DOI: 10.1021/om1003896

ORGANOMETALLICS
Article

Frustrated Lewis Pairs and Ring-Opening of THF, Dioxane, and Thioxane†

Birgit Birkmann,‡ Tanja Voss,‡,§ Stephen J. Geier,‡ Matthias Ullrich,‡ Gerald Kehr,§ Gerhard Erker,§ and Douglas W. Stephan*,‡

‡*Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada M5S 3H6, and* §*Organisch-Chemisches Institut, Westfälische Wilhelms-Universität, Corrensstrasse 40, 48149 Münster, Germany*

Received April 30, 2010

The reaction of tBu$_2$PH and B(p-C$_6$F$_4$H)$_3$ in THF afforded tBu$_2$(H)P(CH$_2$)$_4$OB(p-C$_6$F$_4$H)$_3$ (**1**). Similarly, reactions of N-bases with a THF solution of B(C$_6$F$_5$)$_3$ led to the formation of the THF-ring-opening products C$_5$H$_3$Me$_2$N(CH$_2$)$_4$OB(C$_6$F$_5$)$_3$ (**2**), C$_6$H$_5$CH$_2$NMe$_2$(CH$_2$)$_4$OB(C$_6$F$_5$)$_3$ (**3**), and Me$_2$NC$_6$H$_4$NMe$_2$(CH$_2$)$_4$OB(C$_6$F$_5$)$_3$ (**4**). THF-ring-opening also occurs with aliphatic amines to form the compounds Me$_3$N(CH$_2$)$_4$OB(C$_6$F$_5$)$_3$ (**5**), Et$_3$N(CH$_2$)$_4$OB(C$_6$F$_5$)$_3$ (**6**), Me$_2$N(CH$_2$)$_2$NMe$_2$(CH$_2$)$_4$-OB(C$_6$F$_5$)$_3$ (**7**), and tBuHN(CH$_2$)$_2$NHtBu(CH$_2$)$_4$OB(C$_6$F$_5$)$_3$ (**8**). In related chemistry, reactions of B(C$_6$F$_5$)$_3$, 1,4-dioxane, and the appropriate base yielded tBu$_3$P(CH$_2$)$_2$O(CH$_2$)$_2$OB(C$_6$F$_5$)$_3$ (**10**), C$_6$H$_5$-CH$_2$NMe$_2$(CH$_2$)$_2$O(CH$_2$)$_2$OB(C$_6$F$_5$)$_3$ (**11**), ((tBuN)$_2$C$_3$H$_2$)(CH$_2$)$_2$O(CH$_2$)$_2$OB(C$_6$F$_5$)$_3$ (**12**), Me$_2$NC$_6$-H$_4$NMe$_2$(CH$_2$)$_2$O(CH$_2$)$_2$OB(C$_6$F$_5$)$_3$ (**13**), and C$_5$H$_3$Me$_2$N(CH$_2$)$_2$O(CH$_2$)$_2$OB(C$_6$F$_5$)$_3$ (**14**). In a related fashion, the thioxane adduct (C$_6$F$_5$)$_3$B(SC$_4$H$_8$O) (**15**) reacted with N,N-dimethylbenzylamine, N,N,N',N'-tetramethyl-p-phenylenediamine, 2,6-lutidine, or tBu$_3$P to give the corresponding ring-opened products L(CH$_2$)$_2$S(CH$_2$)$_2$OB(C$_6$F$_5$)$_3$ (L = tBu$_3$P (**16**), C$_6$H$_5$CH$_2$NMe$_2$ (**17**), Me$_2$NC$_6$H$_4$NMe$_2$ (**18**), and C$_5$H$_3$Me$_2$N (**19**)). The crystal structures of **1**−**7**, **10**−**12**, **14**, **18**, and **19** are reported.

Introduction

In recent work, we have demonstrated that a combination of sterically encumbered donors with Lewis acids results in unique reactivity.[1−3] Such systems, referred to as "frustrated Lewis pairs" (FLPs), react with a variety of small molecules, including H$_2$,[4−9] olefins,[10] dienes,[11] alkynes,[12] boranes,[13] disulfides,[14] CO$_2$,[15,16] and N$_2$O.[17,18] While broadening implications of the chemistry of FLPs continue to develop, it is interesting to note that our initial studies of these systems were prompted by an earlier finding that phosphine/borane combinations react with THF to effect ring opening, affording zwitterionic phosphonium borates of the form R$_3$P(CH$_2$)$_4$-OB(C$_6$F$_5$)$_3$.[19] While this reactivity is understandable in the context of the reactivity of FLPs, this ring opening of THF is not unprecedented. Indeed, in 1950, Wittig and Rückert[20] described the reaction of [Ph$_3$C]$^-$ with THF(BPh$_3$), affording the borate anion [Ph$_3$C(CH$_2$)$_4$OBPh$_3$]$^-$. Some 40 years later we reported the related reaction of PCy$_3$ with ZrCl$_4$(THF)$_2$, which resulted in the formation of the dimeric zwitterionic species (Cy$_3$P(CH$_2$)$_4$OZrCl$_4$)$_2$ (Scheme 1).[21] Subsequently, other transition-metal Lewis acids, including complexes derived from U,[22,23] Sm,[24] Ti,[25] and Zr[26,27] as well

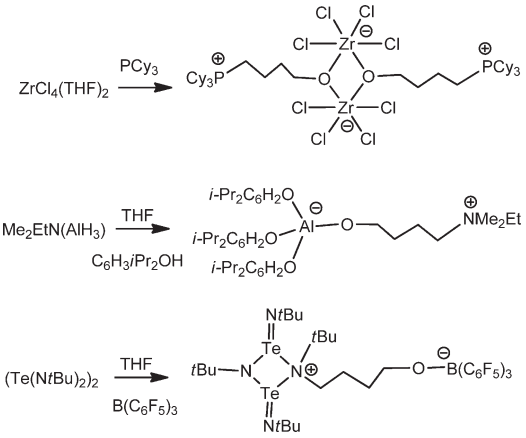
† Part of the Dietmar Seyferth Festschrift. Dedicated to Professor Dietmar Seyferth on the occasion of his retirement as Editor of Organometallics.

*To whom correspondence should be addressed. E-mail: dstephan@chem.utoronto.ca.

(1) Stephan, D. W. *Org. Biomol. Chem.* **2008**, *6*, 1535–1539.
(2) Stephan, D. W. *Dalton Trans.* **2009**, 3129–3136.
(3) Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 46–76.
(4) Spies, P.; Erker, G.; Kehr, G.; Bergander, K.; Fröhlich, R.; Grimme, S.; Stephan, D. W. *Chem. Commun.* **2007**, 5072–5074.
(5) Spies, P.; Schwendemann, S.; Lange, S.; Kehr, G.; Fröhlich, R.; Erker, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 7543–7546.
(6) Sumerin, V.; Schulz, F.; Atsumi, M.; Wang, C.; Nieger, M.; Leskelä, M.; Repo, T.; Pyykkö, P.; Rieger, B. *J. Am. Chem. Soc.* **2008**, *130*, 14117–14119.
(7) Sumerin, V.; Schulz, F.; Nieger, M.; Leskelä, M.; Repo, T.; Rieger, B. *Angew. Chem., Int. Ed.* **2008**, *47*, 6001–6003.
(8) Welch, G. C.; San Juan, R. R.; Masuda, J. D.; Stephan, D. W. *Science* **2006**, *314*, 1124–1126.
(9) Welch, G. C.; Stephan, D. W. *J. Am. Chem. Soc.* **2007**, *129*, 1880–1881.
(10) McCahill, J. S. J.; Welch, G. C.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 4968–4971.
(11) Ullrich, M.; Seto, K. S.-H.; Lough, A. J.; Stephan, D. W. *Chem. Commun.* **2009**, 2335–2337.
(12) Dureen, M. A.; Stephan, D. W. *J. Am. Chem. Soc.* **2009**, *131*, 8396–8397.
(13) Dureen, M. A.; Lough, A.; Gilbert, T. M.; Stephan, D. W. *Chem. Commun.* **2008**, 4303–4305.
(14) Dureen, M. A.; Welch, G. C.; Gilbert, T. M.; Stephan, D. W. *Inorg. Chem.* **2009**, *48*, 9910–9917.
(15) Mömming, C. M.; Otten, E.; Kehr, G.; Fröhlich, R.; Grimme, S.; Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 6643–6646.
(16) Ménard, G.; Stephan, D. W. *J. Am. Chem. Soc.* **2010**, *132*, 1796–1797.
(17) Neu, R. C.; Otten, E.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2009**, *48*, 9709–9712.
(18) Otten, E.; Neu, R. C.; Stephan, D. W. *J. Am. Chem. Soc.* **2009**, *131*, 9918–9919.
(19) Welch, G. C.; Masuda, J. D.; Stephan, D. W. *Inorg. Chem.* **2006**, *45*, 478–480.
(20) Wittig, G.; Rückert, A. *Liebigs Ann. Chem.* **1950**, *566*, 101–113.
(21) Breen, T. L.; Stephan, D. W. *Inorg. Chem.* **1992**, *31*, 4019–4022.
(22) Avens, L. R.; Barnhart, D. M.; Burns, C. J.; McKee, S. D. *Inorg. Chem.* **1996**, *35*, 537–539.
(23) Campello, M. P. C.; Domingos, A.; Santos, I. *J. Organomet. Chem.* **1994**, *484*, 37–46.

 Published on Web 07/08/2010

Scheme 1. Examples of Lewis Acid−Lewis Base Mediated Ring-Opening Reactions



as Mn−carborane complexes,[28] were also shown to induce similar THF-ring-opening, while Campbell and Gladfelter[29] showed that the main group species amine−alane adduct reacts in THF to give a zwitterionic ammonium aluminate (Scheme 1). Similarly, Te nucleophiles and Lewis acids have resulted in related ring-openings:[30,31] for example, Chivers and Schatte[30] described the ring-opening of THF by reaction of a tellurium diimide dimer with $B(C_6F_5)_3$ in THF (Scheme 1). While these previous studies were not described as such, it is clear that these ring-opening reactions are conceptually related to the more recent FLP chemistry as each involves attack of Lewis acid activated THF by a nucleophile. In this paper, we undertake an effort to further generalize such FLP ring-opening reactions. Herein we first probe the generality of such THF-ring-opening reactions by FLPs, exploring analogous reactions with combinations of phosphines, amines, pyridines, and carbenes with electron-deficient boranes. In a second aspect, we further probe the extension of such reactivity in ring-opening reactions of dioxane and thioxane.

