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Notes

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Titanium(IV) and Zirconium(IV) Tetrahydroborate Moieties Supported by a Phenoxo Ligand

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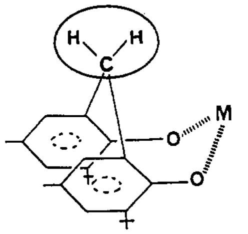
The interest in transition-metal tetrahydroborate derivatives[2] is associated with their potential use as selective reducing agents,[3] as precursors of metal hydrides,[4] and as models for studying the bonding modes of BH_4^- to metals.[5] The tetrahydroborate anion is very rarely found bonded to metals having oxygen donor atoms as ancillary ligands,[6a] in spite of the interest for metal oxide matrix-based reducing agents.[6b] Such ligands should change considerably the reducing properties of the BH_4^- unit toward metals and substrates.

The present report deals with tetrahydroborate derivatives of titanium(IV) and zirconium(IV) bonded to the bisphenoxo dianion ligand (BP) shown in structure I.[7]



I (MBP)

In spite of the very recent impressive development of early-transition-metal alkoxo and phenoxo chemistry,[8] tetrahydroborate derivatives have not been studied. The ligand sketched in I allowed us to isolate a quite unique tetrahydroborate derivative of titanium(IV)[9] and somehow to probe the hapticity of the BH_4^- ligand via the ^1H NMR signals associated with the diastereotopic hydrogens of the bridging methylene.[7] Ligands isoskeletal with that in I but with different donor atoms have been recently designed by us for functioning as spectroscopic probe for the coordination sphere of the metal.[10]

Table I. Crystal Data for Complexes **2** and **4**

complex	**2**	**4**
formula	$C_{23}H_{38}B_2O_2Ti$	$C_{27}H_{46}B_2O_3Zr$
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
cell params at 295 K		
a, Å	9.829 (1)	17.046 (2)
b, Å	13.050 (2)	15.706 (2)
c, Å	9.677 (1)	13.215 (1)
α, deg	90.19 (1)	90
β, deg	93.07 (1)	108.92 (1)
γ, deg	87.11 (1)	90
V, Å^3	1237.9 (3)	3346.8 (7)
Z	2	4
no. of unique obsd data	2607	2902
intens measmt	*a*	*a*
struct refinement	*b*	*b*
R	0.056	0.045

[a] For intensity and background individual profiles were analyzed by following: Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A: Struct. Crystallogr. Cryst. Chem.* **1974**, *A30*, 580. [b] Data reduction, structure solution, and refinement were carried out on a GOULD 32/77 computer using: Sheldrick, G. *SHELX-76. System of Crystallographic Computer Programs*; University of Cambridge: Cambridge, England, 1976. Refinement was by full-matrix least squares anisotropically for all the non-hydrogen atoms except for the C26 carbon atom (complex **4**), which was considered statistically distributed over two positions (A and B) isotropically refined with a site occupation factor of 0.5.

Experimental Section

All operations were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. Infrared spectra were recorded with a Perkin-Elmer 283 spectrophotometer, and NMR spectra with Bruker instruments (AC-200 for ^1H and AC-200 WB for ^{11}B).

Solid-State Structures of 2 and 4. Crystallographic data, atomic coordinates, and selected bond distances and angles are reported in Tables I-V.

Preparation of [(BP)TiCl$_2$] (1).[7] To an *n*-hexane solution (300 mL) of H_2BP (21.0 g, 61.8 mmol) was added $TiCl_4$ (11.6 g, 61.8 mmol). HCl evolution took place, and a red solution suddenly formed, which was kept on stirring for 12 h. A red crystalline solid precipitated, which was filtered off and washed with pentane (100 mL) (25.0 g, yield 88%). ^1H NMR (200 MHz, CD_2Cl_2, ppm, room temperature): δ 7.21 (d, 2 H, Ph), 7.02 (d, 2 H, Ph), 4.07 (d, 1 H, J_{H-H} = 14.2 Hz, CH_2), 3.74 (d, 1 H, J_{H-H} = 14.2 Hz, CH_2), 2.34 (s, 6 H, *p*-Me), 1.46 (s, 18 H, *o*-Bu^t).

