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Borohydrides from Organic Hydrides: Reactions of Hantzsch's Esters with $B(C_6F_5)_3$

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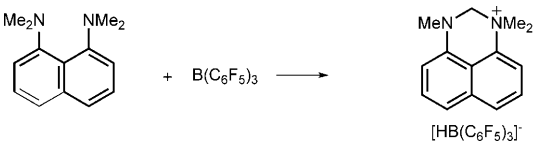
Abstract: We report herein that the reaction between a series of Hantzsch's ester analogues **1a–d** with the Lewis acidic species $B(C_6F_5)_3$ results in facile transfer of hydride to boron. The main products of this reaction are pyridinium borohydride salts **2a–d**, which are obtained in high to moderate yields. The *N*-substituted substrates (*N*-Me, *N*-Ph) reacted in high yield 90–98% and the connectivity of the products were confirmed by an X-ray crystallographic analysis of the *N*-Me borohydride salt **2a**. Unsubstituted Hanztsch's ester **1a** reacted less effectively generating only 60% of the corresponding borohydride salt, with the balance of the material sequestered as the ester-bound Lewis acid–base adduct **3a**. Formation of the Lewis acid–base adduct could be minimized by increasing the steric bulk about the ester groups as in **1d**. The connectivity of the carbonyl-bound adduct was confirmed by an X-ray crystallographic analysis of **3e** the product of the reaction of methyl ketone **1e** with $B(C_6F_5)_3$. We also explored the generation of these pyridinium salts by employing frustrated Lewis pair methodology. However, the reaction of mixtures of the corresponding pyridine and $B(C_6F_5)_3$ with hydrogen gas only resulted in formation of trace amounts of the pyridinium borohydride, along with the Lewis acid–base adduct of the starting material and $B(C_6F_5)_3$. The 1,2-dihydropyridine adduct was the final product of this reaction. This was ascribed to the low basicity of the pyridine nitrogen and the complicating formation of an ester bound Lewis acid–base adduct.

Keywords: boron · C–H activation · Frustrated Lewis pairs · Hantzsch's ester · hydride transfer

Introduction

Reactions that utilize the reactivity of boron–hydrogen bonds are of considerable importance. In organic chemistry, hydroboration and borohydride reagents that perform selective reductions as well as C–H functionalizations are critically important.[1–3] On the other hand, boron–hydride species such as ammonia borane[4–7] are of considerable interest as molecular hydrogen storage materials. Standard methods of borohydride synthesis involve the use of inorganic hydrides such as sodium hydride.[4,7–14] While these methods are effective, the preparation of inorganic hydrides is energy intensive. This is particularly problematic for borohydrides destined for use in energy storage applications where cost effective reconstitution of the boron hydride is essential.[4,6] Other methods for hydride transfer to boron have included less reactive species such as R_3SiH,[9] Bu_3SnH,[10] and Rh hydrides,[14] although the use of these reagents on stoichiometric scale is prohibitive.

An alternative strategy for the formation of B–H species that would involve the use of electron-rich "organic hydrides" has received surprisingly little attention.[15–20] In scattered examples, bulky amines have been shown to act as hydride donors[21] in reactions with $B(C_6F_5)_3$ via a C–H activation alpha to nitrogen [Eqs. (1–3)].[15–18]



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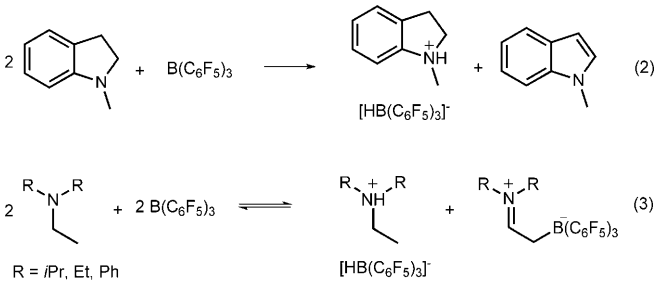


The quintessential organic hydride donor is NADH,[22] its stable analogues Hantzsch's ester[23] and derivatives **1a–e**, (Figure 1) have a reducing power comparable to that of NEt_3BH_3[24] and unusually low C4–H heterolytic bond dissociation energies of ~70 kcal mol^{-1}.[25,26] 1,4-Dihydropyridines[24–27] such as Hantzsch's ester have found widespread application as reducing agents in organic and bioorganic chemistry, however, few reports have probed their application in hydride transfer reactions to Lewis acidic organoelement species such as $B(C_6F_5)_3$.

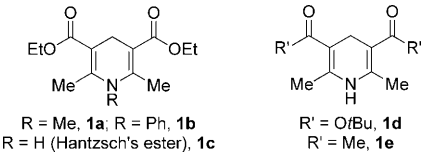
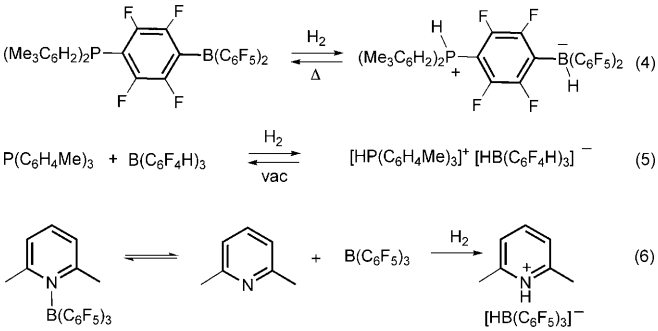


Figure 1. Hantzsch's ester and its derivatives

An alternative strategy for the formation of B–H bonds would employ the recently developed concept of "frustrated Lewis pairs".[28–34] In these cases, sterically hindered phosphines,[29] carbenes,[33,35,36] amines[17] or pyridines[37,38] act in concert with Lewis acids to affect the heterolytic activation of H_2 [Eqs. (4–6)].

