Metal–Free Hydrogen Activation by the Frustrated Lewis Pairs of ClB(C 6 F 5) 2 and HB(C 6 F 5) 2 and Bulky Lewis Bases

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Metal-Free Hydrogen Activation by the Frustrated Lewis Pairs of $ClB(C_6F_5)_2$ and $HB(C_6F_5)_2$ and Bulky Lewis Bases

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The frustrated Lewis pair (FLP) derived from $ClB(C_6F_5)_2$ and the bulky Lewis bases 2,2,6,6-tetramethylpiperidine (**TMP**), tri-*tert*-butylphosphine, and tris(2,4,6-trimethylphenyl)phosphine cleaved H_2 heterolytically to form the intermediate anion $[HClB(C_6F_5)_2]^-$, which quickly underwent hydride/chloride exchange with the remaining $ClB(C_6F_5)_2$ to give the known compound $[HB(C_6F_5)_2]_n$ (n = 1 or 2) and the anion $[Cl_2B(C_6F_5)_2]^-$ present in the products [**TMP**H]-$[Cl_2B(C_6F_5)_2]$ (**1a**), [*t*-Bu_3PH]$[Cl_2B(C_6F_5)_2]$ (**2a**), and $[Mes_3PH][Cl_2B(C_6F_5)_2]$ (**3a**). $[HB(C_6F_5)_2]_n$ forms Lewis adducts with **TMP** and *t*-Bu_3P: **TMP**-$BH(C_6F_5)_2$ (**1b**) and *t*-Bu_3P-$BH(C_6F_5)_2$ (**2b**). The Lewis adduct *t*-Bu_3P-$BH(C_6F_5)_2$ was found capable of generating a FLP at elevated temperature and was reacted with H_2, producing the splitting product [*t*-Bu_3PH]$[H_2B(C_6F_5)_2]$ (**2c**). Mes_3P forms no Lewis adduct with $[HB(C_6F_5)_2]_n$, but a FLP, which was also capable of splitting H_2 to yield initially $[Mes_3PH][H_2B(C_6F_5)_2]$. The $[H_2B(C_6F_5)_2]^-$ anion underwent disproportionation to form $[Mes_3PH]$-$[HB(C_6F_5)_3]$ (**3b**), Mes_3P, $[H_2B(C_6F_5)]_2$, and H_2. Similarly, 2,4,6-tri-*tert*-butylpyridine (**TTBP**) and $[HB(C_6F_5)_2]_n$ gave in the presence of H_2 the final products [**TTBP**H]$[HB(C_6F_5)_3]$ salt and $[H_2B(C_6F_5)]_2$. The contrasting reactivities of the *t*-$Bu_3P/[BH(C_6F_5)_2]_n$, $Mes_3P/[HB(C_6F_5)_2]_n$, and **TTBP**/$[HB(C_6F_5)_2]_n$ pairs were explained on the basis of the different pK_a's of the $[LBH]^+$ cations. After disproportionation of the $[H_2B(C_6F_5)_2]^-$ anion to give $[Mes_3PH][HB(C_6F_5)_3]$ (**3b**) or [**TTBP**H]-$[HB(C_6F_5)_3]$ (**4a**), the also formed $[H_3B(C_6F_5)]^-$ anion reacted with the more acidic cations ($[Mes_3PH]^+$, [**TTBP**H]$^+$) to give H_2 and *syn*- and *anti*-$[H_2B(C_6F_5)]_2$ (**3c**). **1a**, **2a**, **3a**, and **4a** were studied by single-crystal X-ray diffraction analysis.

Introduction

The concept of frustrated Lewis pairs (FLPs) was put forward by D. W. Stephan et al. in 2006 after their remarkable discovery that H_2 can reversibly be activated by the "metal-free" compound $[(2,4,6\text{-}C_6H_2Me_3)_2P(H)(C_6F_5)B(H)\text{-}(C_6F_5)_2]$.[1] As one of the fruitful applications of this concept, "metal-free" catalysts could be developed for the hydrogenation of bulky imines.[2] In such systems sterically hindered Lewis donors and acceptors are combined to establish encounter complexes. Their steric congestion precludes the formation of classical Lewis adducts, and their relatively close proximity indeed provokes H_2 activation and also "unquenched" reactivity toward small molecules.[3,4] For instance, the mixtures of frustrated phosphine and borane pairs can activate H_2 heterolytically under very mild conditions[5] and can undergo addition of olefins, as well.[6,7] Similarly following their pioneering work an increasing number of related FLPs were created, which were capable of activating both H_2 heterolytically and also other small molecules.[8−17] Some of the zwitterionic products resulting from H_2 splitting were shown to serve as active catalysts for the hydrogenation of imines, nitriles, and aziridines, as well as enamine and

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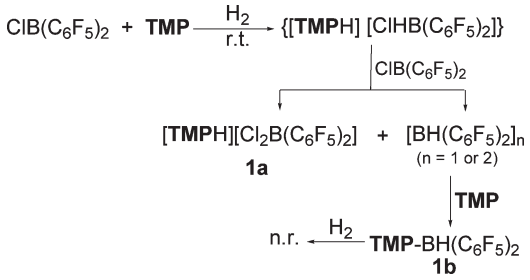
Scheme 1



C=C double bonds of enol silyl ether.[18−20] Presently FLP formation is no longer limited to boron/phosphine systems, since Stephan et al. and Tamm et al. extended the range of FLPs to boron/carbene combinations, in which for H_2 activation the steric demands of the Lewis pair constituents are very crucial to their reactivity.[9,10] For the same purpose Rieger et al. introduced the borane/amine variant for FLPs.[11] The majority of Lewis acids used were trispentafluorophenylborane, $B(C_6F_5)_3$, or closely related molecules. The $ClB(C_6F_5)_2$ and $HB(C_6F_5)_2$ compounds were chosen to act as a highly active hydroboration reagents or as synthons for the incorporation of Lewis acidic $-B(C_6F_5)_2$ groups into molecular frameworks building new intramolecular FLPs.[8,13,18,19] However, as yet, these compounds have not been used as Lewis acidic components in FLPs to activate H_2. We therefore tried to approach utilization of the "robust" molecules $ClB(C_6F_5)_2$[21] and $HB(C_6F_5)_2$[22] in FLPs together with 2,2,6,6-tetramethylpiperidine (**TMP**) or phosphines R_3P (R = *t*-Bu, 2,4,6-trimethylphenyl = Mes) for cleavage of H_2.

Results and Discussion

Toluene solutions of stoichiometric mixtures of 2,2,6,6-tetramethylpiperidine (**TMP**) or of the sterically hindered phosphines R_3P (R = *t*-Bu, 2,4,6-trimethylphenyl) and $ClB(C_6F_5)_2$ were at first explored for Lewis adduct formation by ^1H, ^{19}F, and ^{11}B NMR spectroscopy. We found only unchanged signals due to the free starting materials and no hint of Lewis adduct formation by these sterically quite congested molecules. We can, however, suppose that contact pairs, the FLPs, had formed, since, for instance, exposure of a **TMP**/$ClB(C_6F_5)_2$ toluene solution to an atmosphere of H_2 (1000 mbar) induced a reaction proceeding at ambient temperature. Initial formation of [**TMP**H][$ClHB(C_6F_5)_2$] is assumed, but this species is not stable in the presence of $ClB(C_6F_5)_2$ and is transformed subsequently into the [**TMP**H][$Cl_2B(C_6F_5)_2$] salt **1a**. The chloride/hydride metathesis also produces the known equilibrium mixture of the monomeric and dimeric borohydride $[HB(C_6F_5)_2]_n$ ($n = 1, 2$)[23] (Scheme 1). $[HB(C_6F_5)_2]_n$ quickly associates with the remaining **TMP** to afford the stable Lewis acid−base adduct **TMP**-$BH(C_6F_5)_2$, **1b**. **1b** apparently is such a tight adduct that FLP reactivity toward

