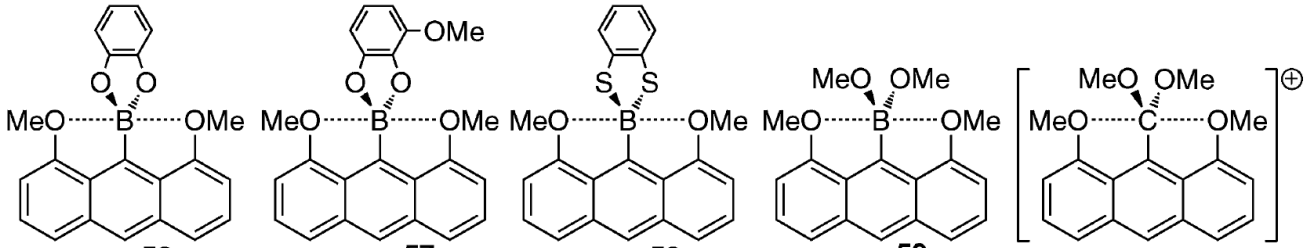
60



δ 19-25

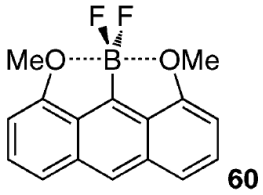
Yamashita, Makato; Yamamoto, Yohsuke; Akiba, Kin-ya; Hashizume, Daisuke; Iwasaki, Fujiko; Takagi, Nozumi; Nagase, Shigeru. *J. Am. Chem. Soc.* **2005**, *127,* 4354

loose pentacoordinate



	56	57	58	59	27
	2.379(2), 2.441(2)	2.398(4), 2.412(4)	2.436(2) identical	2.405(6), 2.462(6) 2.448(6), 2.456(5) 2.414(6), 2.457(6)	2.43(1), 2.45(1)
total O-B(or C)-O distance(av.)	4.82	4.81	4.87	4.88	4.88

tight pentacoordinate

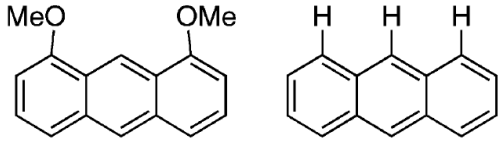


60

2.246(8), 2.340(7)
2.257(8), 2.330(8)

total O-B-O distance(av.) 4.59

Cf.

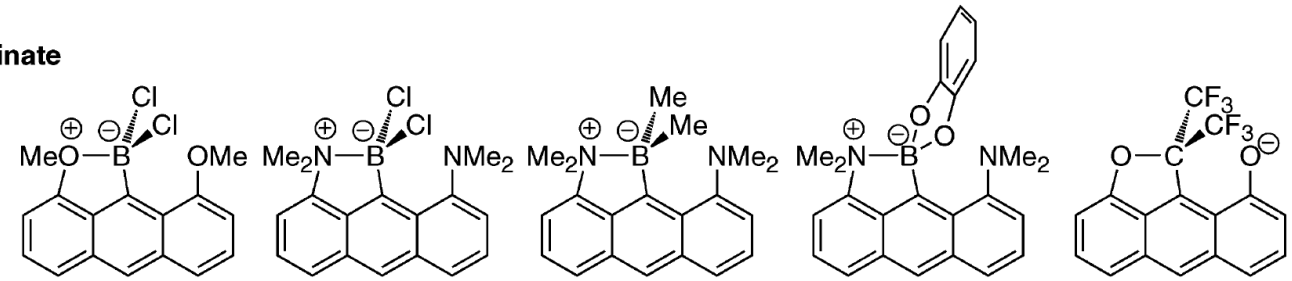


6

O-O distances 4.752(3)

H-H distances 2.46(2)