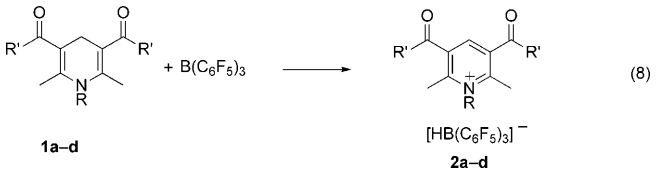


Judicious tuning of the steric and electronic features of the reagents allows some of these reactions to be reversible.[28,34,39] Most notably, Equation (6) describes the use of substituted pyridines which are capable of promoting the activation of hydrogen to yield $HB(C_6F_5)_3^-$ and the corresponding pyridinium cation.[37,38] This salt is closely related to the product that would be prepared by the direct C-H activation using Hantzsch's ester as the hydride donor and $B(C_6F_5)_3$ as the acceptor [Eq. (7)]. Herein, we report the use

of both of these methods, C–H activation from 1,4-dihydropyridines and H_2 activation via the corresponding pyridine, to generate B–H bonds with Lewis acidic boranes such as $B(C_6F_5)_3$. Although hydride transfer to $B(C_6F_5)_3$ with other reagents has been shown to occur via a stepwise process involving an initial electron transfer followed by hydrogen-atom transfer,[21] based on the oxidation potential of Hantzsch's ester and the estimated reduction potential of $B(C_6F_5)_3$, we anticipate that the hydride transfers described herein occur via a concerted mechanism.[40] However, definitive mechanistic studies have not been carried out on these particular systems to rule out stepwise processes.

Results and Discussion

Initially focusing on C-H activation chemistry, we examined the reaction of *N*-alkylated 1,4-dihydropyridines **1a** (*N*-Me) and **1b** (*N*-Ph) with $B(C_6F_5)_3$ (Table 1). These reactions cleanly transfer hydride to boron generating the salts **2a** and **2b** [Eq. (8)] in good yields, 98 and 90%, respectively (Table 1, entries 1–3).



Formation of the borohydride anion was confirmed by its characteristic doublet at −25 ppm in the ^{11}B NMR spectra. The reactions initiate rapidly at temperatures below −40 °C, with no further conversion being observed after 30 min at −20 °C.[40]

Table 1. Product distribution for reactions of **1a–e** with $B(C_6F_5)_3$.

Entry	Substrate	R, R′	**1**/$B(C_6F_5)_3$	Yield **2** [%][a]
1	**1a**	Me, OEt	1:1	95
2	**1a**	Me, OEt	1:1	98[b]
3	**1b**	Ph, OEt	1:1	90[b]
4	**1c**	H, OEt	1:1	60
5	**1c**	H, OEt	2:1	>90
6	**1c**	H, OEt	1:2	60
7	**1d**	H, O*t*Bu	1:1	90[c]

[a] Reactions carried out in 0.03 M **1** in CD_2Cl_2 at −20 °C, ^1H NMR yields based on limiting reagent with bibenzyl as an internal standard. [b] Reaction carried out at 25 °C. [c] Reaction carried out at −30 °C.

Salts **2a** and **2b** can also be formed at room temperature in less than 5 min, although decomposition is observed after extended times in solution (see below). An X-ray crystal structure of the salt **2a** confirmed the expected connectivity (Figure 2). The metric parameters are analogous to those recently reported for pyridinium hydridoborate $[C_5H_3Me_2NH][HB(C_6F_5)_3]$.[37] The closest approach of the BH and N–Me fragments in the solid state is 3.59 Å.

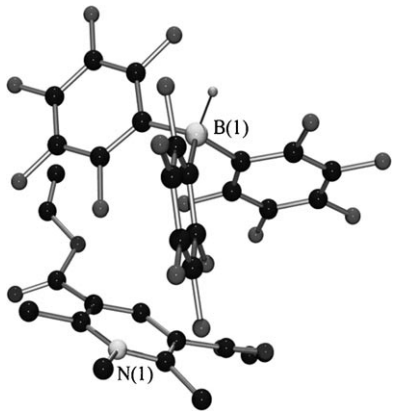
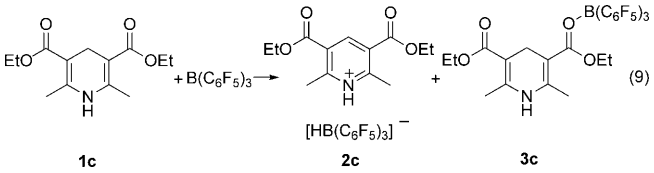


Figure 2. POV-ray depiction of the X-ray crystal structure of **2a**. All hydrogen atoms except for the BH have been omitted for clarity

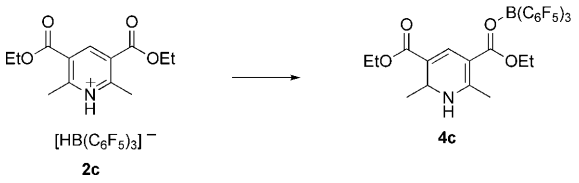
In a similar fashion, the reaction of Hantzsch's ester itself, **1c**, generates the borohydride salt **2c** in 60% yield at −20 °C. At this temperature, the remaining 1,4-dihydropyridine is sequestered as the Lewis acid–base adduct **3c** (entry 4, [Eq. (9)]).



