336 *Inorg. Chem.* **2011**, *50*, 336–344
DOI: 10.1021/ic102003x

Inorganic Chemistry
Article

Synthesis and Reactivity of the Phosphinoboranes $R_2PB(C_6F_5)_2$

Stephen J. Geier,[†] **Thomas M. Gilbert,**[‡] **and Douglas W. Stephan***[,†]

[†]*Department of Chemistry, University of Toronto, Toronto, Ontario M5S 3H6, Canada, and*
[‡]*Department of Chemistry & Biochemistry, Northern Illinois University, DeKalb, Illinois 60115, United States*

Received September 30, 2010

The phosphinoboranes $[R_2PB(C_6F_5)_2]_2$ (R = Et **1**, Ph **2**) and $R_2PB(C_6F_5)_2$ (R = *t*Bu **3**, Cy **4**, Mes **5**) were synthesized from the reaction of $(C_6F_5)_2BCl$ and the corresponding lithium phosphide. The relationships between B—P distance, P pyramidality, and the extent of BP multiple bonding were further explored computationally. Natural Bond Order (NBO) analyses of **3** and **4** showed that the π-bonding highest occupied molecular orbitals (HOMOs) were highly polarized. In addition the Lewis acid—base adducts, $R_2(H)P \cdot B(H)(C_6F_5)_2$ (R = Et **6**; Ph **7**; *t*Bu **8**; Cy **9**; Mes **10**) were prepared via the reaction of the phosphines R_2PH with the borane $HB(C_6F_5)_2$. Compounds **1** and **2** showed no signs of reaction with H_2; however, reaction of compounds **3** and **4** with H_2 was observed to give **8** and **9**. In a related set of reactions compounds **3** and **4** were reacted with H_3NBH_3 or $Me_2(H)NBH_3$ also led to the generation of **8** and **9**, respectively. The reaction profile of the reaction of $(CF_3)_2BPR_2$ with H_2 was examined computationally and shown to be exothermic. Efforts to effect the reverse reaction, that is, dehydrogenation of adducts **6**—**10** were unsuccessful. Compound **4** was also shown to react with 4-*tert*-butylpyridine to give $Cy_2PB(C_6F_5)_2(4\text{-}t\text{BuC}_5H_4N)$ **11** while reactions of **3** and **4** with the Lewis acid BCl_3 gave the dimers $(R_2PBCl_2)_2$ (R = *t*Bu **12**, Cy **13**) and the byproduct $ClB(C_6F_5)_2$.

Introduction

Combinations of group 13 Lewis acids and group 15 Lewis bases are of significant interest as a result of their potential for use as hydrogen storage materials.[1] To that end many recent experimental[2−16] and theoretical studies[17−22] have focused on main group compounds and amino-boranes in particular. The dehydrogenation of ammonia-borane and related amine-borane or phosphine-borane adducts have been shown to occur under thermal duress[23] or catalytically, using transition metals,[2,10−12,14−16,24−30] Lewis acid[4] or Lewis base catalysts.[31] The resulting products contain group13-group 15 multiple bonds, and the nature of these materials has also generated interest in the fundamental nature of the bonding modes in these products. Moreover these dehydrogenation products are thermodynamically downhill from the precursors, and thus hydrogenation of such materials is strongly endothermic.

---

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

(1) Grochala, W.; Edwards, P. P. *Chem. Rev.* **2004**, *104*, 1283.
(2) Keaton, R. J.; Blacquiere, J. M.; Baker, R. T. *J. Am. Chem. Soc.* **2007**, *129*, 1844.
(3) Stephens, F. H.; Baker, R. T.; Matus, M. H.; Grant, D. J.; Dixon, D. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 746.
(4) Stephens, F. H.; Pons, V.; Baker, R. T. *Dalton Trans.* **2007**, 2613.
(5) Marder, T. B. *Angew. Chem., Int. Ed.* **2007**, *46*, 8116.
(6) Cheng, F.; Ma, H.; Li, Y.; Chen, J. *Inorg. Chem.* **2007**, *46*, 788.
(7) Pun, D.; Lobkovsky, E.; Chirik, P. J. *Chem. Commun.* **2007**, 3297.
(8) Jiang, Y.; Berke, H. *Chem. Commun.* **2007**, 3571.
(9) Denney, M. C.; Pons, V.; Hebden, T. J.; Heinekey, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2006**, *128*, 12048.
(10) Clark, T. J.; Russell, C. A.; Manners, I. *J. Am. Chem. Soc.* **2006**, *128*, 9582.
(11) Jaska, C. A.; Bartole-Scott, A.; Manners, I. *Phosphorus, Sulfur Silicon Relat. Elem.* **2004**, *179*, 685.
(12) Jaska, C. A.; Dorn, H.; Lough, A. J.; Manners, I. *Chem.—Eur. J.* **2003**, *9*, 271.
(13) Jaska, C. A.; Manners, I. *J. Am. Chem. Soc.* **2004**, *126*, 1334.
(14) Jaska, C. A.; Manners, I. *J. Am. Chem. Soc.* **2004**, *126*, 2698.
(15) Jaska, C. A.; Temple, K.; Lough, A. J.; Manners, I. *Chem. Commun.* **2001**, 962.
(16) Jaska, C. A.; Temple, K.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2003**, *125*, 9424.
(17) Chen, Y.; Fulton, J. L.; Linehan, J. C.; Autrey, T. *J. Am. Chem. Soc.* **2005**, *127*, 3254.
(18) Luo, Y.; Ohno, K. *Organometallics* **2007**, *26*, 3597.
(19) Yang, X.; Hall, M. B. *J. Am. Chem. Soc.* **2008**, *130*, 1798.
(20) Li, Q. S.; Zhang, J.; Zhang, S. *Chem. Phys. Lett.* **2005**, *404*, 100.
(21) Nguyen, M. T.; Nguyen, V. S.; Matus, M. H.; Gopakumar, G.; Dixon, D. A. *J. Phys. Chem. A* **2007**, *111*, 679.
(22) Paul, A.; Musgrave, C. B. *Angew. Chem., Int. Ed.* **2007**, *46*, 8153.
(23) Niedenzu, K.; Dawson, J. W. *Boron-Nitrogen Compounds*; Academic Press, Inc: New York, 1965.
(24) Dorn, H.; Jaska, C. A.; Singh, R. A.; Lough, A. J.; Manners, I. *Chem. Commun.* **2000**, 1041.
(25) Dorn, H.; Singh, R. A.; Massey, J. A.; Lough, A. J.; Manners, I. *Angew. Chem., Int. Ed.* **1999**, *38*, 3321.
(26) Dorn, H.; Vejzovic, E.; Lough, A. J.; Manners, I. *Inorg. Chem.* **2001**, *40*, 4327.
(27) Bartole-Scott, A.; Jaska, C. A.; Manners, I. *Pure Appl. Chem.* **2005**, *77*, 1991.
(28) Clark, T. J.; Jaska, C. A.; Turak, A.; Lough, A. J.; Lu, Z. H.; Manners, I. *Inorg. Chem.* **2007**, *46*, 7394.
(29) Clark, T. J.; Lee, K.; Manners, I. *Chem.—Eur. J.* **2006**, *12*, 8634.
(30) Clark, T. L.; Rodezno, J. M.; Clendenning, S. B.; Aouba, S.; Brodersen, P. M.; Lough, A. J.; Ruda, H. E.; Manners, I. *Chem.—Eur. J.* **2005**, *11*, 4526.
(31) Himmelberger, D. W.; Yoon, C. W.; Bluhm, M. E.; Carroll, P. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **2009**, *131*, 14101.

Indeed the regeneration of ammonia borane has proven to be challenging.[4,32−34]

More generally, while early studies described the interactions of H_2 with main group species in an argon matrix,[35] it was not until the work of Power and co-workers[36] that a main group species was shown to react with H_2. In that case, germynes were hydrogenated to give a mixture of digermene, digermane, and primary germane products. More recently we have developed the concept of "frustrated Lewis pairs" (FLPs) and shown that such systems are capable of a number of small molecule activation reactions including heterolytic cleave of H_2.[37−39] This reactivity has been extended to effect metal-free catalytic hydrogenations of a variety of polar substrates.[37−46] This unprecedented reactivity prompted us to probe the chemistry of sterically encumbered and electron deficient phosphino-boranes. Previous computational and experimental studies on directly bound phosphinoboranes suggest that there is limited interaction between the lone pair at phosphorus and the vacant p-orbital on boron because of a mismatch of donor and acceptor orbital energies.[47,48] Thus, such systems might exhibit FLP-like behavior as these systems should have residual donor and acceptor ability despite being adjacent. In this manuscript we probe this possibility. Phosphino-boranes are prepared and characterized, the nature of the bonding is studied computationally, and the reactivity of these species is examined. We note that a preliminary communication of a small portion of this work has appeared previously.[49]

