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PAPER

Reactions of substituted pyridines with electrophilic boranes†

Christopher B. Caputo,[a] Stephen J. Geier,[a] Daniel Winkelhaus,[a,b] Norbert W. Mitzel,[b] V. Nicolas Vukotic,[c] Stephen J. Loeb[c] and Douglas W. Stephan*[a]

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The lutidine derivative (2,6-Me_2)(4-Bpin)C_5H_2N when combined with $B(C_6F_5)_3$ yields a frustrated Lewis pair (FLP) which reacts with H_2 to give the salt $[(2,6\text{-}Me_2)(4\text{-Bpin})C_5H_2NH][HB(C_6F_5)_3]$ (**1**). Similarly 2,2′-$(C_5H_2(4,6\text{-}Me_2)N)_2$ and (4,4′-$(C_5H_2(4,6\text{-}Me_2)N)_2$ were also combined with $B(C_6F_5)_3$ and exposed to H_2 to give $[(2,2'\text{-}HN(2,6\text{-}Me_2)C_5H_2C_5H_2(4,6\text{-}Me_2)N][HB(C_6F_5)_3]$ (**2**) and $[(4,4'\text{-}HN(2,6\text{-}Me_2)C_5H_2C_5H_2(2,6\text{-}Me_2)N]$ $[HB(C_6F_5)_3]$ (**3**), respectively. The mono-pyridine-*N*-oxide 4,4′-$N(2,6\text{-}Me_2)C_5H_2C_5H_2(2,6\text{-}Me_2)NO$ formed the adduct $(4,4'\text{-}N(2,6\text{-}Me_2)C_5H_2C_5H_2(2,6\text{-}Me_2)NO)\text{-}(B(C_6F_5)_3)$ (**4**) which reacts further with $B(C_6F_5)_3$ and H_2 to give $[(4,4'\text{-}HN(2,6\text{-}Me_2)C_5H_2C_5H_2(2,6\text{-}Me_2)NO)B(C_6F_5)_3][HB(C_6F_5)_3]$ (**5**). In a related sense, 2-amino-6-CF_3-C_5H_3N reacts with $B(C_6F_5)_3$ to give $(C_5H_3(6\text{-}CF_3)NH)(2\text{-}NH(B(C_6F_5)_3))$ (**6**). Similarly, the species, 2-amino-quinoline, 8-amino-quinoline and 2-hydroxy-6-methyl-pyridine were reacted with $B(C_6F_5)_3$ to give the products as $(C_9H_6NH)(2\text{-}NHB(C_6F_5)_3)$ (**7**), $(C_9H_6N)(8\text{-}NH_2B(C_6F_5)_3)$ (**8**) and $(C_5H_3(6\text{-Me})NH)(2\text{-}OB(C_6F_5)_3)$ (**9**), respectively; while 2-amino-6-picoline, 2-amino-6-CF_3-pyridine, 2-amino-quinoline, 8-amino-quinoline and 2-hydroxy-6-methyl-pyridine react with $ClB(C_6F_5)_2$ to give the species $(C_5H_3(6\text{-R})NH)(2\text{-NH-}(ClB(C_6F_5)_2))$ (R = Me (**10**), R = CF_3 (**11**)) $(C_9H_6NH)(2\text{-NH}(ClB(C_6F_5)_2))$ (**12**), $(C_9H_6N)(8\text{-}NH_2ClB(C_6F_5)_2)$ (**13**) and $(C_5H_3(6\text{-Me})NH)(2\text{-}OClB(C_6F_5)_2)$ (**14**), respectively. In a similar manner, 2-amino-6-picoline and 2-amino-quinoline react with $B(C_6F_5)_2H$ to give $(C_5H_3(6\text{-Me})NH)(2\text{-}NH(HB(C_6F_5)_2))$ (**15**) and $(C_9H_6NH)(2\text{-NH}(HB(C_6F_5)_2))$ (**16**). The corresponding reaction of 8-amino-quinoline yields $(C_9H_6N)(8\text{-}NHB(C_6F_5)_2)$ (**17**). In a similar fashion, reaction of 2-amino-6-CF_3-pyridine resulted in the formation of (**18**) formulated as $(C_5H_3(6\text{-}CF_3)N)\text{-}(2\text{-}NH(B(C_6F_5)_2)$. Finally, treatment of **15** with *i*PrMgCl gave $(C_9H_6N)(2\text{-}NH(B(C_6F_5)_2))$ **(19)**. Crystallographic studies of **1**, **2**, **4**, **6**, **7**, **10**, **11**, **12** and **15** are reported.

Introduction

Over the last five years we and others[1–5] have explored a variety of novel main group systems derived from mixtures of Lewis acids and bases that do not form adducts. Such systems, referred to as "frustrated Lewis pairs" (FLPs) react with a variety of small molecules including H_2. This development has led to the unveiling of metal-free hydrogenation catalysts[1,3] for imines, aziridines, borane-bound nitriles,[6,7] enamines, silylenol-ethers,[8] dimines and a variety of N-based heterocycles. In other efforts, FLPs have been shown to effect the activation of tetrahydrofuran,[9–12] catecholborane,[13] olefins,[14] dienes,[15] terminal alkynes,[16–18] disulfides,[19] CO_2,[20] N_2O,[21] and cyclopropanes.[22] The initial reports of FLP systems were based on combinations of bulky phosphines and electrophilic borane centers.[23,24] Since then linked phosphinoboranes[25] pairs of bulky carbenes,[26–29] and amines[30–33] with $B(C_6F_5)_3$ and alkyl-linked phosphine-boranes [34–36] have been shown to be effective FLPs.

Of particular note is the use of sterically demanding pyridine as the base component of an FLP. Such systems are interesting as they were foreshadowed by the early work of Brown *et al.*[37] In that 1942 work, these authors described the inability of 2,6-lutidine to form a classical Lewis adduct with BMe_3. This was attributed to steric conflict of the B-bound methyl groups and the substituents on pyridine. In our more recent work we have shown[38,39] that combination of lutidine and $B(C_6F_5)_3$ gave an equilibrium between the classical adduct and the FLP (Scheme 1). Indeed the adduct could be isolated at low temperatures while at ambient temperatures FLP reactivity was exhibited.

In this paper, we continue to probe the reactivity of pyridine derivatives with electrophilic boranes. Herein, we report the activation of H_2 by several substituted pyridines in combination with $B(C_6F_5)_3$. In addition, a series of amino-pyridines are shown

[a]*Department of Chemistry, University of Toronto, 80 St George St, Toronto, Ontario, Canada, M5S3H6. E-mail: dstephan@chem.utoronto.ca; Tel: 01-416-946-3294*
[b]*Inorganic Chemistry and Structural Chemistry, Universität Bielefeld, Bielefeld, Germany*
[c]*Department of Chemistry & Biochemistry, University of Windsor, Windsor, Ontario, Canada, N9B 3P4*

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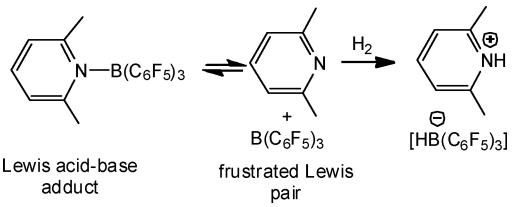


Scheme 1 Reactions of lutidine and $B(C_6F_5)_3$.

to react with electrophilic boranes. The nature of the products are presented and the implications for the further development of FLP chemistry are considered.

Experimental

General data

All preparations were done under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and an Innovative Technologies, Vacuum Atmospheres or a MBraun inert atmosphere glove box. Solvents (pentane, hexanes, toluene, diethyl ether and CH_2Cl_2) were purified employing a Grubbs' type column systems manufactured by Innovative Technology and stored over molecular sieves (4 Å). Molecular sieves (4 Å) were purchased from Aldrich Chemical Company and dried at 140 °C under vacuum for 24 h prior to use. Uninhibited THF was purchased from Caledon and distilled from sodium/benzophenone. Deuterated solvents were dried over Na/benzophenone (C_6D_6, C_7D_8, THF-d_8) or CaH_2 (CD_2Cl_2, C_6D_5Br). All common organic reagents were purified by conventional methods unless otherwise noted. ^1H, ^{13}C, ^{11}B, ^{19}F and ^{31}P NMR spectra were recorded on a Bruker Avance-300 spectrometer, a Varian NMR System 400 MHz or a Bruker Avance III 400 MHz spectrometer at 298 K. ^1H and ^{13}C NMR spectra were referenced to $SiMe_4$ using the residual solvent peak impurity of the given solvent. ^{31}P, ^{11}B and ^{19}F NMR spectra are referenced to 85% H_3PO_4, $BF_3(OEt_2)$, and $CFCl_3$, respectively. Chemical shifts are reported in ppm and coupling constants in Hz as absolute values. Combustion analyses were performed in house employing a Perkin Elmer CHN Analyzer. In some cases, repeated attempts to obtain satisfactory elemental analyses led to low C values. This was attributed to the formation of boron carbide during combustion. $B(C_6F_5)_3$ was purchased from Boulder Scientific Corporation. $(2,6\text{-}Me_2)C_5H_2NO$, $Br(2,6\text{-}Me_2)C_5H_2NO$, $(2,6\text{-}Me_2)(4\text{-Bpin})C_5H_2N$ and $6\text{-}NO_2(2,6\text{-}Me_2)C_5H_2NO$ were prepared following modified literature methods.[40–42]