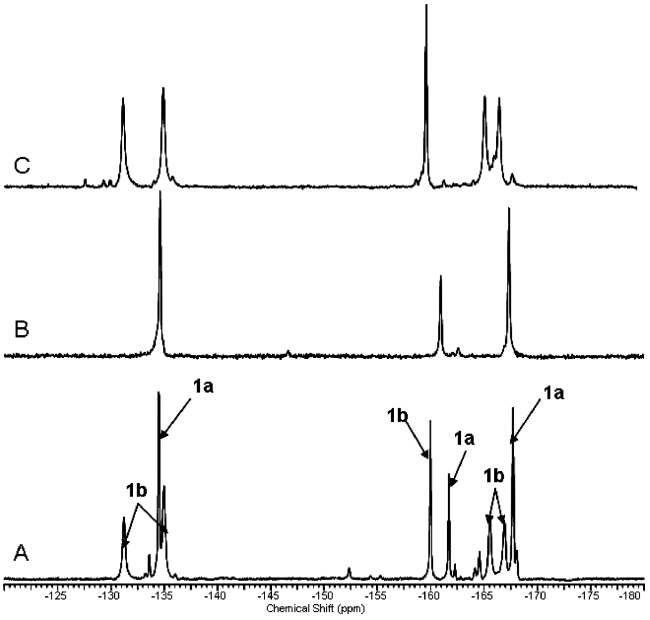


Figure 1. (A) ^{19}F NMR spectra of the mixture of **TMP**-$ClB(C_6F_5)_2$ with H_2 after ca. 30 min in toluene-d_8; (B and C) ^{19}F NMR spectra of pure **1a** and **1b** in toluene-d_8.

H_2 could not be initiated even at elevated temperatures (Scheme 1). The formation of **1a** and **1b** according to Scheme 1 could be analyzed by ^{19}F NMR spectroscopy. The ^{19}F NMR spectrum of the reaction mixture (spectrum A) and its assignments are shown in Figure 1 in comparison with spectra of pure **1a** (B) and **1b** (C). **1a** could be isolated from the reaction mixture as a white solid in ca. 35% yield. The ^1H NMR spectrum of **1a** features a broad NH_2 resonance at 5.90 ppm, and the ^{19}F NMR spectrum shows signals at δ −134.56 (*o*-), −160.92 (*p*-), and −167.32 ppm (*m*-C_6F_5), consistent with the four-coordinate boron atom of the anion ($\Delta\delta_{m,p} = 3.4$). The X-ray diffraction study of **1a** (Figure 2) reveals an overall centrosymmetric chair form of pairs of **1a** held together by hydrogen bonding. Each boron atom is connected to two chlorine atoms and two C_6F_5 groups in a tetrahedral environment.[24] The N1−H1 and N1−H2 distances are 0.90(2) and 0.85(2) Å, and the H1−N1−H2 angle is 104.7(2)°. The Cl1−B1−Cl2 angle is 105.42(8)°, and the B−Cl bonds possess an average length of 1.89 Å. Intermolecular N−H···Cl hydrogen bonds link the pairs of ions with H1···Cl1 and H2···Cl2^i separations of 2.50(2) and 2.47(2) Å, respectively.

Pure **1b** was prepared from the reaction of a stoichiometric mixture of $[HB(C_6F_5)_2]_n$ ($n = 1$ or 2) and **TMP** obtained as a white solid in 86% yield. In the ^1H NMR spectrum **1b** features a broad H_B resonance at 4.18 ppm, and the ^{11}B NMR resonance is located at δ −11.82 ppm. The ^{19}F NMR spectrum provides further evidence for the inequivalence of the phenyl rings, since two sets of signals are attributable to the *ortho*- (δ −131.23, −135.06 ppm) and *meta*-fluorine atoms (δ −165.56, −166.92 ppm), but just one signal is found for the *para*-fluorine atoms (δ −160.01 ppm). This

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(23) In benzene or toluene solution, bis(pentafluorophenyl)borane exhibits a dimer/monomer equilibrium.

(24) Crystal data for **1a**: $C_{21}H_{20}BCl_2F_{10}N$, $M = 558.09$, monoclinic, $P2_1/c$, $a = 12.0763(2)$ Å, $b = 11.2761(2)$ Å, $c = 18.3912(3)$ Å, $\beta = 108.351(2)°$, $V = 2377.04(7)$ Å^3, $Z = 4$, $D_c = 1.559$ g cm^{-1}, $\mu = 0.362$ mm^{-1}, $\lambda = 0.71073$ Å, $T = 183(2)$ K, 23 392 reflections collected, 4844 independent [$R_{(int)} = 0.0309$] and 4150 observed reflections [$I > 2\sigma(I)$], 328 refined parameters, $R = 0.0298$, $wR_2 = 0.0796$. CCDC 736257.

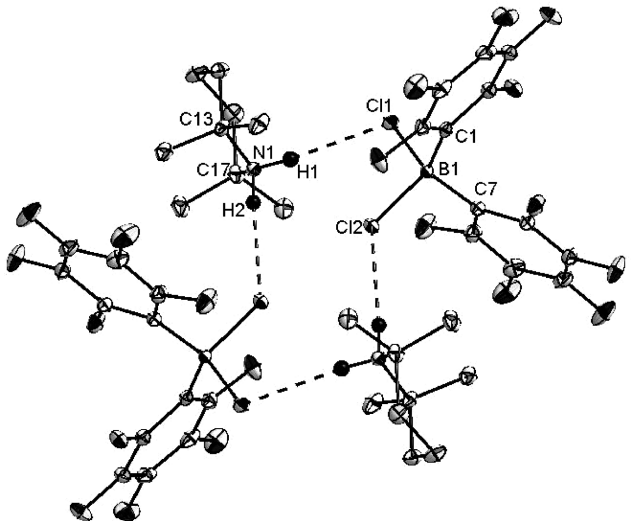
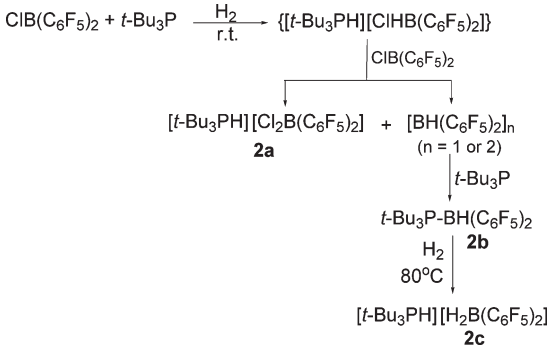


Figure 2. Molecular structure of **1a** with 30% probability thermal ellipsoids. Hydrogen atoms except for the H_N atom are omitted for clarity. Selected bond lengths [Å]: N1−H1 0.90(2), H1···Cl1 2.50(2), N1−H2 0.85(2), H2···Cl2^{i} 2.47(2), N1−C13 1.532(2), N1−C17 1.529(2), B1−Cl1 1.905(2), B1−Cl2 1.885(2), B1−C1 1.618(2), B1−C7 1.623(2). Selected bond angles [deg]: H1−N1−H2 104.7(2), H1−N1−C17 105.1(1), H1−N1−C13 107.9(1), H2−N1−C13 108.7(1), H2−N1−C17 108.7(1), C13−N1−C17 120.8(1), Cl1−B−Cl2 105.42(8), Cl2−B1−C1 113.89(1), Cl2−B1−C7 104.57(9), C1−B1−C7 115.92(1), Cl1−B1−C7 111.8(1), Cl1−B1−C1 104.95(9). N1−H1···Cl1 174.8(15), N2−H2···Cl2^{i} 173.6(15). Symmetry transformation (i) used to generate equivalent atoms: $1-x$, $1-y$, $-z$.