Experimental Section

General Remarks. All manipulations were carried out under an atmosphere of dry, O_2-free N_2 by employing an Innovative Technology glovebox and a Schlenk vacuum line. Solvents were purified with a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled Schlenk glass bombs equipped with Young-type Teflon valve stopcocks (hexanes, toluene, CH_2Cl_2) or were dried over the appropriate agents and distilled into the same kind of Young bombs (C_6H_5Br). All solvents were thoroughly degassed after purification (repeated freeze−pump−thaw cycles). Deuterated solvents were dried over the appropriate agents, vacuum-transferred into Young bombs, and degassed accordingly (C_6D_5Br, CD_2Cl_2). When intended to be used in the glovebox, all solvents were transferred through the antechambers in bombs with evacuated headspaces and refilled inside into brown glass bottles equipped with 4 Å molecular sieves (small pieces of silver foil were further added to CH_2Cl_2 and CD_2Cl_2). ^1H, ^{11}B, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded at 25 °C on Varian 300 and 400 MHz Bruker spectrometers. Chemical shifts are given relative to $SiMe_4$ and referenced to the residual solvent signal (^1H, ^{13}C) or relative to an external standard (^{11}B, $(Et_2O)BF_3$; ^{19}F, $CFCl_3$; ^{31}P, 85% H_3PO_4). In some instances, signal and/or coupling assignment was derived from two-dimensional NMR experiments. Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. For more detailed assignments of the NMR data, please see the Supporting Information. Combustion analyses were performed in house by employing a Perkin-Elmer CHN analyzer. tBu_3P and 1,3-di-*tert*-butylimidazol-2-ylidene were obtained from Strem Chemicals, Inc. (USA) and used as received. $B(C_6F_5)_3$ was doubly sublimed prior to use. Dimethylbenzylamine, 2,6-lutidine, 1,4-dioxane, and 1,4-thioxane were obtained from Sigma-Aldrich and stored over molecular sieves.

Synthesis of $tBu_2(H)P(CH_2)_4OB(p\text{-}C_6F_4H)_3$ (1), $C_5H_3Me_2N\text{-}(CH_2)_4OB(C_6F_5)_3$ (2), $C_6H_5CH_2NMe_2(CH_2)_4OB(C_6F_5)_3$ (3), and $Me_2NC_6H_4NMe_2(CH_2)_4OB(C_6F_5)_3$ (4). These compounds were prepared in a similar fashion, and thus only the preparation of **3** is detailed: *N*,*N*-dimethylbenzylamine (30 mg, 0.223 mmol) in 0.5 mL of THF was added to a solution of $B(C_6F_5)_3$ (114 mg, 0.223 mmol) in 0.5 mL of THF and the resulting mixture stirred at room temperature for 4 h, before the solvent was removed in vacuo. A 0.5 mL portion of dichloromethane and 6 mL of pentane were added, so that a white powder started to precipitate. The mixture was stored at −39 °C overnight and the supernatant removed via syringe. After drying in vacuo, the product **3** was obtained in 81% yield (130 mg, 0.181 mmol). Crystals suitable for X-ray diffraction analysis were obtained by layering a dichloromethane solution with hexane.

1: yield 74 mg (0.112 mmol, 87%). ^1H NMR (CD_2Cl_2): 6.75 (tt, 3H, $^3J_{HF}$ = 9.8 Hz, $^4J_{HF}$ = 7.6 Hz, *p*-CH), 5.45 (dt, $^1J_{HP}$ = 447 Hz, $^3J_{HH}$ = 4.6 Hz, 1H, PH), 3.27 (t, $^3J_{HH}$ = 5.1 Hz, 2H, CH_2), 2.57 (tdm, br, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 4.6 Hz, 2H, CH_2), 1.97 (m, 2H, CH_2), 1.68 (t, br, $^3J_{HH}$ = 5.1 Hz, 2H, CH_2), 1.41 (d, $^3J_{HP}$ = 16.5 Hz, 27H, *t*Bu). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 148.6 (dm, $^1J_{CF} \approx 238$ Hz, *o*-C_6F_4H), 145.8 (dm, $^1J_{CF} \approx 247$ Hz, *m*-C_6F_4H), 132.3 (br, C_q), 102.0 (t, $^2J_{CF} \approx 23$ Hz, *p*-C_6F_4H), 64.0 (CH_2), 33.4 (d, $^1J_{CP}$ = 34.5 Hz, *t*Bu), 32.1 (d, br, $^3J_{CP}$ = 10.5 Hz; CH_2), 27.5 (*t*Bu), 26.2 (d, $^2J_{CP}$ = 6.5 Hz, CH_2), 15.4 (d, $^1J_{CP}$ = 38.5 Hz, PCH_2). ^{19}F NMR (CD_2Cl_2): −134.4 (br, 6F, *o*-C_6F_4H), −142.9 (m, 6F, *m*-C_6F_4H). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): −2.8 (s). ^{31}P NMR (CD_2Cl_2): 51.3 (dm, $^1J_{PH}$ = 447 Hz). Anal. Calcd for $C_{30}H_{30}BF_{12}OP$: C, 53.28; H, 4.47. Found: C, 52.92; H; 4.66.

2: yield 120 mg (89%). X-ray-quality crystals were grown from CH_2Cl_2 at room temperature. ^1H NMR (THF-d_8): 8.09 (t, $^3J_{HH}$ = 8 Hz, CH), 7.65 (d, $^3J_{HH}$ = 8 Hz, CH), 4.68 (m, 2H, CH_2), 3.18 (t, $^3J_{HH}$ = 8 Hz, 2H, CH_2), 2.74 (s, 6H, CH_3), 1.90 (m, 2H, CH_2), 1.62 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR (THF-d_8; partial): 158.0, 150.1 (dm, $^1J_{CF} \approx 241$ Hz, C_6F_5), 145.7, 140.3 (dm, $^1J_{CF} \approx 244$ Hz, C_6F_5), 138.5 (dm, $^1J_{CF} \approx 244$ Hz, C_6F_5), 129.8, 65.4 (CH_2), 55.5 (CH_2), 30.2 (CH_3), 28.7 (CH_2), 22.0 (CH_2), n.o. (*ipso*-C_6F_5). ^{19}F NMR (THF-d_8): −132.5 (d, 6F, $^3J_{FF}$ = 21 Hz, *o*-C_6F_5), −163.3 (t, 3F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), −166.6 (t, 6F, $^3J_{FF}$ = 19 Hz, *m*-C_6F_5). ^{11}B NMR (THF-d_8): −6.3 (s). Anal. Calcd for $C_{29}H_{17}BF_{15}NO$: C, 50.39; H, 2.48; N, 2.03. Found: C, 50.30; H, 2.66; N, 2.17.

3: yield given above. ^1H NMR (CD_2Cl_2): 7.55 (m, 3H, C_6H_5), 7.37 (m, 2H, C_6H_5), 4.26 (s, 2H, CH_2), 3.84 (m, 2H, CH_2), 3.24 (m, 2H, CH_2), 2.90 (s, 6H, CH_3), 2.04 (m, 2H, CH_2), 1.64 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2; partial): 132.8, 131.9, 130.2 (C_6H_5), 126.4 (C_q), 69.2 (CH_2), 66.9 (CH_2), 63.9 (CH_2), 50.2 (CH_3), 28.2 (CH_2), 22.2 (CH_2). ^{19}F NMR (CD_2Cl_2): −134.5 (m, 6F, *o*-C_6F_5), −162.8 (t, $^3J_{FF}$ = 20.1 Hz, 3F, *p*-C_6F_5), −166.8 (m,

(24) Evans, W. J.; Leman, J. T.; Ziller, J. W.; Khan, S. I. *Inorg. Chem.* **1996**, *35*, 4283–4291.
(25) Mommertz, A.; Leo, R.; Massa, W.; Harms, K.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1647–1652.
(26) Guo, Z. Y.; Bradley, P. K.; Jordan, R. F. *Organometallics* **1992**, *11*, 2690–2693.
(27) Polamo, M.; Mutikainen, I.; Leskelä, M. *Acta Crystallogr., Sect. C* **1997**, *C53*, 1036–1037.
(28) Gomez-Saso, M.; Mullica, D. F.; Sappenfield, E.; Stone, F. G. A. *Polyhedron* **1996**, *15*, 793–801.
(29) Campbell, J. P.; Gladfelter, W. L. *Inorg. Chem.* **1997**, *36*, 4094–4098.
(30) Chivers, T.; Schatte, G. *Eur. J. Inorg. Chem.* **2003**, 3314–3317.
(31) Kunnari, S. M.; Oilunkaniemi, R.; Laitinen, R. S.; Ahlgren, M. *Dalton Trans.* **2001**, 3417–3418.

6F, *m*-C_6F_5). ^{11}B NMR (CD_2Cl_2): −3.0 (s, $\nu_{1/2}$ = 22 Hz). Anal. Calcd for $C_{31}H_{21}BF_{15}NO$: C, 51.76; H, 2.94; N, 1.95. Found: C, 51.38; H, 3.36; N, 2.14.

4: yield 72 mg (0.096 mmol, 92%). ^{1}H NMR (CD_2Cl_2): 7.34 (m, 2H, Ar H), 6.73 (m, 2H, Ar H), 4.28 (m, 2H, CH_2), 3.42 (s, 6H, CH_3), 3.19 (m, 2H, CH_2), 3.04 (s, 6H, CH_3), 1.63 (m, 2H, CH_2), 1.57 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2; partial): 150.9 (C_q), 147.9 (dm, $^1J_{CF} \approx$ 238 Hz, C_6F_5), 138.3 (dm, $^1J_{CF} \approx$ 246 Hz, C_6F_5), 136.5 (dm, $^1J_{CH} \approx$ 242 Hz, C_6F_5), 131.5 (C_q), 120.4 (Ar C), 112.2 (Ar C), 70.5 (CH_2), 63.9 (CH_2), 54.9 (CH_3), 39.8 (CH_3), 27.9 (CH_2), 23.0 (CH_2), n.o. (i-C_6F_5). ^{19}F NMR (CD_2Cl_2): −134.4 (m, 2F, *o*-C_6F_5), −163.0 (t, $^3J_{FF}$ = 20.6 Hz, 1F, *p*-C_6F_5), −166.9 (m, 2F, *m*-C_6F_5). ^{11}B NMR (CD_2Cl_2): −3.0 (s, $\nu_{1/2}$ = 20 Hz). Anal. Calcd for $C_{32}H_{24}BF_{15}N_2O$: C, 51.36; H, 3.23; N, 3.74. Found: C, 50.97; H, 3.23; N, 3.35.

Synthesis of $Me_3N(CH_2)_4OB(C_6F_5)_3$ (5), $Et_3N(CH_2)_4OB(C_6F_5)_3$ (6), $Me_2N(CH_2)_2NMe_2(CH_2)_4OB(C_6F_5)_3$ (7), *t*BuHN-$(CH_2)_2NH$*t*Bu$(CH_2)_4OB(C_6F_5)_3$ (8). The preparation of **5** is detailed: 10 μL of thf was added to $B(C_6F_5)_3$ (50 mg, 0.098 mmol) dissolved in 0.5 mL of BrC_6D_5, and the mixture was stirred for 5 min. Tetramethylmethanediamine (9 mg, 0.102 mmol) was added to the solution, and the reaction mixture was stirred for 4 h at room temperature. A 2 mL portion of pentane was added to the solution to yield a white precipitate. Single crystals of **5** were obtained from a concentrated CH_2Cl_2 solution and diffusion of pentane.

5: yield 34 mg (0.053 mmol, 54%). ^{1}H NMR (CD_2Cl_2): 3.88 (m, 2H, CH_2), 3.25 (m, 2H, CH_2), 3.08 (s, 9H, CH_3), 1.97 (m, 2H, CH_2), 1.65 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2; partial): 147.9 (dm, $^1J_{CF} \approx$ 236 Hz, C_6F_5), 138.3 (dm, $^1J_{CF} \approx$ 245 Hz, C_6F_5), 136.5 (dm, $^1J_{CF} \approx$ 248 Hz, C_6F_5), 68.0 (CH_2), 63.6 (CH_2), 53.5 (CH_2), 27.6 (CH_2), 22.2 (CH_2), n.o. (*ipso*-C_6F_5). ^{19}F NMR (CD_2Cl_2): −134.6 (m, 2F, *o*-C_6F_5), −162.9 (t, $^3J_{FF}$ = 20.0 Hz, 1F, *p*-C_6F_5), −166.8 (m, 2F, *m*-C_6F_5). ^{11}B{^{1}H} NMR (CD_2Cl_2): −3.0 (s, $\nu_{1/2}$ = 15 Hz).