Synthesis of $[(2,6\text{-}Me_2)(4\text{-Bpin})C_5H_2NH][HB(C_6F_5)_3]$ (1). $B(C_6F_5)_3$ (100 mg, 0.20 mmol) was dissolved in toluene (5 mL) and added to a solution of 45 mg of $(2,6\text{-}Me_2)(4\text{-Bpin})C_5H_2N$ (0.20 mmol) in toluene (5 mL). The solution was freeze–pump thawed for three cycles and backfilled with H_2 77 K (~4 atm). The solution was allowed to stir over night and pumped to dryness. The residue was washed two times with pentane (2 mL) and again pumped to dryness to give a white solid. Crystals were grown from slow evaporation of a toluene solution. Yield: 131 mg (90%). ^1H NMR (CD_2Cl_2): 11.89 (br s, 1H, N*H*); 7.90 (s, 2H, *m*-C*H*), 3.68 (q, 1H, $^1J_{B\text{-}H}$ = 85 Hz, *H*B), 2.71 (s, 6H, CH_3), 1.37 (s, 12H, CH_3), $^{13}C\{^1H\}$ (CD_2Cl_2) partial: 20.1 (*o*-C(*C*H_3)), 25.0 (OC_qCH_3), 86.8 (OC_q), 130.6 (*m*-CH), 137.0 (dm, $^1J_{C\text{-}F}$ = 245 Hz, C*F*), 138.5 (dm, $^1J_{C\text{-}F}$ = 245 Hz, C*F*), 148.6 (dm, $^1J_{C\text{-}F}$ = 240 Hz, C*F*), 152.6 (*o*-*C*(CH_3)), ^{19}F NMR (CD_2Cl_2): −134.2 (br d, 6F, $^3J_{F\text{-}F}$ = 22 Hz, *o*-C_6F_5), −163.3 (t, 3F, $^3J_{F\text{-}F}$ = 20 Hz, *p*-C_6F_5), −164.2 (m, 6F, *m*-C_6F_5); ^{11}B NMR (CD_2Cl_2): 29.6 (br s, *B*pin), −24.7 (d, $^1J_{B\text{-}H}$ = 85 Hz, H*B*); Anal. calcd. for $C_{31}H_{22}F_{15}NO_2$ (%): C, 49.84; N, 2.97; H, 1.87. Found: C, 50.07; N, 3.25; H, 2.06.

Synthesis of $[(2,2'\text{-}HN(4,6\text{-}Me_2)C_5H_2C_5H_2(4,6\text{-}Me_2)N][HB(C_6F_5)_3]$ (2). $(2,2'\text{-}(C_5H_2(4,6\text{-}Me_2)N)_2$ (0.041 g, 0.20 mmol) was added to a solution of $B(C_6F_5)_3$ (0.10 g, 0.20 mmol) in dichloromethane (5 mL). The solution was subjected to three freeze–pump–thaw cycles and backfilled with H_2 at 77 K (~4 atm). The solution was allowed to stir overnight at room temperature and then pumped to dryness. The solid was washed with hexane (2 × 2 mL) and again pumped to dryness. Yield: 136 mg (95%).

^1H NMR (CD_2Cl_2): 13.07 (br. s, N*H*, 1H), 7.87 (s, C*H*, 2H), 7.41 (s, C*H*, 2H), 3.48 (q, $^1J_{B\text{-}H}$ = 94 Hz, B*H*, 1H), 2.73 (s, CH_3 6H), 2.57 (s, CH_3 6H); ^{13}C NMR (CD_2Cl_2) partial: 22.04, 22.30, 120.77, 128.70, 144.83, 156.39, 157.18; ^{19}F NMR (CD_2Cl_2): −134.95 (d, $^3J_{F\text{-}F}$ = 22 Hz, 6F, *o*-C_6F_5), −165.53 (t, $^3J_{F\text{-}F}$ = 20 Hz, 3F, *p*-C_6F_5), −168.48 (td, $^3J_{F\text{-}F}$ = 22 Hz, $^4J_{F\text{-}F}$ = 7 Hz, 6F, *m*-C_6F_5); ^{11}B NMR (CD_2Cl_2): −25.51 (d, B*H*, $^1J_{B\text{-}H}$ = 94 Hz); Anal. Calcd. for $C_{32}H_{15}BF_{15}N_2$ (%) C: 52.92, H: 2.50, N: 3.86; found C: 52.34, H: 2.68, N: 3.74

Synthesis of $[(4,4'\text{-}HN(2,6\text{-}Me_2)C_5H_2C_5H_2(2,6\text{-}Me_2)N][HB(C_6F_5)_3]$ (3). $(2,2'\text{-}(C_5H_2(4,6\text{-}Me_2)N)_2$ (0.04 g, 0.188 mmol) was added to a solution of $B(C_6F_5)_3$ (0.096 g, 0.19 mmol) in 10 mL of dichloromethane. The solution was subjected to three freeze–pump–thaw cycles and backfilled with H_2 at 77 K (~4 atm). The solution was allowed to stir overnight at room temperature, but precipitate was immediately observed. The precipitate was filtered off and washed with hexanes (2 × 2 mL) and dried. Yield 0.064 g, 47%.

^1H NMR (d^8 THF) partial: 7.73 (s, C*H*, 2H), 3.62 (q, $^1J_{B\text{-}H}$ = 88 Hz, B*H*, 1H), 2.66 (s, CH_3 6H); ^{13}C NMR (CD_2Cl_2) partial: 19.22, 118.12, 133.17 (br), 134.57 (br), 135.58 (br), 136.94 (br), 145.25 (br), 154.87; ^{19}F NMR (CD_2Cl_2): −134.51 (d, $^3J_{F\text{-}F}$ = 21 Hz, 6F, *o*-C_6F_5), −167.32 (t, $^3J_{F\text{-}F}$ = 20 Hz, 3F, *p*-C_6F_5), −169.84 (td, $^3J_{F\text{-}F}$ = 22 Hz, $^4J_{F\text{-}F}$ = 7 Hz, 6F, *m*-C_6F_5); ^{11}B NMR (CD_2Cl_2): −25.48 (d, B*H*, $^1J_{B\text{-}H}$ = 88 Hz);. Anal. Calcd. for $C_{32}H_{18}BF_{15}N_2$ (%) C: 52.92 H: 2.50 N: 3.86; found C: 51.83 H: 2.47 N: 3.49

Synthesis of $(4,4'\text{-}N(2,6\text{-}Me_2)C_5H_2C_5H_2(2,6\text{-}Me_2)NO)(B(C_6F_5)_3$ (4). $4,4'\text{-}N(2,6\text{-}Me_2)C_5H_2C_5H_2(2,6\text{-}Me_2)NO$ (0.045 g, 0.20 mmol) was added to a solution of $B(C_6F_5)_3$ (0.10 g, 0.20 mmol) in 5 mL of dichloromethane. The solution was allowed to stir for 2 h; the solvent was removed *in vacuo* and the residue was washed with hexanes (2 × 2 mL). X-Ray quality crystals were grown from a CH_2Cl_2/Hex mixture. Yield: 140 mg (97%) ^1H NMR (CD_2Cl_2): 7.48 (s, N-Ox C*H*, 2H), 7.12 (s, C*H*, 2H), 2.66 (s, N-Ox CH_3, 6H), 2.58 (s, CH_3 6H); ^{13}C NMR (CD_2Cl_2) partial: 19.64, 24.63, 111.03, 123.82, 142.21, 149.71, 156.43, 160.07; ^{19}F NMR (CD_2Cl_2): −127.75 (s, 2F, *o*-C_6F_5), −132.17 (s, 2F, *o*-C_6F_5) – 133.96 (s, 2F, *o*-C_6F_5), −155.20 (br s, 1F *p*-C_6F_5), −159.76 (s, 2F *p*-C_6F_5), −163.93 (s, 2F, *m*-C_6F_5), −164.89 (s, 2F, *m*-C_6F_5), −165.38 (s, 2F, *m*-C_6F_5); ^{11}B NMR (CD_2Cl_2): 2.02 (br. s); Yield: Anal. Calcd. for $C_{32}H_{16}BF_{15}N_2O$ (%) C: 51.92, H: 2.18, N: 3.78; found C: 51.84, H: 2.76, N: 3.33.