Scheme 2



observation suggests hindered rotation of the C_6F_5 rings around the B−C bonds, which presumably arises from steric contacts between the methyl substituents of the piperidine moiety and the fluorine atoms or forms $H_{TMP}\cdots F$ hydrogen bonding.

Similar to the reaction with **TMP**, the phosphines t-Bu_3P and Mes_3P (Mes = 2,4,6-trimethylphenyl) were reacted with $ClB(C_6F_5)_2$ under an atmosphere of H_2 to yield initially salts of the phosphonium ions with the unstable $[ClHB(C_6F_5)_2]^-$ anion (Schemes 2 and 3). As for the **TMP** reaction, this anion then undergoes fast hydride/chloride exchange with $ClB(C_6F_5)_2$ to generate the $[Cl_2B(C_6F_5)_2]^-$ anion and the equilibrium mixture of the monomeric and dimeric hydrides $[HB(C_6F_5)_2]_n$ ($n = 1$ or 2). The products thus were $[t\text{-}Bu_3PH][Cl_2B(C_6F_5)_2]$ (**2a**) and $[Mes_3PH][Cl_2B(C_6F_5)_2]$ (**3a**), which exhibit ^{19}F and ^{11}B NMR spectra similar to those resonances

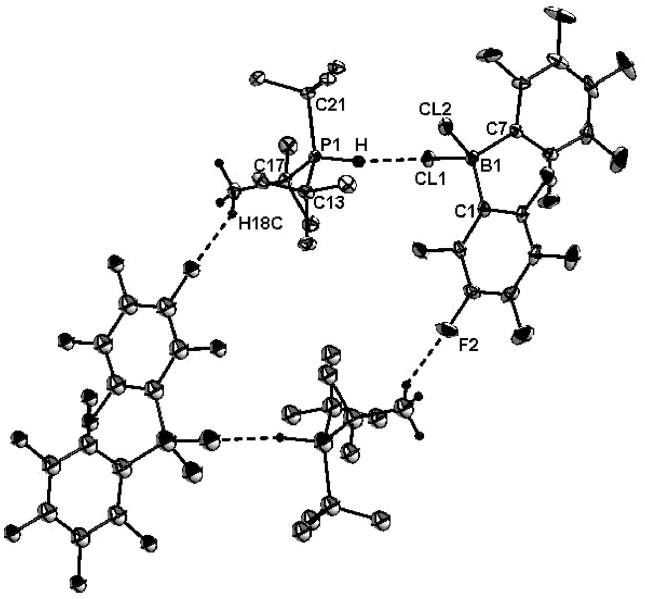


Figure 3. Molecular structure of **2a** with 30% probability thermal ellipsoids. Hydrogen atoms except for the H_P and H_{C18} atoms are omitted for clarity. Selected bond lengths [Å]: P1−H 1.30(2), H···Cl1 2.78(2), H18C···F2^{i} 2.54, P1−C21 1.869(2), P1−C17 1.867(2), P1−C13 1.871(2), B1−Cl1 1.891(2), B1−Cl2 1.895(2), B1−C1 1.625(2), B1−C7 1.630(2). Selected bond angles [deg]: C21−P1−H 103.7(7), C13−P1−H 104.3(7), C17−P1−H 104.1(6), C21−P−C17 114.72(7), C17−P1−C13 113.95(7), C21−P1−C13 114.26(8), Cl1−B−Cl2 107.64(9), Cl1−B1−C1 113.8(1), Cl1−B1−C7 114.1(1), C1−B1−C7 114.3(1), Cl2−B1−C7 113.28(1), Cl2−B1−C1 103.8(1), P1−H···Cl1 148.1(9), C18−H18C···F2^{i} 156. Symmetry transformation (i) used to generate equivalent atoms: $-x$, $-y$, $1-z$.

seen for the $[Cl_2B(C_6F_5)_2]^-$ anion of **1a**. The cations of **2a** and **3a** show ^{31}P NMR resonances at 51.79 and −25.69 ppm with typically large J(P,H) coupling constants of 440 and 472 Hz, respectively. The ^1H NMR signals of the H_P protons are found at δ 5.12 (**2a**) and 8.48 ppm (**3a**). A crystallographic study of **2a** reveals a square-type structure similar to **1a** (Figure 3). The ions are connected through weak P−H···Cl and C−H···F hydrogen bonds with a H···Cl1 distance of 2.78(2) and H18C···F2A of 2.54 Å.[25] The P−H distance is 1.30(2) Å, and the Cl1−B1−Cl2 angle and the Cl−B distance are quite close to those of **1a**. Strong hydrogen bonding could not be traced in the structure of **3a**, and the Cl2···H1 distance amounts to 2.95 Å, which is significantly longer than the corresponding interactions in **1a** (2.50(2) Å) and **2a** (2.47(2) Å) (Figure 4).[26] The Cl1−B1−Cl2 angle and the Cl−B distance of **3a** are comparable to those of **2a**.

The equilibrium mixture of $[HB(C_6F_5)_2]_n$ formed initially according to Schemes 2 and 3 reacted differently with t-Bu_3P and Mes_3P. t-Bu_3P produced the isolable Lewis adduct

(25) Crystal data for **2a**: $C_{24}H_{28}BCl_2F_{10}P$, $M = 619.14$, monoclinic, $P2_1/m$, $a = 8.8527(1)$ Å, $b = 15.7511(2)$ Å, $c = 19.8253(3)$ Å, $\beta = 95.993(2)°$, $V = 2749.33(6)$ Å^3, $Z = 4$, $D_c = 1.496$ g cm^{-1}, $\mu = 0.376$ mm^{-1}, $\lambda = 0.71073$ Å, $T = 183(2)$ K, 27 971 reflections collected, 6555 independent [$R_{(int)}$ = 0.0455] and 4858 observed reflections [$I > 2\sigma(I)$], 356 refined parameters, $R = 0.0352$, $wR_2 = 0.0830$. CCDC 736258.

(26) Crystal data for **3a**: $C_{39}H_{34}BCl_2F_{10}P$, $M = 805.34$, monoclinic, $P2_1/c$, $a = 8.2098(1)$ Å, $b = 19.2927(2)$ Å, $c = 23.8105(2)$ Å, $\beta = 95.018(1)°$, $V = 3756.87(7)$ Å^3, $Z = 4$, $D_c = 1.424$ g cm^{-1}, $\mu = 0.294$ mm^{-1}, $\lambda = 0.71073$ Å, $T = 183(2)$ K, 79 873 reflections collected, 11466 independent [$R_{(int)}$ = 0.0331] and 8553 observed reflections [$I > 2\sigma(I)$], 491 refined parameters, $R = 0.0455$, $wR_2 = 0.1165$. CCDC 736259.