6: yield 58 mg (0.085 mmol, 87%). ^{1}H NMR (CD_2Cl_2): 3.59 (m, 2H, CH_2), 3.23 (m, 2H, CH_2), 3.16 (q, $^3J_{HH}$ = 7.4 Hz, 6H, CH_3), 1.80 (m, 2H, CH_2), 1.66 (m, 2H, CH_2), 1.29 (t, $^3J_{HH}$ = 7.4 Hz, 9H, CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2; partial): 148.0 (dm, $^1J_{CF} \approx$ 240 Hz, C_6F_5), 138.3 (dm, $^1J_{CF} \approx$ 245 Hz, C_6F_5), 136.5 (dm, $^1J_{CF} \approx$ 248 Hz, C_6F_5), 63.6 (CH_2), 58.1 (CH_2), 52.7 (CH_3), 28.0 (CH_2), 20.5 (CH_2), 7.0 (CH_2), n.o. (*ipso*-C_6F_5). ^{19}F NMR (CD_2Cl_2): −133.5 (m, 2F, *o*-C_6F_5), −162.2 (t, $^3J_{FF}$ = 20.5 Hz, 1F, *p*-C_6F_5), −166.1 (m, 2F, *m*-C_6F_5). ^{11}B NMR (CD_2Cl_2): −3.0 (s, $\nu_{1/2}$ = 20 Hz).

7: yield 56 mg (0.080 mmol, 82%). ^{1}H NMR (CD_2Cl_2): 3.80 (m, 2H, CH_2), 3.26 (m, 4H, CH_2), 3.11 (s, 6H, CH_3), 2.71 (m, 2H, CH_2), 2.27 (s, 6H, CH_3), 1.94 (m, 2H, CH_2), 1.65 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2; partial): 147.9 (dm, $^1J_{CF} \approx$ 239 Hz, C_6F_5), 138.3 (dm, $^1J_{CF} \approx$ 245 Hz, C_6F_5), 136.5 (dm, $^1J_{CF} \approx$ 247 Hz, C_6F_5), 67.0 (CH_2), 63.5 (CH_2), 60.9 (CH_2), 53.4 (CH_2), 51.3 (CH_3), 44.7 (CH_3), 27.8 (CH_2), 21.6 (CH_2), n.o. (i-C_6F_5). ^{19}F NMR (CD_2Cl_2): −134.5 (m, 2F, *o*-C_6F_5), −163.0 (t, $^3J_{FF}$ = 20.6 Hz, 1F, *p*-C_6F_5), −166.8 (m, 2F, *m*-C_6F_5). ^{11}B NMR (CD_2Cl_2): −3.0 (s, $\nu_{1/2}$ = 20 Hz).

8: yield 56 mg (0.074 mmol, 76%). ^{1}H NMR (CD_2Cl_2): 4.42 (br s, 2H, N−H), 3.39 (br, 2H, CH_2), 3.26 (m, 2H, CH_2), 3.11 (br, 2H, CH_2), 2.96 (br, 2H, CH_2), 1.95 (m, 2H, CH_2), 1.60 (m, 2H, CH_2), 1.40 (s, 9H, CH_3), 1.16 (s, 9H, CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2; partial): 147.9 (dm, $^1J_{CF} \approx$ 237 Hz, C_6F_5), 138.4 (dm, $^1J_{CF} \approx$ 243 Hz, C_6F_5), 138.4 (dm, $^1J_{CF} \approx$ 243 Hz, C_6F_5), 64.1 (C_q), 63.1 (CH_2), 52.9 (CH_2), 52.0 (C_q), 50.6 (CH_2), 37.7 (CH_2), 28.5 (CH_2), 28.4 (CH_3), 25.8 (CH_2), 25.4 (CH_3), n.o. (i-C_6F_5). ^{19}F NMR (CD_2Cl_2): −134.0 (m, 2F, *o*-C_6F_5), −162.9 (t, $^3J_{FF}$ = 20.5 Hz, 1F, *p*-C_6F_5), −166.7 (m, 2F, *m*-C_6F_5). ^{11}B NMR (CD_2Cl_2): −2.9 (s, $\nu_{1/2}$ = 20 Hz). Anal. Calcd for $C_{32}H_{32}BF_{15}N_2O$: C, 50.81; H, 4.26; N, 3.70. Found: C, 50.67; H, 4.33; N, 3.49.

Generation of $(O((CH_2)_2)_2O)B(C_6F_5)_3$ (9). 1,4-Dioxane (11 mg, 0.124 mmol, 1.1 equiv) and $B(C_6F_5)_3$ (58 mg, 0.113 mmol) were mixed in toluene-d_8, and the product was characterized via NMR spectroscopy.

9: ^{1}H NMR (toluene-d_8): 3.17 (br, $\nu_{1/2} \approx$ 3 Hz, CH_2). ^{13}C{^{1}H} NMR (toluene-d_8): 147.9 (dm, $^1J_{CF} \approx$ 245 Hz, C_6F_5), 141.3 (dm, $^1J_{CF} \approx$ 255 Hz, C_6F_5), 137.7 (dm, $^1J_{CF} \approx$ 248 Hz, C_6F_5), 114.3 (br m, *i*-C_6F_5), 70.2 (br, $\nu_{1/2} \approx$ 28 Hz, CH_2). ^{19}F NMR (toluene-d_8): −133.1 (br, 2F, *o*-C_6F_5), −155.3 (m, 1F, *p*-C_6F_5), −163.6 (m, 2F, *m*-C_6F_5). ^{11}B{^{1}H} NMR (toluene-d_8): 6.8 ($\nu_{1/2} \approx$ 400 Hz). ^{1}H NMR (toluene-d_8, 203 K): 3.28 (t, $^3J \approx {}^2J \approx$ 12 Hz, OCH_2), 3.24 (d, $^2J \approx$ 12 Hz, $BOCH_2$), 2.81 (d, $^2J \approx$ 12 Hz, OCH_2), 2.63 (t, $^3J \approx {}^2J \approx$ 12 Hz, $BOCH_2$). ^{13}C{^{1}H} NMR (toluene-d_8, 203 K): 75.5 ($\nu_{1/2} \approx$ 12 Hz, $BOCH_2$), 64.4 ($\nu_{1/2} \approx$ 15 Hz, OCH_2). n.a. (C_6F_5). ^{19}F NMR (toluene-d_8, 203 K): −130.9 (*o*), −152.5 (t, $^3J_{FF}$ = 20.0 Hz, *p*), −163.2 (*m*) ($C_6F_5^A$), −131.1 (*o*), −156.2 (*p*), −163.0 (*m*) ($C_6F_5^B$), −137.7 (*o*), −156.3 (*p*), −163.1 (*m*) ($C_6F_5^C$). 1,4-dioxane/$B(C_6F_5)_3$ (ca. 1:2): ^{1}H NMR (toluene-d_8): 3.17 (br, $\nu_{1/2} \approx$ 5 Hz, CH_2). ^{13}C{^{1}H} NMR (toluene-d_8): 148.1 (dm, $^1J_{CF} \approx$ 247 Hz, C_6F_5), 142.6 (dm, $^1J_{CF} \approx$ 261 Hz, C_6F_5), 137.9 (dm, $^1J_{CF} \approx$ 255 Hz, C_6F_5), 113.9 (br m, *i*-C_6F_5), 70.5 (br, $\nu_{1/2} \approx$ 25 Hz, CH_2). ^{19}F NMR (toluene-d_8): −133.8 (br, 2F, *o*-C_6F_5), −150.3 (br, 1F, *p*-C_6F_5), −162.8 (m, 2F, *m*-C_6F_5). ^{11}B{^{1}H} NMR (toluene-d_8): 31 ($\nu_{1/2} \approx$ 1400 Hz).

Synthesis of $tBu_3P(CH_2)_2O(CH_2)_2OB(C_6F_5)_3$ (10), $C_6H_5CH_2NMe_2(CH_2)_2O(CH_2)_2OB(C_6F_5)_3$ (11), $((tBuN)_2C_3H_2)(CH_2)_2O(CH_2)_2OB(C_6F_5)_3$ (12), and $Me_2NC_6H_4NMe_2(CH_2)_2O(CH_2)_2OB(C_6F_5)_3$ (13). These compounds were prepared in a similar fashion, and thus only the preparation of **11** is detailed: 10 μL of 1,4-dioxane was added to a solution of 10 mg (0.074 mmol) of *N*,*N*-dimethylbenzylamine and 38 mg (0.074 mmol) of $B(C_6F_5)_3$ in 1 mL of C_6D_5Br, and the mixture was heated to 50 °C until NMR control showed full conversion (∼12 h). After layering with 5 mL of hexane and storing the solution at −39 °C for several days, 46 mg (0.063 mmol, 85%) of white powder precipitated. Single crystals were grown from slow evaporation of a concentrated dichloromethane solution at room temperature.

10: yield 34 mg (0.042 mmol, 86%). ^{1}H NMR (C_6D_5Br): 4.05 (m, 2H, CH_2), 3.71 (br m, 2H, CH_2), 3.47 (br m, 2H, CH_2), 1.93 (m, 2H, CH_2), 0.87 (d, $^3J_{PH}$ = 14.2 Hz, 27H, *t*Bu). ^{19}F NMR (C_6D_5Br): −133.1 (m, 6F, *o*-C_6F_5), −161.9 (t, $^3J_{FF}$ = 21.0 Hz, 3F, *p*-C_6F_5), −165.6 (m, 6F, *m*-C_6F_5). ^{11}B NMR (C_6D_5Br): −2.9 (s, $\nu_{1/2}$ = 26 Hz). ^{31}P{H} NMR (C_6D_5Br): 49.4 (s). Anal. Calcd for $C_{31}H_{21}BF_{15}NO_2$: C, 50.89; H, 4.40. Found: C, 50.30; H, 4.51.

11: yield given above. ^{1}H NMR (CD_2Cl_2): 7.58 (m, 1H, *p*-C_6H_5), 7.50 (m, 2H, *o*-C_6H_5), 7.35 (m, 2H, *m*-C_6H_5), 4.40 (s, 2H, CH_2), 4.25 (br, 2H, CH_2), 3.68 (m, 2H, CH_2), 3.42 (m, 2H, CH_2), 3.29 (m, 2H, CH_2), 3.02 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2; partial): 133.1 (*m*-C_6H_5), 131.8 (*p*-C_6H_5), 130.0 (*o*-C_6H_5), 126.6 (C_q), 73.9 (CH_2), 70.8 (CH_2), 65.3 (CH_2), 65.1 (CH_2), 65.0 (CH_2), 51.9 (CH_3). ^{19}F NMR (CD_2Cl_2): −134.5 (m, 6F, *o*-C_6F_5), −162.7 (t, $^3J_{FF}$ = 21.0 Hz, 3F, *p*-C_6F_5), −166.4 (m, 6F, *m*-C_6F_5). ^{11}B NMR (CD_2Cl_2): −2.9 (s, $\nu_{1/2}$ = 22 Hz). Anal. Calcd for $C_{31}H_{21}BF_{15}NO_2$: C, 50.64; H, 2.80; N, 1.90. Found: C, 50.38; H, 2.87; N, 1.92.