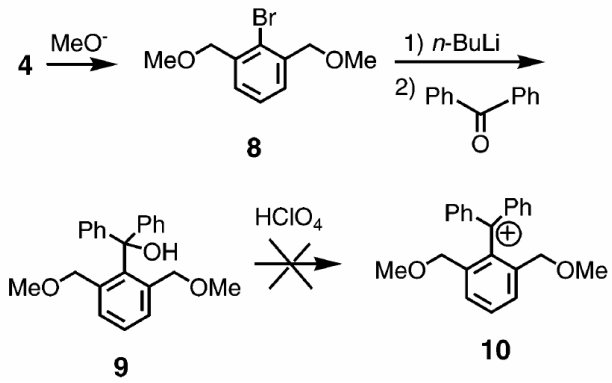
tetracoordinate



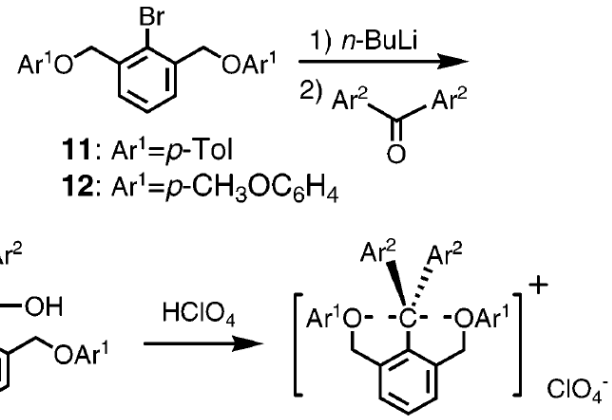
	61	52	51	50	38
	1.686(7), 2.790(7)	1.664(3), 3.129(3)	1.739(2), 3.124(3)	1.809(2), 2.941(2)	1.471(5), 2.986(5)
total O-B(or C)-O distance(av.)	4.48	4.79	4.86	4.75	4.46

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

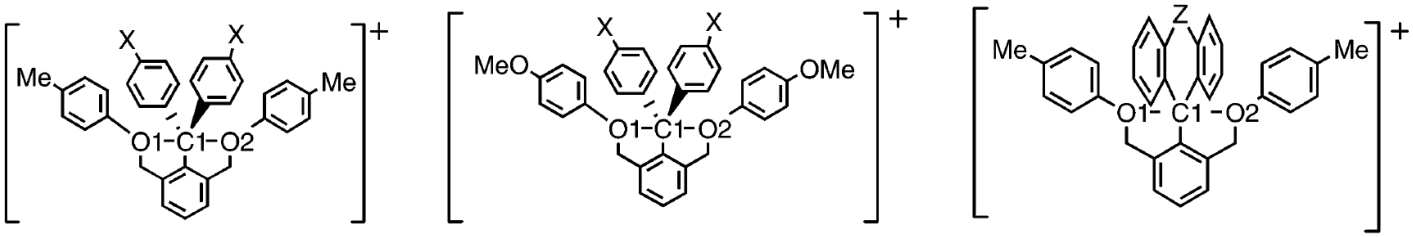


13a(alcohol), **15a**(cation): Ar^1=*p*-Tol, Ar^2=Ph
13b(alcohol), **15b**(cation): Ar^1=*p*-Tol, Ar^2=*p*-FC_6H_4
13c(alcohol), **15c**(cation): Ar^1=*p*-Tol, Ar^2=*p*-ClC_6H_4
13d(alcohol) : Ar^1=*p*-Tol, Ar^2=*p*-$CH_3OC_6H_4$
14a(alcohol), **16a**(cation): Ar^1=*p*-$CH_3OC_6H_4$, Ar^2=Ph
14b(alcohol), **16b**(cation): Ar^1=*p*-$CH_3OC_6H_4$, Ar^2=*p*-FC_6H_4
14c(alcohol), **16c**(cation): Ar^1=*p*-$CH_3OC_6H_4$, Ar^2=*p*-ClC_6H_4
14d(alcohol), **16d**(cation): Ar^1=*p*-$CH_3OC_6H_4$, Ar^2=*p*-$CH_3OC_6H_4$

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^1) and the Donating Oxygen Atoms (O^1 and O^2) and the $O^1{-}C^1{-}O^2$ Angles Revealed by X-ray Analysis of **15b-ClO_4**, **15c-ClO_4**, **15e-ClO_4**, **15f-ClO_4**, **16a-ClO_4**, **16b-PF_6**, and **16d-PF_6**



15b (X=F) ClO_4^-
15c (X-Cl)