Experimental Section

General Considerations. All preparations were done under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and an Innovative Technologies or Vacuum Atmospheres inert atmosphere glovebox. Solvents (pentane, hexanes, toluene, and methylene chloride) were purified employing a Grubbs' type column systems manufactured by Innovative Technology and stored over molecular sieves (4 Å), purchased from Aldrich Chemical Co. and dried at 140 °C under vacuum for 24 h prior to use. Deuterated solvents were dried over Na/benzophenone (C_6D_6, C_7D_8) or CaH_2 (CD_2Cl_2, $CDCl_3$) and distilled prior to use. All common organic reagents were purified by conventional methods unless otherwise noted. ^1H, ^{13}C, ^{11}B, ^{19}F, and ^{31}P nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance-300 or Avance-400 spectrometer at 300 K unless otherwise noted. ^1H and ^{13}C NMR spectra are referenced to $SiMe_4$ using the residual solvent peak impurity of the given solvent. ^{11}B and ^{19}F NMR experiments were referenced to 15% BF_3-Et_2O in $CDCl_3$ and ^{31}P NMR experiments were referenced to 85% H_3PO_4. Chemical shifts are reported in parts per million (ppm) and coupling constants in hertz (Hz) as absolute values. Combustion analyses were performed in house employing a Perkin-Elmer CHN Analyzer. Despite repeated attempts, elemental analyses gave low C values for several compounds reported herein. This was attributable to the formation of boron-carbide during combustion. H_2 was passed through a drierite column prior to use. R_2PLi (R = Et, Ph, *t*Bu, Cy, Mes) were prepared by treating the corresponding phosphine with 1.1 equiv of *t*BuLi in toluene and collecting the precipitate. $(C_6F_5)_2BCl$ was prepared by the literature method.[50]

Synthesis of $[R_2PB(C_6F_5)_2]_2$ (R = Et 1, Ph 2) and $R_2PB(C_6F_5)_2$ (R = *t*Bu 3, Cy 4, Mes 5). These compounds were prepared in a similar fashion, and thus only one preparation is detailed. To a slurry of Et_2PLi (51 mg, 0.53 mmol) in toluene (5 mL) was added a solution of $(C_6F_5)_2BCl$ (200 mg, 0.53 mmol) in toluene (5 mL) at −35 °C. The mixture was allowed to stir overnight and was then run through Celite. The filtrate was concentrated to ~2 mL and stored at −35 °C overnight. The solution was dried in vacuo and washed with cold pentane (2 × 2 mL). **1** was isolated as a colorless polycrystalline solid. Yield: 192 mg (84%).

1: Yield: 192 mg (84%). Anal. Calcd. for $C_{16}H_{10}BF_{10}P$: C, 44.28; H, 2.32; Found: C, 44.66; H, 2.64. Crystals of **1** were grown from a pentane solution at room temperature. ^1H NMR (CD_2Cl_2): 1.07 (6H, dt, $^3J_{P-H} = 16$ Hz,$^3J_{H-H} = 8$ Hz, CH_3), 2.16 (4H, m, CH_2). ^{19}F NMR (CD_2Cl_2): −125.0 (d, $^3J_{F-F} = 20$ Hz, 4F, o-C_6F_5), −153.5 (t, $^3J_{F-F} = 23$ Hz, 2F, p-C_6F_5), −160.3 (t, $^3J_{F-F} = 20$ Hz, 4F, m-C_6F_5). ^{31}P NMR (CD_2Cl_2): −23.4 (br m). ^{11}B NMR (CD_2Cl_2): −12.9 (t, $^1J_{P-B} = 72$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) partial: 8.3 (*C*P), 16.2 (m, CH_3), 137.4 (dm, $^1J_{C-F} = 248$ Hz, *C*F), 140.4 (dm, $^1J_{C-F} = 209$ Hz, *C*F), 147.3 (dm, $^1J_{C-F} = 227$ Hz, *C*F).

2: Yield: 184 mg (65%). Anal. Calcd. for $C_{24}H_{10}BF_{10}P$: C, 54.38; H, 1.90; Found: C, 55.32; H, 2.30. Crystals were grown by slow evaporation from a 1:1 dichloromethane:pentane solution. ^1H NMR (CD_2Cl_2): 7.26 (4H, t, $^3J_{H-H} = 8$ Hz, m-C_6H_5), 7.41 (6H, m, o-C_6H_5, p-C_6H_5). ^{19}F NMR (CD_2Cl_2): −121.3 (m, 4F, o-C_6F_5), −156.3 (t, $^3J_{F-F} = 20$ Hz, 2F, p-C_6F_5), −164.2 (m, 4F, m-C_6F_5). ^{31}P NMR (CD_2Cl_2): −0.8 (s). ^{11}B NMR (CD_2Cl_2): −2.2 (t, $^1J_{P-B} = 66$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) partial: 127.8 (m, C_6H_5), 129.2 (d, $^1J_{P-C} = 32$ Hz, P*C*), 130.8 (C_6H_5), 134.3 (C_6H_5), 137.0 (dm, $^1J_{C-F} = 228$ Hz, *C*F), 140.3 (dm, $^1J_{C-F} = 242$ Hz, *C*F), 146.8 (dm, $^1J_{C-F} = 239$ Hz, *C*F).

3: Yield: 160 mg (61%). Anal. Calcd. for $C_{20}H_{18}BF_{10}P$: C, 49.01; H,3.70; Found: C, 48.16; H, 3.54. Crystals were grown from hexanes at −35 °C.^1H NMR (CD_2Cl_2): 1.40 (d, $^3J_{P-H} = 15$ Hz). ^{19}F NMR (CD_2Cl_2): −130.7 (m, 4F, o-C_6F_5), −156.0 (t, $J_{F-F} = 23$ Hz, 2F, p-C_6F_5), −163.4 (m, 4F, m-C_6F_5). ^{31}P NMR (CD_2Cl_2): 120.7 (br m). ^{11}B NMR (CD_2Cl_2): 41.8 (d, $^1J_{P-B} = 150$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) partial: 32.9 (CH_3), 39.6 (d, $^1J_{P-C} = 23$ Hz, P*C*), 115.9 (m, B*C*), 137.5 (dm, $^1J_{C-F} = 253$ Hz, *C*F), 140.9 (dm, $^1J_{C-F} = 253$ Hz, *C*F), 143.0 (dm, $^1J_{C-F} = 239$ Hz, *C*F).

4: Yield: 235 mg (83%). Anal. Calcd. for $C_{24}H_{22}BF_{10}P$: C, 53.16; H, 4.09; Found: C, 52.28; H, 4.20. Crystals were grown from hexanes at −35 °C. ^1H NMR (CD_2Cl_2): 1.15 (tt, $J = 13$, $J = 3$, 2H), 1.25 (m, $J = 13$ Hz, $J = 3$ Hz, 4H), 1.49 (m, $J = 13$ Hz, $J_{P-H} = 5$ Hz, $J = 3$ Hz, 4H), 1.64 (d, $J = 13$ Hz, 2H), 1.75 (dd, $J = 13$ Hz, $J_{P-H} = 3$ Hz, 4H), 1.99 (d, $J = 13$ Hz, 4H), 2.33 (dtt, $J = 13$ Hz,

---

(32) Hausdorf, S.; Baitalow, F.; Wolf, G.; Mertens, F. O. R. L. *Int. J. Hydrogen Energy* **2008**, *33*, 608.

(33) Ramachandran, P. V.; Gagare, P. D. *Inorg. Chem.* **2007**, *46*, 7810.

(34) Davis, B. L.; Dixon, D. A.; Garner, E. B.; Gordon, J. C.; Matus, M. H.; Scott, B.; Stephens, F. H. *Angew. Chem., Int. Ed.* **2009**, *48*, 6812.

(35) Spies, P.; Erker, G.; Kehr, G.; Bergander, K.; Froehlich, R.; Grimme, S.; Stephan, D. W. *Chem. Commun.* **2007**, 5072.

(36) Spikes, G. H.; Fettinger, J. C.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 12232.

(37) Stephan, D. W. *Org. Biomol. Chem.* **2008**, *6*, 1535.

(38) Stephan, D. W. *Dalton Trans.* **2009**, 3129.

(39) Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 46.

(40) Axenov, K. V.; Kehr, G.; Fröhlich, R.; Erker, G. *J. Am. Chem. Soc.* **2009**, *131*, 3454.

(41) Chase, P. A.; Jurca, T.; Stephan, D. W. *Chem. Commun.* **2008**, 1701.

(42) Chase, P. A.; Welch, G. C.; Jurca, T.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 8050.

(43) Geier, S. J.; Chase, P. A.; Stephan, D. W. *Chem. Commun.* **2010**, *46*, 4884.

(44) Spies, P.; Schwendemann, S.; Lange, S.; Kehr, G.; Fröhlich, R.; Erker, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 7543.

(45) Sumerin, V.; Schulz, F.; Atsumi, M.; Wang, C.; Nieger, M.; Leskela, M.; Repo, T.; Pyykko, P.; Rieger, B. *J. Am. Chem. Soc.* **2008**, *130*, 14117.

(46) Wang, H. D.; Frohlich, R.; Kehr, G.; Erker, G. *Chem. Commun.* **2008**, 5966.

(47) Gilbert, T. M.; Bachrach, S. M. *Organometallics* **2007**, *26*, 2672.