Although the carbonyl oxygen atoms are expected to be less basic than the amine nitrogen, the steric congestion about nitrogen and its vinylogous placement presumably accounts for the formation of these adducts. When a solution that contained **3c** was cooled below −40 °C, the peaks representing the distinct ethyl ester moiety were resolved, suggesting a dissymmetric complex resulting from a carbonyl–borane adduct. A NOESY experiment revealed a correlation between the protic NH (δ 12.5 ppm) and the BH hydride (δ 3.5 ppm) for compound **2c** in solution, consistent with ion pairing. Similar interactions have been observed in related compounds.[16,17,29,37]

The product distribution was altered by varying the stoichiometry. Formation of the adduct **3c** was minimized in the presence of excess **1c** relative to $B(C_6F_5)_3$; alternatively formation of **2c** was driven by increasing the amount of the 1,4-dihydropyridine (entry 5).[41]

Upon warming from −20 °C to room temperature, borohydride salt **2c** converts into the corresponding 1,2-dihydropyridine-$B(C_6F_5)_3$ adduct **4c**. A significant amount (55% yield) of the 1,2-dihydropyridine adduct is observed after 30 min at room temperature with a maximum yield of 70% after 24 h in CD_2Cl_2 [Eq. (10)].



This stands in contrast to the corresponding 1,2-dihydropyridine adducts **4a** and **4b**, derived from **1a** and **1b**, which are formed in solutions of **2a** and **2b**, respectively, upon standing at room temperature for several hours. The 1,2-dihydropyridine adduct **4c** is readily identifiable by its ^{1}H NMR spectrum,[42,43] which is characterized by a pentet at δ 4.60 ppm (p, 1H, $^3J_{H-H}=7$ Hz) in CD_2Cl_2 representing the methine proton and a doublet at δ 1.10 ppm (d, 3H, $^3J_{H-H}=7$ Hz) from the adjacent methyl group.[44] The ^{19}F and ^{11}B NMR spectra were consistent with $B(C_6F_5)_3$ remaining complexed to the carbonyl oxygen. Product **4c** was isolated in 45% yield when the reaction of **1c** and $B(C_6F_5)_3$ is carried out in a mixture of CH_2Cl_2 and hexanes at room temperature for 1 h and cooled to induce crystallization.

The structure of **4c**, in which the $B(C_6F_5)_3$ fragment is bound to the ester *trans* to the center of hydride addition, was confirmed by X-ray crystallographic analysis (Figure 3). However, solution data indicate that the $B(C_6F_5)_3$ moiety is likely exchanging between both ethyl esters in solution. The geometry about the B centre of **4c** is pseudo-tetrahedral with an O–B distance of 1.547(4) Å, similar in length to analogous ester adducts.[45,46] Formation of the corresponding 1,2-dihydropyridine adduct is negligible for all substrates at −20 °C even after several hours.

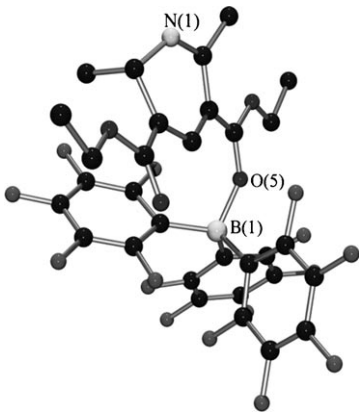
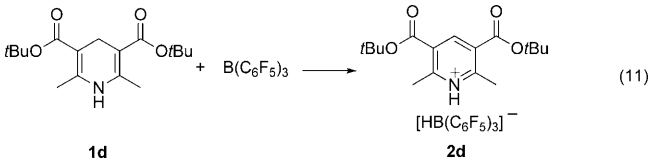


Figure 3. POV-ray depiction of one of the molecules of **4c** in the asymmetric unit of the X-ray crystallographic structure. All hydrogen atoms were omitted for clarity.

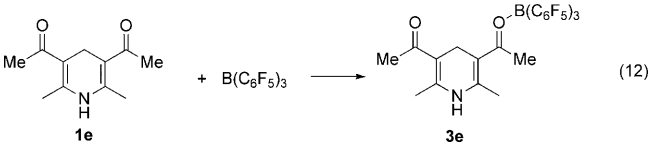
Clearly for the reactions of **1a–c** with $B(C_6F_5)_3$, the formation of 1,2-dihydropyridine adducts and Lewis acid–base adducts has an impact on the effectiveness of hydride transfer. In an effort to disfavor the formation of these adducts, the reaction of the *tert*-butyl-ester derivative **1d** with $B(C_6F_5)_3$ was examined. This approach proved successful, as a 1:1 molar ratio of these species afforded the pyridinium hydridoborate salt **2d** in good yield (90%) [Eq. (11)].