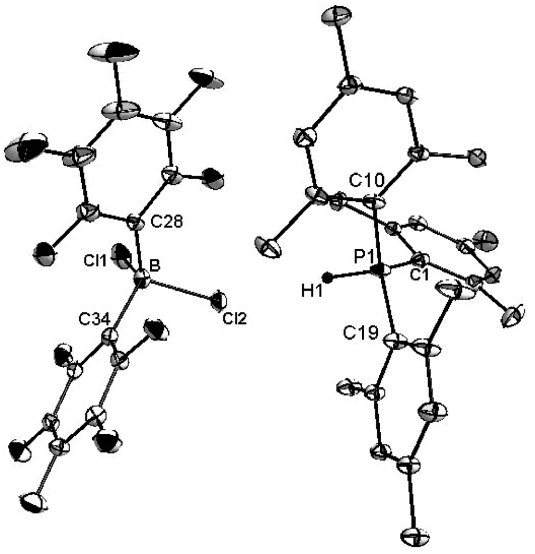


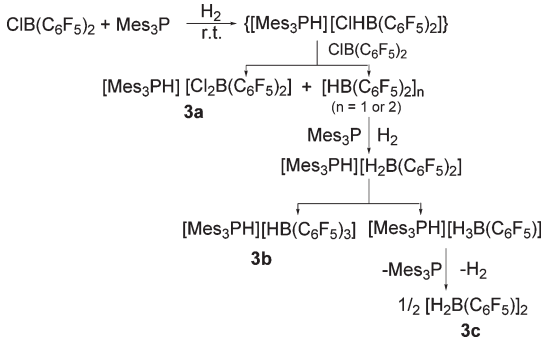
Figure 4. Molecular structure of **3a** with 30% probability thermal ellipsoids. Hydrogen atoms except for the H_P atom are omitted for clarity. Selected bond lengths [Å]: P1−H1 1.30(1), P1−C1 1.80(1), P1−C10 1.80(1), P1−C19 1.81(1), B−Cl1 1.86 (2), B−Cl2 1.93(2), B1−C28 1.626(2), B1−C34 1.631(2). Selected bond angles [deg]: C1−P1−C10 114.05(6), C1−P1−C19 115.73(6), C10−P1−C19 115.80(6), C1−P1−H1 103.4(6), C10−P1−H1 102.8(6), C19−P1−H1 102.4(6) Cl1−B−Cl2 107.43(8), Cl2−B−C34 102.99(1), Cl2−B−C28 110.4(1), Cl1−B−C34 114.1(1), Cl1−B−C28 105.9(1), C28−B−C34 115.8(1).

t-Bu_3P-$BH(C_6F_5)_2$ **2b**. **2b** could independently be prepared from a stoichiometric mixture of $[HB(C_6F_5)_2]_n$ and t-Bu_3P in toluene. In the ^{19}F NMR spectrum it is characterized by a set of signals at δ −124.56 (*o*-), −158.87 (*p*-), and −164.18 ppm (*m*-C_6F_5). The ^{31}P NMR signal of this adduct is found at δ 47.64 ppm, and the ^{11}B NMR resonance is at −27.40 ppm, which is consistent with the tetrahedral boron center of **2b**. Interestingly, upon a raise in temperature to 80 °C, **2b** reacted further with H_2, affording the isolable ionic species $[t$-$Bu_3PH][H_2B(C_6F_5)_2]$, **2c**. The elevated temperature apparently promotes dissociation of the Lewis adduct to form a FLP.

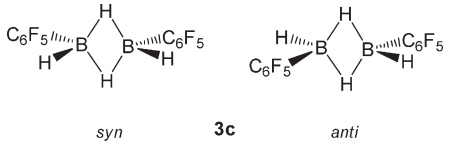
The relative stability of **2c** is mainly attributed to the stability of the anion in the presence of the $[t$-$Bu_3PH]^+$ cation, displaying too low acidity[27] for further transformation like the salt of this anion with the $[Mes_3PH]^+$ cation (*vide infra* Scheme 3). The ^1H and ^{31}P NMR spectra of **2c** exhibited the expected resonances. The ^{11}B NMR spectrum shows a triplet at −30.2 ppm with a B−H coupling constant of 90 Hz, and the corresponding ^1H NMR resonance is found at 3.01 ppm (q, br, B−H). Moreover, the $\Delta\delta$ (*m*-F)−(*p*-F) separation is consistent with the presence of an anionic four-coordinate boron atom.

Toluene solutions of stoichiometric mixtures of Mes_3P and $[HB(C_6F_5)_2]_n$ did not lead to formation of a Lewis adduct. The mixture was however found to act as a FLP

Scheme 3



capable of splitting H_2 heterolytically under ambient conditions and generate—somewhat unexpectedly—the $[Mes_3PH]$-$[HB(C_6F_5)_3]$ salt **3b** as one of the final products. Compound **3b** possesses the following data after exposure of the toluene solution of Mes_3P-$[HB(C_6F_5)_2]_n$ at H_2 atmosphere for 30 min: ^1H NMR δ 7.93 ppm (d, $^1J_{P-H} = 460$ Hz); ^{11}B NMR δ −20.21 ppm (d, J_{B-H} = 82 Hz); ^{19}F NMR δ −133.65, −164.61, −168.34 ppm. Another ^{11}B NMR resonance at 9.5 ppm (br) and a set of ^{19}F NMR signals at δ −136.79, −137.51, −160.69, −162.14, −166.23, and −166.59 ppm were additionally recognized in the spectra of the reaction solution. These signals were attributed to the *syn* and *anti* isomers of $[H_2B(C_6F_5)]_2$ (**3c**) formed via disproportionation of the $[H_2B(C_6F_5)_2]^-$ anion.[28] But *syn*-$[H_2B(C_6F_5)]_2$ (^{19}F NMR signals at δ −136.79, −162.14, −166.59 ppm) was not stable in solution and was completely converted after several hours into *anti*-$[H_2B(C_6F_5)]_2$, **3c** (^{19}F NMR signals at δ −137.51, −160.69, −166.23 ppm). The ^1H NMR spectrum of **3c** was less informative, since resonances for the hydride substituents (terminal or bridging) could not be detected. This was explained on the basis of a broadening of these resonances due to the direct neighborhood with the ^{11}B quadrupole nuclei.



syn **3c** *anti*

Mes_3P cannot form a stable Mes_3P-$BH(C_6F_5)_2$ Lewis adduct, but a reactive $Mes_3P\cdots BH(C_6F_5)_2$ FLP, since reactivity similar to that of the t-$Bu_3P\cdots BH(C_6F_5)_2$ FLP was found. The $Mes_3P\cdots BH(C_6F_5)_2$ encounter complex can apparently split H_2 to initially generate the $[H_2B(C_6F_5)_2]^-$ anion, which can be detected via ^{11}B NMR as a transient during the reaction process. As a subsequent reaction step, disproportionation of this anion occurs, producing in equilibrium the substituent exchange products $[HB(C_6F_5)_3]^-$ and $[H_3B(C_6F_5)]^-$[29] (Scheme 3). The quite basic $[H_3B(C_6F_5)]^-$ anion is quickly withdrawn from equilibrium via the acid−base reaction with the acidic $[Mes_3PH]^+$ cation, evolving H_2

(27) pK_a values, t-Bu_3P: 11.4; Ph_3P: 2.73; (o-$MeC_6H_4)_3P$: 3.08; (p-$MeC_6H_4)_3P$: 3.84; **TMP**: 11.07; **TTBP**: 4.02. (a) Streuli, C. A. *Anal. Chem.* **1960**, *32*, 985. (b) Bush, R. C.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 681. (c) Cappellani, E. P.; Drouin, S. D.; Jia, G.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T. *J. Am. Chem. Soc.* **1994**, *116*, 3375. (d) Graton, J.; Berthelot, M.; Laurence, C. *J. Chem. Soc., Perkin Trans.* **2001**, 2130. (e) Hall, H. K. *J. Am. Chem. Soc.* **1957**, *79*, 5444. (f) Deutsch, E.; Cheung, N. K. V. *J. Org. Chem.* **1973**, *38*, 1123.

(28) The monoalkylboranes usually exist as the dimers, and usually the *anti* isomer is thermodynamically more stable than the other. (a) Brown, H. C.; Singaram, B.; Cole, T. E. *J. Am. Chem. Soc.* **1985**, *107*, 460. (b) Soundararajan, R.; Matteson, D. S. *Organometallics* **1995**, *14*, 4157. (c) Wehmschulte, R. J.; Diaz, A. A.; Khan, M. A. *Organometallics* **2003**, *22*, 83.