(48) Pestana, D. C.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 8426.

(49) Geier, S. J.; Gilbert, T. M.; Stephan, D. W. *J. Am. Chem. Soc.* **2008**, *130*, 12632.

(50) Parks, D. J.; Piers, W. E.; Yap, G. P. A. *Organometallics* **1998**, *17*, 5492.

J_{P-H} = 9 Hz,, J = 3 Hz, 2H). ^{19}F NMR (CD_2Cl_2): −130.78 (m, 4F, o-C_6F_5), −155.46 (t, $^3J_{F-F}$ = 20 Hz, 2F, p-C_6F_5), −163.51 (m, 4F, m-C_6F_5). ^{31}P NMR (CD_2Cl_2): 92.1 (br m). ^{11}B NMR (CD_2Cl_2): 39.5 (d, $^1J_{B-P}$ = 142 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2): 25.4 (C_6H_{11}), 26.8 (d, $^2J_{C-P}$ = 34 Hz, C_6H_{11}), 33.7 (d, $^3J_{C-P}$ = 4 Hz, C_6H_{11}), 35.0 (d, $^1J_{C-P}$ = 27 Hz, P*C*), 113.1 (B*C*), 137.6 (dm, $^1J_{C-F}$ = 260 Hz, *C*F), 141.0 (dm,$^1J_{C-F}$ = 264 Hz, *C*F), 145.2 (dm, $^1J_{C-F}$ = 247 Hz, *C*F).

5: Yield: 220 mg (68%). Anal. Calcd. for $C_{30}H_{22}BF_{10}P$: C, 58.66; H, 3.61; Found: C, 57.51; H, 3.53. ^{1}H NMR (CD_2Cl_2): 2.25 (s, 6H, p-CH_3), 2.29 (s, 12H, o-CH_3), 6.89 (d, $^4J_{P-H}$ = 6 Hz, 4H, C*H*). ^{19}F NMR (CD_2Cl_2)δ: −131.2 (m, 4F, o-C_6F_5), −154.6 (t, $^3J_{F-F}$ = 20 Hz, 2F, p-C_6F_5), −163.5 (m, 4F, m-C_6F_5). ^{31}P NMR (CD_2Cl_2, 121 MHz): 29.3 (br m). ^{11}B NMR (CD_2Cl_2): 40.1 (br m). ^{13}C{^{1}H} NMR (CD_2Cl_2) partial: 20.9 (p-CH_3), 22.6 (d, $^3J_{C-P}$ = 7.7 Hz, o-CH_3), 123.1 (d, J_{C-P} = 72 Hz, P*C*), 129.3 (d,^{3} J_{C-P} = 11 Hz, *C*H), 137.2 ($^1J_{C-F}$ = 246 Hz, *C*F), 141.2 (d, $^1J_{C-F}$ = 252 Hz, *C*F), 141.4 (d, $^4J_{C-P}$ = 3 Hz, p-*C*CH_3), 143.6 (d,$^2J_{C-P}$ = 7 Hz, o-*C*CH_3), 146.0 (d, $^1J_{C-F}$ = 248 Hz, *C*F).

Synthesis of $R_2(H)PB(H)(C_6F_5)_2$ (R = Et 6, Ph 7, *t*Bu 8, Cy 9, Mes 10). These compounds were prepared in a similar fashion and thus only one preparation is detailed. A solution of Et_2PH (12 mg, 0.15 mmol) in toluene (1 mL) was added to $(C_6F_5)_2BH$ (50 mg, 0.15 mmol) in hexanes (2 mL). The mixture was stirred for 1 h, then stored at −35 °C for 2 h. The solution was decanted and the white precipitate **6** was dried in vacuo.

6: Yield: 48 mg (77%). Anal. Calcd. for $C_{16}H_{12}BF_{10}P$: C, 44.07; H, 2.77; Found: C, 43.80; H, 2.73. Crystals were grown from hexanes at −35 °C. ^{1}H NMR (CD_2Cl_2): 1.17 (dt, $^3J_{H-P}$ = 17 Hz, $^2J_{H-H}$ = 8 Hz, 6H, CH_3), 1.84 (dq, $^2J_{P-H}$ = 24 Hz, $^2J_{P-H}$ = 8 Hz, 4H, CH_2), 3.43 (br m, 1H, B*H*), 4.95 (dm, $^1J_{P-H}$ = 388 Hz, 1H, P*H*). ^{19}F NMR (CD_2Cl_2): −131.7 (m, 4F, o-C_6F_5), −159.2 (t, $^3J_{F-F}$ = 20 Hz, 2F, p-C_6F_5), −164.7 (m, 4F, m-C_6F_5). ^{31}P NMR (CD_2Cl_2): −4.6 (br m). ^{11}B NMR (CD_2Cl_2): −30.0 (d, $^1J_{B-P}$ = 65 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2) partial: 8.5 (d, J_{C-P} = 6 Hz), 10.6 (d, J_{C-P} = 38.5 Hz), 137.1 (dm, $^1J_{C-F}$ = 208 Hz, *C*F), 140.3 (dm, $^1J_{C-F}$ = 235 Hz, *C*F), 148.0 (dm, $^1J_{C-F}$ = 233 Hz, *C*F).

7: Yield: 58 mg (74%). Anal. Calcd. for $C_{2\ 4}H_{12}BF_{10}P$: C, 54.17; H, 2.27; Found: C, 53.82; H, 2.25. Crystals were grown from 1:1 dichloromethane:hexanes at −35 °C. ^{1}H NMR (CD_2Cl_2): 3.94 (br m, 1H, B*H*), 6.81 (ddm, $^1J_{P-H}$ = 409 Hz, $^3J_{H-H}$ = 15 Hz, 1H, P*H*), 7.44 (ddd, $^3J_{H-H}$ = 8 Hz, $^3J_{H-H}$ = 6 Hz, $^4J_{H-P}$ = 1 Hz, 4H, m-C_6H_5), 7.54 (tt, $^3J_{H-H}$ = 6 Hz, $^4J_{H-H}$ = 2 Hz, 2H, p-C_6H_5), 7.60 (ddd, $^3J_{H-P}$ = 12 Hz, $^3J_{H-H}$ = 8 Hz, $^4J_{H-H}$ = 2 Hz, 3H, o-C_6H_5). ^{19}F NMR (CD_2Cl_2): −131.2 (m, 4F, o-C_6F_5), −158.8 (t, 2F, $^3J_{F-F}$ J = 20 Hz, p-C_6F_5), −164.7 (m, 4F, m-C_6F_5). ^{31}P NMR (CD_2Cl_2,): −1.5 (br m). ^{11}B NMR (CD_2Cl_2): −28.5 (d, $^1J_{P-B}$ = 71 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2) partial: 122.9 (d, $^1J_{C-P}$ = 65 Hz, *C*H), 129.5 (dm, $^2J_{C-P}$ = 164 Hz, *C*H), 133.7(*C*H), 135.3 (*C*H) 136.9 (dm, $^1J_{C-F}$ = 248 Hz, *C*F), 140.7 (dm, $^1J_{C-F}$ = 254 Hz, *C*F), 148.0 (dm, $^1J_{C-F}$ = 235 Hz, *C*F).

8: Yield: 48 mg (65%). Anal. Calcd. for $C_{20}H_{20}BF_{10}P$: C, 48.81; H, 4.10; Found: C, 48.42; H, 3.90. Crystals were grown from the hexane wash layer. ^{1}H NMR (CD_2Cl_2): 1.27 (d, $^3J_{H-P}$ = 14 Hz, 18H, CH_3), 3.48 (br m, 1H, B*H*), 4.84 (dd, $^1J_{H-P}$ = 375 Hz, $^3J_{H-H}$ = 11 Hz, 1H, P*H*). ^{19}F NMR (CD_2Cl_2): −129.7 (m, 4F, o-C_6F_5), −159.4 (t, $^3J_{F-F}$ = 20 Hz, 2F, p-C_6F_5), −164.7 (m, 4F, m-C_6F_5). ^{31}P NMR (CD_2Cl_2): 32.0 (br m). ^{11}B NMR (CD_2Cl_2): −30.0 (d, $^1J_{P-B}$ = 48 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2): 29.2 (CH_3), 33.0 (d, $^1J_{C-P}$ = 29 Hz, *C*P), 117.9 (br m, B*C*), 137.1 (dm, $^1J_{C-F}$ = 255 Hz, *C*F), 139.6 (dm, $^1J_{C-F}$ = 250 Hz, *C*F), 148.0 (dm, $^1J_{C-F}$ = 239 Hz, *C*F).