Preparation of [(BP)ZrCl$_2$(THF)$_2$] (3). To a thf solution (200 mL) of H_2BP (30.3 g, 89.2 mmol) was slowly added NaH (4.3 g, 178.3 mmol). H_2 evolution took place, and a colourless solution suddenly

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Table II. Fractional Atomic Coordinates ($\times 10^4$) for Complex **2**

atom	*x*/*a*	*y*/*b*	*z*/*c*
Ti	89 (1)	2400 (1)	1913 (1)
O1	−1043 (3)	1660 (2)	2847 (3)
O2	1101 (3)	2981 (2)	3220 (3)
C1	−1520 (5)	1521 (3)	4133 (5)
C2	−2952 (5)	1452 (3)	4273 (5)
C3	−3362 (5)	1390 (4)	5611 (5)
C4	−2471 (6)	1353 (4)	6770 (5)
C5	−1072 (5)	1352 (4)	6586 (5)
C6	−602 (5)	1428 (3)	5273 (5)
C7	948 (5)	1374 (3)	5120 (5)
C8	1641 (5)	2374 (3)	5479 (5)
C9	2232 (5)	2511 (4)	6791 (5)
C10	2876 (5)	3429 (4)	7135 (5)
C11	2894 (5)	4189 (4)	6135 (5)
C12	2316 (4)	4092 (3)	4798 (5)
C13	1682 (4)	3153 (3)	4508 (4)
C14	−3972 (5)	1434 (4)	3011 (5)
C15	−5451 (6)	1328 (5)	3471 (7)
C16	−3625 (6)	493 (5)	2113 (6)
C17	−3982 (6)	2423 (5)	2148 (7)
C18	−3013 (7)	1336 (5)	8201 (6)
C19	3541 (7)	3565 (5)	8550 (6)
C20	2359 (5)	4956 (4)	3718 (5)
C21	904 (6)	5364 (4)	3270 (6)
C22	3132 (6)	4562 (4)	2478 (6)
C23	3116 (6)	5889 (4)	4322 (7)
B1	−1044 (8)	3640 (6)	775 (8)
B2	1300 (9)	1366 (6)	592 (8)

Table III. Fractional Atomic Coordinates ($\times 10^4$) for Complex **4**

atom	*x*/*a*	*y*/*b*	*z*/*c*
Zr	5851.5 (4)	2651.6 (4)	1240.0 (5)
O1	6512 (2)	2616 (3)	2727 (3)
O2	6742 (2)	3074 (3)	766 (3)
O3	5018 (2)	3107 (3)	−375 (3)
C1	7012 (3)	2931 (4)	3685 (5)
C2	7108 (3)	2494 (4)	4642 (4)
C3	7619 (4)	2889 (5)	5581 (5)
C4	8007 (4)	3668 (5)	5595 (5)
C5	7895 (4)	4070 (4)	4621 (5)
C6	7402 (4)	3714 (4)	3656 (5)
C7	7319 (4)	4167 (4)	2620 (5)
C8	7869 (4)	3818 (4)	2012 (5)
C9	8704 (4)	4027 (4)	2373 (5)
C10	9236 (4)	3749 (4)	1851 (6)
C11	8911 (4)	3266 (4)	919 (5)
C12	8088 (4)	3025 (4)	519 (5)
C13	7567 (4)	3303 (4)	1098 (5)
C14	6690 (4)	1640 (4)	4696 (5)
C15	6977 (5)	967 (5)	4060 (6)
C16	6927 (5)	1300 (5)	5843 (6)
C17	5746 (5)	1746 (6)	4251 (7)
C18	8515 (5)	4060 (5)	6628 (6)
C19	10143 (5)	3981 (6)	2254 (8)
C20	7778 (4)	2467 (5)	−485 (5)
C21	8452 (5)	2333 (6)	−1017 (6)
C22	7530 (6)	1602 (6)	−205 (7)
C23	7043 (6)	2888 (7)	−1307 (6)
C24	4192 (4)	2777 (5)	−912 (5)
C25	3844 (5)	3320 (5)	−1901 (6)
C27	5119 (4)	3920 (5)	−862 (6)
C26A	4287 (11)	4146 (11)	−1602 (14)
C26B	4538 (11)	3875 (11)	−2008 (14)
B1	5589 (6)	1205 (6)	794 (7)
B2	4821 (6)	3606 (8)	1769 (8)