16a (X=H) PF_6^-
16b (X=F) or ClO_4^-
16d (X=OMe)

15e (Z=S) ClO_4^-
15f (Z=O)

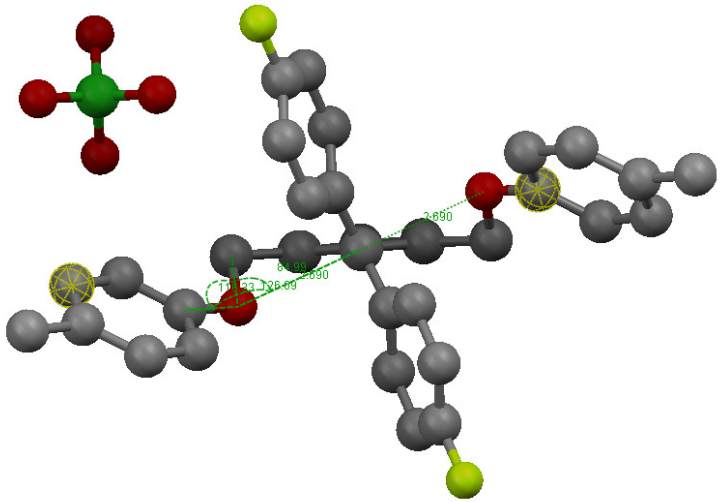
distance (Å)	**15c-ClO_4** (X = Cl)	**15b-ClO_4** (X = F)	**16a-ClO_4** (X = H)	**16b-PF_6** (X = F)	**16b-PF_6** (X = OCH_3)	**15e-ClO_4** (Z = S)	**15f-ClO_4** (Z = O)
$C^1{-}O^1$	2.671(4)	2.690(4)	2.705(2)	2.718(5)	2.77(1)	2.776(4) 2.617(4)	3.026(4)
$C^1{-}O^2$	2.682(4)	2.690(4)	2.705(2)	2.718(5)	2.78(1)	2.855(5) 2.827(4)	4.23
$O^1{-}C^1{-}O^2$	161.9(1)	162.3(1)	158.9(2)	160.4(4)	159.1(4)	155.7(2) 165.0(2)	

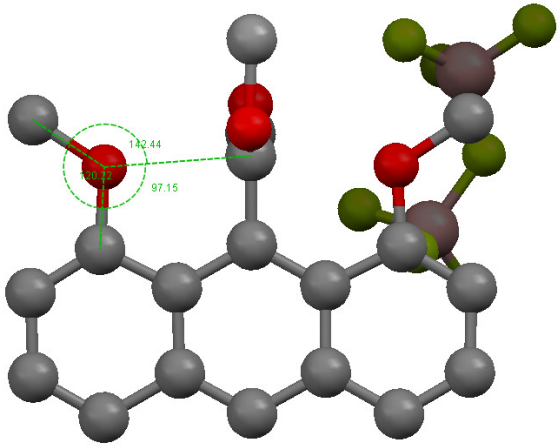
Akiba, Kin-ya; Moriyama, Yuji; Mizozoe, Mitsuhiro; Inohara, Hideki; Nishii, Takako; Yamamoto, Yohsuke; Minoura, Mao; Hashizume, Daisuke; Iwasaki, Fujiko; Takagi, Nozumi; Ishimura, Kazuya; Nagase, Shigeru. *J. Am. Chem. Soc.* **2005**, *127,* 5893

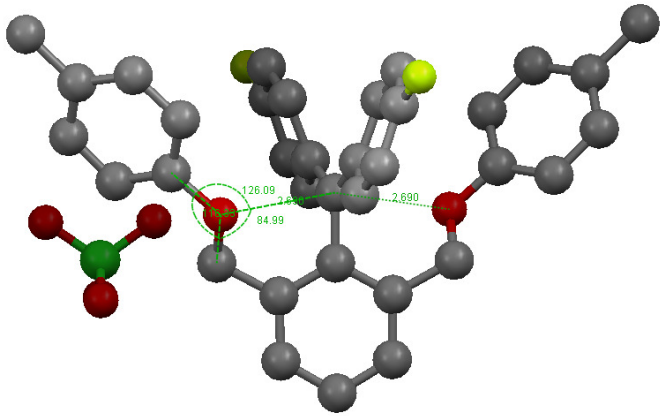
Benzene skeleton cont.