9: Yield: 61 mg (77%). Anal. Calcd. for $C_{24}H_{24}BF_{10}P$: C, 52.97; H, 4.45; Found: C, 52.50; H, 4.56. Crystals were grown from hexanes at −35 °C. ^{1}H NMR (CD_2Cl_2): 1.15 (m, 2H, PC_6H_{11}), 1.20−1.29 (br m, 6H, PC_6H_{11}), 1.37 (m, 2H, PC_6H_{11}), 1.68 (br d, $^2J_{H-H}$ = 13 Hz, 2H, PC_6H_{11}), 1.75−1.84 (br m, 6H, PC_6H_{11}), 1.89 (m, 2H, PC_6H_{11}), 2.00 (m, 2H, PC_6H_{11}), 3.33 (1H, br m, B*H*), 4.78 (ddm, $^1J_{P-H}$ = 381 Hz, $^3J_{H-H}$ = 13 Hz,1H, P*H*). ^{19}F NMR (CD_2Cl_2): −131.0 (m, 4F, o-C_6F_5), −159.4 (t, $^3J_{F-F}$ = 20 Hz, 2F, p-C_6F_5), −164.7 (t, $^3J_{F-F}$ = 17 Hz, 4F, m-C_6F_5). ^{31}P NMR (CD_2Cl_2): 7.1 (br m). ^{11}B NMR (CD_2Cl_2): −28.1 (d,$^1J_{P-B}$ = 68 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2) partial: 25.4(*C*H_2), 26.7 (m, *C*H_2), 29.2, (d, J = 17 Hz, *C*H_2), 29.7 (d, J = 35 Hz, *C*H), 136.6 (m, $^1J_{C-F}$ = 185 Hz, *C*F), 148.0 (dm, $^1J_{C-F}$ = 237 Hz, *C*F).

10: Yield: 70 mg (78%). Anal. Calcd. for $C_{30}H_{24}BF_{10}P$: C, 58.47; H, 3.93; C, 57.82; H, 3.91. ^{1}H NMR (CD_2Cl_2): 2.24 (s, 12H, o-CH_3), 2.26 (s, 6H, p-CH_3), 6.88 (s, 4H, C*H*), 7.06 (dd, $^1J_{H-P}$ = 402 Hz, $^3J_{H-H}$ = 13 Hz, 1H, P*H*). ^{19}F NMR (CD_2Cl_2): −131.4 (m, 4F, o-C_6F_5), −158.7 (t, $^3J_{F-F}$ = 20 Hz, 2F, p-C_6F_5), −164.8 (m, 4F, m-C_6F_5). ^{31}P NMR (CD_2Cl_2): −39.0 (br m). ^{11}B NMR (CD_2Cl_2): −25.4 (d, $^1J_{P-B}$ = 48 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2) partial: 20.7 (CH_3), 21.6 (CH_3), 118.0 (d, $^1J_{C-P}$ = 58 Hz, *C*P), 130.5 (d, J = 9 Hz, *C*H), 136.9 (dm, $^1J_{C-F}$ = 245 Hz, C*F*), 142.4 (p-*C*-CH_3), 143.0 (d, J = 8 Hz, o-*C*-CH_3), 148.4 (dm, $^1J_{C-F}$ = 240 Hz, C*F*).

Alternate Generation of 8 and 9. These compounds were prepared in a similar fashion and thus only one preparation is detailed. (A) A resealable NMR tube was charged with **3** (20 mg, 0.041 mmol) and tol-d_8 (0.75 mL); the solution was subjected to 3 freeze−pump−thaw cycles, and 1 atm of H_2 was added at 77 K (~4 atm at room temperature). 80% conversion to **8** was achieved in 4 weeks at 25 °C, while quantitative conversion was achieved over 48 h at 60 °C. (B) An NMR tube was charged with **3** (20 mg, 0.041 mmol), Me_2NH-BH_3 (2 mg, 0.04 mmol), and CD_2Cl_2 (0.75 mL) After 15 min at 25 °C, ^{1}H, ^{11}B, ^{31}P, and ^{19}F NMR spectroscopy revealed quantitative conversion to **8** and 0.5 $(Me_2NBH_2)_2$.

Synthesis of $Cy_2PB(C_6F_5)_2$(4-*t*BuC_5H_4N) 11. A solution of **3** (25 mg) in $CDCl_3$ (0.75 mL) was added to 4-*tert*-butylpyridine (1 equiv). The solution was monitored by multinuclear NMR spectroscopy.

11: ^{1}H NMR ($CDCl_3$): 0.41−2.00 (m, 22H, C_6H_{11}), 1.41 (s, 9H, C(CH_3)$_3$), 7.32 (d, $^3J_{H-H}$ = 7 Hz, 2H, C*H*), 9.05 (br s, 2H, C*H*). ^{19}F NMR ($CDCl_3$): −128.0 (br m, 4F, o-C_6F_5), −157.2 (br s, 2F, p-C_6F_5), −162.2 (m, m-C_6F_5). ^{13}C NMR ($CDCl_3$, partial): 26.5, 27.6 (d, J_{P-C} = 6 Hz), 28.2 (J_{P-C} = 13 Hz), 30.1, 31.7 (ov), 35.8, 120.8, 122.6, 146.5 (d, J_{P-C} = 20 Hz), 167.6. ^{31}P NMR ($CDCl_3$): −28.3 (br s). ^{11}B NMR ($CDCl_3$): −1.3. Using toluene (1 mL) as the solvent gave X-ray quality crystals. Rapid decomposition precluded characterization by elemental analysis and ^{13}C NMR spectroscopy.

Generation of $(R_2PBCl_2)_2$ (R = *t*Bu 12, Cy 13). These compounds were prepared in a similar fashion and thus only one preparation is detailed. BCl_3 (1 equiv) is added to a solution of **3** (25 mg) in toluene. The solution was allowed to stir for 3 h. Volatiles were then removed in vacuo, and the residue was taken up in $CDCl_3$ for NMR spectroscopy. Resonances attributed to $ClB(C_6F_5)_2$ and species **12** were observed. The former resonance corresponded to those previously reported $ClB(C_6F_5)_2$[50,51] Although crystals of compound **12** were obtained for X-ray diffraction, efforts to obtain bulk samples of **12** and **13** from these reactions for elemental analysis proved problematic as separation from $ClB(C_6F_5)_2$ was not possible.

(**12**) ^{1}H NMR ($CDCl_3$): 1.33 (d, $^3J_{P-H}$ = 15 Hz, 9H, C(CH_3)$_3$). ^{31}P NMR ($CDCl_3$): −14.8 (sept, $^1J_{P-B}$ = 90 Hz). ^{11}B NMR ($CDCl_3$): 4.2 (t, $^1J_{P-B}$ = 90 Hz, (^{t}Bu$_2$P*B*Cl$_2$)$_2$), 2.7 (d, $^1J_{P-B}$ = 135 Hz, ^{t}Bu$_2$P*B*Cl$_2$).

(**13**) ^{1}H NMR ($CDCl_3$): 1.11−2.58 (m, 22H, *Cy*). ^{31}P NMR ($CDCl_3$): −14.5 (sept, $^1J_{P-B}$ = 99 Hz). ^{11}B NMR ($CDCl_3$): −0.5 (t, $^1J_{P-B}$ = 99 Hz).

X-ray Data Collection and Reduction. Crystals were coated in Paratone-N oil in the glovebox, mounted on a MiTegen Micromount and placed under an N_2 stream, thus maintaining a dry, O_2-free environment for each crystal. The data were collected on

---

(51) Parks, D. J.; Spence, R. E. V. H.; Piers, W. E. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 809.

Table 1. Crystallographic Data for **1**−**4**, **6**−**8**, **12**, and **14**[a]

	1[d]	**2**·**CH_2Cl_2**[d]	**3**[d]	**4**[d]	**6**[d]
formula	$C_{32}H_{20}P_2F_{20}B_2$	$C_{50}H_{22}P_2F_{20}B_2Cl_2$	$C_{20}H_{18}BF_{10}P$	$C_{24}H_{22}BF_{10}P$	$C_{16}H_{12}BF_{10}P$
formula weight	868.04	1131.10	490.12	542.20	436.04
crystal system	triclinic	triclinic	orthorhombic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	*Pbca*	$P\bar{1}$	$P\bar{1}$
a (Å)	9.699(2)	10.3197(16)	12.194(9)	9.4503(13)	9.198(6)
b (Å)	9.703(2)	12.0982(19)	18.331(13)	10.4530(14)	12.989(8)
c (Å)	10.404	20.926(3)	19.774(14)	13.7545(19)	15.681(9)
α (deg)	67.072(2)	74.492(2)	90.00	110.6870(10)	83.854(6)
β (deg)	80.770(3)	76.700(2)	90.00	99.036(2)	87.955(7)
γ (deg)	67.852(2)	68.458(2)	90.00	95.566(2)	75.462(6)
V (Å^3)	835.1(3)	2316.1(6)	4420(5)	1238.1(3)	1803.0(19)
Z	1	2	8	2	4
d(calc) g cm^{-1}	1.726	1.622	1.473	1.454	1.606
abs coeff, *μ*, cm^{-1}	0.269	0.327	0.212	0.197	0.249
data collected	2933	8128	3891	4354	6329
data $F_o^2 > 3\sigma(F_o^2)$	2274	3801	2640	2870	5186
variables	253	676	289	325	521
R[b]	0.0390	0.0573	0.0553	0.0631	0.0493
R_w[c]	0.0942	0.1347	0.1889	0.2154	0.1449
goodness of fit	1.035	0.919	1.059	1.043	1.050