12: yield 26 mg (0.033 mmol, 68%). ^{1}H NMR (CD_2Cl_2): 7.34 (s, 2H, =CH), 4.05 (t, $^3J_{HH}$ = 6.8 Hz, 2H, CH_2), 3.64 (t, $^3J_{HH}$ = 6.8 Hz, 2H, CH_2), 3.60 (br, 2H, CH_2), 3.25 (br, 2H, CH_2), 1.74 (s, 18H, *t*Bu). ^{13}C{^{1}H} NMR (CD_2Cl_2; partial): 147.9 (dm, $^1J_{CF} \approx$ 235 Hz, C_6F_5), 138.2 (dm, $^1J_{CF} \approx$ 236 Hz, C_6F_5), 136.4 (dm, $^1J_{CF} \approx$ 245 Hz, C_6F_5), 145.2 (C_q), 119.2 (=CH), 73.5 (CH_2), 67.9 (CH_2), 64.4 (CH_2), 63.5 (C_q-*t*Bu), 30.2 (*t*Bu), 27.6 (CH_2), n.o. (i-C_6F_5). ^{19}F NMR (CD_2Cl_2): −134.0 (m, 6F, *o*-C_6F_5), −163.5 (t, $^3J_{FF}$ = 20.8 Hz, 3F, *p*-C_6F_5), −167.1 (m, 6F, *m*-C_6F_5). ^{11}B NMR (CD_2Cl_2): −3.0 (s, $\nu_{1/2}$ = 18 Hz). Anal. Calcd for $C_{31}H_{21}BF_{15}NO_2$: C, 50.72; H, 3.74; N, 3.59. Found: C, 50.47; H, 3.51; N, 3.61.

13: yield 49 mg (0.065 mmol, 66%). ^{1}H NMR (CD_2Cl_2): 7.22 (m, 2H, C_6H_4), 6.62 (m, 2H, C_6H_4), 3.79 (m, 2H, CH_2), 3.70 (m, 2H, CH_2), 3.49 (m, 2H, CH_2), 3.42 (s, 6H, CH_3), 3.18 (m, 2H, CH_2), 2.93 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2; partial): 151.4 (C_q), 148.4 (dm, $^1J_{CF} \approx$ 235 Hz, C_6F_5), 138.9 (dm, $^1J_{CF} \approx$ 235 Hz, C_6F_5), 137.0 (dm, $^1J_{CF} \approx$ 247 Hz, C_6F_5), 132.9 (C_q), 120.9 (C_6H_4), 112.5 (C_6H_4), 74.9 (CH_2), 71.2 (CH_2), 66.2 (CH_2), 64.6

(CH_2), 55.9 (CH_3), 40.2 (CH_3), n.o. (*ipso*-C_6F_5). ^{19}F NMR (CD_2Cl_2): −133.4 (m, 6F, *o*-C_6F_5), −162.0 (t, $^3J_{FF}$ = 20.7 Hz, 3F, *p*-C_6F_5), −165.9 (m, 6F, *m*-C_6F_5). ^{11}B NMR (CD_2Cl_2): −2.9 (s, $\nu_{1/2}$ = 19 Hz). Anal. Calcd for $C_{32}H_{24}BF_{15}N_2O_2$: C, 50.28; H, 3.16; N, 3.67. Found: C, 49.77; H, 3.20; N, 3.61.

Synthesis of $(C_5H_3Me_2N)(CH_2)_2O(CH_2)_2OB(C_6F_5)_3$ (14). A 5 mg portion (0.049 mmol) of 2,6-lutidine was added to a solution of 25 mg (0.049 mmol) of $B(C_6F_5)_3$ in 0.7 mL of BrC_6D_5 in a J. Young NMR tube. The solution was stirred for 10 min, and then 5 μL of 1,4-dioxane was added and the mixture was heated to 50 °C for 2 days. The reaction was monitored by NMR spectroscopy and showed formation of the Lewis 2,6-lutidine−borane adduct and ring-opening product in a ratio of approximately 5:2. The product was purified by repetitive recrystallization and was isolated as a white powder in 24% yield (8 mg, 0.012 mmol). Single crystals were obtained from a concentrated dichloromethane solution layered with hexane at −39 °C. ^1H NMR (CD_2Cl_2): 8.15 (t, $^3J_{HH}$ = 7.9 Hz, 1H, *p*-CH), 7.65 (d, $^3J_{HH}$ = 7.9 Hz, 2H, *m*-CH), 4.72 (t, $^3J_{HH}$ = 5.2 Hz, 2H, CH_2), 4.32 (t, $^3J_{HH}$ = 4.7 Hz, 2H, CH_2), 3.57 (m, 2H, CH_2), 3.16 (br m, 2H, CH_2), 2.93 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2; partial): 156.4 (C_q-lutidine), 144.2, 128.0 (Ar C-lutidine), 73.2 (CH_2), 68.4 (CH_2), 64.6 (CH_2), 53.8 (CH_2), 22.0 (CH_3-lutidine), n.o. (C_6F_5). ^{19}F NMR (CH_2Cl_2): −134.2 (m, 6F, *o*-C_6F_5), −163.2 (t, $^3J_{FF}$ = 20.7 Hz, 3F, *p*-C_6F_5), −166.9 (m, 6F, *m*-C_6F_5). ^{11}B NMR (CH_2Cl_2): −3.0 (s, $\nu_{1/2}$ = 20 Hz). Anal. Calcd for $C_{31}H_{21}BF_{15}NO_2$: C, 49.25; H, 2.42; N, 1.98. Found: C, 48.75; H, 2.49; N, 2.13.

Synthesis of $(C_6F_5)_3B(SC_4H_8O)$ (15). A 5.0 μL portion of 1,4-thioxane was added to a solution of 51 mg (0.1 mmol) of $B(C_6F_5)_3$ in 0.7 mL of BrC_6H_5, and the mixture was stirred at room temperature for 30 min. All volatile materials were removed, and the residue was dissolved in CD_2Cl_2 and analyzed by NMR spectroscopy. The solution was transferred into a vial, layered with hexane, and stored at −39 °C overnight to give colorless crystals in 92% yield (57 mg, 0.092 mmol). ^1H NMR (CD_2Cl_2): 4.09 (m, 2H, CH_2), 2.67 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2; partial): 148.1 (dm, $^1J_{CF} \approx$ 234 Hz, C_6F_5), 141.2 (dm, $^1J_{CF} \approx$ 236 Hz, C_6F_5), 137.5 (dm, $^1J_{CF} \approx$ 243 Hz, C_6F_5), 67.8 (CH_2), 30.6 (CH_2), n.o. (i-C_6F_5). ^{19}F NMR (CD_2Cl_2): −130.0 (d, $^3J_{FF}$ = 21.0 Hz, 6F, *o*-C_6F_5), −154.2 (t, $^3J_{FF}$ = 21.0 Hz, 3F, *p*-C_6F_5), −162.8 (m, 6F, *m*-C_6F_5). ^{11}B NMR (CD_2Cl_2): 4.0 (s, $\nu_{1/2}$ = 245 Hz). Anal. Calcd for $C_{31}H_{21}BF_{15}NO_2$: C, 42.88; H, 1.31. Found: C, 42.56; H, 1.02. Additional NMR experiments: 1,4-thioxane (10 mg, 0.096 mmol) and $B(C_6F_5)_3$ (49 mg, 0.096 mmol) were mixed in toluene-d_8 and characterized via NMR spectroscopy.

15: ^1H NMR (toluene-d_8): 3.18 (m, OCH_2), 1.85 (m, SCH_2). $^{13}C\{^1H\}$ NMR (toluene-d_8): 148.6 (dm, $^1J_{CF} \approx$ 254 Hz, C_6F_5), 141.3 (dm, $^1J_{CF} \approx$ 254 Hz, C_6F_5), 137.8 (dm, $^1J_{CF} \approx$ 255 Hz, C_6F_5), 113.9 (br m, *i*-C_6F_5), 67.8 (br, $\nu_{1/2} \approx$ 11 Hz, OCH_2), 30.0 (br, $\nu_{1/2} \approx$ 6 Hz, SCH_2). ^{19}F NMR (toluene-d_8): −131.4 (m, 2F, *o*-C_6F_5), −154.3 (m, 1F, *p*-C_6F_5), −163.4 (m, 2F, *m*-C_6F_5). ^{11}B NMR (toluene-d_8): 2.4 ($\nu_{1/2} \approx$ 330 Hz).

15-O: ^1H NMR (toluene-d_8, 183 K): 3.98 (m, 1H, $BOCH_2$), 2.90 (m, 1H, $BOCH_2'$), 2.72 (t, $^3J \approx {}^3J \approx$ 11 Hz, 1H, SCH_2), 1.21 (m, 1H, SCH_2'). $^{13}C\{^1H\}$ NMR (from ghsqc experiment; toluene-d_8, 183 K): 78.3 ($BOCH_2$), 26.1 (SCH_2).

15-S: 3.09 (d, $^3J \approx$ 11 Hz, 3H, OCH_2'), 2.44 (t, $^3J \approx {}^3J \approx$ 11 Hz, 3H, OCH_2'), 1.61 (m, 3H, $BSCH_2$), 1.12 (m, 3H, $BSCH_2'$). $^{13}C\{^1H\}$ NMR (from ghsqc experiment; toluene-d_8, 183 K): 64.7 (OCH_2), 30.8 (SCH_2). 1,4-thioxane/$B(C_6F_5)_3$ (1: 2): ^1H NMR (toluene-d_8): 3.11 (m, OCH_2), 1.80 (m, SCH_2). $^{13}C\{^1H\}$ NMR (toluene-d_8): 148.3 (dm, $^1J_{CF} \approx$ 254 Hz, C_6F_5), 144.0 (dm, $^1J_{CF} \approx$ 254 Hz, C_6F_5), 137.7 (dm, $^1J_{CF} \approx$ 240 Hz, C_6F_5), 113.9 (br m, *i*-C_6F_5), 67.7 (br, $\nu_{1/2} \approx$ 5 Hz, OCH_2), 30.6 (br, $\nu_{1/2} \approx$ 4 Hz, SCH_2). ^{19}F NMR (toluene-d_8): −130.7 (m, 2F, *o*-C_6F_5), −147.4 (br, 1F, *p*-C_6F_5), −162.4 (m, 2F, *m*-C_6F_5). ^{11}B NMR (toluene-d_8): 39.4 ($\nu_{1/2} \approx$ 1000 Hz). ^1H NMR (toluene-d_8, 203 K): 3.45 (br, 1H, OCH_2), 2.46 (br, 1H, OCH_2'), 2.09 (br, 1H, SCH_2), 1.14 (br, 1H, SCH_2').