1d **2d** (11)

However, isolation of borohydride salt **2d** was hampered by its low solubility and instability above −20°C. Thus the reaction was carried out at −30°C and characterization was performed at low temperature. Nonetheless, the formation of **2d** in good yield without the need for excess hydride donor is consistent with steric congestion at the carbonyl oxygen precluding Lewis acid–base adducts formation. Furthermore, the low temperature at which hydride transfer occurs illustrates the very high reactivity of 1,4-dihydropyridines with $B(C_6F_5)_3$.

In contrast, the dimethyl ketone analogue **1e** reacts with $B(C_6F_5)_3$ affording exclusively the Lewis acid–base adduct **3e** with no evidence of the hydride transfer product [Eq. (12)].



1e **3e** (12)

The preferential formation of the adduct **3e** is consistent with the decreased steric congestion around the carbonyl, and increased Lewis basicity of the carbonyl oxygen,[45,47] **1e** is a vinylogous amide. Again, exchange between the two carbonyl groups is facile at room temperature, as desymmetrization of the Me resonances is observed in CD_2Cl_2 only on cooling to 0°C. Binding to the carbonyl group is also supported by crystallography data for **3e** (Figure 4). Similar to **4c**, the structure of **3e** shows the $B(C_6F_5)_3$ fragment bound with a pseudo-tetrahedral geometry about B and an O–B distance of 1.538(5) Å.[45] The adduct **3e** is thermally sensitive, degrading slowly at room temperature in solution to an inseparable mixture of the corresponding pyridine and 1,2-dihydropyridine adducts.

The formation of **2d** and **3e** demonstrate that electronic and steric factors impact the stability of the competing products derived from hydride transfer and Lewis acid–base adduct formation. Indeed these two cases represent either extreme in these reactions of 1,4-dihydropyridines with $B(C_6F_5)_3$.

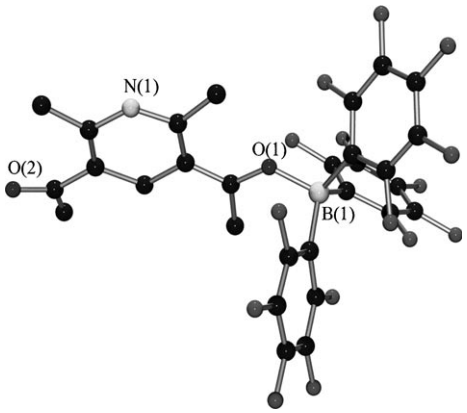


Figure 4. POV-ray depiction of one of the molecules of **3e** in the asymmetric unit of the X-ray crystallographic structure. All hydrogen atoms were omitted for clarity.

An alternative strategy for the preparation of pyridinium borohydride salts employs the recently developed frustrated Lewis pair (FLP) methodology.[30,37,38] As was previously shown [Eq. (6)], sterically hindered pyridines and $B(C_6F_5)_3$ could be employed to affect the heterolytic cleavage of H_2, the resulting pyridinium–borohydride salts would be similar to those obtained from C–H activation from a 1,4-dihydropyridine. Thus we explored this methodology as a complementary synthetic approach for the synthesis of **2c**.

The pyridine analogue of **1c**, $(C_5HMe_2(CO_2Et)_2N)$ **5c** was combined with $B(C_6F_5)_3$ in a 1:1 ratio. This produced **6c**, attributable to the Lewis acid–base adduct formed via binding of $B(C_6F_5)_3$ to the carbonyl group [Eq. (13)]. Compound **6c** was isolated and crystallographically characterized confirming the proposed binding of B to one of the carbonyl oxygen atoms (Figure 5). In this case, the O–B bond length was determined to be 1.589(2) Å which was slightly longer than that observed for **4c**.[45] In solution, **6c** gives rise to three resonances in the ^{19}F NMR spectrum, even at −60°C, consistent with binding at oxygen. It should be noted that 2,6-disubstituted pyridine adducts of $B(C_6F_5)_3$ show inequivalent C_6F_5 rings.[37,38] Low-temperature ^1H NMR spectroscopy did not resolve the methyl and ethyl resonances, suggesting the borane is rapidly exchanging between the two carbonyl groups.

The equilibrium between **5c** and **6c**, allows the combination of Lewis acid and base to react as a FLP with H_2 in $[D_8]$-toluene, albeit slowly [Eq. (14)]. At room temperature, over two days this reaction affords a product mixture including the oxygen-bound pyridine adduct **6c**, oxygen-bound 1,2-dihydropyridine adduct **4c**, and ion pair **2c** in a 40:51:9 ratio. At low temperature no H_2 activation is observed. At −15°C, only trace amounts of **2c** and **4c** appear slowly on standing (weeks), whereas no reaction was observed at −30°C. In contrast, reaction of **5c** with two equivalents of $B(C_6F_5)_3$ under 4 atm H_2 in $[D_8]$-toluene, affords **4c**/**2c**/**6c** in an 86:11:3 ratio.

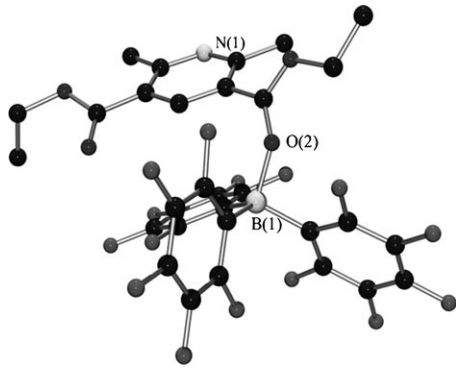
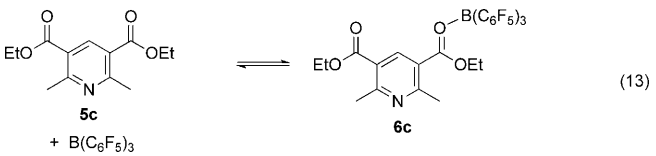


Figure 5. POV-ray depiction of the X-ray crystal structure of **6c**. All hydrogens were omitted for clarity.