	7[e]	**8**[d]	**11**[e]	**13**[e]
formula	$C_{24}H_{22}BF_{15}P$	$C_{20}H_{20}BF_{10}P$	$C_{40}H_{43}BF_{10}NP$	$C_{16}H_{36}B_2Cl_4P_2$
formula weight	542.20	492.14	769.53	453.81
crystal system	triclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	8.9820(6)	9.5420(17)	9.8554(5)	8.8289(3)
b (Å)	10.3690(6)	12.872(2)	12.3799(6)	14.3784(5)
c (Å)	12.4150(6)	19.447(3)	16.4730(8)	9.0538(3)
α (deg)	106.381(3)	96.656(2)	72.596(2)	90.00
β (deg)	94.690(3)	95.583(2)	78.921(2)	92.991(1)
γ (deg)	96.226(3)	109.144(2)	86.032(2)	90.00
V (Å^3)	1095.11(1)	2217.9(2)	1881.95(16)	1147.77(7)
Z	2	4	2	2
d(calc) g cm^{-1}	1.644	1.474	1.358	1.313
abs coeff, *μ*, cm^{-1}	0.223	0.212	0.153	0.654
data collected	4947	7778	19836	2633
data $F_o^2 > 3\sigma(F_o^2)$	3199	2777	13490	2416
variables	333	594	478	115
R[b]	0.0573	0.0949	0.0441	0.0277
R_w[c]	0.1834	0.2839	0.1333	0.0770
goodness of fit	1.078	0.952	1.038	1.050

[a] All data were collected with Mo Kα radiation ($\lambda = 0.71069$ Å). [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = \{\sum w(F_o^2 - F_c^2)^2/\sum[w(F_o)^2]\}^{1/2}$. [d] These data were collected at 293 K. [e] These data were collected at 150 K.

a Bruker Apex II diffractometer (Table 1). The data were collected at 150(±2) K for all crystals. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multiscan method (SADABS).

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[52] The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine.[53] The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on *F*, minimizing the function $\omega\ (F_o - F_c)^2$ where the weight ω is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases atoms were treated isotropically. C−H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C−H bond length of 0.95 Å. H-atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C-atom to which they are bonded. The H-atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of residual electron densities in each case were of no chemical significance. Additional details are provided in the Supporting Information (Table 1).

Computational Methods. Optimizations were performed with the GAUSSIAN (G98) suite.[54] Phosphinoboranes and phosphineboranes were first optimized without constraints at modest computational levels, typically HF/3-21G or HF/BS0, where the BS0 basis set uses the 6-31+G(d) basis set on non-hydrogen atoms and the 3-21G basis set on hydrogens. Examination of the optimized

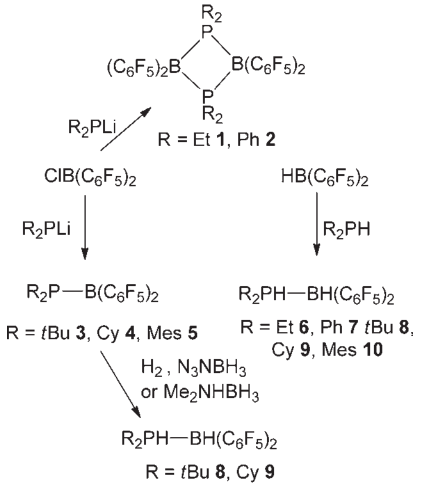
---

(52) Cromer, D. T.; Waber, J. T. *Int. Tables X-Ray Crystallogr.* **1974**, *4*, 71.

(53) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.

(54) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, A. D.; Rabuck, K. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S. *Gaussian 98*, Revision A.11.4; Gaussian, Inc: Pittsburgh, PA, 1998.

Scheme 1. Synthesis of **1**−**10**



structures by analytical frequency analyses at these levels demonstrated them to be minima (no imaginary frequencies). The structures were reoptimized at higher levels, either at the density functional theory (DFT)-based MPW1K[55] /6-31+G(d) level, or using a two-layer ONIOM[56,57] approach (denoted ONIOM-(MPW1K/6-31+G(d)), using the MPW1K/6-31+G(d) model for high layers, and the MPW1K/3-21G model for low layers. Partitioning of the layers for $B(C_6F_5)_3$ and PR_3 moieties was described previously.[58] In some cases, to assess the dependence of structural parameters on model and basis set, different ONIOM combinations were employed for further optimizations, including MPW1K/6-311+G(d):MPW1K/3-21G (denoted ONIOM-(MPW1K/6-311+G(d)), PBE1PBE/6-311++G(d, p):HF/3-21G (denoted ONIOM(PBE1/6-311++G(d, p), and PBE1PBE/6-311++G(2df, p):HF/3-21G (denoted ONIOM(PBE1/6-311++G(2df, p)). Natural Bond Order (NBO) calculations were performed using a upgraded version of the NBO subroutine in the Gaussian98 program,[59,60] using the MPW1K/BS0-optimized structures and wave functions.

Scans of the potential energy surface for H_2 loss from phosphine-boranes $(F_5C_6)_2(H)BP(H)(R)_2$ employed a slightly different ONIOM(MPW1K/6-311++G(d, p)) approach, with the high layer encompassing the B and P atoms and the H atoms bound to them. The 6-311++G(d, p) basis set was used in the high layer, the 3-21G basis set in the low layer. Relative energies from the scan steps were corrected using unscaled zero point energies (ZPEs) from the frequency analyses. Optimized Cartesian coordinates of molecules studied are available as Supporting Information.

Results and Discussion

The phosphinoboranes $R_2PB(C_6F_5)_2$ (R = Et **1**, Ph **2**) were synthesized from the reaction of $(C_6F_5)_2BCl$ and the corresponding lithium phosphide (Scheme 1). The products were isolated in 84 and 65% yield, respectively. Compounds **1** and **2** are characterized by triplet resonances at −12.9 ($^1J_{P-B}$ = 72 Hz) and −2.2 ($^1J_{P-B}$ = 68 Hz) ppm in the ^{11}B NMR spectra, respectively. In addition, the ^{19}F NMR spectra show gaps between the *meta*- and *para*-fluorine signals of 6.85 and 7.82 ppm for **1** and **2**, respectively. These latter data are typical of neutral, 4 coordinate boron centers, consistent with the postulate of the dimeric formulations, $[R_2PB(C_6F_5)_2]_2$ (R = Et **1**, Ph **2**).[61,62] These structural assignments were additionally supported by X-ray crystallography (Figure 1).

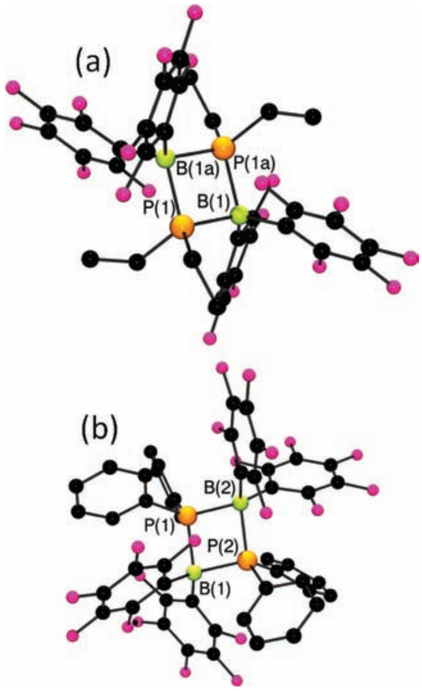


Figure 1. POV-Ray depictions of phosphinoborane dimers (a) **1** and (b) **2**. C, black; B, yellow-green; F, deep pink; P, orange. Solvent and hydrogen atoms are omitted for clarity. Selected metrical parameters (distance Å, angle deg) **1**: B(1)−P(1) 2.056(3), B(1)−P(1a) 2.058(3), B(1)−P(1)−B(1a) 92.30(10), P(1)−B(1)−P(2) 87.70(10). **2**: P(1)−B(1) 2.096(5), P(1)−B(2) 2.088(5), P(2)−B(1) 2.022(5), P(2)−B(2) 2.080(5), B(1)−P(1)−B(2) 92.65(19), B(1)−P(2)−B(2) 95.05(18), P(1)−B(1)−P(2) 86.57(18), P(1)−B(2)−P(2) 85.32(18).

The crystal structure of **1** reveals a dimer with crystallographic 2-fold symmetry. The P−B distances are 2.056(3) and 2.058(3) Å, while the B−P−B and P−B−P bond angles are 92.30(10)° and 87.70(10)° respectively. The structure of **2** shows similar metrical parameters, with average P−B bond lengths of 2.072 Å, average P−B−P angle of 85.95° and average B−P−B angle of 93.87°. The data for the related species $[(Et_2P)_2B(\mu\text{-}PEt_2)]_2$ (2.012(6) Å, 2.033(5) Å),[63]$[i\text{Bu}(H)B(\mu\text{-}P(t\text{Bu})_2)]_2$ (2.004(4), 2.022(4) Å)[64] and 1,1-ferrocene-$[B(CH_3)(\mu\text{-}PPh_2)]_2$ (2.036(4) Å, 2.033(4) Å)[65] show P−B bond lengths that are slightly shorter than those reported for the present compounds. This is presumably due to crowding resulting from the larger substituents at boron.