***t*Bu$_3$P(CH$_2$)$_2$S(CH$_2$)$_2$OB(C$_6$F$_5$)$_3$ (16).** A 10 μL portion of 1,4-thioxane was added to a solution of 10 mg (0.049 mmol) of tri-*tert*-butylphosphine and 25 mg (0.049 mmol) of $B(C_6F_5)_3$ in 0.7 mL of C_6D_5Br, and the mixture was heated to 50 °C until NMR control showed full conversion (∼12 h). After it was layered with 1 mL of hexane, the solution was stored at −39 °C for several days to yield a white solid (15 mg, 0.018 mmol, 37%) . The compound was purified through crystallizations. Single crystals were grown from slow evaporation of a concentrated dichloromethane solution at −39 °C. ^1H NMR (CD_2Cl_2): 3.48 (t, $^3J_{HH}$ = 5.7 Hz, 2H, CH_2), 3.33 (m, 2H, CH_2), 2.77 (t, $^3J_{HH}$ = 5.7 Hz, 2H, CH_2), 2.47 (m, 2H, CH_2), 1.59 (d, $^3J_{PH}$ = 14.1 Hz, 2H, *t*Bu). $^{13}C\{^1H\}$ NMR (CD_2Cl_2; partial): 148.0 (dm, $^1J_{CF} \approx$ 237 Hz, C_6F_5), 138.3 (dm, $^1J_{CF} \approx$ 237 Hz, C_6F_5), 136.5, (dm, $^1J_{CF} \approx$ 246 Hz, C_6F_5), 66.8 (CH_2), 39.4 (d, $^1J_{PC}$ = 28.4 Hz, C_q-*t*Bu), 34.6 (CH_2), 29.5 (br, *t*Bu), 26.4 (d, $^2J_{PC}$ = 6.4 Hz, CH_2), 20.4 (d, $^1J_{PC}$ = 29.0 Hz, PCH_2), n.o. (i-C_6F_5) . ^{19}F NMR (CD_2Cl_2): −134.0 (m, 6F, *o*-C_6F_5), −163.3 (t, $^3J_{FF}$ = 20.4 Hz, 3F, *p*-C_6F_5), −166.8 (m, 6F, *m*-C_6F_5). ^{11}B NMR (CD_2Cl_2): −2.90 (s, $\nu_{1/2}$ = 17.3 Hz). $^{13}P\{^1H\}$ NMR (CD_2Cl_2): 50.2 (s). Anal. Calcd for $C_{32}H_{33}BF_{15}OPS*1/2CH_2Cl_2$: C, 48.13; H, 4.21. Found: C, 48.72; H, 4.40.

Synthesis of $C_6H_5CH_2NMe_2(CH_2)_2S(CH_2)_2OB(C_6F_5)_3$ (17) and $Me_2NC_6H_4NMe_2(CH_2)_2S(CH_2)_2OB(C_6F_5)_3$ (18). These two compounds were prepared in a similar fashion and thus only the preparation of **17** is detailed: after a solution of 50 mg (0.370 mmol) of *N*,*N*-dimethylbenzylamine, 190 mg (0.370 mmol) of $B(C_6F_5)_3$ and 50 μL of 1,4-thioxane in 5 mL of bromobenzene was stirred at 80 °C overnight, all volatiles were removed in vacuo. The remaining oil was dissolved in 1 mL of dichloromethane, before ∼50 mL of hexanes was added to yield a white powder. This was filtered off and dried in vacuo (165 mg, 0.220 mmol, 60%).

17: ^1H NMR (CD_2Cl_2): 7.52 (m, 2H, C_6H_5), 7.28 (m, 3H, C_6H_5), 4.17 (s, 2H, CH_2), 3.73 (m, 2H, CH_2), 3.53 (m, 2H, CH_2), 3.26 (m, 2H, CH_2), 2.82 (s, 6H, CH_3), 2.75 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2; partial): 148.3 (dm, $^1J_{CF} \approx$ 245 Hz, C_6F_5), 136.9 (dm, $^1J_{CF} \approx$ 248 Hz, C_6F_5), 132.7, 131.8, 130.1 (C_6H_5), 125.8 (C_q), 69.2 (CH_2), 68.3 (CH_2), 66.9 (CH_2), 50.2 (CH_3), 35.6 (CH_2), 25.2 (CH_2). ^{19}F NMR (CD_2Cl_2): −134.1 (m, 6F, *o*-C_6F_5), −162.3 (t, $^3J_{FF}$ = 20.0 Hz, 3F, *p*-C_6F_5), −166.2 (m, 6F, *m*-C_6F_5). ^{11}B NMR (CD_2Cl_2): −2.9 (s, $\nu_{1/2}$ = 29 Hz). Anal. Calcd for $C_{31}H_{21}BF_{15}NOS$: C, 49.55; H, 2.82; N, 1.86; Found C, 49.26; H, 2.97; N, 2.01.

18: yield 55 mg (0.070 mmol, 72%). ^1H NMR (CD_2Cl_2): 7.26 (m, 2H, C_6H_4), 6.75 (m, 2H, C_6H_4), 4.20 (m, 2H, CH_2), 3.47 (m, 2H, CH_2), 3.32 (s, 6H, CH_3), 3.04 (s, 6H, CH_3), 2.75 (m, 2H, CH_2), 2.70 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2; partial): 151.0 (C_q, C_6H_4), 147.9 (dm, $^1J_{CF} \approx$ 237 Hz), 138.4 (dm, $^1J_{FC} \approx$ 249 Hz), 136.6 (dm, $^1J_{CF} \approx$ 247 Hz), 130.9 (C_q, C_6H_4), 120.2 (C_6H_4), 112.2 (C_6H_4), 70.6 (CH_2), 67.2 (CH_2), 54.8 (CH_3), 39.8 (CH_3), 35.9 (CH_2), 25.9 (CH_2), n.o. (*ipso*-C_6F_5). ^{19}F NMR (CD_2Cl_2): −134.1 (m, 6F, *o*-C_6F_5), −162.5 (t, $^3J_{FF}$ = 20.6 Hz, 3F, *p*-C_6F_5), −166.4 (m, 6F, *m*-C_6F_5). ^{11}B NMR (CD_2Cl_2): −2.9 (s, $\nu_{1/2}$ = 22 Hz). Anal. Calcd for $C_{32}H_{24}BF_{15}N_2OS$: C, 49.25; H, 3.10; N, 3.59. Found: C, 48.87; H, 2.97; N, 3.59.

Synthesis of $C_5H_3Me_2N(CH_2)_2S(CH_2)_2OB(C_6F_5)_3$ (19). A 5 mg (0.049 mmol) portion of 2,6-lutidine was added to a solution of 25 mg (0.049 mmol) of $B(C_6F_5)_3$ in 0.7 mL of BrC_6D_5 in a J. Young NMR tube. The solution was stirred for 10 min, and then 5 μL of 1,4-thioxane was added and the mixture was heated to 80 °C for 2 days. The reaction was monitored by NMR spectroscopy and showed formation of the FLP adduct and ring-opening product in a ratio of approximately 3:1. The product was purified through crystallization and was isolated as a colorless solid powder in 20% yield (7 mg, 0.010 mmol). Single crystals were obtained from a concentrated bromobenzene solution layered with pentane at −39 °C. ^1H NMR (CD_2Cl_2): 8.19 (t, $^3J_{HH}$ = 7.6 Hz, 1H, *p*-CH), 7.65 (d, $^3J_{HH}$ = 7.6 Hz, 2H, *m*-CH), 4.77 (m, 2H, CH_2), 3.52 (m, 2H, CH_2), 3.44 (br m, 2H, CH_2), 2.92 (s, 6H, CH_3 lutidine), 2.74 (br m, 2H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2;

Table 1. Crystallographic Data

	1	**2**	**3**	**4**	**5**	**6**	**7**
formula	$C_{30}H_{30}BF_{12}OP$	$C_{29}H_{17}BF_{15}NO$	$C_{31}H_{21}BF_{15}NO$	$C_{32}H_{24}BF_{15}N_2O$	$C_{25}H_{17}BF_{15}NO$	$C_{62}H_{50}B_2F_{30}N_2O_2$	$C_{28}H_{24}BF_{15}N_2O$
formula wt	676.32	691.25	719.30	748.34	643.21	1526.57	700.30
cryst syst	orthorhombic	orthorhombic	monoclinic	triclinic	triclinic	triclinic	monoclinic
space group	$P2_12_12_1$	$Pna2_1$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	9.1959(6)	17.4334(9)	10.3639(9)	10.4026(12)	10.1478(10)	10.0758(6)	11.0576(6)
b (Å)	15.6009(10)	10.6793(6)	18.5069(15)	11.8821(13)	11.5115(12)	13.0173(8)	12.6641(6)
c (Å)	20.3479(11)	14.4679(8)	15.0807(10)	13.3039(16)	13.3066(15)	13.2239(7)	20.5009(9)
α (deg)	90.00	90.00	90.00	93.177(5)	93.857(7)	67.466(3)	90.00
β (deg)	90.00	90.00	92.054(4)	108.859(6)	106.083(7)	80.503(3)	94.936(2)
γ (deg)	90.00	90.00	90.00	97.387(5)	107.488(6)	83.416(3)	90.00
V (Å^3)	2919.2(3)	2693.6(3)	2890.7(4)	1535.0(3)	1405.2(2)	1577.55(16)	2860.2(2)
Z	4	4	4	2	2	1	4
T (K)	296(2)	150(2)	150(2)	149(2)	150(2)	150(2)	150(2)
D (g/cm^3)	1.539	1.705	1.653	1.619	1.520	1.607	1.626
R(int)	0.0397	0.0205	0.0516	0.0272	0.0567	0.0315	0.0406
μ (cm^{-1})	0.196	0.175	0.166	0.161	0.161	0.786	0.166
total no. of data	58 263	35 400	25 095	25 998	35 230	35 031	23 948
no. of obsd data	8006	13 352	6612	7031	9777	9534	6521
no. of variables	416	424	444	486	391	454	428
R ($>2\sigma$)	0.0301	0.0389	0.0436	0.0459	0.0574	0.0497	0.0403
R_w	0.0730	0.1146	0.0988	0.1211	0.1493	0.1408	0.1044
GOF	1.021	1.046	1.011	1.039	0.957	1.046	1.019

	10·0.5C_6H_5Br	**11**·0.5CH_2Cl_2	**12**	**14**	**15**	**18**	**19**·C_6H_5Br
formula	$C_{37}H_{34.5}BBr_{0.5}F_{15}O_2P$	$C_{31.5}H_{22}BClF_{15}NO_2$	$C_{33}H_{28}BF_{15}N_2O_2$	$C_{29}H_{17}BF_{15}NO_2$	$C_{22}H_8BF_{15}OS$	$C_{32}H_{24}BF_{15}N_2OS$	$C_{35}H_{22}BBrF_{15}NOS$
formula wt	880.90	777.76	780.38	707.25	616.15	780.40	880.32
cryst syst	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	Cc	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a (Å)	15.6780(6)	10.8022(11)	20.136(3)	10.7712(6)	11.3535(9)	10.385(9)	12.5351(3)
b (Å)	13.9752(5)	12.5626(12)	18.474(3)	17.1693(10)	9.8755(8)	11.969(9)	28.6052(6)
c (Å)	18.5333(7)	12.7031(12)	9.9822(15)	15.3473(9)	19.2199(15)	13.687(11)	10.0729(2)
α (deg)	90.00	72.288(5)	90.00	90.00	90.00	92.10(4)	90.00
β (deg)	110.439(2)	89.924(5)	112.825(4)	101.361(3)	94.300(4)	108.09(4)	106.3280(10)
γ (deg)	90.00	74.042(4)	90.00	90.00	90.00	95.89(3)	90.00
V (Å^3)	3805.1(2)	1572.5(3)	3422.5(9)	2782.6(3)	2148.9(3)	1604(2)	3466.16(13)
Z	4	2	4	4	4	2	4
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
D (g/cm^3)	1.538	1.643	1.514	1.688	1.905	1.615	1.687
R(int)	0.0782	0.0375	0.0503	0.0527	0.0375	0.0757	0.0477
μ (cm^{-1})	0.705	0.244	0.150	0.174	0.298	0.220	1.359
total no. of data	58 814	35 421	10 623	24 428	18 297	24 565	35 796
no. of obsd data	8758	9501	5735	6282	4913	7218	8946
no. of variables	523	498	475	435	361	473	498
R ($>2\sigma$)	0.0769	0.0586	0.0628	0.0439	0.0360	0.0498	0.0449
R_w	0.2348	0.2037	0.1596	0.1071	0.0874	0.1742	0.1044
GOF	1.019	0.951	1.008	1.007	1.021	0.899	1.023

partial): 155.9 (*ipso*-C lutidine), 147.0 (dm, $^1J_{CF} \approx 235$ Hz, C_6F_5), 144.5 (C Ar lutidine), 138.3 (dm, $^1J_{CF} \approx 237$ Hz, C_6F_5), 136.0, (dm, $^1J_{CF} \approx 244$ Hz, C_6F_5), 128.3 (C Ar lutidine), 67.0 (CH_2), 54.1 (CH_2), 34.9 (CH_2), 30.1 (CH_2), 21.7 (CH_3 lutidine). ^{19}F NMR (CD_2Cl_2): −134.2 (m, 6F, *o*-C_6F_5), −162.9 (t, $^3J_{FF}$ = 20.4 Hz, 3F, *p*-C_6F_5), −166.8 (m, 6F, *m*-C_6F_5). ^{11}B NMR (CD_2Cl_2): −3.0 (s, $\nu_{1/2}$ = 20 Hz). Anal. Calcd for $C_{31}H_{21}BF_{15}NOS$*1/2C_6H_5Br: C, 47.93; H, 2.45; N, 1.75. Found: C, 47.49; H, 2.53; N, 1.92.