Synthesis of $[(4,4'\text{-}HN(2,6\text{-}Me_2)C_5H_2C_5H_2(2,6\text{-}Me_2)NO)\ B(C_6F_5)_3][HB(C_6F_5)_3]$ (5). $4,4'\text{-}N(2,6\text{-}Me_2)C_5H_2C_5H_2(2,6\text{-}Me_2)NO$

(0.022 g, 0.098 mmol) was added to two equivalents of $B(C_6F_5)_3$ (0.10 g, 0.20 mmol) in 5 mL of dichloromethane. The solution was subjected to three freeze–pump–thaw cycles and backfilled with H_2 at 77 K (4 atm). The solution was allowed to stir overnight at room temperature and then pumped to dryness. The solid was washed with hexane (2 × 2 mL) and again pumped to dryness. Yield: 112 mg (90%)

^{1}H NMR (CD_2Cl_2): 12.69 (br. s, N*H*, 1H), 7.69 (s, C*H*, 2H), 7.55 (s, C*H*(NO-ring), 2H), 3.48 (q, $^1J_{B-H}$ = 60 Hz, B*H*, 1H), 2.80 (s, CH_3, 6H), 2.72 (s, CH_3(NO-ring), 6H); ^{13}C NMR (CD_2Cl_2) partial: 19.98, 20.67, 123.88, 124.43, 144.04, 152.40, 155.98, 158.48; ^{19}F NMR (CD_2Cl_2): −127.80 (s, 2F, *o*-C_6F_5), −132.20 (s, 2F, *o*-C_6F_5) −133.73 (s, 2F, *o*-C_6F_5), −134.26 (d, $^3J_{F-F}$ = 20 Hz, *o*-C_6F_5, 6F) −154.69 (br s, 1F *p*-C_6F_5), −159.37 (br. s, 2F *p*-C_6F_5), −162.95 (t, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5, 3F) −163.55 (s, 2F, *m*-C_6F_5), −164.61 (s, 2F, *m*-C_6F_5), −165.25 (s, 2F, *m*-C_6F_5), −166.56 (td, $^3J_{F-F}$ = 20 Hz, $^4J_{F-F}$ = 8 Hz, *m*-C_6F_5, 6F); ^{11}B NMR (CD_2Cl_2): 2.85 (br. s), −24.70 (d, B*H*, $^1J_{B-H}$ = 83 Hz); Anal. Calcd. for $C_{32}H_{16}BF_{15}N_2O$ (%) C: 51.92, H: 2.18, N: 3.78; found C: 51.84, H: 2.76, N: 3.33.

Synthesis of $(C_5H_3(6\text{-}CF_3)NH)(2\text{-}NH(B(C_6F_5)_3))$ (6), $(C_9H_6NH)(2\text{-}NHB(C_6F_5)_3)$ (7), $(C_9H_6N)(8\text{-}NH_2B(C_6F_5)_3)$ (8), $(C_5H_3(6\text{-}Me)NH)(2\text{-}OB(C_6F_5)_3)$ (9), $(C_5H_3(6\text{-}R)NH)(2\text{-}NH(ClB(C_6F_5)_2))$ (R = Me (10), R = CF_3 (11)) $(C_9H_6NH)(2\text{-}NH(ClB\text{-}(C_6F_5)_2))$ (12), $(C_9H_6N)(8\text{-}NH_2ClB(C_6F_5)_2)$ 13, $(C_5H_3(6\text{-}Me)NH)(2\text{-}OClB(C_6F_5)_2)$ 14, $(C_5H_3(6\text{-}Me)NH)(2\text{-}NH(HB(C_6F_5)_2))$ 15, $(C_9H_6NH)(2\text{-}NH(HB(C_6F_5)_2))$ 16, $(C_9H_6N)(8\text{-}NHB(C_6F_5)_2)$ 17, $(C_5H_3(6\text{-}CF_3)N)(2\text{-}NH(B(C_6F_5)_2)$ 18). These compounds were prepared in a similar fashion and thus only one preparation is detailed. For example: 2-amino-6-CF_3-pyridine (32 mg, 0.040 mmol) was added to a solution of $B(C_6F_5)_3$ (100 mg, 0.039 mmol) in CH_2Cl_2 (2 mL), The solution was allowed to stand for 2 h, then all volatiles were removed and the residue was washed with pentane (2 × 2 mL). The resulting white solid **6** was dried *in vacuo*.

6: Yield: 124 mg (95%). Crystals for X-ray diffraction were grown from the hexane wash layer. ^{1}H NMR ($CDCl_3$): 8.96 (br s, 1H, N*H*), 7.64 (dd, $^3J_{H-H}$ = 8 Hz, $^3J_{H-H}$ = 7 Hz, 1H, C*H*), 7.01 (d, $^3J_{H-H}$ = 9 Hz, 1H, C*H*), 6.87 (d, $^3J_{H-H}$ = 7 Hz, 1H, C*H*), 6.74 (br s, 1H, N*H*); ^{19}F NMR ($CDCl_3$): −67.8 (s, 3F, CF_3), −133.3 (d, $^3J_{F-F}$ = 22 Hz, 6F, *o*-C_6F_5), −155.3 (t, $^3J_{F-F}$ = 21 Hz, 3F, *p*-C_6F_5), −164.1 (tm, $^3J_{F-F}$ = 22 Hz, 6F, *m*-C_6F_5); ^{11}B NMR ($CDCl_3$): −10.9 (s); ^{13}C NMR ($CDCl_3$) partial: 108.5, 122.0, 137.4, (dm, $^1J_{C-F}$ = 255 Hz, *C*F), 140.0, 148.1, (dm, $^1J_{C-F}$ = 239 Hz, *C*F), 154.6. Anal. Calcd. for $C_{24}H_5BF_{18}N_2$ (%) C: 42.76, H: 0.75, N: 4.16; found C: 42.73, H: 0.95, N: 4.24.

7: Yield: 119 mg (93%). ^{1}H NMR ($CDCl_3$): 8.91 (br s, 1H, N*H*), 7.94 (d, $^3J_{H-H}$ = 10 Hz, 1H), 7.71 (d, $^3J_{H-H}$ = 8 Hz, 1H), 7.67 (t, $^3J_{H-H}$ = 8 Hz, 1H), 7.45 (t, $^3J_{H-H}$ = 8 Hz, 1H), 7.08 (d, $^3J_{H-H}$ = 8 Hz, 1H), 6.86 (dd, $^3J_{H-H}$ = 7 Hz, $^4J_{H-H}$ = 2 Hz, 1H), 6.70 (br s, 1H, N*H*); ^{13}C NMR ($CDCl_3$) partial: 116.1, 116.9, 120.4, 125.5, 128.8, 133.0, 135.2, 137.3 (dm, $^1J_{C-F}$ = 260 Hz, *C*F), 148.1 (dm, $^1J_{C-F}$ = 246 Hz, *C*F), 154.4. ^{19}F NMR ($CDCl_3$): −132.7 (d, $^3J_{F-F}$ = 20 Hz, 6F, *o*-C_6F_5), −155.8 (t, $^3J_{F-F}$ = 21 Hz, 3F, *p*-C_6F_5), −162.0 (tm, $^3J_{F-F}$ = 20 Hz, 6F, *m*-C_6F_5); ^{11}B NMR ($CDCl_3$): −10.7 (s); Anal. Calcd. for $C_{27}H_8BF_{15}N_2$ (%) C: 49.42, H: 1.23, N: 4.27; found C: 48.45, H: 1.18, N: 4.47.

8: Yield: 111 mg (87%). ^{1}H NMR ($CDCl_3$): 8.84 (d, $^3J_{H-H}$ = 4 Hz, 1H), 8.39 (br s, 2H, NH_2), 8.25 (d, $^3J_{H-H}$ = 8 Hz, 1H), 7.82 (d, $^3J_{H-H}$ = 8 Hz, 1H), 7.67 (d, $^3J_{H-H}$ = 7 Hz, 1H), 7.55 (m, 2H); ^{13}C NMR ($CDCl_3$) partial: 122.4, 122.8, 126.4, 128.0, 131.4, 136.7, 149.9; ^{19}F NMR ($CDCl_3$): −133.0 (br s, 6F, *o*-C_6F_5), −156.4 (t, $^3J_{F-F}$ = 20 Hz, 3F, *p*-C_6F_5), −163.1 (t, $^3J_{F-F}$ = 20 Hz, 6F, *m*-C_6F_5); ^{11}B NMR ($CDCl_3$): −5.8 (br s); Anal. Calcd. for $C_{27}H_8BF_{15}N_2$ (%) C: 49.42, H: 1.23, N: 4.27; found C: 48.92, H: 1.23, N: 4.08.

9: Yield: 110 mg (91%). ^{1}H NMR ($CDCl_3$): 9.90 (br s, 1H, N*H*), 7.88 (dd, $^3J_{H-H}$ = 9 Hz, $^3J_{H-H}$ = 7 Hz, 1H, *p*-C*H*), 6.88 (d, $^3J_{H-H}$ = 7 Hz, 1H), 6.71 (d, $^3J_{H-H}$ = 10 Hz, 1H), 2.65 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) partial: 19.9, 112.7, 114.4, 147.0, 147.3, 161.7. ^{19}F NMR ($CDCl_3$): −134.1 (d, $^3J_{F-F}$ = 23 Hz, 6F, *o*-C_6F_5), −157.8 (t, $^3J_{F-F}$ = 20 Hz, 3F, *p*-C_6F_5), −164.0 (tm, $^3J_{F-F}$ = 22 Hz, 6F, *m*-C_6F_5); ^{11}B NMR ($CDCl_3$): −1.5 (s); Anal. Calcd. for $C_{24}H_7BF_{15}NO$ (%) C: 46.41, H: 1.14, N: 2.26; found C: 45.97, H: 1.37, N: 2.79.

