# Notes

## Crystal Structure of the Molecular Addition Compound Diphenylchloroborane·Tetrahydrofuran

**Wendy I. Cross, Matthew P. Lightfoot,**
**Francis S. Mair,* and Robin G. Pritchard**

Department of Chemistry, UMIST, P.O. Box 88, Manchester
M60 1QD, U.K.

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### Introduction

A very common usage of haloboranes in organic synthesis is in the cleavage of ethers.[1] Diorganohaloboranes in particular are valued in this capacity.[2] Ether cleavage is particularly facilitated in the case of cyclic ethers, such as tetrahydrofuran (THF), so much so that it is common practice to employ low temperatures when utilizing haloboranes in such solvents. Indeed, cleavage of tetrahydrofuran can even occur with short reaction times at 0 °C, such as was observed in the only crystallographic confirmation of the course of a boron-mediated ether cleavage reaction in the literature,[3] that of tetraphenylphosphonium 2-(4-chlorobut-1-oxy)-1-carba-*closo*-undecahydrododecaborate(1-) (**1**; Chart 1). This was obtained from the insertion reaction of $BCl_3{\cdot}SMe_2$ with $Li_3[CB_{10}H_{11}]$ in THF.

It was particularly surprising for us to discover, therefore, that from the reaction of diphenylchloroborane with a THF solution of tetralithiated tetra-*tert*-butyl calix(4)arene, the well-formed colorless crystals isolated were in fact the pseudotetrahedral complex $Ph_2BCl{\cdot}THF$ (**2**, Figure 1).

### Experimental Section

$Ph_2BCl$ and tetra-*tert*-butyl calix[4]arene were prepared according to literature methods.[4,5] To a THF solution (7 mL) of tetra-*tert*-butyl calix[4]arene (0.34 g, 0.52 mmol) was added dropwise $^nBuLi$ (1.35 M in hexanes, 1.56 mL, 2.1 mmol). The solution was stirred for 2 h, and an orange solution was formed. The solution was cooled to −78 °C, and $BPh_2Cl$ (0.58 g, 2.89 mmol) in hexane (2 mL) was added. Gradual warming produced a white, cloudy suspension. As the solution reached room temperature, a clear, yellow solution was formed that was left stirring for 1 h. Some of the solvent (6 mL) was removed under vacuum, and the remaining solution was placed at −50 °C to form colorless rhomboidal crystals of **2**, mp = 124−130 °C. $^1H$ NMR (200 MHz, $C_6D_6$): $\delta$ 8.08 (dd, 4H), 7.34 (m, 6H), 3.61 (m, 4H, THF), 1.12 (m, 4H, THF). Found: C, 70.28; H, 6.91; Cl, 12.89. Calcd for $C_{16}H_{18}BClO$(%): C, 70.50; H, 6.66; Cl, 13.00. Details of the structure analysis are summarized in Table 1.

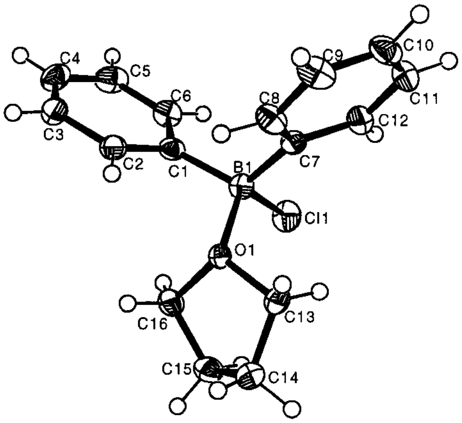
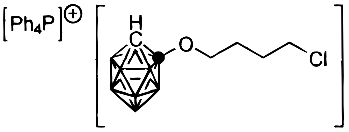


**Figure 1.** Molecular structure of **2**. See Table 2 for significant bond lengths and angles.

### Chart 1



**1**

● = B; unmarked vertices = BH

**Table 1.** X-ray Data Collection and Processing Parameters for **1**

| | |
|---|---|
| molecular formula | $C_{16}H_{18}BClO$ |
| fw | 272.56 |
| temp/°C | −70(2) |
| wavelength/Å | 0.710 73 |
| space group | $P2_1/c$ |
| $a$/Å | 9.087(2) |
| $b$/Å | 14.019(4) |
| $c$/Å | 11.680(2) |
| $\beta$/deg | 108.324(10) |
| $V$/Å$^3$ | 1412.4(6) |
| $Z$ | 4 |
| $D$(calcd)/g cm$^{-3}$ | 1.282 |
| abs coeff/mm$^{-1}$ | 0.258 |
| final $R$ indices: $R_1$,[a] w$R_2^b$ | 0.0301, 0.0821 |

[a] $R_1 = \sum||F_o| - |F_c|/\sum|F_o|$ (observed reflections). [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum(wF_o^2)^2]^{1/2}$ (all data).