X-ray Data Collection, Reduction, Solution, and Refinement. Single crystals were mounted in thin-walled capillaries either placed under an atmosphere of dry N_2 in a glovebox and flame-sealed or coated in Paratone-N oil. The data were collected using the SMART software package on a Siemens SMART System CCD diffractometer using a graphite monochromator with Mo Kα radiation (λ = 0.710 73 Å). A hemisphere of data was collected in 1448 frames with 10 s exposure times unless otherwise noted. Data reduction was performed using the SAINT software package and an absorption correction applied using SADABS. The structures were solved by direct methods using XS and refined by full-matrix least squares on F^2 using XL as implemented in the SHELXTL suite of programs.[32] All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors. Crystal data for compounds **1**−**7**, **10**·0.5C_6H_5Br, **11**·0.5CH_2Cl_2, **12**, **14**, **15**, **18**, and **19**·C_6H_5Br are given in Table 1.

Results and Discussion

Noting that sterically hindered phosphines in combination with $B(C_6F_5)_3$ have been previously[19] shown to effect THF ring-opening, we probed the corresponding reaction of the borane $B(p\text{-}C_6F_4H)_3$[34] with tBu$_2$PH in THF. The species tBu$_2$(H)P(CH$_2$)$_4$OB(*p*-$C_6F_4H)_3$ (**1**) was obtained in 87% yield. The ^{31}P NMR signal at 51.3 ppm exhibited P−H coupling of about 447 Hz, consistent with the formation of a phosphonium center. The ^{19}F NMR data showed signals at

(32) Sheldrick, G. M. *SHELXTL*; Bruker AXS Inc., Madison, WI, 2000.

(33) Geier, S. J.; Stephan, D. W. *J. Am. Chem. Soc.* **2009**, *131*, 3476–3477.

(34) Ullrich, M.; Lough, A. J.; Stephan, D. W. *J. Am. Chem. Soc.* **2009**, *131*, 52–53.

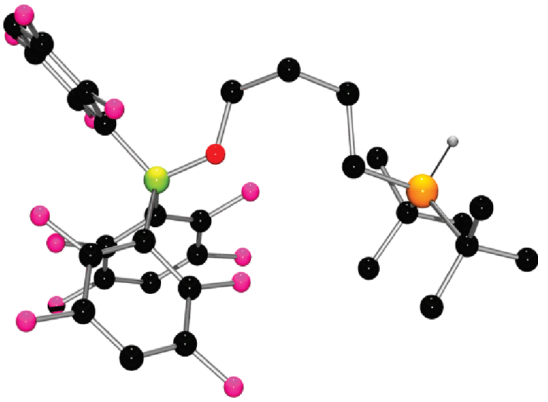
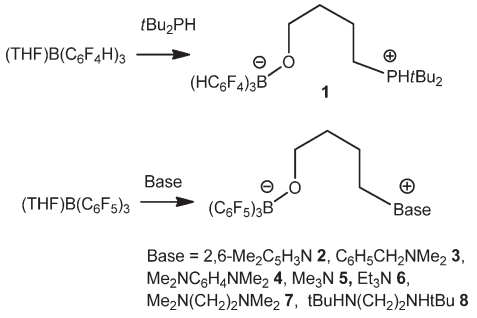


Figure 1. POV-ray depiction of **1**. Legend for atoms: C, black; B, yellow-green; F, pink; O, red; N, aquamarine.

Scheme 2. Synthesis of 1−8[a]



Base = 2,6-$Me_2C_5H_3N$ **2**, $C_6H_5CH_2NMe_2$ **3**, $Me_2NC_6H_4NMe_2$ **4**, Me_3N **5**, Et_3N **6**, $Me_2N(CH_2)_2NMe_2$ **7**, $tBuHN(CH_2)_2NHtBu$ **8**

[a] Note: the base used in the formation of **5** was $CH_2(NMe_2)_2$.

−134.4 and −142.9 ppm, while the $^{11}B\{^1H\}$ resonance was observed at −2.8 ppm, as expected for the borate fragment. Crystallographic data (Figure 1) confirmed this interpretation. It is noted that, in the absence of THF, the combination of $B(C_6F_5)_3$ and tBu_2PH has been previously shown to give $tBu_2(H)P(C_6F_4)BF(C_6F_5)_2$ from nucleophilic attack by the phosphine at the para position of one of the fluoroarene rings.[35] Thus, the inclusion of protons in the para positions of the borane precludes such substitution.

To broaden the scope of such ring-opening reactions, we considered related reactions of sterically encumbered N-bases. In this regard, we previously communicated that the reaction of 2,6-lutidine with a THF solution of $B(C_6F_5)_3$ led to the formation of the THF-ring-opening product $(C_5H_3Me_2N)$-$(CH_2)_4OB(C_6F_5)_3$ (**2**), as evidenced by NMR and X-ray crystallographic data (Scheme 2, Figure 2).[33] The reactions of *N*,*N*-dimethylbenzylamine with a THF solution of $B(C_6F_5)_3$ were performed. Following workup the new species **3** was isolated in 81% yield. ^1H NMR data showed five methylene resonances at 4.26, 3.84, 3.24, 2.04, and 1.64 ppm consistent with the incorporation of the amine and ring-opening of a THF molecule. ^{19}F and ^{11}B NMR spectral data were consistent with the formation of a borate moiety, and thus **3** was formulated as $C_6H_5CH_2NMe_2(CH_2)_4OB(C_6F_5)_3$. Crystals suitable for X-ray diffraction analysis were obtained from CH_2Cl_2/hexane. The subsequent analysis confirmed the proposed formulation of **3** (Figure 3). The B−O bond distance of 1.462(3) Å was similar to that seen in the phosphine THF-ring-opened product **1** and in **2**. The N−C distances were unexceptional.

(35) Welch, G. C.; Cabrera, L.; Chase, P. A.; Hollink, E.; Masuda, J. D.; Wei, P.; Stephan, D. W. *Dalton Trans.* **2007**, 3407–3414.

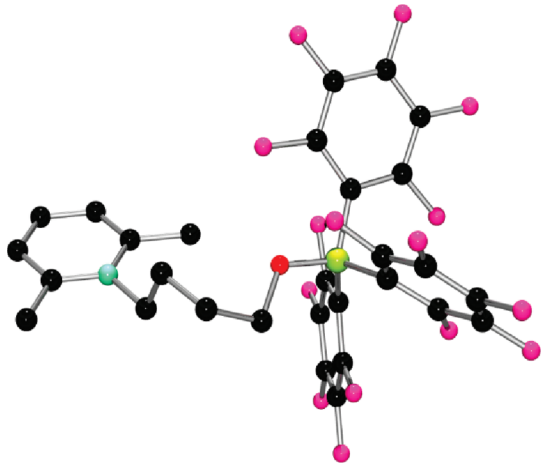


Figure 2. POV-ray depiction of **2**. Legend for atoms: C, black; B, yellow-green; F, pink; O, red; N, aquamarine.

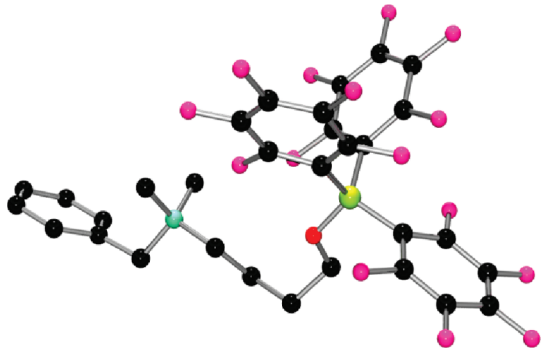


Figure 3. POV-ray depiction of **3**. Legend for atoms: C, black; B, yellow-green; F, pink; O, red; P, orange.

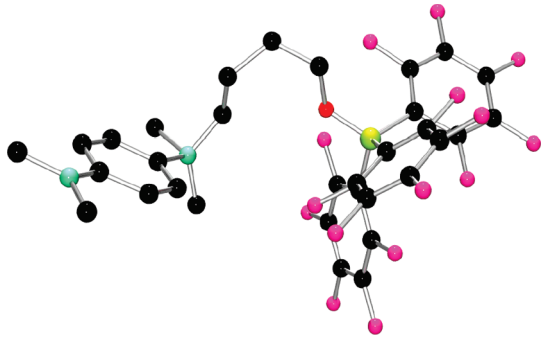


Figure 4. POV-ray depiction of **4**. Legend for atoms: C, black; B, yellow-green; F, pink; O, red; N, aquamarine.

The corresponding reaction of *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine with $B(C_6F_5)_3$ and THF gave $Me_2NC_6H_4NMe_2(CH_2)_4OB(C_6F_5)_3$ (**4**) in 92% yield (Scheme 2). ^{19}F and ^{11}B NMR spectra were consistent with the formation of a borate moiety. Four methylene resonances at 4.28, 3.19, 1.63, and 1.57 ppm were detected in the ^1H NMR data and are consistent with the ring-opening of a THF molecule. Single crystals suitable for X-ray diffraction analysis (Figure 4) confirmed the proposed formulation. The corresponding reactions of $B(C_6F_5)_3$(THF) with *N*,*N*,*N*′,*N*′-tetramethylmethanediamine, triethylamine, *N*,*N*,*N*′,*N*′-tetramethylethanediamine, and *N*,*N*′-di-*tert*-butylethanediamine in C_6D_5Br at 25 °C gave the corresponding ring-opened products **5**−**8** in 54, 87, 82, and 76% yields, respectively (Scheme 2). The

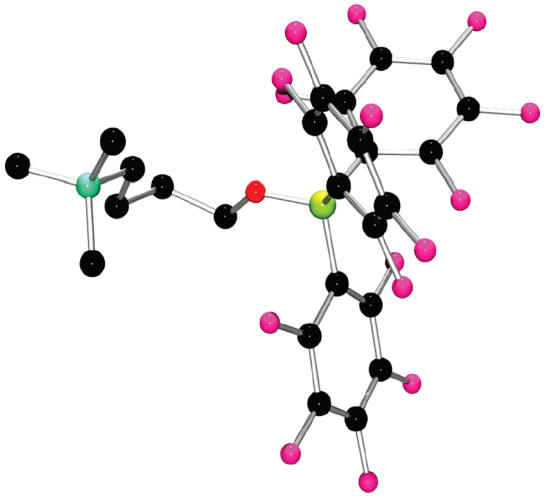


Figure 5. POV-ray depiction of **5**. Legend for atoms: C, black; B, yellow-green; F, pink; O, red; N, aquamarine.