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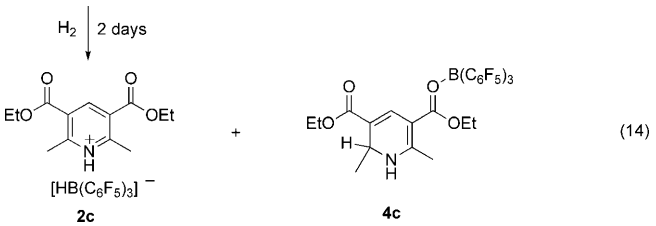

(14)

These results are consistent with increased hydrogen activation with increased availability of free $B(C_6F_5)_3$. Moreover, it suggests the barrier to activation of H_2 by the pyridine–borane pair is significantly higher than the barrier for hydride abstraction from **1c** which occurs rapidly at low temperature. This barrier to activation of H_2 and the facile conversion of **2c** to **4c** thus precludes the isolation of the desired salt **2c**. These observations also demonstrate that **5c**/borane activates hydrogen to a much lesser extent than the mixture of 2,6-lutidine/$B(C_6F_5)_3$,[37,38] consistent with the reduced basicity at the pyridine nitrogen in **5c**, and the effect of the formation of the adduct, **6c** on the reaction with H_2.

Conclusion

In summary, we have shown that Hantzsch's ester and particularly its *N*-alkylated or arylated analogues are highly effective hydride donors for the organic Lewis acid $B(C_6F_5)_3$, such that hydride transfer is observed at temperatures as low as −50 °C. The analogue in which the ethyl esters are replaced by methyl ketones reacts only by formation of a Lewis acid–base adduct at the carbonyl carbon, and no hydride transfer is observed. Increasing steric bulk at this location by the use of a *t*Bu ester results in significantly less adduct formation and a very facile hydride transfer; however, the products of this reaction display limited stability. For the most stable products, resulting from hydride transfer from the *N*-Me and *N*-Ph analogues of Hantzsch's ester, a slow reaction between the borohydride and the pyridinium ions is observed which results in the gradual accumulation of 1,2-dihydropyridine adduct in solution at room temperature. FLP-type activation of H_2 by the fully aromatic pyridine analogue of Hantzsch's ester was also shown to yield the borohydride/pyridinium salt, although this reaction was considerably slowed by comparison with the hydride transfer from the 1,4-dihydropyridine analogues. The increased time for reaction provided the opportunity for the transfer of hydride back to the pyridinium salt such that the major products observed were the pyridine–$B(C_6F_5)_3$ adduct, and the 1,2-dihydropyridine. This decreased reactivity is attributed to the lower basicity of the pyridine nitrogen and the presence of a second complexation site for boron at the carbonyl oxygen. Work is in progress to identify hydride donors that are as effective as Hantzsch's ester without providing alternative coordination sites for boron.

Experimental Section

General: Manipulations were performed either in an mBraun glovebox or on a double manifold Ar/vacuum line using standard Schlenk technique unless otherwise noted. All solvents were of Certified A.C.S. grade, purchased from Aldrich Chemical Co. unless otherwise note and distilled prior to use from an appropriate drying agent (pentane: P_2O_5; hexanes: Na; THF: Na/benzophenone; Et_2O, CH_2Cl_2, CD_2Cl_2 and 1,2-dichloroethane: CaH_2; $CDCl_3$: Na_2SO_4) degassed by three freeze–pump–thaw cycles and stored in a glovebox over 4 Å molecular sieves and basic Al_2O_3. CD_2Cl_2 was purchased from Cambridge Isotopes, ethyl acetoacetate from Acros Organics and ammonium acetate from BDH Chemicals, $B(C_6F_5)_3$ was purchased from Strem and sublimed under static vacuum at 80 °C prior to use. Compounds **(**$(C_5H_2Me_2(CO_2tBu)_2N)$ (**1d**) and $(C_5HMe_2(CO_2Et)_2N)$ (**5c**) were purchased from the Aldrich Chemical Co while compounds $(C_5H_2Me_2(CO_2Et)_2NPh)$ (**1b**),[48,49] $(C_5H_2Me_2(CO_2Et)_2NH)$ (**1c**)[50] and $(C_5H_2Me_2(COMe)_2NH)$ (**1e**)[50] were prepared by literature methods. ^1H, ^{13}C, ^{11}B and ^{19}F NMR spectra were obtained on Bruker Advance 400, 500 and 600 MHz NMR spectrometers as indicated and referenced to residual solvent (^1H, ^{13}C) or externally (^{11}B: BF_3OEt_2, ^{19}F: $CFCl_3$).