formed, which was refluxed for 24 h. Then $ZrCl_4(THF)_2$ (33.6 g, 89.15 mmol) was added, and no color change was observed. The solution was refluxed for 12 h, and then the solvent was evaporated to dryness. By extraction of the white residue with Et_2O, a white crystalline solid was obtained (47.4 g, yield 82.5%). Anal. Calcd for $[(BP)ZrCl_2(THF)_2]$, $C_{31}H_{40}Cl_2O_4Zr$: C, 57.74; H, 7.19. Found: C, 57.68; H, 7.17. ^1H NMR (200 MHz, CD_2Cl_2, ppm, room temperature): δ 7.08 (d, 2 H, Ph), 6.90 (d, 2 H, Ph), 4.32 (d, 1 H, J_{H-H} = 14.5 Hz, CH_2), 3.75 (b, 8 H, thf), 3.63 (d, 1 H, J_{H-H} = 14.5 Hz, CH_2), 2.24 (s, 6 H, *p*-Me), 1.72 (b, 8 H, thf), 1.38 (s, 18 H, *o*-Bu^t).

Table IV. Selected Bond Distances (Å) and Angles (deg) for Complex **2**

Ti–O1	1.791 (3)	Ti–H3B1	1.951
Ti–O2	1.761 (3)	Ti–H1B2	1.875
Ti–B1	2.184 (7)	Ti–H2B2	2.013
Ti–B2	2.205 (8)	Ti–H3B2	1.984
Ti–H1B1	1.978	O1–C1	1.368 (5)
Ti–H2B1	1.870	O2–C13	1.365 (5)
B1–Ti–B2	113.7 (3)	O1–Ti–B1	110.6 (3)
O2–Ti–B2	112.4 (2)	O1–Ti–O2	103.9 (2)
O2–Ti–B1	106.7 (2)	Ti–O1–C1	142.9 (3)
O1–Ti–B2	109.1 (2)	Ti–O2–C13	158.6 (3)

Table V. Selected Bond Distances (Å) and Angles (deg) for Complex **4**

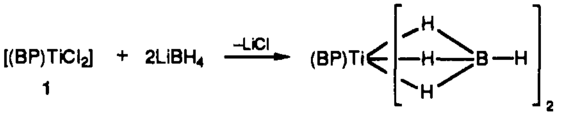
Zr–O1	1.922 (3)	Zr–H2B1	2.036
Zr–O2	1.937 (4)	Zr–H3B1	2.162
Zr–O3	2.263 (3)	Zr–H1B2	2.125
Zr–B1	2.354 (8)	Zr–H2B2	1.999
Zr–B2	2.572 (12)	O1–C1	1.370 (6)
Zr–H1B1	2.068	O2–C13	1.379 (7)
B1–Zr–B2	122.7 (4)	O1–Zr–B2	87.9 (3)
O3–Zr–B2	78.3 (3)	O1–Zr–B1	103.2 (3)
O3–Zr–B1	93.4 (2)	O1–Zr–O3	162.5 (2)
O2–Zr–B2	124.3 (3)	O1–Zr–O2	94.6 (2)
O2–Zr–B1	110.8 (3)	Zr–O1–C1	156.5 (4)
O2–Zr–O3	84.5 (2)	Zr–O2–C13	144.3 (4)

Preparation of 2. To a pentane (100 mL) suspension of $[(BP)TiCl_2]$ (3.0 g, 6.81 mmol) was added $LiBH_4$ (0.3 g, 13.63 mmol), and the mixture was kept on stirring for 24 h. LiCl was filtered off and the red solution kept on standing at 0 °C for 24 h. A red crystalline solid precipitated (2.1 g, yield 74%). ^1H NMR (200 MHz, C_6D_6, ppm, room temperature): δ 6.90 (d, 2 H, Ph), 6.85 (d, 2 H, Ph), 4.66 (d, 1 H, J_{H-H} = 13.9 Hz, CH_2), 3.22 (d, 1 H, J_{H-H} = 13.9 Hz, CH_2), 2 (broad, 8 H, BH_4), 2.04 (s, 6 H, *p*-Me), 1.37 (s, 18 H, *o*-Bu^t). ^{11}B NMR [200 MHz, THF, ppm, F_3BOEt_2 used as a reference ($\delta(F_3BOEt_2) = 0$)]: $\delta(^{11}B) = -18.8$ (broad, BH_4). IR (Nujol): 2559, 2542 cm^{-1} (tridentate B–H$_t$ stretching); 2209, 2118 cm^{-1} (tridentate B–H$_b$ sym and antisym stretching). Anal. Calcd for $[(BP)Ti(BH_4)_2]$, $C_{23}H_{38}B_2O_2Ti$: C, 66.40; H, 9.21. Found: C, 66.40; H, 9.30.