(29) (a) Biscoe, M. R.; Uyeda, C.; Breslow, R. *Org. Lett.* **2004**, *6*, 4331. (b) Biscoe, M. R.; Breslow, R. *J. Am. Chem. Soc.* **2003**, *125*, 12718.

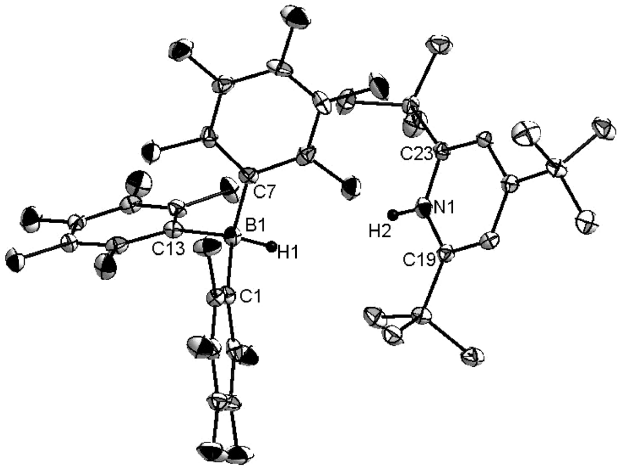
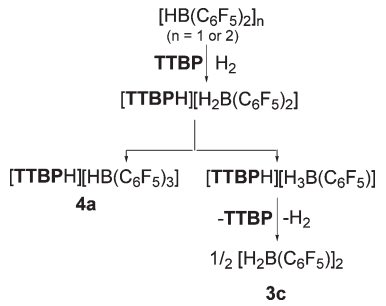


Figure 5. Molecular structure of **4a** with 30% probability thermal ellipsoids. Hydrogen atoms except for the H_N and H_B atoms are omitted for clarity. Selected bond lengths [Å]: B1−H1 1.15(3), B1−C7 1.636(4), B1−C13 1.637(4), B1−C1 1.648(4), N1−H1 0.96(3), N1−C23 1.363(3), N1−C19 1.354(3). Selected bond angles [deg]: C7−B1−H1 107.0(2), C1−B1−H1 103.7(1), C13−B1−H1 108.6(1), C7−B1−C13 112.6(2), C7−B1−C1 114.4(2), C13−B1−C1 110.0(2), H2−N1−C23 115.9(2), H2−N1−C19 119.9(2), C19−N1−C23 124.3 (3).

Scheme 4



and forming $[H_2B(C_6F_5)]_2$ (Scheme 3). It should be mentioned at this point that the $[H_2B(C_6F_5)_2]^-$ anion of **2c** is also believed to undergo this disproportionation process. The disproportionation occur for the $[H_2B(C_6F_5)_2]^-$ anions of both salts $[t\text{-}Bu_3PH][H_2B(C_6F_5)_2]$ and $[Mes_3PH][H_2B(C_6F_5)_2]$ (Schemes 2 and 3), however with low actual equilibrium concentrations of the $[H_3B(C_6F_5)]^-$ anion, too low to enable acid−base reaction with the less acidic $[t\text{-}Bu_3PH]^+$ cation, but sufficient for the reaction with the more acidic $[Mes_3PH]^+$ cation.[27]

In order to acquire more information about this H_2 splitting reaction with $[HB(C_6F_5)_2]_n$, the bulky Lewis base 2,4,6-tri-*tert*-butylpyridine (**TTBP**) was applied. **TTBP** was considered to behave similarly to Mes_3P, since its protonated form possesses a pK_a similar to that of the $[Mes_3PH]^+$ cation,[27] and in addition the sterically congested **TTPB** was expected to form a FLP with $[HB(C_6F_5)_2]_n$.

Indeed, the reaction of the **TTBP**/$[HB(C_6F_5)_2]_n$ pair with H_2 led to a split of this molecule and also to subsequent disproportionation of the $[\mathbf{TTBP}H][H_2B(C_6F_5)_2]$ salt to afford the stable $[\mathbf{TTBP}H][HB(C_6F_5)_3]$ compound **4a** and the *syn* and *anti* mixture of **3c** (Scheme 4). **4a** features the same ^1H, ^{11}B, and ^{19}F NMR resonances as the anion of **3b** and also as a compound prepared independently from $B(C_6F_5)_3$ and **TTBP** with H_2. Crystals grown from the crude mixture allowed a X-ray crystallographic study of **4a** (Figure 5), which showed that the B−H and N−H units are oriented toward each other with a BH···HN nonbonding distance of 3.51(1) Å, which is much longer than that of other related intermolecular dihydrogen bonding separations.[30]

In continuation of these investigations, reduction of imines was probed using $HB(C_6F_5)_2$ or $[t\text{-}Bu_3PH][H_2B(C_6F_5)_2]$ as catalyst. However, in many cases of the applied imines, the formation of too stable amine-boron adducts prevented the formation of FLPs and consequently also catalytic activity. As a result, only PhCH=N*t*-Bu could be reduced to the corresponding amine in 95% yield at 120 °C in the presence of 10% $HB(C_6F_5)_2$ at a hydrogen pressure of 1300 mbar within 24 h. For the sterically less hindered imines PhCH=NPh and $PhCH{=}NCHPh_2$ the conversions were usually less than 50% under the same conditions as mentioned before. This observation supports the idea that FLP formation is crucial to metal-free hydrogenation catalysis, and anything precluding such a step leads to suppression of catalysis.

Conclusion

In summary, $ClB(C_6F_5)_2$ and $HB(C_6F_5)_2$ were employed as Lewis acids (LAs) in FLP chemistry, and heterolytic splitting of H_2 was observed in the presence of the bulky Lewis bases (LBs) **TMP**, $t\text{-}Bu_3P$, Mes_3P, and **TTBP**. The bulkiness of the LB components, the stability of the $[LAH]^-$ anions toward substituent exchanges, and the acidities of the $[LBH]^+$ cations were decisive parameters determining the courses of the reactions following the initial H_2 splitting. On the LB side the $[LBH]^+$ cations $[\mathbf{TMP}H]^+$, $[t\text{-}Bu_3PH]^+$, $[Mes_3PH]^+$, and $[\mathbf{TTBP}H]^+$ were formed and the more acidic ones caused follow-up reactions. On the LA side the initially formed $[LAH]^-$ anions were subjected to different reaction courses depending on the mentioned parameters. The $[ClHB(C_6F_5)_2]^-$ anions initially formed from $ClB(C_6F_5)_2$ underwent hydride/chloride exchange with $ClB(C_6F_5)_2$ to give $[Cl_2B(C_6F_5)_2]^-$ and $[HB(C_6F_5)_2]_n$ ($n = 1$ or 2). **TMP** and $[HB(C_6F_5)_2]_n$ (n = 1 or 2) formed a tight Lewis adduct, unreactive toward H_2. At higher temperatures the Lewis adduct $t\text{-}Bu_3P\text{-}BH(C_6F_5)_2$ reacted in the form of its $t\text{-}Bu_3P\cdots BH(C_6F_5)_2$ FLP with H_2 to generate the salt $[t\text{-}Bu_3PH][H_2B(C_6F_5)_2]$. The FLPs $Mes_3P\cdots[HB(C_6F_5)_2]$ and $\mathbf{TTBP}\cdots[HB(C_6F_5)_2]$ effected formation of the $[H_2B(C_6F_5)_2]^-$ anion as a first intermediate, which then underwent disproportionation of the substituents to form $[Mes_3PH][HB(C_6F_5)_3]$ or $[\mathbf{TTBP}H][HB(C_6F_5)_3]$ and the quite basic $[H_3B(C_6F_5)]^-$ anion. Unlike $[t\text{-}Bu_3PH][H_2B(C_6F_5)_2]$, where the anticipated equilibrium formation of the $[H_3B(C_6F_5)]^-$ anion did not lead to a subsequent acid−base reaction with the $[t\text{-}Bu_3PH]^+$ cation, the $[H_3B(C_6F_5)]^-$ anion was withdrawn from the disproportionation equilibrium with the more acidic $[Mes_3PH]^+$ and $[\mathbf{TTBP}H]^+$ cations, affording H_2, LB, and *syn*- and *anti*-$[H_2B(C_6F_5)]_2$.