"both oxygens (O^1 and O^2) are sp^2; that is, the sum of the angles (C^5-O^1-C^6, C^1-O^1-C^6, C^1-O^1-C^5) around O^1 is 360.0º"

116.33+126.09+84.99=327.41º







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.

Bader, R. F. W. *J. Phys. Chem. A,* **1998,** *102*, 7314
Haaland, A.; Shorokhov, D. I.; Tverdova, N. V. *Chem. Eur. J.* **2004,** *10*, 4416
Bader, R. F. W.; Fang, D-C. *J. Chem. Theory Comput.* **2005**, *1,* 403

Bond Paths and Experimental Electron Density

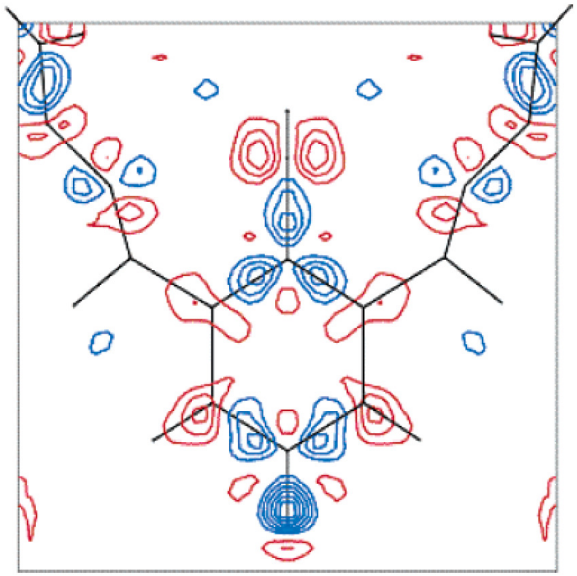


Figure 9. Static model map of **15b-ClO$_4$** based on the accurate X-ray analysis. Positive and negative regions are shown as blue and red lines, respectively, and zero contours are omitted.

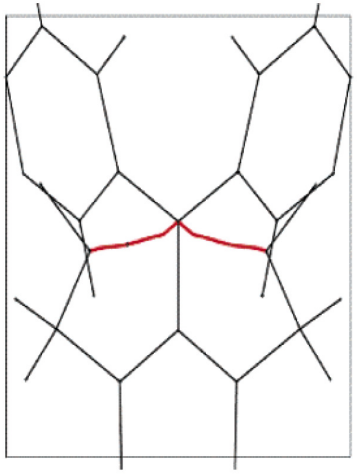


Figure 10. Bond paths of **15b-ClO$_4$** between the central carbon and the oxygen of the arm based on the accurate X-ray analysis.

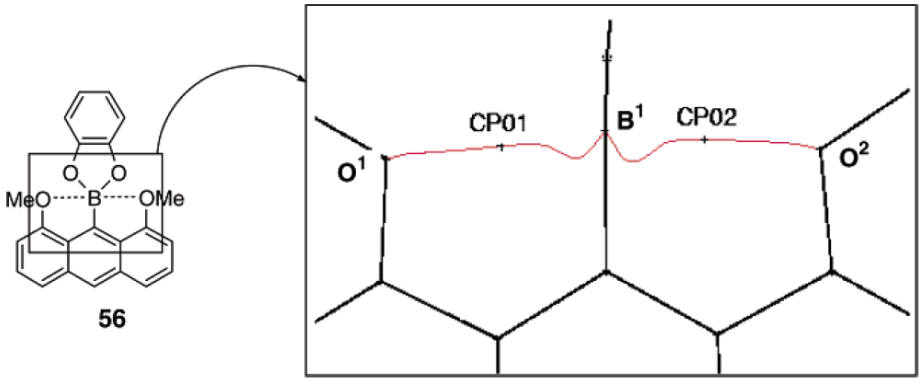


Figure 18. Bond paths of the B^1–O^1 and B^1–O^2 bonds of **56** obtained by the accurate X-ray analysis. Bond paths are shown as red lines.

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.