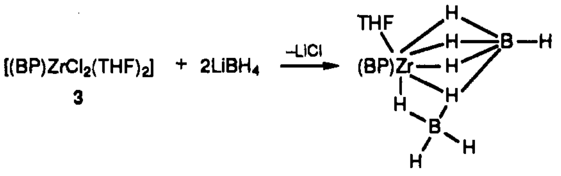
Preparation of 4. To a Et_2O (100 mL) suspension of $[(BP)ZrCl_2(THF)_2]$ (5.0 g, 7.76 mmol) was added $LiBH_4$ (0.34 g, 15.52 mmol), and the mixture was kept on stirring for 12 h. LiCl was filtered off and the colorless solution evaporated to dryness. The white residue was dissolved in *n*-hexane (100 mL), and after the solution was standing for 12 h, a white crystalline solid was obtained (3.0 g, yield 72%). ^1H NMR (200 MHz, C_6D_6, ppm, room temperature): δ 7.08 (d, 2 H, Ph), 6.99 (d, 2 H, Ph), 4.81 (d, 1 H, J_{H-H} = 13.7 Hz, CH_2), 3.80 (m, 4 H, thf), 3.59 (d, 1 H, J_{H-H} = 13.7 Hz, CH_2), 2.13 (s, 6 H, *p*-Me), 1.80 (broad, 8 H, BH_4), 1.48 (s, 18 H, *o*-Bu^t), 1.18 (m, 4 H, thf). ^{11}B NMR [200 MHz, THF, ppm, $BF_3(Et_2O)_2$ used as a reference ($\delta(BF_3\,(Et_2O)) = 0$)]: $\delta(^{11}B) = -15.9$ (q, $J_{^{11}B-H}$ = 91.5 Hz, BH_4). IR (Nujol): 2539 cm^{-1} (tridentate B–H$_t$ stretching); 2458, 2400 cm^{-1} (bidentate B–H$_t$ sym and antisym stretching); 2219, 2117 cm^{-1} (tridentate B–H$_b$ sym and antisym stretching); 2020 cm^{-1} (bidentate B–H$_b$ sym and antisym overlapped bands stretching). Anal. Calcd for $[(BP)Zr(BH_4)_2(THF)_2]$, $C_{31}H_{54}B_2O_4Zr$: C, 61.69; H, 9.02. Found: C, 62.10; H, 9.26.

Results and Discussion

Complexes **1**[7] and **3** react with $LiBH_4$ according to eqs 1 and 2.



1 2 (1)



3 4 (2)

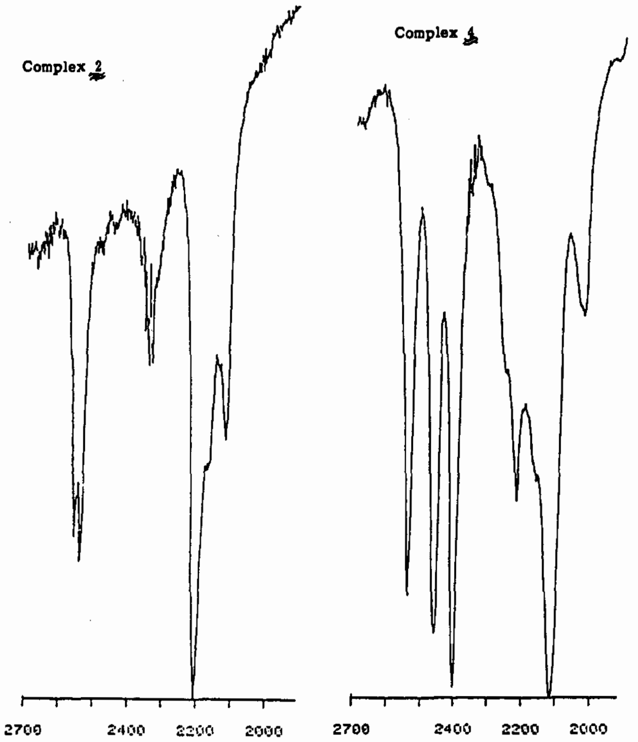


Figure 1. IR spectrum in the B–H region of complexes **2** and **4**.