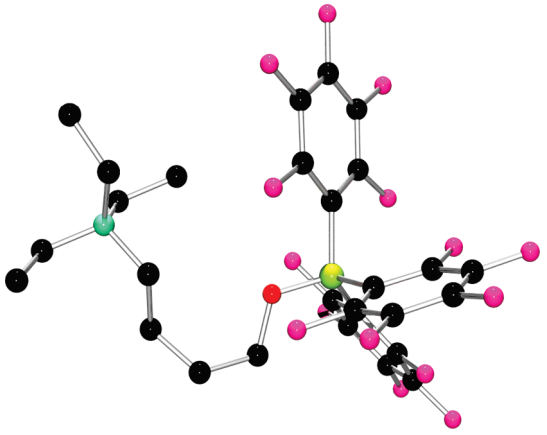


Figure 6. POV-ray depiction of **6**. Legend for atoms: C, black; B, yellow-green; F, pink; O, red; N, aquamarine.

resonances of the ^{19}F and ^{11}B NMR data showed signals expected for the borate fragment. ^{1}H NMR data of **5** showed an unexpected intensity ratio of 9:2 for the methyl and methylene groups, respectively, suggesting the formulation of **5** as $Me_3N(CH_2)_4OB(C_6F_5)_3$, a formulation that was subsequently confirmed crystallographically (Figure 5). This product presumably arises from the instability of transient ammonium aminomethane with respect to methyl migration and elimination of $MeN{=}CH_2$.

In the case of compound **8**, upon ring-opening, the resulting chiral N atom generates diastereotopic methylene groups, as evidenced by low-temperature NMR data in dichloromethane at −75 °C. While preliminary X-ray data confirmed the formulation of **8**, poor crystal quality precluded publishable data. Nonetheless, crystallographic data were also obtained for **6** and **7** (Figures 6 and 7).

In further extending this chemistry, we investigated the possibility that such Lewis acid/Lewis base combinations might also induce the ring-opening of other cyclic ethers. While derivatization of cyclic oxonium derivatives has been reported for polyhedral boron hydrides,[36] it has not been demonstrated for combinations of Lewis acids and bases.

(36) Semioshkin, A. A.; Sivaev, I. B.; Bregadze, V. I. *Dalton Trans.* **2008**, 977–992.

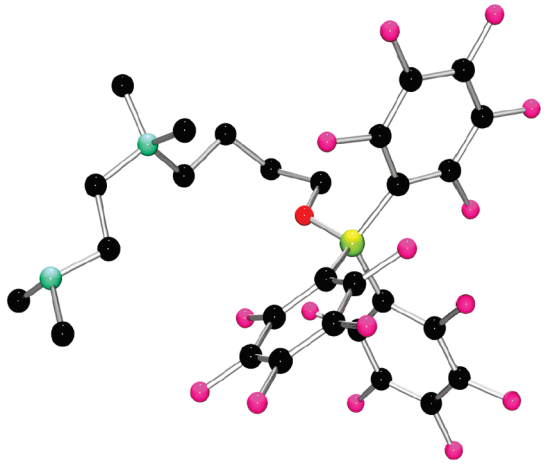


Figure 7. POV-ray depiction of **7**, Legend for atoms: C, black; B, yellow-green; F, pink; O, red; N, aquamarine.

The combination of 1,4-dioxane and $B(C_6F_5)_3$ in a ca. 1.1:1 ratio afforded formation of the $(O(CH_2CH_2)_2O)B(C_6F_5)_3$ adduct **9**. At 25 °C only one broad methylene resonance was observed ($\delta(^1H)$ 3.17, $\delta(^{13}C)$ 70.2), consistent with a fast exchange of the borane, involving both oxygen atoms of the 1,4-dioxane. When the temperature was lowered to −70 °C, two different CH_2 groups, each with diastereotopic protons, were detected ($\delta(^1H)$ 3.28/2.81 ($\delta(^{13}C)$ 64.4) (OCH_2); 3.24/2.63 ($\delta(^{13}C)$ 75.5) ($BOCH_2$)). The ^{19}F NMR spectrum at −70 °C shows three sets of signals for three different C_6F_5 groups, −130.9 (*o*), −152.5 (*p*), −163.2 (*m*) ($C_6F_5{}^A$), −131.1 (*o*), −156.2 (*p*), −163.0 (*m*) ($C_6F_5{}^B$), and −137.7 (*o*), −156.3 (*p*), −163.1 (*m*) ($C_6F_5{}^C$), due to hindered rotation around the B−O vector. Similar NMR experiments were also carried out with a 1:2 mixture of 1,4-dioxane and $B(C_6F_5)_3$. At 25 °C the ^{19}F and ^{11}B NMR spectra ($\delta(^{19}F)$ −133.8 (*o*), −150.3 (*p*), −162.8 (*m*); $\delta(^{11}B)$ 31 ($\nu_{1/2} \approx 1400$ Hz)) clearly show an equilibrium between the adduct **9** and free borane. At −70 °C the sample became heterogeneous due to precipitation of $B(C_6F_5)_3$, although the very broad ^1H and ^{19}F resonances were consistent with the presence of **9** and free $B(C_6F_5)_3$.

The phosphine tBu$_3$P, $B(C_6F_5)_3$, and 1,4-dioxane were mixed and heated to 50 °C for 2 days. This resulted in the formation of the new species **10** in 86% yield. The ^1H NMR spectrum revealed resonances consistent with four inequivalent methylene groups in addition to resonances arising from the *tert*-butyl groups. ^{19}F and ^{11}B NMR data were consistent with the formation of a borate anion with resonances very similar to those seen for **2**. The $^{13}P\{^1H\}$ NMR signal was clearly consistent with the quaternization of P, with a resonance at 49.4 ppm. This suggested the formulation of **10** as tBu$_3$P$(CH_2)_2O(CH_2)_2OB(C_6F_5)_3$, a formulation that was subsequently confirmed crystallographically (Figure 8).

In a similar fashion, reaction of $B(C_6F_5)_3$−1,4-dioxane with *N*,*N*-dimethylbenzylamine, the carbene $(t\text{BuN})_2C_3H_2$, *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine, and 2,6-lutidine afforded $C_6H_5CH_2NMe_2(CH_2)_2O(CH_2)_2OB(C_6F_5)_3$ (**11**), $((t\text{BuN})_2C_3H_2)(CH_2)_2O(CH_2)_2OB(C_6F_5)_3$ (**12**), $Me_2NC_6H_4NMe_2(CH_2)_2O(CH_2)_2OB(C_6F_5)_3$ (**13**), and $C_5H_3Me_2N(CH_2)_2O(CH_2)_2OB(C_6F_5)_3$ (**14**) in 85, 68, 66, and 24% isolated yields, respectively (Scheme 3). The observation of a ^{13}C resonance for **12** at 145.2 ppm was consistent with the participation of the carbene C in C−C bond formation. The formulation of these zwitterionic salts was confirmed crystallographically

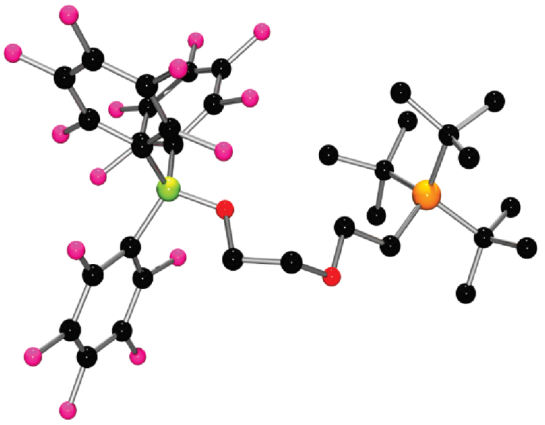
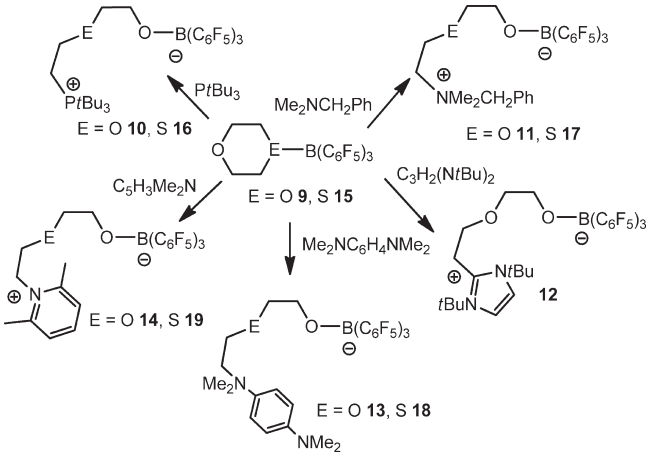


Figure 8. POV-ray depiction of **10**. Legend for atoms: C, black; B, yellow-green; F, pink; O, red; N, aquamarine.

Scheme 3. Synthesis of 9−19



(Figures 9−11). The new N−C bond distance was unexceptional and was similar to that seen in the previously reported THF-ring-opened analogues. For compound **13** ^{19}F and ^{11}B NMR spectral data were consistent with the formation of a borate moiety. In the case of **14**, the low yield resulted from the simultaneous formation of the 2,6-lutidine−$B(C_6F_5)_3$ adduct. The ratio of adduct **14** was approximately 5:2.

A further extension of this chemistry targeted 1,4-thioxane ring-opening. To this end, the borane complex of thioxane ($(C_6F_5)_3B(SC_4H_8O)$ (**15-S**) was isolated in 92% yield. The ^{1}H NMR spectrum showed resonances at 4.09 and 2.67 ppm, while the ^{19}F NMR signals were observed at −130.0, −154.2, and −162.8 ppm. The ^{11}B NMR signal at 4.0 ppm was quite broad, suggesting the possibility of an equilibrium governing a donor−acceptor interaction. The X-ray structure of **15-S** (Figure 12) was determined, and it revealed that in the solid state the thioxane is S-bound to B with a S−B distance of 2.111(2) Å. This bond length is considerably longer than that seen for ether adducts and thus is consistent with the suggestion of facile exchange in solution. The observation of S binding in the solid state is perhaps surprising, given the oxophilicity of B. However, S-bonded thioxane adducts are known with BH_3[37,38] and BX_nH_{n-1},[39] whereas BF_3 and BCl_3 prefer O binding.[40]

(37) Brown, H. C.; Mandal, A. K. *J. Org. Chem.* **1992**, *18*, 4970–4976.
(38) Brown, H. C.; Mandal, A. K. *Synthesis* **1980**, *2*, 153–155.
(39) Zaidlewicz, M.; Kanth, J. V. B.; Brown, H. C. *J. Org. Chem.* **2000**, *20*, 6697–6702.