### Results and Discussion

The successful structural characterization of **2** constitutes the first case of THF found intact in the presence of a boron−halogen bond. We therefore have confirmed structural data on both the precursor and postcursor[3] of the ether cleavage reaction.

In **2**, the C−O lengths (see Table 2) of 1.4835(18) and 1.4899(18) Å are longer than those in free THF (1.429 Å at −175 °C, 1.435 Å at −125 °C) and significantly longer than the mean value of all crystallographically determined uncoordinated THF C−O bond lengths (1.403 Å).[6] This lengthening can be ascribed to the Lewis acid nature of the boron. The lengthening is significant, the THF C−O bond lengths in **2** being among the longest known for accurately determined[6] structures.

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**Table 2.** Bond Lengths [Å] and Angles [deg] for **2**

| | | | |
|---|---|---|---|
| Cl(1)−B(1) | 1.8932(17) | O(1)−B(1) | 1.5691(19) |
| O(1)−C(13) | 1.4835(18) | B(1)−C(1) | 1.599(2) |
| O(1)−C(16) | 1.4899(18) | B(1)−C(7) | 1.602(2) |
| C(13)−O(1)−C(16) | 108.80(11) | C(1)−B(1)−C(7) | 114.75(12) |
| C(13)−O(1)−B(1) | 118.51(11) | O(1)−B(1)−Cl(1) | 104.14(10) |
| C(16)−O(1)−B(1) | 118.00(11) | C(1)−B(1)−Cl(1) | 111.17(10) |
| O(1)−B(1)−C(1) | 106.77(11) | C(7)−B(1)−Cl(1) | 111.65(11) |
| O(1)−B(1)−C(7) | 107.61(12) | C(6)−C(1)−C(2) | 116.66(14) |

While the isolation and characterization of **2** does not directly *prove* that it is the precursor to the ether cleavage reaction, this observation strengthens the view of **2** as a model for the immediate precursor to B−X insertion into the C−O bond. However, the presence of the two phenyl groups appears to moderate the reactivity of the B−X bond. Gillespie has recently championed a novel way of rationalizing the structures and behaviors of many first-row compounds, including haloboranes, using the results of the atoms-in-molecules approach.[7] This view emphasizes the ionic component of bonding[8] and asserts that arguments based on $p\pi-p\pi$ interaction are likely to be spurious because it is not chemically sensible to consider a halogen atom as donating $\pi$-electron density to a boron atom on grounds of electronegativity.[8] The conventional argument may run thus. The phenyl groups, unlike halides, do not donate $\pi$ density. Therefore, they free the boron's unutilized p orbital to accept $\pi$ density from the single remaining chlorine; indeed, through their electron-withdrawing capacity, they increase the demand of the boron for $\pi$ density from the chlorine. A less reactive B−Cl bond than in $BCl_3$ results. However, the B−Cl bond length in **2** is longer than that in the recently computed $Cl_3B\cdot OMe_2$ molecule (mean, 1.835 Å).[9] Conversely, an assumption of predominantly ionic bonding[8] means that the principal determinant of bond strength/length is the closest packing of anionic ligands. Reexamination of experimental and computational structural data in a wide variety of molecular oxides and fluorides supports this view.[8] Applied to **2**, this view explains the observations rather better (vide infra), without the need to employ arguments requiring $p\pi-p\pi$ back-bonding.