10: Yield: 119 mg (91%). ^{1}H NMR ($CDCl_3$): 11.10 (br s, 1H, N*H*), 7.48 (dd, $^3J_{H-H}$ = 9 Hz, $^3J_{H-H}$ = 7 Hz, 1H, *p*-C*H*), 6.58 (d, $^3J_{H-H}$ = 9 Hz, 1H), 6.46 (br s, 1H, N*H*), 6.38 (d, $^3J_{H-H}$ = 7 Hz, 1H), 2.39 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) partial: 19.6, 110.4, 114.4, 142.5, 144.8, 155.2. ^{19}F NMR ($CDCl_3$): −133.5 (dd, $^3J_{F-F}$ = 23 Hz, $^4J_{F-F}$ = 8 Hz 6F, *o*-C_6F_5), −155.9 (t, $^3J_{F-F}$ = 21 Hz, 3F, *p*-C_6F_5), −162.3 (td, $^3J_{F-F}$ = 21 Hz, $^4J_{F-F}$ = 8 Hz, 6F, *m*-C_6F_5); ^{11}B NMR ($CDCl_3$): −2.8 (br. s); Anal. Calcd. for $C_{18}H_8BClF_{15}N_2$ (%) C: 44.25, H: 1.65, N: 5.73; found C: 44.19, H: 1.94, N: 5.55.

11: Yield: 73 mg (87%). Crystals for X-ray diffraction were grown from the hexane wash layer. ^{1}H NMR ($CDCl_3$): 11.59 (br s, 1H, N*H*); 7.79 (t, $^3J_{H-H}$ = 8 Hz, $^3J_{H-H}$ = 7 Hz, 1H, *p*-C*H*), 7.07 (br m, 3H), ^{13}C NMR ($CDCl_3$) partial: 109.9, 117.8, 120.6, 121.3, 137.4 (dm, $^1J_{C-F}$ = 255 Hz, *C*F), 140.6 (dm, $^1J_{C-F}$ = 255 Hz, *C*F), 140.9, 147.8, (dm, $^1J_{C-F}$ = 244 Hz, *C*F), 154.9; ^{19}F NMR ($CDCl_3$): −66.9 (s, 3F, CF_3), −133.3 (br d, $^3J_{F-F}$ = 19 Hz, 4F, *o*-C_6F_5), −154.7 (br s, 2F, *p*-C_6F_5), −161.9 (br s, 4F, *m*-C_6F_5); ^{11}B NMR ($CDCl_3$): 0.4 (br s); Anal. Calcd. for $C_{18}H_9BF_{15}N_2$ (%) C: 39.85, H: 0.93, N: 5.16; found C: 40.12, H: 0.93, N: 5.00.

12: Yield: 87 mg (96%). Crystals for X-ray diffraction were grown from the hexane wash layer. ^{1}H NMR ($CDCl_3$): 11.10 (br s, 1H, N*H*), 8.03, (d, $^3J_{H-H}$ = 9 Hz, 1H), 7.76 (t, $^3J_{H-H}$ = 8 Hz, 1H), 7.75 (d, $^3J_{H-H}$ = 8 Hz, 1H), 7.52 (d, $^3J_{H-H}$ = 8 Hz, 1H), 7.50 (t, $^3J_{H-H}$ = 8 Hz, 1H), 7.06 (br s, 1H, N*H*), 6.89 (d, $^3J_{H-H}$ = 9 Hz, 1H), ^{13}C NMR ($CDCl_3$) partial: 116.9, 117.4, 120.8, 125.7, 128.7, 133.0, 141.8, 154.5; ^{19}F NMR ($CDCl_3$): −133.5 (d, $^3J_{F-F}$ = 21 Hz, 6F, *o*-C_6F_5), −155.7 (t, $^3J_{F-F}$ = 20 Hz, 3F, *p*-C_6F_5), −162.2 (td, $^3J_{F-F}$ = 20 Hz, $^4J_{F-F}$ = 8 Hz, 6F, *m*-C_6F_5); ^{11}B NMR ($CDCl_3$): −3.0 (s); Anal. Calcd. for $C_{21}H_8BClF_{10}N_2$ (%) C: 48.08, H: 1.54, N: 5.34; found C: 47.84, H: 1.79, N: 5.41.

13: Yield: 78 mg (86%). ^{1}H NMR ($CDCl_3$) partial: 8.88 (d, $^3J_{H-H}$ = 5 Hz, 1H), 8.43 (d, $^3J_{H-H}$ = 8 Hz, 1H), 7.65 (dd, $^3J_{H-H}$ = 7 Hz, $^3J_{H-H}$ = 5 Hz, 1H), 7.50 (t, $^3J_{H-H}$ = 8 Hz, 1H), 6.98 (d, $^3J_{H-H}$ = 7 Hz, 1H), 6.76 (d, $^3J_{H-H}$ = 7 Hz, 1H); ^{13}C NMR ($CDCl_3$) was not obtained due to poor solubility; ^{19}F NMR ($CDCl_3$): −134.9 (br s, 6F, *o*-C_6F_5), −156.3 (br s, 3F, *p*-C_6F_5), −163.1 (br s, 6F, *m*-C_6F_5); ^{11}B NMR ($CDCl_3$): 2.7 (br s); Anal. Calcd. for $C_{21}H_8BClF_{10}N_2$ (%) C: 48.08, H: 1.54, N: 5.34; found C: 47.26, H: 1.83, N: 5.17

14: Yield: 80 mg (90%). ^{1}H NMR ($CDCl_3$): 11.96 (br s, 1H, N*H*), 8.00 (t, $^3J_{H-H}$ = 8, 1H, *p*-C*H*), 7.16 (d, $^3J_{H-H}$ = 8 Hz, 1H), 6.96 (d, $^3J_{H-H}$ = 7 Hz, 1H), 2.65 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) partial: 19.9, 115.4, 116.0, 146.6, 146.8, 161.2;. ^{19}F NMR ($CDCl_3$): −134.0 (dd, $^3J_{F-F}$ = 22 Hz, $^4J_{F-F}$ = 7 Hz, 6F, *o*-C_6F_5), −156.8 (t, $^3J_{F-F}$ = 21 Hz, 3F, *p*-C_6F_5), −163.8 (td, $^3J_{F-F}$ = 21 Hz, $^4J_{F-F}$ = 8 Hz, 6F, *m*-C_6F_5); ^{11}B NMR ($CDCl_3$): 3.4 (s); Anal. Calcd. for $C_{18}H_7BClF_{10}NO$ (%) C: 44.17, H: 1.44, N: 2.86; found C: 44.12, H: 1.31, N: 3.19.

15: Yield: 119 mg (91%). Crystals for X-ray diffraction were grown from the hexane wash layer. ^{1}H NMR ($CDCl_3$): 9.85 (br s, 1H, N*H*), 7.32 (dd, $^3J_{H-H}$ = 9 Hz, $^3J_{H-H}$ = 7 Hz, 1H, *p*-C*H*), 6.47 (d, $^3J_{H-H}$ = 9 Hz, 1H), 6.26 (br s, 1H, N*H*), 6.18 (d, $^3J_{H-H}$ = 7 Hz, 1H), 3.85 (q, $^1J_{H-B}$ = 94 Hz, 1H, B*H*), 2.37 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) partial: 19.9, 108.7, 114.3, 141.5, 144.1, 155.2. ^{19}F NMR ($CDCl_3$): −135.4 (d, $^3J_{F-F}$ = 23 Hz, 6F, *o*-C$_6F_5$), −159.4 (t, $^3J_{F-F}$ = 20 Hz, 3F, *p*-C$_6F_5$), −164.1 (tm, $^3J_{F-F}$ = 20 Hz, 6F, *m*-C$_6F_5$); ^{11}B NMR ($CDCl_3$): −18.3 (d, $^3J_{H-B}$ = 94 Hz); Anal. Calcd. for $C_{18}H_9BF_{15}N_2$ (%) C: 47.61, H: 2.00, N: 6.17; found C: 47.26, H: 2.38, N: 6.36.

16: Yield: 82 mg (96%). ^{1}H NMR ($CDCl_3$): 9.97 (br s, 1H, N*H*), 7.88 (d, $^3J_{H-H}$ = 9 Hz, 1H), 7.71 (t, $^3J_{H-H}$ = 8 Hz, 1H), 7.68 (d, $^3J_{H-H}$ = 8 Hz, 1H), 7.47 (d, $^3J_{H-H}$ = 8 Hz, 1H), 7.42 (t, $^3J_{H-H}$ = 8 Hz, 1H), 6.87 (br s, 1H, N*H*), 6.80 (dd, $^3J_{H-H}$ = 9 Hz, $^3J_{H-H}$ = 2 Hz,1H), 4.11 (q, $^1J_{B-H}$ = 90 Hz, 1H, B*H*); ^{13}C NMR ($CDCl_3$) partial: 116.9, 117.1, 120.7, 125.2, 128.8, 132.8, 135.9, 140.9, 154.2; ^{19}F NMR ($CDCl_3$): −134.3 (d, $^3J_{F-F}$ = 22 Hz, 6F, *o*-C$_6F_5$), −158.2 (t, $^3J_{F-F}$ = 20 Hz, 3F, *p*-C$_6F_5$), −163.0 (tm, $^3J_{F-F}$ = 22 Hz, 6F, *m*-C$_6F_5$); ^{11}B NMR ($CDCl_3$): −18.0 (d, $^1J_{B-H}$ = 90 Hz); Anal. Calcd. for $C_{21}H_9BF_{10}N_2$ (%) C: 51.46, H: 1.85, N: 5.72; found C: 52.17, H: 2.06, N: 6.13.