(30) Crystal data for **4a**: $C_{38}H_{38}BF_{15}N$, $M = 804.50$, triclinic, $P\bar{1}$, $a = 9.8216(3)$ Å, $b = 10.7921(3)$ Å, $c = 18.7474(6)$ Å, $\alpha = 74.768(3)°$, $\beta = 77.215(3)°$, $\gamma = 78.314(3)°$, $V = 1847.65(10)$ Å^3, $Z = 2$, $D_c = 1.446$ g cm^{-1}, $\mu = 0.136$ mm^{-1}, $\lambda = 0.71073$ Å, $T = 183(2)$ K, 19 560 reflections collected, 6995 independent [$R_{(int)} = 0.0421$] and 3529 observed reflections [$I > 2\sigma(I)$], 514 refined parameters, $R = 0.0495$, $wR_2 = 0.1148$. CCDC 736260.

Experimental Section

General Considerations. All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques or in a glovebox (M. Braun 150B-G-II) filled with dry nitrogen. Solvents were freshly distilled under N_2 by employing standard procedures and were degassed by freeze−thaw cycles prior to use. All organic reagents were purchased from Aldrich and used without further purification. $ClB(C_6F_5)_2$ and $HB(C_6F_5)_2$ were prepared according to the literature.[21,22] ^1H NMR, ^{19}F NMR, $^{11}B\{^1H\}$ NMR, and $^{31}P\{^1H\}$ NMR data were recorded on a Varian Gemini-200 or -300 spectrometer. Chemical shifts are expressed in parts per million (ppm) referenced to the deuterated solvent used. ^{19}F, ^{11}B, and ^{31}P NMR were referenced to $CFCl_3$, $BF_3 \cdot OEt_2$, and 85% H_3PO_4, respectively. Microanalyses were carried out at the Anorganisch-Chemisches Institut of the University of Zürich.

Crystallographic data were collected at 183(2) K on an Oxford Xcalibur diffractometer (4-circle kappa platform, Ruby CCD detector, and a single-wavelength Enhance X-ray source with Mo Kα radiation, $\lambda = 0.71073$ Å).[31] The selected suitable single crystals were mounted using polybutene oil on the top of a glass fiber fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, face-indexing analytical absorption correction,[32] and data reduction were performed with the Oxford program suite CrysAlisPro.[33] The structures were solved with the direct methods and were refined by full-matrix least-squares methods on F^2 with SHELXL-97.[34] All programs used during the crystal structure determination process are included in the WINGX software.[35] The program PLATON[36] was used to check the results of the X-ray studies and to analyze the hydrogen-bonding systems. The hydrogen atoms bound to nitrogen or phosphorus were located in a difference Fourier map and refined without restraints. All other hydrogen positions were calculated after each cycle of refinement using a riding model with C−H distances in the range 0.93−0.97 Å and their isotropic displacement parameters constrained to $1.2U_{eq}$(C) or $1.5U_{eq}$(C).

[TMPH][Cl$_2$B(C$_6$F$_5$)$_2$], 1a. $ClB(C_6F_5)_2$ (0.076 g, 0.2 mmol) and 2,2,6,6-tetramethylpiperidine (**TMP**) (0.0283 g, 0.2 mmol) were dissolved in 5 mL of toluene, giving a colorless solution. The reaction vessel was filled with H_2 (1000 mbar), and the solution was stirred at room temperature for 4 h. The reaction mixture was then concentrated to half of its volume, and hexane was added to induce precipitation. The mixture was filtered, washed with hexane, and dried *in vacuo*. **1a** was collected as a white solid. Yield: 35%. Anal. Calcd for $C_{21}H_{20}BCl_2F_{10}N$: C, 45.19; H, 3.61; N, 2.51. Found: C, 45.12; H, 3.63; N, 2.49. ^1H NMR (toluene-d_8, 300 MHz, 293 K): δ 5.90 (br, 2H, N-H), 0.91 ppm (m, overlap, 18H, TMP-C*H*). $^{11}B\{^1H\}$ NMR (toluene-d_8, 96 MHz, 293 K): δ −1.68 ppm (br). ^{19}F NMR (toluene, 282 MHz, 293 K): δ −134.56 (d, 4F, $^3J_{F-F}$ = 25 Hz, *o*-C_6F_5), −160.92 (t, 2F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −167.32 ppm (t, 4F, $^3J_{F-F}$ = 23 Hz, *m*-C_6F_5). $^{13}C\{^1H\}$ NMR (toluene-d_8, 75 MHz, 293 K): δ 148.32 (dm, $^1J_{C-F}$ = 258 Hz, *o*-C_6F_5), 140.51 (dm, $^1J_{C-F}$ = 263 Hz, *p*-C_6F_5), 138.15 (dm, $^1J_{C-F}$ = 262 Hz, *m*-C_6F_5), 59.17 (*o*-C_5H_7N), 34.37 (*m*-C_5H_7N), 26.93 (*C*H$_3$), 15.45 ppm (*p*-C_5H_7N). X-ray quality crystals were obtained from a mixture of toluene/hexane at 25 °C.

TMP-BH(C$_6$F$_5$)$_2$, 1b. $HB(C_6F_5)_2$ (0.0692 g, 0.2 mmol) and 2,2,6,6-tetramethylpiperidine (**TMP**) (0.0283 g, 0.2 mmol) were dissolved in 2 mL of toluene, and the colorless solution was stirred at room temperature for 30 min. The solvent was then removed to half of its original volume *in vacuo*. Hexane was added to induce precipitation, and the product was collected as a white solid. Yield: 86%. Anal. Calcd for $C_{21}H_{20}BF_{10}N$: C, 51.77; H, 4.14; N, 2.88. Found: C, 51.69; H, 4.22; N, 2.95. ^1H NMR (toluene-d_8, 300 MHz, 293 K): δ 4.18 (s, 1H, B-H), 1.16 (m, 2H, −CH$_2$), 0.96 (s, 6H, −CH$_3$), 0.87 (m, overlap, 4H, −CH$_2$), 0.82 (s, 6H, −CH$_3$), 0.73 ppm (s, 1H, N-H). $^{11}B\{^1H\}$ NMR (toluene-d_8, 96 MHz, 293 K): δ −11.82 ppm (br). ^{19}F NMR (toluene, 282 MHz, 293 K): δ −131.23 (s, 2F, *o*-C_6F_5), −135.06 (s, 2F, *o*-C_6F_5), −160.01 (t, 2F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −165.56 (s, 2F, *m*-C_6F_5), −166.92 ppm (s, 2F, *m*-C_6F_5). $^{13}C\{^1H\}$ NMR (toluene-d_8, 75 MHz, 293 K): δ 149.61 (dm, $^1J_{C-F}$ = 245 Hz, *o*-C_6F_5), 140.50 (dm, $^1J_{C-F}$ = 242 Hz, *p*-C_6F_5), 137.93 (dm, $^1J_{C-F}$ = 241 Hz, *m*-C_6F_5), 62.03 (*o*-C_5H_7N), 41.82 (*m*-C_5H_7N), 32.33 (*C*H$_3$), 16.01 ppm (*p*-C_5H_7N).