Unfortunately, no data are available for a direct comparison of uncomplexed $Ph_2BCl$. However, from those uncomplexed diorganochloroboranes that have been structurally characterized, the expected trends are discernible. The mean B−Cl length in this class is 1.768 Å, similar to the distance in $BCl_3$ (1.75(2) Å).[10] While the carbon ligands are smaller than chlorine, thereby allowing a closer approach for the remaining chloride, they are also much less electronegative so that the positive charge on boron is much less well developed, leading to cancellation of the two effects. The shortest in this group is 1.746(5) Å for $(C_6F_5)_2BCl$;[11] the electron-withdrawing character of the perfluorophenyl substituents increases the positive charge on boron and hence maximizes its electrostatic attraction for chloride. The longest, 1.799 Å in 1-chloroborepin ($\overline{C_6H_6B}Cl$), is presumably ascribable to the involvement of the carbocyclic $\pi$ system in reducing the positive charge on boron.[12] The donation of $\pi$ density from a carbon to boron is much more plausible on the grounds of electronegativity than from a halide to boron. The full range of B−Cl lengths in these three-coordinate analogues lies outside the observed B−Cl length of 1.8932(17) Å in **2**. This value is in fact very close to the mean B−Cl value (1.905 Å) found in four-coordinate neutral Lewis base adducts of diorganochloroboranes.[13] The systematic lengthening on increasing coordination number is in full accord with Gillespie's "ligand-close-packing" model of molecular structure. There is no necessity to invoke lost back-bonding as a further reason for lengthening in the case of group 13 halides. The most pertinent comparisons to draw, then, are between similar four-coordinate ether solvates. Experimental data are available for $Ph_3B\cdot THF$[14] but, of course, not for the reactive $Cl_3B\cdot THF$. However, a model of $Cl_3B\cdot OMe_2$ has been recently computed at the B3LYP density functional level.[9]

The B−O bond is marginally shorter in **2** than in the (computed) $Cl_3B\cdot OMe_2$ (1.633 Å)[9] because the carbon atoms of the phenyl groups take up less room around the boron atom than chlorine ligands, allowing closer approach of the ether oxygen in **2**. The B−O bond in **2** is shorter than in $Ph_3B\cdot THF$ (1.660(4) Å),[14] despite the presence of the chlorine, because the positive charge on boron in **2** is greater than in $Ph_3B\cdot THF$. This short B−O bond in **2** is at the expense of a long B−Cl bond; the presence of three first-row elements in the coordination sphere of boron forces the remaining, more weakly held chlorine ligand out further than in comparable trichloroborane complexes ($Cl_3B\cdot OMe_2$, 1.831 and 1.844 Å;[9] $Cl_3B\cdot NMe_3$, 1.839(9) and 1.827(9) Å).[15] The charge on boron in monochlorinated **2** is presumably less than in these two trichloroborane complexes, thus re-enforcing the ligand close-packing argument. Thus, the ionic model, in concert with ligand close-packing, deals satisfactorily with the apparent paradox of an isolable compound with a *shorter* B−O and a *longer* B−Cl bond than those computed for a reactive and as yet unisolated $Cl_3B$ analogue.

The reduced reactivity of B−Cl bonds in diorganochloroboranes with respect to $BCl_3$, and therefore the lack of THF cleavage in **2**, is in stark contrast to **1**. While solutions of **2** require extended reflux to promote reaction, conversion of $BCl_3\cdot SMe_2$ and $Li_3[CB_{10}H_{11}]$ in THF to **1** is quantitative after 30 min of stirring at 0 °C.[3] It is an open question as to whether the insertion reaction itself resulted in facilitating the ether cleavage. Aside from the issue of C−O cleavage reactivity, the sluggishness of $Ph_2BCl\cdot THF$ in reacting with the lithiated calix-4-arene is also quite unexpected. In contrast, $Ph_2BCl$ reacts smoothly at low temperatures with $LiNC(^tBu)_2$ in hexane.[16] In the realm of lithium chemistry, movement from hexane to THF as reaction solvent normally results in an increase in reactivity, through the breakdown of aggregated species. Here the opposite is true. We ascribe this result to a combination of protection of the boron

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(6) Luger, P.; Buschmann, J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 410. A search of the Cambridge Crystallographic Database for uncoordinated THF molecules free of disorder yielded 342 hits. The mean C−O length of these was 1.403 Å, significantly shorter than the distances in **2**. However, the range was 0.931−1.721 Å! Clearly, many of the entries, even those allegedly free of disorder, were subject to crystallographic error. While there was significant clustering of values around the mean (lower quartile = 1.326 Å, higher quartile = 1.471 Å), we consider the safest comparison to draw is with the accurate low-temperature data from pure, crystalline THF.

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from alkoxide attack by the saturation of its coordination sphere by THF and the reluctance of the extensively chelated calixarene to break down its aggregated form[17] even in THF. After extended reflux, some conversion of parent calixarene is apparent, but we have so far failed to isolate pure products.

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**Supporting Information Available:** X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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