17: Yield: 64 mg (76%). ^{1}H NMR ($CDCl_3$): 8.87 (d, $^3J_{H-H}$ = 5 Hz, 1H), 8.42 (d, $^3J_{H-H}$ = 8 Hz, 1H), 7.65 (t, $^3J_{H-H}$ = 8 Hz, 1H), 7.47 (d, $^3J_{H-H}$ = 8 Hz, 1H), 6.97 (d, $^3J_{H-H}$ = 8 Hz, 1H), 6.74 (d, $^3J_{H-H}$ = 7 Hz, 1H), 4.85 (br s, 1H, N*H*); ^{13}C NMR ($CDCl_3$) partial: 105.8, 108.9, 122.4, 129.1, 133.2, 140.4, 142.2, 147.9; ^{19}F NMR ($CDCl_3$): −134.9 (dd, $^3J_{F-F}$ = 21 Hz, $^4J_{F-F}$ = 8 Hz, 6F, *o*-C$_6F_5$), −155.9 (t, $^3J_{F-F}$ = 21 Hz, 3F, *p*-C$_6F_5$), −162.0 (tm, $^3J_{F-F}$ = 21 Hz, $^4J_{F-F}$ = 8 Hz, 6F, *m*-C$_6F_5$); ^{11}B NMR ($CDCl_3$): 2.4 (br s); Anal. Calcd. for $C_{21}H_7BF_{10}N_2$ (%) C: 51.68, H: 1.45, N: 5.74; found C: 51.44, H: 1.68, N: 5.60.

18: Yield: 58 mg (76%). ^{1}H NMR ($CDCl_3$): 7.82 (t, $^3J_{H-H}$ = 8 Hz, 1H, *p*-C*H*), 7.74 (br. s, 1H, N*H*), 7.46 (d, $^3J_{H-H}$ = 8 Hz, 1H), 7.02 (d, $^3J_{H-H}$ = 8 Hz, 1H),; ^{13}C NMR ($CDCl_3$) partial: 116.8, 117.0, 119.4, 122.1, 137.6 (dm, $^1J_{C-F}$ = 255 Hz, *C*F), 139.9, 142.8 (dm, $^1J_{C-F}$ = 264 Hz, *C*F), 147.4, (dm, $^1J_{C-F}$ = 246 Hz, *C*F), 153.7; ^{19}F NMR ($CDCl_3$): −67.9 (s, 3F, CF_3), −130.9 (br s, 4F, *o*-C$_6F_5$), −147.6 (br s, 1F, *p*-C$_6F_5$), −150.7 (br s, 1F, *p*-C$_6F_5$), −160.2 (br s, 4F, *m*-C$_6F_5$); ^{11}B NMR ($CDCl_3$): 37.0 (br s); Anal. Calcd. for $C_{18}H_4BF_{13}N_2$ (%) C: 42.72, H: 0.80, N: 5.54; found C: 42.34, H: 1.05, N: 5.83.

Synthesis of (C$_5$H$_3$(6-Me)N)(2-NHB(C$_6$F$_5$)$_2$) 19. *i*PrMgCl (0.657 mL of a 2.0 M solution in diethyl ether, 1.31 mmol) was added dropwise to a solution of **16** (642 mg, 1.31 mmol) in 10 mL of diethyl ether. The cloudy solution was allowed to stir for 2 h, hexanes (10 mL) was added and the solution was filtered. The filtrate was dried *in vacuo*. Yield: 543 mg (92%). ^{1}H NMR ($CDCl_3$): 7.79 (br s, 1H, N*H*), 7.46 (t, $^3J_{H-H}$ = 8 Hz, 1H, *p*-C*H*), 6.94 (d, $^3J_{H-H}$ = 8 Hz, 1H), 6.55 (d, $^3J_{H-H}$ = 8 Hz, 1H), 2.40 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) partial: 24.0, 111.0, 120.1, 138.5, 152.3, 158.1; ^{19}F NMR ($CDCl_3$): −131.7(m, 4F, *o*-C$_6F_5$), −148.9 (t, $^3J_{F-F}$ = 21 Hz, 1F, *p*-C$_6F_5$), −152.1 (t, $^3J_{F-F}$ = 20 Hz, 1F, *p*-C$_6F_5$), −160.9 (td, $^3J_{F-F}$ = 21 Hz, $^4J_{F-F}$ = 8 Hz, 2F, *m*-C$_6F_5$), −161.5 (td, $^3J_{F-F}$ = 22 Hz, $^4J_{F-F}$ = 8 Hz, 2F, *m*-C$_6F_5$); ^{11}B NMR ($CDCl_3$): 36.0 (br s);. Anal. Calcd. for $C_{18}H_7BF_{10}N_2$ (%) C: 47.82, H: 1.56, N: 6.20; found C: 47.44, H: 1.98, N: 6.23.

X-Ray crystallography. 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 a Bruker Apex II and Bruker SMART diffractometers employing Mo-Kα radiation (λ = 0.71073 Å). Data collection strategies were determined using Bruker Apex software and optimized to provide >99.5% complete data to a 2θ value of at least 55°. The data were collected at 150(±2) K for all crystals (Table 1). The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multi-scan method (SADABS). Non-hydrogen atomic scattering factors were taken from the literature tabulations.[43] The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine. 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 $w(F_o-F_c)^2$ where the weight w 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 1.20 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 the residual electron densities in each case were of no chemical significance.

Results and discussion

The lutidine derivative (2,6-Me$_2$)(4-Bpin)C$_5$H$_2$N was prepared by literature methods[42] and combined with B(C$_6$F$_5$)$_3$. This resulted in no reaction, yielding an FLP. However subsequent addition of H_2 resulted in the synthesis of the salt [(2,6-Me$_2$)(4-Bpin)C$_5$H$_2$NH][HB(C$_6$F$_5$)$_3$] (**1**) which was isolated in 90% yield. The protonated lutidine nitrogen atom resulted in a ^{1}H NMR signal at 11.89 ppm, while the B–H fragment of the anion gave rise to a quartet at 3.68 ppm with B–H coupling of 85 Hz. The ^{19}F NMR resonances at −134.2, −163.3 and −164.2 ppm were consistent with a borate anion. The ^{11}B NMR peaks at 29.6 and −24.7 ppm were consistent with the presence of the Bpin fragment on the lutidine and the borate anion, respectively. The formulation based on these data was further confirmed *via* X-ray crystallography (Fig. 1). The metric parameters of this salt were unexceptional. The formation of (**1**) is perhaps not surprising given the ability of lutidine and B(C$_6$F$_5$)$_3$ to activate H_2. It seems that the Bpin substituent has little impact on the basicity of the lutidine and thus on its ability to activate H_2.

The 2,2-bis-pyridine species 2,2′-(C$_5$H$_2$(4,6-Me$_2$)N)$_2$ was also combined with B(C$_6$F$_5$)$_3$ and exposed to H_2. The resulting product (**2**) gave rise to a ^{11}B NMR doublet at −25.51 ppm with B–H coupling of 94 Hz. This together with the ^{19}F NMR spectral data were consistent with the presence of a hydridoborate anion. The ^{1}H NMR signals at 13.07 and 3.48 ppm suggested the presence of NH and BH fragments, while the two singlets at 2.73 and 2.57 ppm were consistent with inequivalent lutidine-methyl groups supporting the formulation of (**2**) as

Table 1 Crystallographic data

	1	**2**	**4**	**6**	**7**	**10**
Formula	$C_{31}H_{22}B_2F_{15}NO_2$	$C_{32}H_{18}BF_{15}N_2$	$C_{32}H_{16}BF_{15}N_2O$	$C_{24}H_5BF_{18}N_2$	$C_{27}H_8BF_{15}N_2$	$C_{18}H_8BClF_{10}N_2$
M_r	747.12	726.29	740.28	647.11	656.16	488.52
Cryst. syst.	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	10.8926(6)	11.2901(7)	9.2565(9)	9.8877(10)	9.8040(3)	24.9904(18)
b/Å	11.0691(5)	16.2725(11)	13.5871(14)	11.1457(12)	9.9703(4)	13.1642(11)
c/Å	14.3170(8)	17.1597(12)	14.3235(15)	12.4221(12)	14.3432(5)	11.2738(8)
α (°)	99.984(2)	81.189(3)	69.707(4)	74.787(5)	90.240(2)	90
β (°)	109.274(2)	74.757(3)	83.127(5)	70.681(6)	109.000(2)	91.412(4)
γ (°)	95.546(2)	88.279(4)	79.205(5)	77.611(5)	113.800(2)	90
V/Å^3	1582.65(16)	3005.6(3)	1656.8(3)	1234.3(2)	1197.93(7)	3707.7(5)
Z	2	4	2	2	2	8
d(calc)/g cm^{-3}	1.568	1.605	1.484	1.814	1.819	1.750
R(int)	0.0374	0.0363	0.0296	0.0620	0.0215	0.1410
μ/mm^{-1}	0.157	0.159	0.148	0.203	0.189	0.313
Total data	26474	57933	27083	20118	18932	33247
Unique data	7200	16294	7614	5606	5435	8539
$F_o^2 > 2\sigma(F_o^2)$	4456	9681	5736	2902	4459	3644
Variables	464	917	462	414	406	595
R ($>2\sigma$)	0.0484	0.0632	0.0413	0.0448	0.0341	0.0585
R_w (all)	0.1476	0.1940	0.1278	0.1082	0.0930	0.1254
GOF	0.905	1.042	1.119	0.958	0.893	0.945