[*t*-Bu$_3$PH][Cl$_2$B(C$_6$F$_5$)$_2$], 2a. $ClB(C_6F_5)_2$ (0.076 g, 0.2 mmol) and tri-*tert*-butylphosphine (0.0405 g, 0.2 mmol) were dissolved in 5 mL of toluene, giving a yellow solution. The reaction vessel was filled with H_2 (1000 mbar), and the solution was stirred at room temperature for 2 h. Some precipitate had formed during the process. The reaction mixture was concentrated to half of its original volume, and hexane was added to induce precipitation. The mixture was filtered, washed with hexane, and dried *in vacuo*. **2a** was collected as a white solid. Yield: 47%. Anal. Calcd for $C_{24}H_{28}BCl_2F_{10}P$: C, 46.56; H, 4.56. Found: C, 46.48; H, 4.71. ^1H NMR ($CDCl_3$, 200 MHz, 293 K): δ 5.12 (d, 1H, $^1J_{H-P}$ = 440 Hz, P-*H*), 1.70 ppm (d, 27H, $^3J_{H-P}$ = 16 Hz P{(C(CH$_3$)$_3$}). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 64 MHz, 293 K): δ −4.50 ppm (br). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81 MHz, 293 K): δ 51.79 ppm (s). ^{19}F NMR ($CDCl_3$, 188 MHz, 293 K): δ −134.09 (dd, 4F, $^3J_{FF}$ = 23 Hz, $^4J_{F-Cl}$ = 7 Hz, *o*-C_6F_5), −161.61 (t, 2F, $^3J_{FF}$ = 23 Hz, *p*-C_6F_5), −166.80 ppm (td, 4F, $^3J_{FF}$ = 23 Hz, $^5J_{F-Cl}$ = 7 Hz, *m*-C_6F_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 MHz, 293 K): δ 147.32 (dm, $^1J_{C-F}$ = 242 Hz, *o*-C_6F_5), 139.21 (dm, $^1J_{C-F}$ = 247 Hz, *p*-C_6F_5), 136.9 (dm, $^1J_{C-F}$ = 247 Hz, *m*-C_6F_5), 37.38 (d, $^1J_{C-P}$ = 28 Hz, P{*C*(CH$_3$)$_3$}), 30.04 ppm (s, P(C(*C*H$_3$)$_3$). X-ray quality crystals were obtained from a mixture of toluene/hexane at 25 °C.

***t*-Bu$_3$P-BH(C$_6$F$_5$)$_2$ 2b.** In a NMR tube a suspension of $HB(C_6F_5)_2$ (0.0346 g, 0.1 mmol) in toluene-d_8 (0.5 mL) was prepared. Tri-*tert*-butylphosphine (0.02 g, 0.1 mmol) was then added to the suspension. The tube was capped with a rubber septum, and the suspension was vigorously shaken until all solid had dissolved (approximately 5 min). Anal. Calcd for $C_{24}H_{28}BF_{10}P$: C, 52.58; H, 5.15. Found: C, 52.50; H, 5.14. ^1H NMR (toluene-d_8, 200 MHz, 293 K): δ 4.20 (br, 1H, B-H), 1.11 ppm (d, 27H, $^3J_{H-P}$ = 12 Hz, P{(C(CH$_3$)}). $^{11}B\{^1H\}$ NMR (toluene-d_8, 64 MHz, 293 K): δ −27.40 ppm (br). $^{31}P\{^1H\}$ NMR (toluene-d_8, 81 MHz, 293 K): δ 47.64 ppm (br). ^{19}F NMR (toluene-d_8, 188 MHz, 293 K): δ −124.56 (br, 4F, *o*-C_6F_5), −158.87 (t, 2F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −164.18 ppm (br, 4F, *m*-C_6F_5). $^{13}C\{^1H\}$ NMR (toluene-d_8, 50 MHz, 293 K): δ 148.54 (dm, $^1J_{C-F}$ = 242 Hz, *o*-C_6F_5), 140.28 (dm, $^1J_{C-F}$ = 223 Hz, *p*-C_6F_5), 137.96 (dm, $^1J_{C-F}$ = 242 Hz, *m*-C_6F_5), 39.55 (d, $^1J_{C-P}$ = 18 Hz, P{*C*(CH$_3$)$_3$}), 31.14 ppm (s, P(C(*C*H$_3$)$_3$).

[*t*-Bu$_3$PH][H$_2$B(C$_6$F$_5$)$_2$], 2c. $HB(C_6F_5)_2$ (0.0692 g, 0.2 mmol) and tri-*tert*-butylphosphine (0.0405 g, 0.2 mmol) were dissolved in 5 mL of toluene, giving a slurry. The reaction vessel was filled with H_2 (1000 mbar), and the solution was stirred at 80 °C for 24 h. The reaction mixture was then concentrated to half of its original volume, and hexane was added to induce precipitation. The mixture was filtered, washed with hexane, and dried *in vacuo*. The product was collected as a white solid. Yield: 78%. Anal. Calcd for $C_{24}H_{30}BF_{10}P$: C, 52.39; H, 5.50. Found: C, 52.27; H, 5.41. ^1H NMR ($CDCl_3$, 200 MHz, 293 K): δ 5.12 (d, 1H, $^1J_{H-P}$ = 450 Hz, P-*H*), 3.01 (q, br, 1H, $^1J_{H-B}$ = 90 Hz, B-H), 1.70 ppm (d, 27H, $^3J_{H-P}$ = 16 Hz P{(C(CH$_3$)$_3$}). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 64 MHz, 293 K): δ −30.20 ppm (s). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81 MHz, 293 K): δ 53.88 ppm (s). ^{19}F NMR ($CDCl_3$,

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(33) *CrysAlisPro* (*Versions 1.171.32/33*); Oxford Diffraction Ltd: Abingdon, Oxfordshire, England.
(34) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.
(35) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.
(36) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7–13.

188 MHz, 293 K): δ −134.09 (d, 4F, $^3J_{FF}$ = 20 Hz, *o*-C_6F_5), −165.85 (t, 2F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), −167.97 ppm (t, 4F, $^3J_{FF}$ = 20 Hz, *m*-C_6F_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 MHz, 293 K): δ 147.48 (dm, $^1J_{C-F}$ = 243 Hz, *o*-C_6F_5), 139.65 (dm, $^1J_{C-F}$ = 244 Hz, *p*-C_6F_5), 136.36 (dm, $^1J_{C-F}$ = 247 Hz, *m*-C_6F_5), 36.88 (d, $^1J_{C-P}$ = 28 Hz, P{*C*(CH_3)}$_3$), 30.15 ppm (s, P(C(*C*H_3)$_3$).