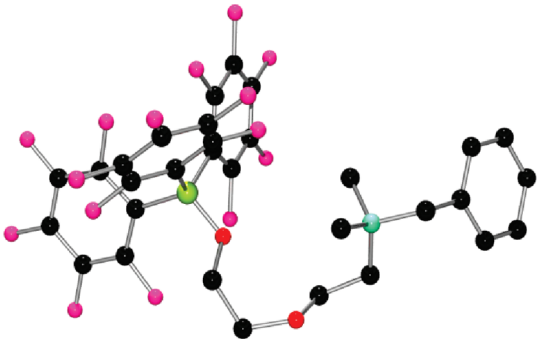


Figure 9. POV-ray depiction of **11**. Legend for atoms: C, black; B, yellow-green; F, pink; O, red; P, orange.

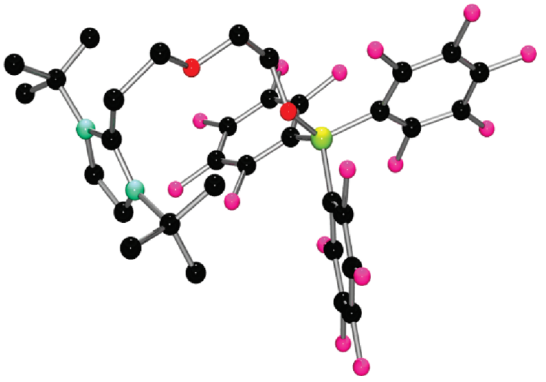


Figure 10. POV-ray depiction of **12**. Legend for atoms: C, black; B, yellow-green; F, pink; O, red; N, aquamarine.

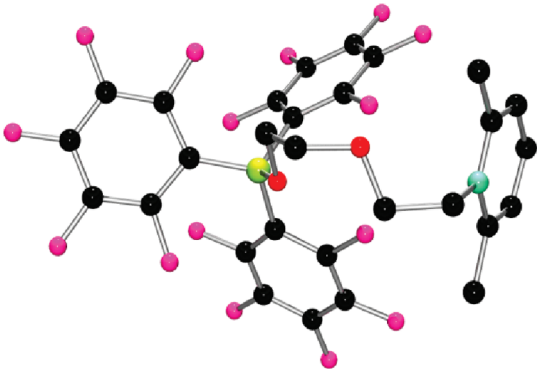


Figure 11. POV-ray depiction of **14**. Legend for atoms: C, black; B, yellow-green; F, pink; O, red; N, aquamarine.

To examine the nature of species present in solution, $B(C_6F_5)_3$ and 1,4-thioxane were mixed in a 1:1 ratio and characterized via variable-temperature NMR spectroscopy. At 25 °C two methylene resonances attributable to an AA′BB′ spin system (δ(^{1}H) 3.18 (δ(^{13}C) 67.8) (OCH_2); δ(^{1}H) 1.85 (δ(^{13}C) 30.0) (SCH_2)) were detected, which indicates fast exchange of the borane taking place under these conditions. At −90 °C, the NMR spectra show two main species in a 1:3 ratio, each exhibiting two different CH_2 groups with diastereotopic protons. In combination with 2D NMR experiments, these were assigned to be most likely the sulfur-bonded adduct (**15-S**) (major compound δ(^{1}H) 3.09/2.44 (δ(^{13}C) 64.7) (OCH_2); δ(^{1}H) 1.61/1.12 (δ(^{13}C) 30.8)

(40) Baker, K. L.; Fowles, G. W. A. *J. Chem. Soc. A* **1968**, *4*, 801–804.

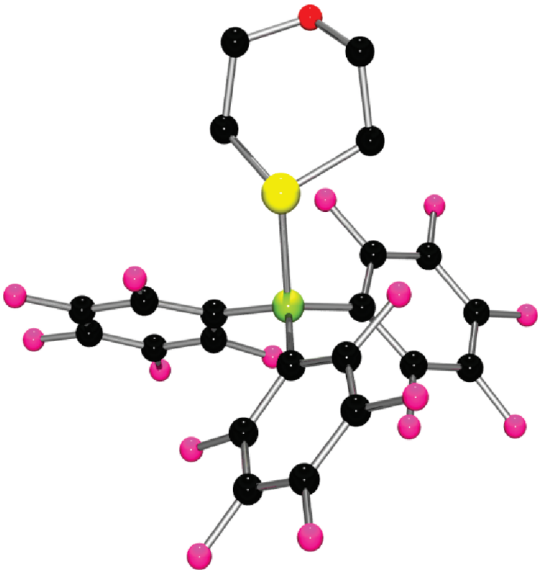


Figure 12. POV-ray depiction of **15**. Legend for atoms: C, black; B, yellow-green; F, pink; O, red; S, yellow.

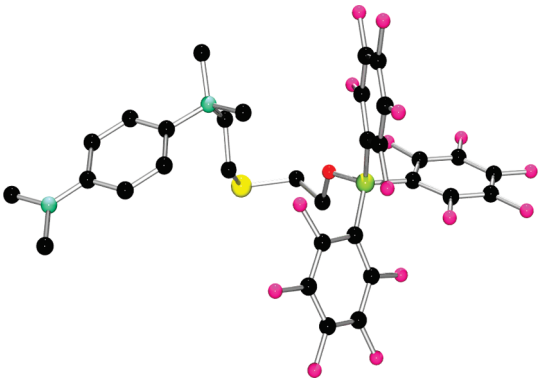
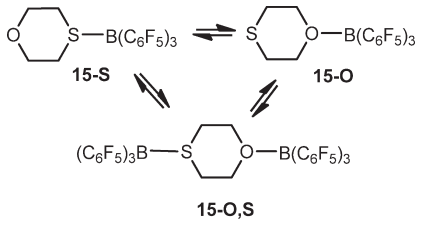


Figure 13. POV-ray depiction of **18**. Legend for atoms: C, black; B, yellow-green; F, pink; O, red; N, aquamarine; S, yellow.

Scheme 4. Equilibria involving Thioxane and $B(C_6F_5)_3$



(SCH_2)) and the O-bonded adduct (**15-O**) (minor compound $\delta(^1H)$ 3.98/2.90 ($\delta(^{13}C)$ 78.3) (OCH_2); $\delta(^1H)$ 2.72/1.21 ($\delta(^{13}C)$ 26.1) (SCH_2)). Similar to the 1,4-dioxane case, a 1:2 mixture of 1,4-thioxane and $B(C_6F_5)_3$ shows fast exchange at 25 °C and thus two methylene resonances in the NMR spectra ($\delta(^1H)$ 3.11 ($\delta(^{13}C)$ 67.7) (OCH_2); $\delta(^1H)$ 1.80 ($\delta(^{13}C)$ 30.6) (SCH_2)) were observed. However, whereas the 1:1 mixture forms two different monoadducts at lower temperatures (Scheme 4), the 1:2 mixture apparently yields the bis-$B(C_6F_5)_3$ adduct **15-O,S**, giving rise to the observation of four different ^1H NMR methylene signals in a 1:1:1:1 ratio ($\delta(^1H)$ 3.45/2.46 (OCH_2), 2.09/1.14 (SCH_2) (all broad)). These data affirm the presence of rapidly interconverting S- and O-bound adducts of B-$(C_6F_5)_3$ in solution despite the isolation of crystalline **15-S**.

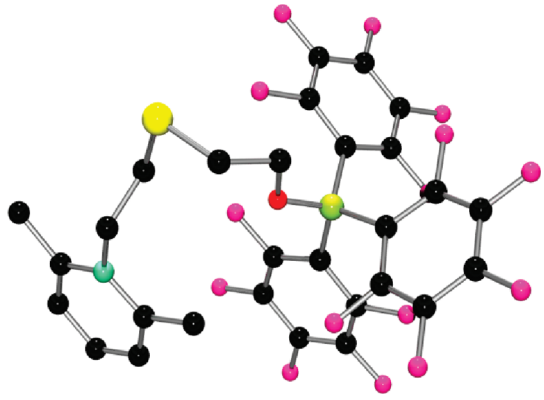


Figure 14. POV-ray depiction of **19**. Legend for atoms: C, black; B, yellow-green; F, pink; O, red; P, orange; S, yellow.

Reactions of $B(C_6F_5)_3$ and thioxane with tBu$_3$P, *N*,*N*-dimethylbenzylamine, *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine, and 2,6-lutidine in C_6D_5Br at 80 °C proceed to give the corresponding ring-opened products **16**−**19** in 37, 60, 72, and 20% yields, respectively (Scheme 3). NMR data were consistent with ring-opening, as each product exhibited four methylene resonances in the ^1H NMR spectrum. In addition, the products **16**−**19** exhibited similar ^{19}F and ^{11}B NMR spectra, suggesting the formulations $L(CH_2)_2S(CH_2)_2OB(C_6F_5)_3$ (L = tBu$_3$P (**16**), $C_6H_5CH_2NMe_2$ (**17**), $Me_2NC_6H_4NMe_2$-$(CH_2)_2S(CH_2)_2OB(C_6F_5)_3$ (**18**), $C_5H_3Me_2N$ (**19**)). These formulations were confirmed with crystallographic data. While preliminary data confirmed the formulations of **16** and **17**, poor crystal quality precluded publishable data. Nonetheless, crystallographic data were also obtained for **18** (Figure 13) and **19** (Figure 14). In these cases, the formation of the B−O bond was confirmed, as the B−O distances were typical of those described for the species above. The formation of these ring-opening products where a C−O bond is cleaved is seemingly in contradiction to isolation of the S-bound isomer (**15-S**). However, the detection of the rapid interconversion of O- and S-coordinated isomers of **15** in solution, together with the shorter bond length of B−O versus B−S, suggests that greater steric congestion in the O-bound adduct may activate the ether linkages to attack by the nucleophilic base. Apparently, 1,4-thioxane/$B(C_6F_5)_3$ is a case where the isolated crystalline product (**15-S**) does not completely represent the situation encountered in solution.

Conclusions

The present results demonstrate the generality of ring-opening of THF, dioxane, and thioxane with a variety of sterically hindered combinations of boranes and bases, including amines, phosphines, carbenes, and pyridines. Such reactivity appears to be generally typical of FLPs. Moreover, the mechanistic similarities to previously reported THF ring-openings by transition-metal and main-group systems suggest that these systems can also be described as FLPs. While this notion opens the door to a broader exploration of FLP reactivity, the present results suggest that ring-opening products may provide a unique synthetic strategy to new mixed-donor ether or thioether ligands. Both of these avenues of research are under examination and will be described in due course.

Acknowledgment. G.E. gratefully acknowledges the financial support of the Deutsche Forschungsgemeinschaft

and the Fonds der Chemischen Industrie. D.W.S. gratefully acknowledges the financial support of the NSERC of Canada, the award of a Canada Research Chair, and a Killam Research Fellowship. B.B. is grateful that this work was supported by a fellowship within the postdoctoral program of the German Academic Exchange Service (DAAD). T.V. is grateful for the Ph.D. fellowship of the Fonds der Chemischen Industrie. S.J.G. is grateful for the support of an NSERC postgraduate scholarship. M.U. is grateful for the award of a Feodor-Lynen Postdoctoral Fellowship by the Alexander-von-Humboldt Foundation.

Supporting Information Available: Text and figures giving additional characterization data for compounds **1**−**19** and CIF files giving crystallographic data for **1**−**7**, **10**·0.5C_6H_5Br, **11**·0.5CH_2Cl_2, **12**, **14**, **15**, **18**, and **19**·C_6H_5Br. This material is available free of charge via the Internet at http://pubs.acs.org.