	11	**12**	**16**
Formula	$C_{18}H_5BClF_{13}N_2$	$C_{21}H_8BClF_{10}N_2$	$C_{18}H_9BF_{10}N_2$
wt	542.50	524.55	454.08
Cryst. syst.	Monoclinic	Monoclinic	Triclinic
Space grp	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a/Å	10.2702(3)	9.9317(4)	8.4351(16)
b/Å	31.6155(10)	17.7746(8)	10.3150(19)
c/Å	12.3047(4)	11.3370(6)	10.496(2)
α (°)	90	90	100.424(9)
β (°)	92.436(2)	97.843(2)	91.554(9)
γ (°)	90	90	109.413(8)
V/Å^3	3991.7(2)	1982.62(16)	843.3(3)
Z	8	4	2
d(calc)/g cm^{-3}	1.805	1.757	1.788
R(int)	0.0353	0.0700	0.0357
μ/mm^{-1}	0.321	0.300	0.183
Total data	35879	16792	26080
Unique data	9116	4556	7306
$>2\sigma(F_o^2)$	6762	3584	5014
Variables	647	324	293
R ($>2\sigma$)	0.0413	0.0352	0.0396
R_w (all)	0.1024	0.0934	0.1210
GOF	1.024	0.999	1.067

[(2,2′-HN(4,6-Me$_2$)C$_5$H$_2$C$_5$H$_2$(4,6-Me$_2$)N][HB(C$_6$F$_5$)$_3$]. The formulation of this salt was also confirmed crystallographically (Fig. 2).

In a similar fashion, the corresponding reaction of (4,4′-(C$_5$H$_2$(4,6-Me$_2$)N)$_2$, B(C$_6$F$_5$)$_3$ and H$_2$ resulting in the formation of the analogous salt [(4,4′-HN(2,6-Me$_2$)C$_5$H$_2$C$_5$H$_2$(2,6-Me$_2$)N][HB(C$_6$F$_5$)$_3$] (**3**) in 47% yield. The spectral data for (**3**) were similar to those for (**2**) although rapid intermolecular proton exchange presumably accounts for the single lutidine methyl resonance and the inability to observe the NH proton. Suzuki style cross coupling reaction between the 4-lutidine boronic ester described above and 4-bromolutidine *N*-oxide[40–42] afforded the mono-pyridine-*N*-oxide 4,4′-N(2,6-Me$_2$)C$_5$H$_2$C$_5$H$_2$(2,6-Me$_2$)NO. This species was shown to form an adduct (**4**) with B(C$_6$F$_5$)$_3$. This was evidenced by the ^{11}B NMR chemical shift at 2.02 ppm and the observation of eight ^{19}F NMR resonances attributable to the fluoroarene-rings which are inequivalent as a result of O binding. ^{1}H NMR data revealed the expected inequivalent pyridine and methyl signals. The formulation of (**4**) as (4,4′-N(2,6-Me$_2$)C$_5$H$_2$C$_5$H$_2$(2,6-Me$_2$)NO)(B(C$_6$F$_5$)$_3$ was confirmed *via* a crystallographic study (Fig. 3). The B–O bond length in (**4**) was determined to be 1.560(2) Å, while the B–O–N angle was 118.5(1)°. The remaining metrics were as expected.

The subsequent reaction of (**4**) with B(C$_6$F$_5$)$_3$ and H$_2$ led to the isolation of a new species (**5**). This species gave rise ^{1}H NMR signals at 12.69 and 3.48 ppm attributable to NH and BH fragments. The ^{19}F NMR spectrum showed 11 sets of peaks consistent with the pyridine-*N*-oxide adduct and a free hydridoborate anion. This was further supported by the observation of ^{11}B NMR signals at 2.85 and –24.70 ppm, respectively.

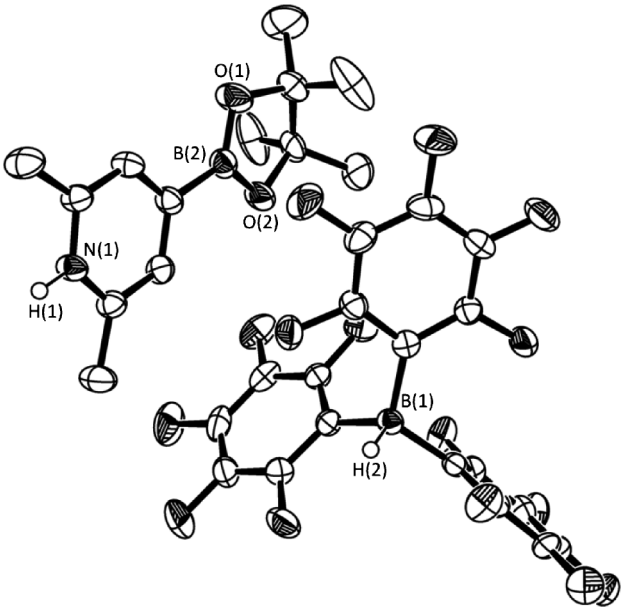


Fig. 1 ORTEP drawing of **1**, hydrogen atoms with the exception of NH and BH protons are omitted for clarity. 50% thermal ellipsoids are shown.

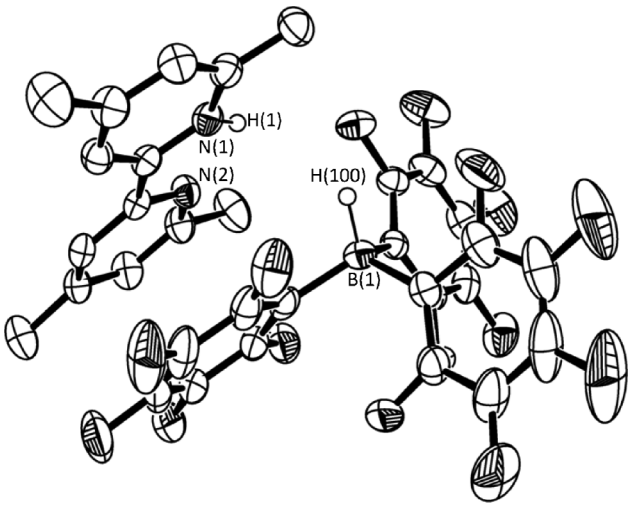


Fig. 2 ORTEP drawing of **2**, hydrogen atoms with the exception of NH and BH protons are omitted for clarity. 50% thermal ellipsoids are shown. One of two independent molecules in the asymmetric unit is shown.

Collectively these data are in accord with the formulation of (**5**) as [(4,4′-HN(2,6-Me_2)$C_5H_2C_5H_2$(2,6-Me_2)NO)$B(C_6F_5)_3$] [HB-(C_6F_5)$_3$] (Scheme 2). The nature of **5** is an interesting example of a product that simultaneously exhibits both classical Lewis acid–base adduct formation and FLP reactivity.

We have previously demonstrated that reaction of 2-amino-6-picoline with $B(C_6F_5)_3$ showed quantitative formation of a new zwitterionic product (C_5H_3(6-Me)NH)(2-NH($B(C_6F_5)_3$)).[38] In a related fashion, herein the reaction of the 2-amino-6-CF_3-pyridine with $B(C_6F_5)_3$ was examined and shown to result in the formation of a new species (**6**) which was isolated in 95% yield (Scheme 3). This species gave rise to a ^{11}B NMR signal at −10.9 ppm while the ^{19}F NMR resonances were observed at −67.8, −133.3, −155.3 and −164.1 ppm. These data suggest the presence of a borate anion. ^{1}H NMR data showed resonances at 8.96 and 6.74 ppm