Reaction of the more sterically demanding lithium phosphides R_2PLi (R = *t*Bu, Cy and Mes) with $(C_6F_5)_2BCl$ resulted in the generation of phosphinoborane monomers $R_2PB(C_6F_5)_2$ (R = *t*Bu **3**, Cy **4**, Mes **5**) (Scheme 1). These formulations are consistent with NMR spectroscopic data. In particular, the ^{11}B NMR spectra show upfield doublet resonances, typical of 3-coordinate boranes, that exhibit coupling to phosphorus

---

(55) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2001**, *105*, 2936.

(56) Vreven, T.; Morokuma, K. *J. Comput. Chem.* **2000**, *21*, 1419.

(57) Dapprich, S.; Komáromi, I.; Byun, K. S.; Morokuma, K.; Frisch, M. J. *J. Mol. Struc.* (*Theochem*) **1999**, *461−462*, 1.

(58) Gille, A. L.; Gilbert, T. M. *J. Chem. Theory Comput.* **2008**, *3*, 1681.

(59) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. *NBO 5.0.*; Theoretical Chemistry Institute, University of Wisconsin: Madison, WI, 2001.

(60) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(61) Horton, A. D.; deWith, J. *Organometallics* **1997**, *16*, 5424.

(62) Blackwell, J. M.; Piers, W. E.; Parvez, M. *Org. Lett.* **2000**, *2*, 695.

(63) Nöth, H. *Z. Anorg. Allg. Chem.* **1987**, *555*, 79.

(64) Karsch, H. H.; Hanika, G.; Huber, B.; Riede, J.; Mueller, G. *J. Organomet. Chem.* **1989**, *361*, C25.

(65) Jakle, F.; Mattner, M.; Priermeier, T.; Wagner, M. *J. Organomet. Chem.* **1995**, *502*, 123.

($^1J_{B-P}$~150 Hz). The ^{31}P NMR resonances are also upfield and significantly broadened because of coupling to the quadrupolar nucleus of the boron atom. Interestingly the gaps between *para*- and *meta*-fluorine resonances in the ^{19}F NMR spectra lie closer to the range for typical neutral 4-coordinate boranes, suggesting that there is substantial electron density being donated into the vacant p-orbital on boron from the lone pair at phosphorus.

The structures of **3** and **4** were confirmed by X-ray crystallography (Figure 2). In compound **3** both phosphorus and boron centers are essentially planar, with sums of angles at 359.1° and 360.0°, although these planes are not coplanar, but canted with respect to each other with C−P−B-C torsion angles of 21.6° and 7.4°. Compound **3** shows a significantly shorter P−B bond length (1.786(4) Å) than the sterically similar compound Mes$_2$BPtBu$_2$ (1.841 Å) suggesting the electron-withdrawing effect of the C$_6$F$_5$ groups result in a contraction of the P−B bond length. Compound **4** shows an even shorter P−B bond length of 1.762(4) Å, presumably a result of a stronger P−B π−bond. This is reflected in the smaller C−P−B−C torsion angles 1.1° and 5.6°. The P−B bonds in the present compounds are much shorter than those observed for the analogous compounds, tBu$_2$PBMes$_2$ (1.839(8), 1843(8) Å),[48] Mes$_2$PBMes$_2$ (1.839(8) Å),[48] Ph$_2$PBMes$_2$ (1.859(3) Å),[48,66] consistent with significant P−B π-bonding. Literature data formulate P−B double bonds with P−B distances in the range 1.79−1.84 Å, and P−B single bonds from 1.90 to 2.00 Å.[67] This infers that **3** and **4** have significant P−B multiple bonding character. Thus it appears that the steric bulk about P and B precludes dimerization of **3**−**5** and encourages planarity and thus P−B π-bonding.

The relationships between B−P distance, P pyramidality, and the extent of BP multiple bonding were further explored computationally. The ONIOM(MPW1K/6-31+G(d))-optimized structure of **3** exhibited a B−P distance of 1.806 Å, somewhat longer than that observed crystallographically, but supporting the view that the electron withdrawing ability of the fluoroarene substituents shortens the interaction. The C−P−B−C torsion angles varied with the model, but were nonetheless consistent with the canting observed crystallographically, averaging about 25° and 10° for the larger and smaller torsions, respectively. The sum of the angles around phosphorus was about 355.5°, in fair agreement with the crystallographic result; however, the more direct measure of phosphorus pyramidality, the "plane angle",[68] was predicted to be about 151° whereas that determined crystallographically was 169.0°. For further comparison, the plane angles for (F$_3$C)$_2$B=PtBu$_2$ and Mes$_2$B = PMes$_2$ were predicted to be 164−180°;[47] and 179.9°, respectively. The plane angle is known to be a "soft" parameter, capable of changing significantly with only a modest energy cost. To probe the effect of the plane angle on the B−P distance and the energetics, **3** was optimized with the plane angle fixed at 180°. This structure was 0.9 kcal/mol less stable than the unrestricted one and exhibited a much smaller B−P distance of 1.785 Å. This demonstrates that planarity at phosphorus affects the B−P distance, but without increasing the stability of the molecule.[69,58,70−72] This in turn implies that the solid state B−P distance cannot be finely correlated with B−P bond order. Thus the seemingly notable changes in structural parameters reflect small energy differences. It is likely that the structural differences in B−P bond lengths and P planarities between experiment and theory for **3** are due to solid state effects such as crystal packing forces distorting the molecules from the gas phase ideal.

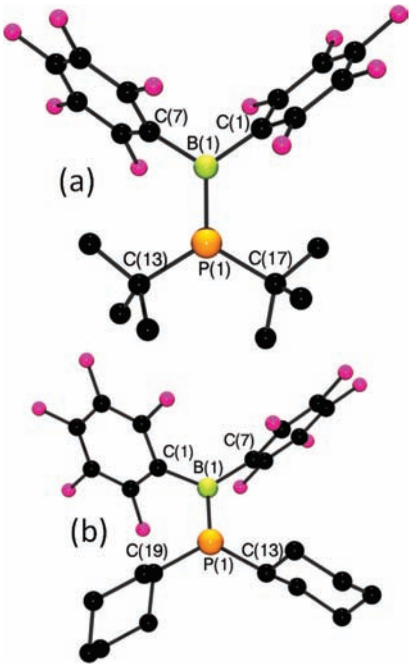


Figure 2. POV-Ray depictions of phosphinoboranes (a) **3** and (b) **4**. C, black; B, yellow-green; F, deep pink; P, orange. Hydrogen atoms are omitted for clarity. Selected metrical parameters (distance Å, angle deg). **3**: P(1)−B(1) 1.786(4), P(1)−C(13) 1.862(3), P(1)−C(17) 1.865(3), B(1)−C(1) 1.580(4), B(1)−C(7) 1.590(4), C(13)−P(1)−C(17) 117.08, B(1)−P(1)−C(13) 120.85(14), B(1)−P(1)−C(17) 121.14(15), C(1)−B(1)−C(7) 113.3(2), C(1)−B(1)−P(1) 124.0(2), C(7)−B(1)−P(1) 122.7(2). **4**: P(1)−B(1) 1.762(4), P(1)−C(13) 1.820(4), P(1)−C(19) 1.835(4), B(1)−C(1) 1.585(5), B(1)−C(7) 1.596(5), C(13)−P(1)−C(19) 112.6(2), B(1)−P(1)−C(13) 126.4(2), B(1)−P(1)−C(19) 120.88(19), C(1)−B(1)−C(7) 117.0(3), C(1)−B(1)−P(1) 119.9(3), C(7)−B(1)−P(1) 123.1(3).

Similar studies of **4** do not support the crystallographic suggestion of a shorter, stronger P−B bond in this molecule; the ONIOM(MPW1K/6-31+G(d)) approach predicts a distance of 1.816 Å, slightly longer than that in **3**. Moreover, computationally, it is not observed that the smaller substituents on phosphorus in **4** allow greater planarity for the C$_2$BPC$_2$ core atoms. The lowered bulk around phosphorus causes its geometry to become notably pyramidal as the plane angle in **4** is predicted to be about 137° while in the solid state, the plane angle is observed to be 175°. As above, an optimization of **4** with a fixed plane angle of 180° was performed at the ONIOM(MPW1K/6-31+G(d)) level. It exhibited a B−P distance of 1.777 Å, comparable to the solid state value, and was only 2.3 kcal/mol less stable than the fully optimized

---

(66) Feng, X.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1986**, *25*, 4615.

(67) Paine, R. T.; Nöth, H. *Chem. Rev.* **1995**, *95*, 343.

(68) The plane angle is the angle between the B−P axis and the bisector of the angle formed by the P atom and the two C atoms attached to it.

(69) Indeed, in phosphinoboranes with small substituents, the conformer with planar phosphorus is a transition state between versions with pyramidal phosphorus, with corresponding decreased stability.

(70) Vogel, U.; Hoemensch, P.; Schwan, K.-C.; Timoshkin, A. Y.; Scheer, M. *Chem.—Eur. J.* **2003**, *9*, 515.