$(C_5H_2Me_2(CO_2Et)_2NMe)$ (1a): NaH (90 mg, 3.79 mmol) was weighed in a glovebox, suspended in dry THF (5 mL) and transferred via cannula to **1c** (400 mg, 1.58 mmol) suspended in THF (5 mL) in a 25 mL round bottom flask at 0 °C. The solution developed a bright orange colour over 10 min and was warmed to room temperature. Methyl *p*-toluene sulfonate (0.60 mL, 5.91 mmol) was added drop wise over 30 min. The suspension was stirred for a further 2 h after which the solvent was removed under vacuum. The residue was cooled in an ice bath, the excess NaH was quenched by slow addition of a dilute aqueous solution of *p*-toluene sulfonic acid (0.05 M, 25 mL) and the crude product was recovered by extraction with CH_2Cl_2. The organic layer was washed with brine and dried with $MgSO_4$, followed by the addition of 1,4-diazabicyclo[2.2.2]octane (500 mg, 4.44 mmol) to quench excess methyl *p*-toluene sulfonate. The solvent was removed under vacuum and the residue was purified by chromatography (hexanes/ethyl acetate 3:1). The recovered white solid was dried over P_2O_5 under vacuum (210 mg, 50 %). ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 1.31 (t, 6H, $^3J_{H-H}$ = 6 Hz, OCH_2CH_3), 2.39 (s, 6H, CH_3), 3.14 (s, 2H, CH_2), 3.18 (s, 3H, N-CH_3), 4.17 ppm (q, 4H, $^3J_{H-H}$ = 6 Hz, OCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 14.4, 15.9, 23.9, 33.8, 59.7, 101.5, 150.6, 167.8 ppm.

$[C_5HMe_2(CO_2Et)_2NMe][HB(C_6F_5)_3]$ (2a): $B(C_6F_5)_3$ (100 mg, 0.19 mmol) was weighed in a glovebox, dissolved in CH_2Cl_2 (1.5 mL) and was added drop wise, in the dark, to a solution of **1b** (50 mg, 0.19 mmol) in CH_2Cl_2 (1.5 mL) in a 4 dram glass vial at room temperature. A bright yellow solution formed on addition and after 5 min Et_2O (15 mL) was added. The solvent was removed under vacuum to yield a white powder. X-ray quality crystals were grown from Et_2O at −25 °C. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 1.45 (t, 6H, $^3J_{H-H}$=7 Hz, OCH_2CH_3), 3.16 (ov s, 6H, CH_3), 3.42 (br ov q, 1H, $^1J_{B-H}$=88 Hz, B-*H*), 4.25 (s, 3H, N-CH_3), 4.52 (q, 4H, $^3J_{H-H}$=7 Hz, OCH_2CH_3), 9.14 ppm (s, 1H, *para*-*H*); ^{13}C NMR (125 MHz, CD_2Cl_2 273 K): δ = 14.1, 20.3, 42.5, 64.6, 125.4 (br m, *C*-B), 130.4, 136.8 (dm, $^1J_{C-F}$=257 Hz, *C*-F), 138.1 (dm, $^1J_{C-F}$=244 Hz, *C*-F), 146.7, 148.28 (dm, $^1J_{C-F}$=244 Hz, *C*-F), 160.7, 162.6 ppm; ^{19}F NMR (376 MHz, CD_2Cl_2, 298 K): δ = −134.6 (br m, 6F, *ortho*-C_6F_5), −164.6 (br m, 3F, *para*-C_6F_5), −167.6 ppm (br m, 6F, *meta*-C_6F_5); ^{11}B NMR (160 MHz, CD_2Cl_2, 298 K): δ = −25.8 ppm (d, $^1J_{B-H}$=88 Hz, *B*-H); elemental analysis calcd (%) for $C_{32}H_{21}BF_{15}NO_4\cdot 0.5\,CH_2Cl_2$: C 47.50, H 2.70, N 1.70; found: C 47.51, H 2.50, N 1.71.

$[C_5HMe_2(CO_2Et)_2NPh][HB(C_6F_5)_3]$ (2b): $B(C_6F_5)_3$ (8.6 mg, 0.015 mmol) was weighed in a glovebox and dissolved in CD_2Cl_2 (0.25 mL) and was added in the dark to a suspension of **1b** (5 mg, 0.015 mmol) frozen in CD_2Cl_2 (0.25 mL) in an NMR tube. On warming, a bright yellow solution formed. The solution was characterized by VT multi-nuclear NMR. ^{1}H (400 MHz, CD_2Cl_2, 243 K): δ = 1.43 (t, 6H, $^3J_{H-H}$=5 Hz, OCH_2CH_3), 2.76 (s, 6H, CH_3), 3.45 (br m, 1H, B-*H*), 4.51 (q, 4H, $^3J_{H-H}$=5 Hz, OCH_2CH_3), 7.24 (d, 2H, $^3J_{H-H}$=4 Hz, *ortho*-Ar*H*), 7.79 (ov m, 3H, *meta* & *para*-Ar*H*), 9.32 ppm (s, 1H, *para*-*H*); partial ^{13}C NMR (150 MHz, CD_2Cl_2, 258 K): δ = 13.8, 21.5, 64.2, 124.6, 129.4, 129.5, 129.9, 132.2, 132.5, 136.3 (dm, $^1J_{C-F}$=244 Hz, *C*-F), 136.9 (dm, $^1J_{C-F}$=238 Hz, *C*-F), 138.2, 147.6 147.8 (dm, $^1J_{C-F}$=244 Hz, *C*-F), 161.5, 162.0 ppm; ^{19}F NMR (376 MHz, CD_2Cl_2, 253 K): δ = −135.3 (br m, 6F, *ortho*-C_6F_5), −164.3 (br m, 3F, *para*-C_6F_5), −167.3 ppm (br m, 6F, *meta*-C_6F_5); ^{11}B (168 MHz, CD_2Cl_2, 298 K): δ = −23.3 ppm (d, $^1J_{B-H}$=93 Hz, *B*-H); elemental analysis calcd (%) for $C_{37}H_{23}BF_{15}NO_4$: C 52.82, H 2.76, N 1.67; found: C 53.25, H 2.68, N 1.67.