Complexes **2** and **4** have been obtained as red and white crystalline solids, respectively, in a yield higher than 70%. The structure given is based on the X-ray analysis (vide infra). In both complexes the ^1H NMR spectrum did not distinguish, regardless of the temperature, spectra being recorded from room temperature down to 193 K, between different types of hydrogens. A broad band was observed in both cases, suggesting a very dynamic behavior, averaging all kinds of hydrogens of the BH_4 ligand. The mechanism of such a fluxional behavior is known, as well as the pathway through which the exchange of hydrogens occurs.[11] ^{11}B NMR[12] spectroscopy shows only one kind of boron atom in the proton-decoupled spectrum of **4**. This is in agreement with their fluxional behavior. The IR spectra, on the contrary, in the solid state are very diagnostic (see Figure 1) for the presence of two tridentate BH_4^- groups in **2**, and one bidentate and one tridentate in **4**, in agreement with well-known examples from the literature[2,9,13] (see Experimental Section). A significant parameter in solution is the $\Delta\delta$ separation of the two doublets belonging to the diastereotopic hydrogens of the BP ligand (see structure I). Such a difference is very indicative of both the coordination number and the volume around the metal. The separation increases from 0.33 to 1.44 ppm going from **1** to **2** and from 0.69 to 1.22 ppm from **3** to **4**. Such high separations in **2** and **4** are diagnostic of a high coordination number ensured by a polydentate bonding mode of the BH_4^- anion.[7]

The structure of complex **2** is reported in Figure 2, while bond distances and angles are listed in Table IV. Oxygen and boron atoms define a tetrahedral coordination around titanium. Both BH_4^- anions act as tridentate ligands as proven by the closeness of the Ti–H distances,[2,9] ranging from 2.00 to 2.17 Å, along with the linearity of the Ti–B–H$_t$ (t = terminal) skeleton (171 and 177°). The Ti–O and Ti⋯H71 distances fall in the range of values usually observed for this kind of compound.[7] The dioxametallacycle Ti(BP) is puckered, the total puckering amplitude being 1.038 (4) Å,[14] with a boat conformation. A projection of the chelation ring into the plane perpendicular to the O2⋯O1 line is reported in Figure 3. The dihedral angle between the two Ph rings is 64.1 (2)°. The structure of **4** is reported in Figure 4, while selected bond distances and angles are in Table V. The structure consists of discrete monomeric units, where the zirconium atom is bonded to a tridentate BH_4^- and a bidentate BH_4^- group, two oxygen atoms of the BP ligand, and an oxygen atom from a THF molecule. The coordination polyhedron of zirconium is a distorted trigonal bipyramid with B1, B2, and O2 atoms defining the equatorial plane, and O1 and O3 the axial positions. The zirconium atom is at 0.196 (1) Å from the equatorial plane toward the O1 oxygen atom. The tridentate bonding mode of one of the B(1)H_4^- anions is proved by the closeness of the Zr–H distances (2.04–2.16 Å),[2,15] as well as the linearity of the Zr–B1–H4 unit (175°). The bidentate bonding mode of the B(2)H_4^- anion is in agreement with the Zr–H distances ranging between 2.00 and 2.12 Å and the Zr–B–H$_t$ angles ranging from 122.5 to 113.4°.[2,15] The dioxametallacycle is puckered, the total puckering amplitude being 1.194 (6) Å with a boat conformation. The projection of the chelation ring into the plane perpendicular to the O1⋯O2 line is reported in Figure 5. The dihedral angle between the two Ph

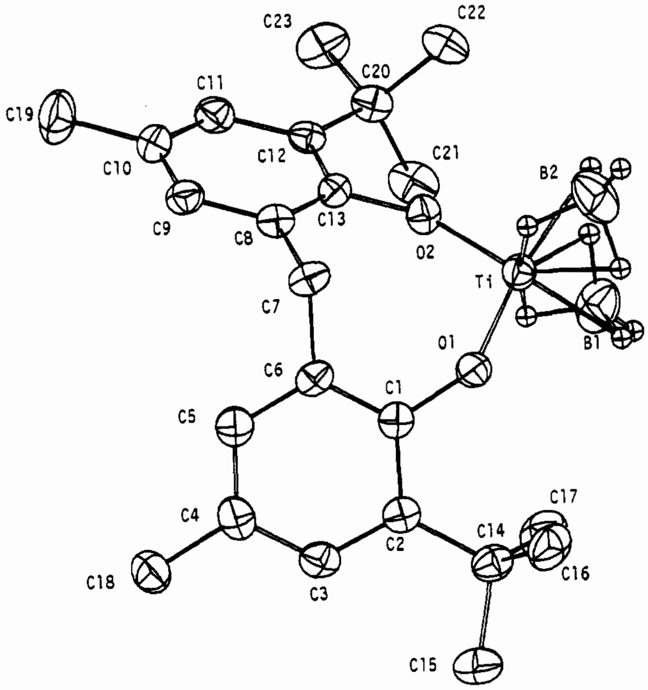


Figure 2. ORTEP drawing of complex **2** (30% probability ellipsoids).