(71) Allen, T. L.; Scheiner, A. C.; Schaefer, H. F., III *Inorg. Chem.* **1990**, *29*, 1930.

(72) Coolidge, M. B.; Borden, W. T. *J. Am. Chem. Soc.* **1990**, *112*, 1704.

version. As above, the differences are on the order of crystal packing energies, so the crystallographic observations cannot be taken as clear evidence of increased or decreased BP bond order. Nonetheless, the data indicate that the BP bond order in $(C_6F_5)_2B{=}PR_2$ phosphinoboranes exceeds that in other $R_2B{=}PR_2$ compounds, making their reactivities of interest. The data also indicate that the presence of a perfectly planar phosphorus atom is not a requirement for substantial B−P π bonding, although greater planarity helps.

To probe the effect of less donating substituents on phosphine, the structure of **5** was also optimized. At the ONIOM-(MPW1K/6-31+G(d)) level, the B−P distance was predicted to be 1.795 Å, and the plane angle to be 151°. This bond distance is shorter than in **3** despite the fact that the plane angles are comparable. This points again to the energetic softness of the latter parameter. Moreover, it appears phosphorus basicity plays a relatively small role in setting the B−P distance, given that the $PMes_2$ moiety should be significantly less basic than the P*t*Bu$_2$ moiety.

NBO analyses of **3** and **4** showed that the π-bonding HOMOs were highly polarized, with 74% of the molecular orbital derived from the phosphorus atom, with only 26% from the boron atom. These values are similar to those predicted for $(F_3C)_2B{=}PtBu_2$, (70 and 30%),[47] suggesting that the C_6F_5 and CF_3 substituents are close in their abilities to inductively attract electrons from the phosphorus to the boron. The Wiberg index in the natural atomic orbital (NAO) basis for **3** is 1.62. This model predicts B−C bond orders of about 0.85, and P−C bond orders of about 0.9. Bond order determinations from other models within the NBO framework give comparable predictions, implying that the π bond in phosphinoboranes like **3**−**5** is similar to that in $(F_3C)_2B{=}PtBu_2$; highly polarized toward phosphorus and best described as about 70% of a perfectly covalent π bond.

Though the experimental data for compounds **3**−**5** suggests significant interaction between the lone pair at phosphorus and the vacant orbital at boron, the computational data suggest that the interaction is highly polarized, and thus subject to chemical attack. To probe this, we examined the ability of these compounds to participate in chemistry attributed to "frustrated Lewis pairs" (FLPs). Initially, we considered the potential for hydrogenation of the P−B bonds. In preparation for these studies, we prepared and characterized the Lewis acid−base adducts, $R_2(H)P\cdot B(H)(C_6F_5)_2$ (R = Et **6**; Ph **7**; *t*Bu **8**; Cy **9**; Mes **10**) (Scheme 1) via the reaction of the phosphines R_2PH with the borane $HB(C_6F_5)_2$. Crystal structures were obtained for compounds **6** (Figure 3), **7**, and **8** (Figure 4). In each case the structures were as anticipated with pseudotetrahedral P and B centers. Of these adducts, **6** has the shortest P−B bond length (1.950(3) Å), while **7** and **8** show indistinguishable P−B bond lengths of 1.966(3) Å and 1.966(9) Å, respectively. These lengths are significantly shorter than those for the related $R_2(H)P\cdot B(C_6F_5)_3$ species (R = Cy, 2.0270(14) Å,[73] cyclopentyl 2.0243(3) Å, Et 2.036(8) Å, Ph 2.098(3) Å),[74] because of the reduced steric congestion about B in $HB(C_6F_5)_2$ compared to that in $B(C_6F_5)_3$. Interestingly, for **6** and **7**, the P-*H* and B-*H* hydrogen atoms are oriented in a *trans* disposition with respect to one another in the solid state exhibiting a typically staggered conformation (H−P−B−H = 176.76° and 178.98°, respectively). In contrast, **8** shows more twisting in the solid state from the staggered conformation with a H−P−B−H torsion angle of 166.55°. This twisting appears to be a solid-state effect as there is no evidence of dissymmetric geometry observed by NMR spectroscopy.

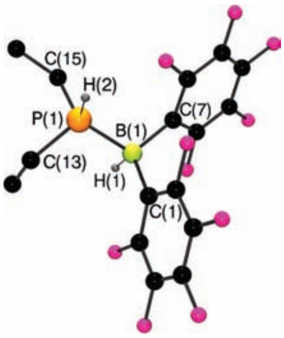


Figure 3. POV-Ray depiction one of two crystallographically independent molecules of **6**. C, black; H, white; B, yellow-green; F, deep pink; P, orange. C-bound H-atoms are omitted for clarity. Selected metrical parameters (distance Å, angle deg). P(1)−B(1) 1.950(3), H(1)−B(1)−P(1)−H(2) 176.76.

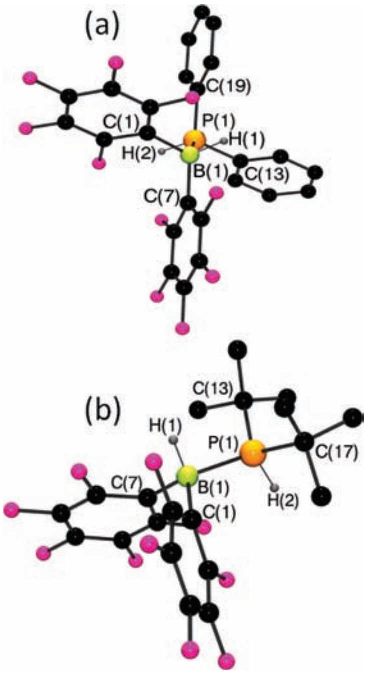


Figure 4. POV-Ray depictions of (a) **7** and (b) of two crystallographically independent molecules of **8**. C, black; H, white; B, yellow-green; F, deep pink; P, orange. C-bound H-atoms are omitted for clarity. Selected metrical parameters (distance Å, angle deg). **7**: P(1)−B(1) 1.966(3), H(1)−B(1)−P(1)−H(2) 178.98. **8**: P(1)−B(1) 1.966(9); H(1)−B(1)−P(1)−H(2) 166.55.

Hydrogenation of compounds **1**−**5** was explored via exposure of these species to 4 atm of H_2 at both room temperature (25 °C) and at 60 °C. Compounds **1** and **2** showed no signs of reaction. However at 25 °C reaction of compounds **3** and **4** was observed to give **8** and **9** in 2 and 4 weeks, respectively (Scheme 1). These products were formed in only 2 days at 60 °C. Compound **5** showed only traces of a new product after several weeks at room temperature.

---

(73) Lancaster, S. J.; Mountford, A. J.; Hughes, D. L.; Schormann, M.; Bochmann, M. *J. Organomet. Chem.* **2003**, *680*, 193.

(74) Welch, G. C.; Prieto, R.; Dureen, M. A.; Lough, A. J.; Labeodan, O. A.; Holtrichter-Rossmann, T.; Stephan, D. W. *Dalton Trans.* **2009**, 1559.

Computations suggest that the reaction of $(CF_3)_2BPR_2$ species with H_2 is exothermic.[47] However, the slow reaction of **5** infers there may be a relatively large kinetic barrier. Efforts to effect the reverse reaction, dehydrogenation of the adducts **6**−**10**, were also undertaken. Heating these species for 2 days at 140 °C showed no loss of H_2. These observations are in contrast to some primary or secondary phosphine adducts of BH_3 which can lose hydrogen under thermal duress[11,12,14−16,24−26] to produce B/P oligomers and polymers. It appears that the presence of electron-withdrawing groups at boron in the present case enhances the affinity for H_2.

In a related set of reactions compounds **3** and **4** were reacted with H_3NBH_3 or $Me_2(H)NBH_3$. This also led to the generation of **8** and **9**, respectively (Scheme 1). The nature of the byproduct from the reaction with H_3NBH_3 was not clear because of poor solubility, although they are thought to be oligomers of formula $(H_2NBH_2)_n$. Similarly the reactions with $Me_2(H)NBH_3$ produced the known dimer $(Me_2N\text{-}BH_2)_2$.[15] These experiments demonstrate the greater affinity for H_2 exhibited by compounds **3** and **4**. This is due in part to the enhanced Lewis acidity at boron in **3** and **4** compared to that of the boron centers of amino-borane. The proton transfer from N to P is aided by the enthalpically favorable formation of B═N double bond, which subsequently oligomerize or dimerize.

Computational studies at the ONIOM(MPW1K/6-311++G-(d, p)) level revealed that H_2 activation by **3** to form **8** is exothermic by 41.4 kcal/mol.[49] In contrast, the formations of the related phosphine-borane species by hydrogenation of Mes_2BPtBu_2 and Mes_2BPMes_2 are exothermic by 23.3 and 11.8 kcal/mol, respectively. This implies that fluoroarene substituents on B and alkyl groups on P increase the affinity for hydrogen. Moreover, in this limited data set, it appears that the former has a greater impact (ca. 18 kcal/mol) than the latter (ca. 12 kcal/mol).