$[C_5HMe_2(CO_2Et)_2NH][HB(C_6F_5)_3]$ (2c) and $(C_5H_2Me_2(CO_2Et)(CO_2EtB(C_6F_5)_3)NH)$ (3c): $B(C_6F_5)_3$ (10 mg, 0.02 mmol) was weighed in a glovebox, dissolved in CD_2Cl_2 (0.25 mL) and was added in the dark to a suspension of **1c** (5 mg, 0.02 mmol) frozen in CD_2Cl_2 (0.25 mL) in an NMR tube. On warming, a bright yellow solution formed. The solution was characterized by VT multi-nuclear NMR. **2c**: ^{1}H (400 MHz, CD_2Cl_2, 253 K): δ = 1.46 (t, 6H, $^3J_{H-H}$=7 Hz, OCH_2CH_3), 3.06 (s, 6H, CH_3), 3.53 (br ov q, 1H, $^1J_{B-H}$=80 Hz, B-*H*), 4.50 (q, 4H, $^3J_{H-H}$=7 Hz, OCH_2CH_3), 9.42 (s, 1H, *para*-*H*), 13.05 ppm (br s, 1H, N-*H*); ^{13}C NMR (125 MHz, CD_2Cl_2 253 K, HSQC and HMBC): δ = 14.3 (s, OCH_2CH_3), 21.2 (s, CH_3), 64.3 (s, OCH_2CH_3), 124.0 (br m, *C*-B), 128.0 (s, py*C*), 136.8 (dm, $^1J_{C-F}$=244 Hz, *C*-F), 138.4 (dm, $^1J_{C-F}$=235 Hz, *C*-F), 148.2 (dm, $^1J_{C-F}$= 231 Hz, *C*-F), 149.5 (s, py*C*H), 159.3 (s, py*C*), 161.7 ppm (s, *C*OOEt); ^{19}F NMR (376 MHz, CD_2Cl_2, 253 K): δ = −135.3 (d, 6F, $^3J_{F-F}$=22 Hz, *ortho*-C_6F_5), −164.1 (t, 3F, $^3J_{F-F}$=20 Hz, *para*-C_6F_5), −167.7 ppm (t, 6F, $^3J_{F-F}$=20 Hz, *meta*-C_6F_5); ^{11}B (168 MHz, CD_2Cl_2, 263 K): δ = −24.4 ppm (d, $^1J_{B-H}$=80 Hz, *B*-H). **3c** ^{1}H (400 MHz, CD_2Cl_2, 253 K): δ = 1.23 (br, 6H, OCH_2CH_3), 2.11 (s, 6H, CH_3), 3.22 (s, 2H, CH_2), 4.20 (q, 4H, $^3J_{H-H}$=7 Hz, OCH_2CH_3), 5.94 ppm (br s, 1H, N-*H*); partial ^{13}C (125 MHz, CD_2Cl_2, 263 K, HSQC and HMBC): δ = 13.1 (s, OCH_2CH_3), 18.9 (s, CH_3), 23.3 (s, CH_2), 66.1 (s, OCH_2CH_3), 97.1 (s, *C*=C), 149.8 (s, C=*C*), 174.9 ppm (s, *C*OOEt); ^{19}F NMR (376 MHz, CD_2Cl_2, 253 K): δ = −135.6 (br m, 6F, *ortho*-C_6F_5), −159.1 (br m, 3F, *para*-C_6F_5), −165.9 ppm (br m, 6F, *meta*-C_6F_5); ^{11}B (168 MHz, CD_2Cl_2, 263 K): δ = 2.4 ppm (br s, *B*-O).

$[(C_5H_2Me_2(CO_2Et)(CO_2EtB(C_6F_5)_3)NH]$ (4c): $B(C_6F_5)_3$ (100 mg, 0.19 mmol) was weighed in a glovebox, dissolved in CH_2Cl_2 (1.5 mL) and was added drop wise, in the dark, to a solution of **1c** (50 mg, 0.19 mmol) in CH_2Cl_2 (1.5 mL) in a 4 dram glass vial at room temperature. A bright yellow solution formed on addition, after 5 min hexanes (10 mL) was added and the solution was allowed to stand at −25 °C. The resulting precipitate was filtered and recrystallized from CH_2Cl_2 layered from pentane, filtered and dried under vacuum (60 mg, 40 %). **3c** slowly decomposed in solution to **2c** and as a result it was not possible to obtain an analytically pure sample. X-ray quality crystals were grown from CH_2Cl_2 layered with pentane at −25 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.10 (ov d, 3H, $^3J_{H-H}$=7 Hz, $CHCH_3$), 1.13 (ov br m, 3H, OCH_2CH_3), 1.44 (br, 3H, OCH_2CH_3), 2.39 (s, 3H, CH_3), 4.13 (br m, 2H, OCH_2CH_3), 4.22 (br m, 2H, OCH_2CH_3), 4.56 (p, 1H, $^3J_{H-H}$=7 Hz, $CHCH_3$), 6.06 (br s), 7.41 ppm (br s); partial ^{13}C (125 MHz, CD_2Cl_2, 298 K, HSQC): δ = 13.5, 13.7, 21.7, 23.7, 48.6, 62.1, 65.4, 138.6 ppm; ^{19}F NMR (376 MHz CD_2Cl_2, 298 K): δ = −134.2 (br m, 6F, *ortho*-C_6F_5), −157.3 (br m, 3F, *para*-C_6F_5), −164.3 ppm (br m, 6F, *meta*-C_6F_5); ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ = 2.9 ppm (br s, *B*-O).