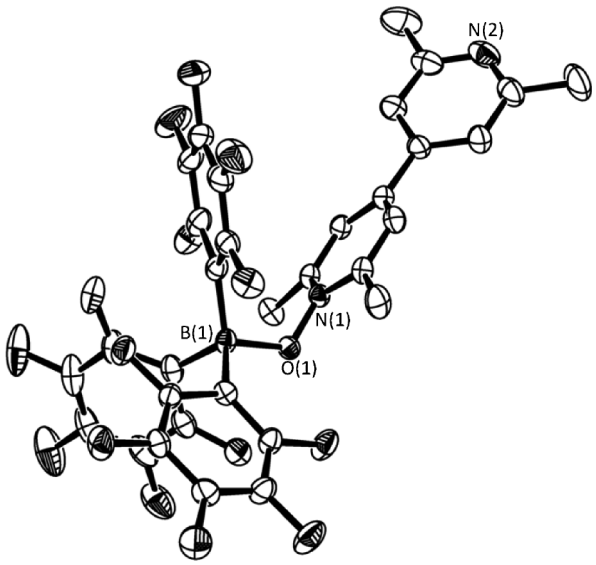
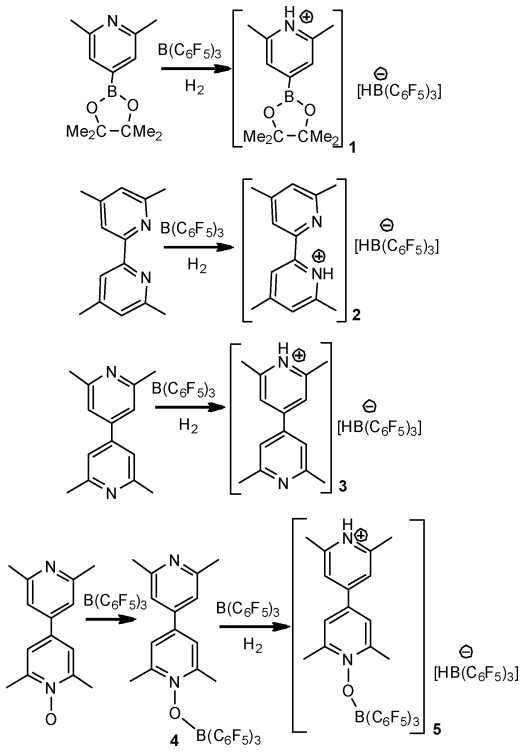


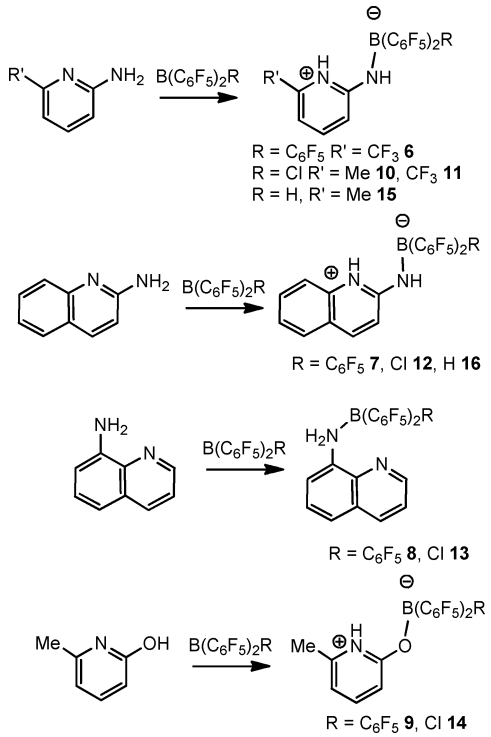
Fig. 3 ORTEP drawing of **4**, hydrogen atoms are omitted for clarity. 50% thermal ellipsoids are shown.



Scheme 2 Synthesis of **1–5**.

attributed to N*H* protons consistent with the proposition of the formulation of (**6**) as (C_5H_3(6-CF_3)NH)(2-NH($B(C_6F_5)_3$)). This zwitterionic formulation was subsequently confirmed *via* an X-ray crystallographic study (Fig. 4). These data confirmed binding of the B to the 2-amido-substituent with concurrent transfer of a proton to the pyridyl-N atom. The N–B distance was determined to be 1.564(3) Å.

It is interesting to note that while the pyridyl N-atom is expected to be more basic than the amino-substituent, it remains inaccessible to the Lewis acid. The result is interaction of the B



Scheme 3 Synthesis of **6–16**.

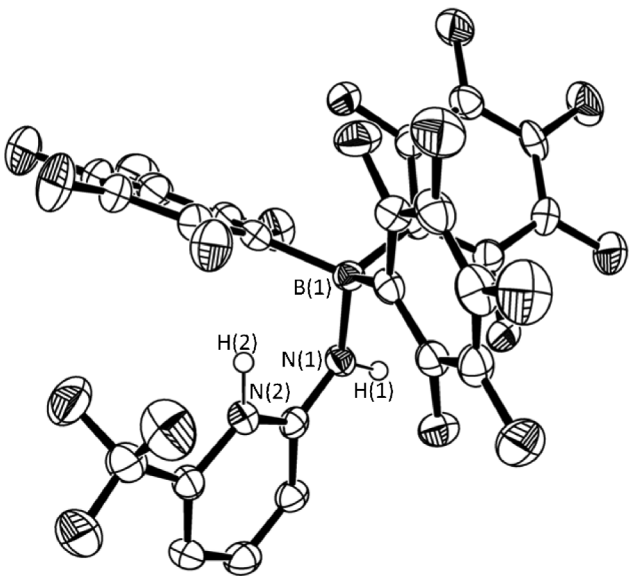


Fig. 4 ORTEP drawing of **6**, hydrogen atoms with the exception of NH and BH protons are omitted for clarity. 50% thermal ellipsoids are shown.

with the amino-substituent which increases the acidity of the NH_2 protons, prompting proton transfer to the more basic pyridyl N-atom.

In a related fashion, the species 2-amino-quinoline, 8-amino-quinoline and 2-hydroxy-6-methyl-pyridine were reacted with $B(C_6F_5)_3$. The resulting products formed in yields ranging from 87–93% and exhibited spectroscopic data similar to those exhibited by (**6**) prompting the formulation to the products as $(C_9H_6NH)(2\text{-}NHB(C_6F_5)_3)$ (**7**), $(C_9H_6N)(8\text{-}NH_2B(C_6F_5)_3)$ (**8**) and $(C_5H_3(6\text{-}Me)NH)(2\text{-}OB(C_6F_5)_3)$ (**9**), respectively. A crystal structure of (**7**)

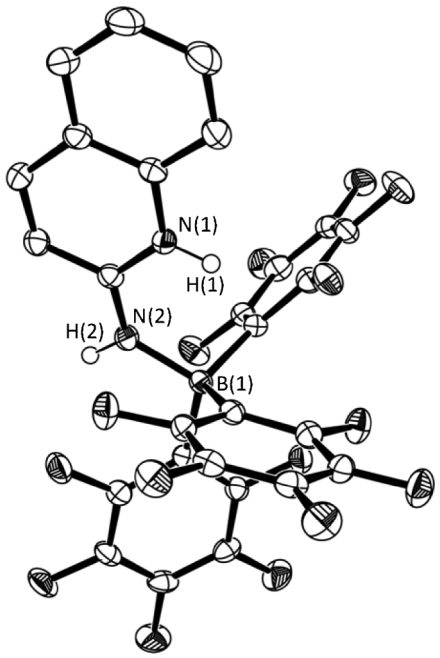


Fig. 5 ORTEP drawing of **7**, hydrogen atoms with the exception of NH protons are omitted for clarity. 50% thermal ellipsoids are shown.

confirmed the nature of this species (Fig. 5). The B–N bond length in this case was determined to be 1.5676(19) Å. It is noteworthy that proton transfer to the pyridyl nitrogen was not observed in **8**. This is indicated by observation of a single ^1H resonance attributable to the two amino protons at 8.39 ppm. This presumably results from the lesser basicity of the ring-N atom in 8-amino-quinoline, in comparison to those in 2-amino-quinoline. In addition, the proximity of the amino-substituent to the quinoline-N in 2-amino-quinoline makes the amine protons more acidic upon interaction with borane than those in 8-amino-quinoline.

A series of analogous species were also derived from reactions with $B(C_6F_5)_2Cl$. Thus reactions of 2-amino-6-picoline, 2-amino-6-CF_3-pyridine, 2-amino-quinoline, 8-amino-quinoline and 2-hydroxy-6-methyl-pyridine lead to the formation of the species $(C_5H_3(6\text{-}R)NH)(2\text{-}NH(ClB(C_6F_5)_2))$ (R = Me (**10**), R = CF_3 (**11**)) $(C_9H_6NH)(2\text{-}NH(ClB(C_6F_5)_2))$ (**12**), $(C_9H_6N)(8\text{-}NH_2ClB(C_6F_5)_2)$ (**13**) and $(C_5H_3(6\text{-}Me)NH)(2\text{-}OClB(C_6F_5)_2)$ (**14**), respectively. These products were isolated in high yields of 86–96%. The species **10–12** and **14** exhibited ^{11}B NMR signals at 0.4 to −3.4 ppm consistent with the presence of an anionic chloroborate center. Crystallographic studies of **10–12** confirmed these formulations (Fig. 6–8). The B–N bonds lengths in these species were found to be 1.536(6), 1.534(3) and 1.544(2) Å while the B–Cl bond lengths were typically falling in the range from 1.945(4), 1.929(2) and 1.907(2) Å, respectively. In the case of **13** the ^{11}B resonance at 2.7 ppm inferred that similar to **8**, amino-proton transfer to the ring N has not occurred, although the ^1H NMR resonance for the NH_2 fragment was not observed. Thus while **10–12** and **14** are best described as zwitterions, **13** is a classical Lewis acid–base adduct.