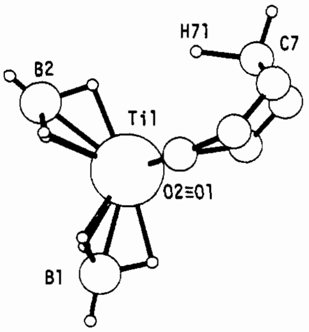


Figure 3. Projection of the chelation ring onto the plane perpendicular to the O2⋯O3 line.

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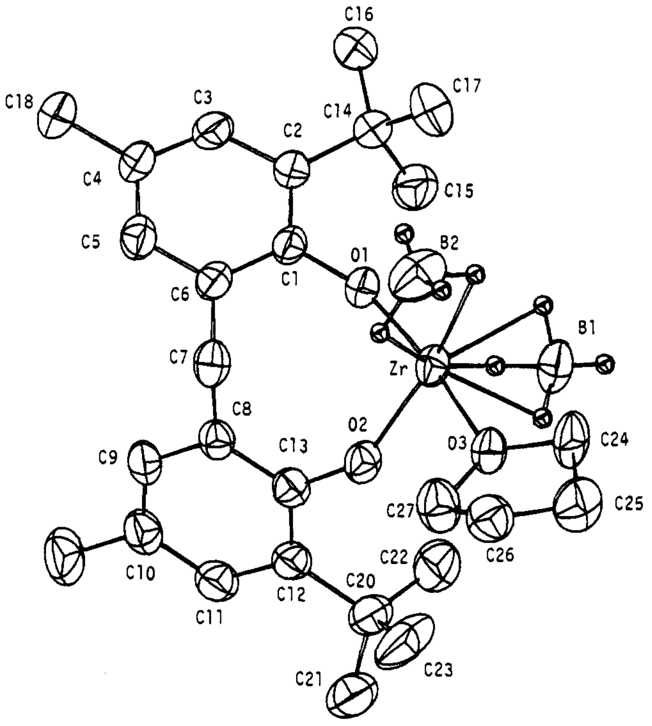

Figure 4. ORTEP drawing of complex **4** (30% probability ellipsoids).

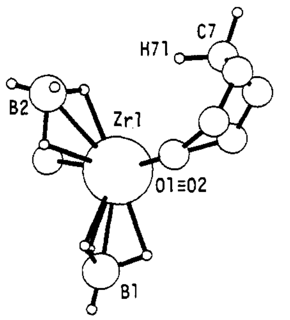

Figure 5. Projection of the chelation ring onto the plane perpendicular to the O1···O2 line.

rings is 68.8 (2)°.

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Supplementary Material Available: Complete listings of crystallographic data, fractional atomic coordinates for hydrogen atoms, anisotropic thermal parameters, and bond distances and angles for complexes **2** and **4** (10 pages); listings of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of (Trifluoroethoxy)boranes[1]

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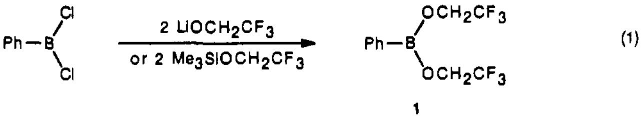
Introduction

The preparative chemistry of several types of boron–nitrogen compounds, especially those containing Si–N–B, B–N–B, and/or P–N–B linkages, is under current investigation in our laboratory.[2] Many of these compounds are of interest either as possible precursors to or structural and stereochemical models[3] for B–N polymer systems. As an aspect of these overall studies, we report here on the synthesis and characterization of several new reagents that should be useful for the introduction of *N*-boryl functional groups into such compounds. In particular, various (*trifluoroethoxy*)boranes were selected as target compounds for synthesis, since the OCH_2CF_3 group is known to be an excellent leaving group in condensation polymerizations [e.g., poly(phosphazenes)].[4]