[Mes$_3$PH][Cl$_2$B(C$_6$F$_5$)$_2$], 3a. $ClB(C_6F_5)_2$ (0.0380 g, 0.1 mmol) and trimesitylphosphine (0.0388 g, 0.1 mmol) were dissolved in 2 mL of toluene, giving a pink solution. The reaction vessel was filled with H_2 (1000 mbar), and the solution was stirred at room temperature for 2 h. The reaction mixture was then concentrated to half of its original volume, and hexane was added to induce precipitation. The mixture was filtered, washed with hexane, and dried *in vacuo*. **3a** was collected as a white solid. Yield: 30%. Anal. Calcd for $C_{39}H_{34}BCl_2F_{10}P$: C, 58.16; H, 4.26. Found: C, 58.08; H, 4.20. ^1H NMR (toluene-d_8, 200 MHz, 293 K): δ 8.48 (d, 1H, $^1J_{H-P}$ = 472 Hz, P-H), 6.52 (s, 6H, P(C_6H_2)$_3$), 2.16 (s, 9H, P(C_6H_2Me-*4*), 1.95 (s, 9H, P(C_6H_2Me-*2*)), 1.65 ppm (s, 9H, P(C_6H_2Me-*6*)). $^{11}B\{^1H\}$ NMR (toluene-d_8, 64 MHz, 293 K): δ −4.72 ppm (br). $^{31}P\{^1H\}$ NMR (toluene-d_8, 81 MHz, 293 K): δ −25.69 ppm (s). ^{19}F NMR (toluene-d_8, 188 MHz, 293 K): δ −132.51 (d, 4F, $^3J_{F-F}$ = 24 Hz, *o*-C_6F_5), −162.46 (t, 2F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −167.08 ppm (t, 4F, $^3J_{F-F}$ = 21 Hz, *m*-C_6F_5). $^{13}C\{^1H\}$ NMR (toluene-d_8, 50 MHz, 293 K): δ 148.32 (dm, $^1J_{C-F}$ = 242 Hz, *o*-C_6F_5), 146.42 (*para*-C_6H_2), 143.87 (*ortho*-C_6H_2), 139.95 (dm, $^1J_{C-F}$ = 247 Hz, *p*-C_6F_5), 137.23 (dm, $^1J_{C-F}$ = 247 Hz, *m*-C_6F_5), 132.49 (*meta*-C_6H_2), 112.28 (d, $^1J_{C-P}$ = 81 Hz, P-*C*$_6H_2$), 21.79 (C_6H_2Me-6), 21.56 (C_6H_2Me-4), 19.25 ppm (C_6H_2Me-2). X-ray quality crystals were obtained from toluene/hexane solution at 25 °C.

[Mes$_3$PH][HB(C$_6$F$_5$)$_3$], 3b. $HB(C_6F_5)_2$ (0.0692 g, 0.2 mmol) and trimesitylphosphine (0.0776 g, 0.2 mmol) dissolved in 5 mL of toluene, giving a slurry solution. The reaction vessel was filled with H_2 (1000 mbar), and the reaction mixture was stirred at room temperature for 8 h. The reaction mixture was concentrated to half of its original volume, and hexane was added to induce precipitation. The mixture was filtered, washed with hexane, and dried *in vacuo*. The product was collected as a white solid. Yield: 56%. Anal. Calcd for $C_{45}H_{35}BF_{15}P$: C, 59.89; H, 3.91. Found: C, 59.67; H, 3.61. ^1H NMR ($CDCl_3$, 200 MHz, 293 K): δ 8.06 (d, 1H, $^1J_{H-P}$ = 456 Hz, P-*H*), 7.12 (d, 6H, $^4J_{H-P}$ = 12 Hz, P(C_6H_2)$_3$), 2.37 (s, 9H, P(C_6H_2Me-*4*), 2.27 (s, 9H, P(C_6H_2Me-*2*)), 1.99 ppm (s, 9H, P(C_6H_2Me-*6*)). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 64 MHz, 293 K): δ −25.63 ppm (s). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81 MHz, 293 K): δ −26.95 ppm (s). ^{19}F NMR ($CDCl_3$, 188 MHz, 293 K): δ −134.64 (d, 6F, $^3J_{FF}$ = 21 Hz, *o*-C_6F_5), −165.74 (t, 3F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), −168.52 ppm (t, 6F, $^3J_{FF}$ = 24 Hz, *m*-C_6F_5).

[H$_2$B(C$_6$F$_5$)]$_2$, 3c. There was no evidence for signals of the bridging or terminal hydrides in the ^1H NMR spectrum. ^{19}F NMR (toluene-d_8, 282 MHz, 293 K): *syn*-$[H_2B(C_6F_5)]_2$ δ −136.79 (d, $^3J_{F-F}$ = 20 Hz, *o*-C_6F_5), −162.14 (t, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −166.59 ppm (t, $^3J_{F-F}$ = 20 Hz, *m*-C_6F_5). *anti*-$[H_2B(C_6F_5)]_2$ δ −137.51 (d, $^3J_{FF}$ = 21 Hz, *o*-C_6F_5), −160.69 (t, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), −166.23 ppm (t, $^3J_{FF}$ = 20 Hz, *m*-C_6F_5). ^{11}B NMR (toluene-d_8, 96 MHz, 293 K): δ 9.5 ppm (br).

[TTBPH][HB(C$_6$F$_5$)$_3$], 4a. $HB(C_6F_5)_2$ (0.0692 g, 0.2 mmol) and 2,4,6-tri-*tert*-butylpyridine (0.05 g, 0.2 mmol) were dissolved in 5 mL of toluene, giving a slurry. The reaction vessel was filled with H_2 (1000 mbar). The solution was stirred at 120 °C for 24 h, during which time a white precipitate formed. The reaction mixture was concentrated to half of its original volume, and hexane was added to induce complete precipitation. The mixture was filtered, washed with hexane, and dried *in vacuo*. The product was collected as a white solid. Yield: 38%. Anal. Calcd for $C_{35}H_{31}BF_{15}N$: C, 55.21; H, 4.10; N, 1.84. Found: C, 55.60; H, 4.18; N, 1.87. ^1H NMR ($CDCl_3$, 200 MHz, 293 K): δ 10.66 (br, 1H, N-*H*), 7.72 (s, 2H, Ar-*H*), 3.40 (q, br, 1H, $^1J_{H-B}$ = 86 Hz, B-*H*), 1.49 (s, 18H, *t*-Bu), 1.40 ppm (s, 9H, *t*-Bu). ^{19}F NMR ($CDCl_3$, 188 MHz, 293 K): δ −134.69 (d, 6F, $^3J_{F-F}$ = 21 Hz, *o*-C_6F_5), −165.41 (t, 3F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −168.43 ppm (t, 6F, $^3J_{F-F}$ = 21 Hz, *m*-C_6F_5). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 64 MHz, 293 K): δ −30.73 ppm (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 MHz, 293 K): δ 163.69 (*o*-C_5H_2N), 150.95 (*p*-C_5H_2N), 147.84 (dm, $^1J_{C-F}$ = 238 Hz, *o*-C_6F_5), 139.27 (dm, $^1J_{C-F}$ = 240 Hz, *p*-C_6F_5), 136.00 (dm, $^1J_{C-F}$ = 243 Hz, *m*-C_6F_5), 120.66 (*m*-C_5H_2N), 37.88 (*o*-*C*(CH_3)), 37.67 (*p*-*C*(CH_3)), 30.16 (*p*-C(*C*H_3)), 28.98 (*o*-C(*C*H_3)). X-ray quality crystals were obtained from a toluene/hexane solution at 25 °C.

[H$_2$B(C$_6$F$_5$)]$_2$, 3c. ^{19}F NMR (toluene-d_8, 282 MHz, 293 K): *syn*-$[H_2B(C_6F_5)]_2$ δ −137.08 (*o*-C_6F_5), −161.85 (*p*-C_6F_5), −166.65 ppm (*m*-C_6F_5); *anti*-$[H_2B(C_6F_5)]_2$ δ −137.70 (*o*-C_6F_5), −161.06 (*p*-C_6F_5), −166.32 ppm (t, $^3J_{F-F}$ = 20 Hz, *m*-C_6F_5). ^{11}B NMR (toluene-d_8, 96 MHz, 293 K): δ 8.2 ppm (br).

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Supporting Information Available: CIF files giving details of the X-ray crystal structure analysis (**1a**, **2a**, **3a**, **4a**). This material is available free of charge via the Internet at http://pubs.acs.org.