In a similar manner, 2-amino-6-picoline and 2-amino-quinoline react with "*Piers borane*" $B(C_6F_5)_2H$ to form the analogous borohydride zwitterions $(C_5H_3(6\text{-}Me)NH)(2\text{-}NH(HB(C_6F_5)_2))$ (**15**) and $(C_9H_6NH)(2\text{-}NH(HB(C_6F_5)_2))$ (**16**) in greater than 90% yields. The presence of the borohydride unit is consistent with the ^{11}B

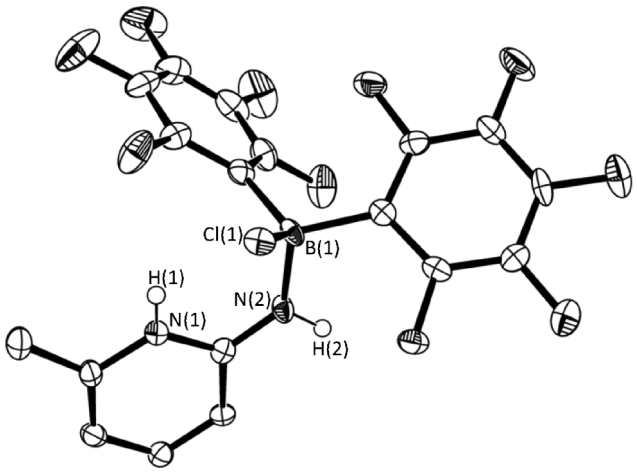


Fig. 6 ORTEP drawing of **10**, hydrogen atoms with the exception of NH protons are omitted for clarity. 50% thermal ellipsoids are shown. One of two independent molecules in the asymmetric unit is shown.

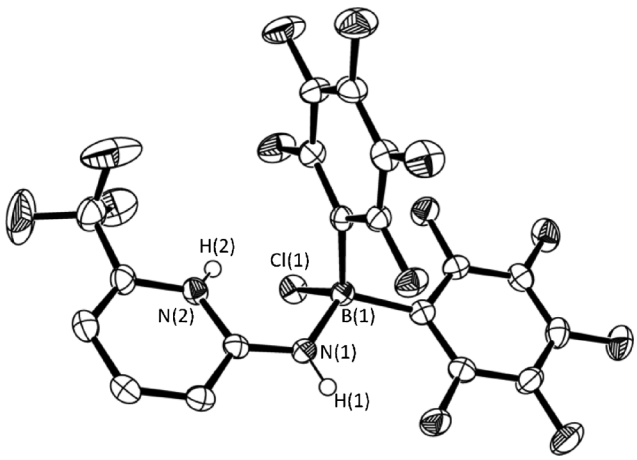


Fig. 7 ORTEP drawing of **11**, hydrogen atoms with the exception of NH protons are omitted for clarity. 50% thermal ellipsoids are shown. One of two independent molecules in the asymmetric unit is shown.

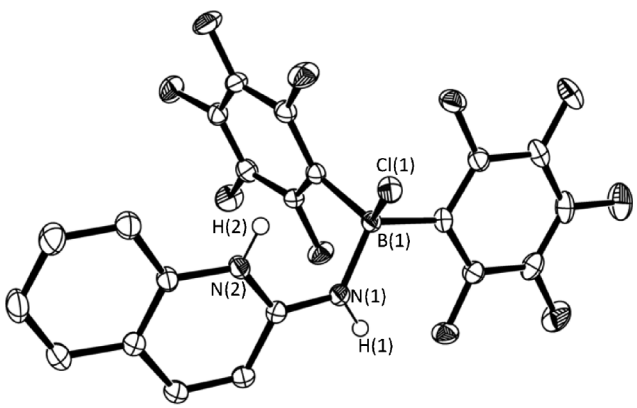


Fig. 8 ORTEP drawing of **12**, hydrogen atoms with the exception of NH protons are omitted for clarity. 50% thermal ellipsoids are shown.

NMR signals at −18.3 and −18.0 ppm, respectively with boron-hydride couplings of 94 and 90 Hz. The structure for (**15**) further confirmed these formulations (Fig. 9). The B–N bond length in **15** was found to be 1.552(1) Å, similar to those observed for other

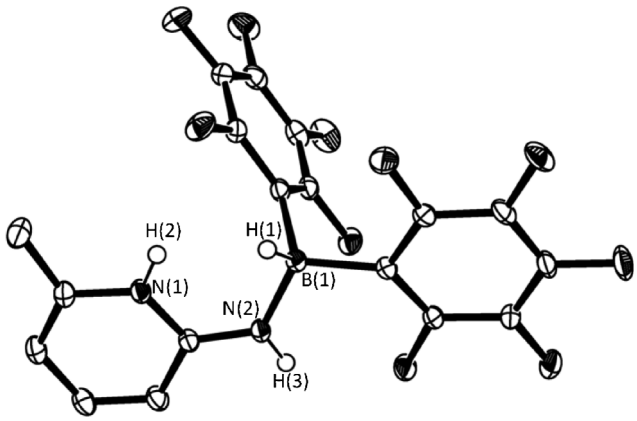
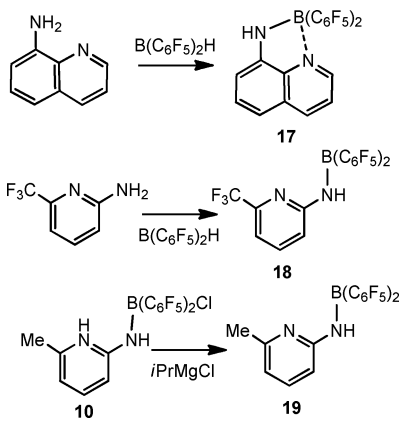


Fig. 9 ORTEP drawing of **15**, hydrogen atoms with the exception of NH and BH protons are omitted for clarity. 50% thermal ellipsoids are shown.

amido-fluoroarylborate anions[27,44,45] and significantly shorter than those seen in amine–borane adducts.[46]

In marked contrast, the corresponding reaction of 8-amino-quinoline with $B(C_6F_5)_2H$ gave rise to a new species (**17**) in 76% yield (Scheme 4). This species exhibited a broad ^{11}B resonance at 2.4 ppm while the ^{19}F NMR signals showed a gap between the *meta* and *para* fluorine atoms of 7.1 ppm. Moreover the ^{1}H NMR data showed only a single resonance attributable to the NH fragment at 4.85 ppm. These data suggest a formulation of (**17**) as an amido-borane derivative $(C_9H_6N)(8\text{-}NHB(C_6F_5)_2)$. Stabilization of **17** is provided by interaction of the B center with the quinoline-N yielding an intramolecular Lewis acid–base adduct. This view is consistent with the ^{11}B chemical shift. This species is proposed to form an initial amine–borane adduct analogous to **8** and **13** with subsequent loss of H_2 to give (**17**). If the quinoline-N atom is transiently protonated, the elimination of H_2 could be imagined to proceed by a six-member transition state involving proton–hydride interaction.



Scheme 4 Synthesis **17–19**.

In a similar fashion, the reaction of 2-amino-6-CF_3-pyridine resulted in the formation of (**18**) formulated as $(C_5H_3(6\text{-}CF_3)N)(2\text{-}NH(B(C_6F_5)_2))$. In this case the three coordinate B was evidenced by the broad ^{11}B resonance at 37.0 ppm and a large *meta–para* gap of 11.0 ppm in the ^{19}F NMR spectrum. This reaction is reminiscent of work by Piers and co-workers, who demonstrated that the *ortho*-substituted ammonium borate 1-(Ph_2HN)-2-$(BH(C_6F_5)_2)C_6H_4$

rapidly loses H_2 to form the linked amine–borane 1-(Ph_2N)-2-($B(C_6F_5)_2$)C_6H_4.[47] As is the case with **17**, inequivalent C_6F_5 rings are observed in the ^{19}F NMR spectrum of **18** due to restricted rotation about the N–B bond.

Employing a strategy used to generate $Mes_2PC_6F_4B(C_6F_5)_2$ from $Mes_2PHC_6F_4BH(C_6F_5)_2$, **10** was treated with *i*PrMgCl to give **19** in 92% yield. This species exhibits a ^{11}B NMR signal at 36.0 ppm similar to that seen for **18**. As well inequivalent C_6F_5 rings are apparent in the ^{19}F NMR data inferring the generation of three coordinate B *via* formal loss of proton and chloride from **10** and thus the formulation of **19** as (C_9H_6N)(2-$NH(B(C_6F_5)_2)$). It is noteworthy that **19** is structurally similar to the phosphine-borane $Mes_2PCH_2CH_2B(C_6F_5)_2$. Consequently the possibility of reaction with H_2 was considered. However addition of H_2 to **19** did not regenerate **15**. Instead, several uncharacterized degradation products were observed. The inability of **19** to activate H_2 cleanly is consistent with previous results for fluoro-arylborane derivatives with p-donating substituents. Such groups diminish the Lewis acidity of the boron center, precluding FLP activation of H_2 between the boron and pyridyl-nitrogen.

Conclusions

Herein we have described a series of lutidine derivatives that exhibit the ability in combination with boranes to effect FLP activation of H_2, even when the other end of the molecule is engaged in a classical Lewis acid–base adduct. In addition, amino-pyridine and amino-quinoline derivatives have been shown to react with boranes. In these cases, these systems show that steric protection of the ring N-atoms prompts N–B bond formation at more accessible amino-substituents. Often this coordination prompts proton transfer to the more basic ring-N, although in the case of 8-amino-quinoline derivatives, such a transfer is not seen due to the result of simple acidity basicity considerations. Efforts to explore the reactivity of other systems that exhibit FLP character continues to be a focus of our research.

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