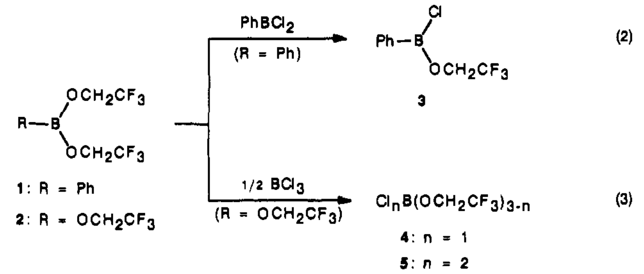
Results and Discussion

The new bis(trifluoroethoxy)borane **1** was prepared via the reaction of $PhBCl_2$ with 2 equiv of lithium trifluoroethoxide. Compound **1** was obtained in 61% yield as a colorless liquid that was characterized by NMR (^1H, ^{13}C, and ^{11}B) spectroscopy (Table I) and elemental analysis (Table II). Alternatively, **1** could be prepared (in 81% yield) via the Si–O cleavage reaction of $PhBCl_2$ with $Me_3SiOCH_2CF_3$ (eq 1). In a similar manner, treatment of BCl_3 with $LiOCH_2CF_3$ in a 1:3 mole ratio afforded tris(trifluoroethoxy)borane, $(CF_3CH_2O)_3B$ (**2**), in 36% isolated yield. A satisfactory elemental analysis of **2** was not obtained, however, due to the presence of a small amount of an unidentified impurity that could not be removed by fractional distillation.



$$PhBCl_2 \xrightarrow[\text{or } 2\ Me_3SiOCH_2CF_3]{2\ LiOCH_2CF_3} PhB(OCH_2CF_3)_2\ (\mathbf{1}) \qquad (1)$$

The desired chlorinated derivatives of these alkoxyboranes were prepared by means of ligand exchange with the appropriate chloroboranes. This type of reaction is well-known in aminoborane chemistry, for example, in the preparation of $ClB(NMe_2)_2$ from $B(NMe_2)_3$ and BCl_3.[5] Thus, treatment of **1** and **2** with $PhBCl_2$ and BCl_3, respectively, in the appropriate proportions afforded the chloro(trifluoroethoxy)boranes **3–5** as colorless, moisture-sensitive liquids (eqs 2 and 3). Compound **3** (eq 2) was isolated in 95% yield and was fully characterized by NMR spectroscopy and elemental analysis (Tables I and II). In an alternate attempt to synthesize **3**, a neat sample of $PhBCl_2$ was treated with an equimolar amount of $Me_3SiOCH_2CF_3$. This process resulted in a nearly 1:1 mixture of mono-(**3**) and disubstituted (**1**) products from which **3** could not be isolated in pure form. The ligand-exchange reaction of the tris(trifluoroethoxy) derivative **2** with $^1/_2$ equiv of BCl_3 (eq 3) also resulted in a mixture (of unreacted **2** and the chloroboranes **4** and **5**) instead of only the monosubstituted product **4** as desired. In this case, however, compound **4** was isolated in 36% yield by fractional distillation as a very air-sensitive, colorless liquid.



$$RB(OCH_2CF_3)_2 \xrightarrow[(R = Ph)]{PhBCl_2} PhBCl(OCH_2CF_3)\ (\mathbf{3}) \qquad (2)$$

$$RB(OCH_2CF_3)_2 \xrightarrow[(R = OCH_2CF_3)]{1/2\ BCl_3} Cl_nB(OCH_2CF_3)_{3-n} \qquad (3)$$

1: R = Ph; **2**: R = OCH_2CF_3; **4**: n = 1; **5**: n = 2

The reactivity of compound **3** was studied in order to test its usefulness for transferring the $PhB(OCH_2CF_3)$– moiety to other substrates such as the diazoboracyclohexane ring. Two types of

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[1] Taken in part from: Shaw, S. Y. Ph.D. Dissertation, Texas Christian University, Fort Worth, TX, 1988.

[2] For accounts of preliminary results presented at meetings, see: (a) Shaw, S. Y.; DuBois, D. A.; Neilson, R. H. *ACS Symp. Ser.* **1988**, *360*, 385. (b) Shaw, Y. S.; Scheide, G. M.; Davis, C. E.; Mukherjee, P.; Neilson, R. H. *Phosphorus, Sulfur Silicon Relat.* **1989**, *41*, 141.

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