Kinetic aspects of H_2 addition/dissociation were explored using relaxed scans of the potential energy surfaces for the processes. Typically a scan began with optimization of the structure of the phosphine-borane adducts, and involved shortening the H−H distance until H_2 "formed", then "dissociated" from the resulting phosphinoborane (Figure 5). Considering the H_2 addition reaction, climbing the barrier to the transition state is initiated by coordination of H_2 to B, followed by a slip of the coordinated H_2 toward P and H−H bond cleavage with concomitant P−H bond formation. These steps do not appear to require individual transition states. Indeed, the transition state region is rather flat and we were unable to locate a stationary point in the area. Nonetheless, the scan data give a value for the barrier of about 18 kcal/mol at the ONIOM(MPW1K/6-311++G(d, p)) level. This seems reasonable, if slightly low, for a reaction that occurs very slowly at 25 °C, but much faster at 60 °C. This barrier energy for addition of H_2 implies that the barrier for dissociation of bound H_2 is nearly 60 kcal/mol. Given the computed exothermicities and associated barriers to hydrogenation, it is not surprising that **8**−**10** do not release hydrogen, even on heating for extended periods at elevated temperatures.

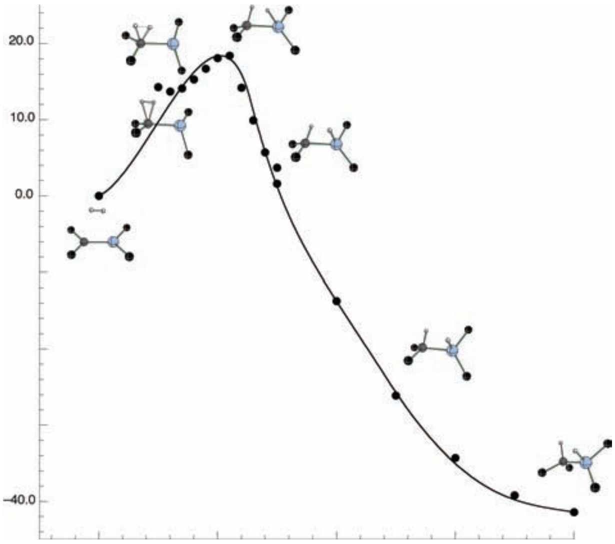


Figure 5. Computed reaction profile (ONIOM(MPW1K/6-311++G-(d,p)) for H_2 addition/dissociation (energies are given in kcal/mol).

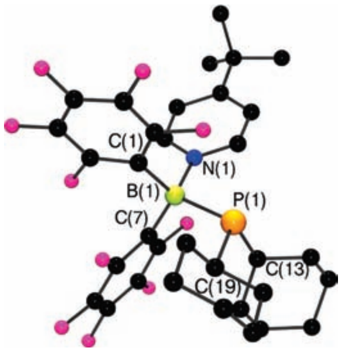
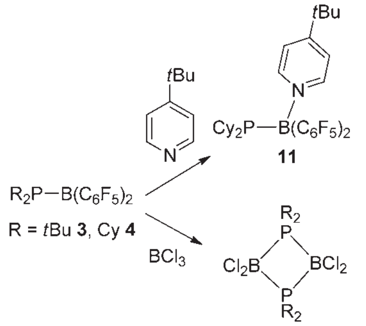


Figure 6. POV-Ray depiction of **11**. C, black; B, yellow-green; F, deep pink; N, blue; P, orange. H- and solvent atoms are omitted for clarity. Selected metrical parameters (distance Å, angle deg). B(1)−N(1) 1.6332(11), B(1)−P(1) 2.0329(9), N(1)−B(1)−P(1) 106.04, N(1)−B(1)−C(1) 101.81(6), N(1)−B(1)−C(7) 109.06(6), C(1)−B(1)−C(7) 113.53(7), P(1)−B(1)−C(1) 115.87(5), P(1)−B(1)−C(7) 109.77(5), B(1)−P(1)−C(13) 101.27(4), B(1)−P(1)−C(19) 109.43(4), C(13)−P(1)−C(19) 104.20(4).

Scheme 2. Synthesis of **11**−**13**



To probe the ambiphilic nature of the monomeric P−B compounds, reactions with simple donors and acceptors were conceived. Initially reactions with donors were considered. For example, reaction of **4** with 4-*tert*-butylpyridine shows evidence of the formation of a new species within 20 min of mixing. The product **11** exhibits a ^{11}B NMR resonance at −1.3 ppm while the ^{31}P signal broadens and shifts to −28.3 ppm. These data suggest B−N adduct formation. The reaction is quantitative although the product was challenging to isolate, and decomposition precluded characterization by elemental analysis. Nonetheless, **11** was characterized crystallographically (Figure 6, Scheme 2) and confirmed to be $Cy_2PB(C_6F_5)_2(4\text{-}tBuC_5H_4N)$. The crystal structure reveals a dramatic lengthening

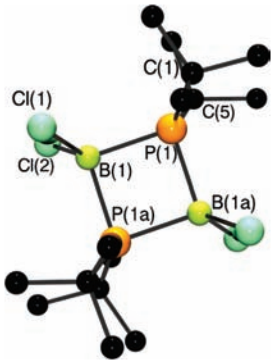


Figure 7. POV-Ray depiction of **13**. C, black; B, yellow-green; Cl, aquamarine; P, orange; F, deep pink. H-atoms are omitted for clarity. Selected metrical parameters (distance Å, angle deg). P(1)−B(1) 2.0552(15), P(1)−B(1a) 2.0557(15), B(1)−Cl(1) 1.8409(15), B(1)−Cl(2) 1.8453(15), B(1)−P(1)−B(1a) 89.01(6), P(1)−B(1)−P(1a) 90.99(6).

of the P−B bond to 2.0329(9) Å as a result of the loss of the π-bonding interaction between the formerly vacant orbital on boron and the lone pair on phosphorus. The B−N bond of 1.6332(11) Å is slightly longer than that reported for the analogous $B(C_6F_5)_3$ adduct of 4-*tert*-butyl pyridine (1.618(2) Å).[75] This longer bond length is a result of diminished Lewis acidity at boron and increased steric crowding caused by the adjacent phosphorus center. As expected, the boron center has become pseudotetrahedral. The N−B−C angles average 105.44° while the P−B−C angles average 112.82°, consistent with greater steric conflict between the $B(C_6F_5)_2$ and the PCy_2 units. The phosphorus center has also pyramidalized with the sum of angles totaling 314.9°. This is somewhat surprising since the planarity of the precursor phosphinoborane was attributed to steric conflict between substituents on P and B. The pyramidalization at phosphorus in **11** suggests that electronic effects and π-bonding facilitates the planarity observed in **4**.

Considering the inverse reactions, the phosphinoboranes **3** and **4** were reacted with the Lewis acid BCl_3. The new products **12** and **13** (Scheme 2) were characterized by new ^{11}B NMR signals at 4.2 and −0.5 ppm respectively. In addition these species gave rise to ^{31}P septets at −14.8 and −14.5 ppm with P−B couplings of 90 and 99 Hz, respectively. These data were consistent with the formation of the dimers $(R_2PBCl_2)_2$ (R = *t*Bu **12**, Cy **13**) (Scheme 2). In addition to these products the byproduct $ClB(C_6F_5)_2$ was also observed spectroscopically. Compound **13** was characterized crystallographically (Figure 7). Metrical parameters for **13** were similar to those of **1** and **2**, with the P−B bond lengths again falling toward the long end of the range for related P−B dimers[63−65] because of the bulky groups at phosphorus. The analogous combination of **5** with BCl_3 under similar conditions led to no reaction. This suggests that the phosphorus center in **5** is too hindered to initiate reaction by coordination to the incoming Lewis acid.

Conclusions

Monomeric phosphinoboranes of the general formula $R_2PB(C_6F_5)_2$ can be readily synthesized and characterized. Large substituents on P prevent dimerization, and the monomeric species exhibit spectroscopic and structural evidence of significant P−B π−bonding. Nonetheless, these bonds are sufficiently polarizable for these species to react with H_2, ammonia-borane, a Lewis acid or base. Lewis acid−base adducts of these ambiphilic phosphinoboranes are rather unstable because of the steric repulsion and weakening of the P−B bond caused by the loss of the π-bonding component of the interaction. The reactivity of these species with hydrogen under mild conditions without a catalyst is particularly interesting in the context of efforts to illuminate new strategies toward hydrogen storage materials that can be regenerated. It is this latter information that we are striving to exploit in ongoing efforts.

Acknowledgment. The authors thank NSERC of Canada for financial support. D.W.S. is grateful for the award of a Canada Research Chair and a Killam Research Fellowship. S.J.G. is grateful for an NSERC postgraduate scholarship.

Supporting Information Available: Crystallographic data in CIF format, and optimized cartesian coordinates of molecules examined computationally. This material is available free of charge via the Internet at http://pubs.acs.org.

---

(75) Geier, S. J.; Gille, A. L.; Gilbert, T. M.; Stephan, D. W. *Inorg. Chem.* **2009**, *48*, 10466.