$[C_5HMe_2(CO_2tBu)_2NH][HB(C_6F_5)_3]$ (2d): $B(C_6F_5)_3$ (9.7 mg, 0.02 mmol) was weighed in a glovebox, dissolved in CD_2Cl_2 (0.25 mL) and was added in the dark, to a suspension of **1c** (5 mg, 0.02 mmol) frozen in CD_2Cl_2 (0.25 mL) in an NMR tube. On warming to −50 °C, a bright yellow heterogeneous solution formed. The yellow precipitate dissolved on shaking and the solution was characterized by VT multi-nuclear NMR. ^{1}H (600 MHz, CD_2Cl_2, 233 K): δ = 1.58 (s, 18H, $OC(CH_3)_3$), 2.90 (s, 6H, CH_3), 3.50 (br m, B-*H*), 9.28 (s, 1H, *para*-*H*), 12.81 ppm (br s, 1H, N-*H*); partial ^{13}C (150 MHz, CD_2Cl_2, 223 K, HSQC and HMBC): δ = 25.1 (s, CCH_3), 27.5 (s, $OC(CH_3)_3$), 85.7 (s, $OC(CH_3)_3$), 127.9 (s, py*C*), 149.2 (s, py*C*H), 158.4 (s, py*C*), 160.4 ppm (s, *C*O*O*t*B*u); ^{19}F NMR (376 MHz, CD_2Cl_2, 233 K): δ = −134.7 (d, 6F, $^3J_{F-F}$=22 Hz, *ortho*-C_6F_5), −162.5 (t, 3F, $^3J_{F-F}$=20 Hz, *para*-C_6F_5), −166.2 ppm (t, 6F, $^3J_{F-F}$=20 Hz, *meta*-C_6F_5); ^{11}B (168 MHz, CD_2Cl_2, 240 K): δ = −24.6 ppm (d, $^1J_{B-H}$=74 Hz, *B*-H).

$(C_5H_2Me_2(COMe)(COMeB(C_6F_5)_3)NH)$ (3e): $B(C_6F_5)_3$ (25 mg, 0.05 mmol) was weighed in a glovebox, dissolved in CD_2Cl_2 (0.25 mL) and was added in the dark, to a suspension of **1e** (9 mg, 0.05 mmol) in CD_2Cl_2 (0.25 mL) in an NMR tube. The solution was characterized by VT multi-nuclear NMR. X-ray quality crystals were grown from 1,2-DCE layered with pentane at −25 °C. ^{1}H (600 MHz, CD_2Cl_2, 273 K): δ = 2.10 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 3.34 (s, 2H, CH_2), 7.10 ppm (s, 1H, *NH*); ^{13}C NMR (125 MHz, CD_2Cl_2, 273 K): δ = 19.1, 23.9, 25.3, 27.0, 30.4, 105.9, 116.6, 119.6 (br m, *C*-B), 137.3 (dm, $^1J_{C-F}$=246 Hz, *C*-F), 139.3, 140.2 (dm, $^1J_{C-F}$=253 Hz, *C*-F), 148.0 (dm, $^1J_{C-F}$=240 Hz, *C*-F), 164.7, 197.9, 198.5 ppm; ^{19}F NMR (376 MHz, CD_2Cl_2, 250 K): δ = −134.0 (br m, 6F, *ortho*-C_6F_5), −155 (br m, 3F, *para*-C_6F_5), −163.3 ppm (br m, 6F, *meta*-C_6F_5); ^{11}B (168 MHz, CD_2Cl_2, 273 K): δ = −2.0 ppm (br s, *B*-O); elemental analysis calcd (%) for $C_{32}H_{21}BF_{15}NO_4\cdot 0.5\,CH_2Cl_2$: C 49.39, H 2.14, N 1.99; found: C 49.22, H 2.03, N 1.96.

$(C_5H_2Me_2(CO_2Et)(CO_2EtB(C_6F_5)_3)N)$ (6c): $B(C_6F_5)_3$ (100 mg, 0.20 mmol) was added to **5c** (48 mg, 0.20 mmol) in toluene (2 mL). The solution was allowed to stir for 4 h and then pumped to dryness. The solid was washed with pentane (2×2 mL) and again pumped to dryness (110 mg, 74 %). X-ray quality crystals were grown from pentane at −35 °C. Cooling to −60 °C resulted in only broadening of the peaks, not in resolution. ^{1}H NMR (CD_2Cl_2): δ = 1.40 (t, $^3J_{H-H}$=8 Hz, CH_2-CH_3), 2.75 (s, C-CH_3), 4.47 (q, $^3J_{H-H}$=8 Hz, CH_2-CH_3), 8.48 ppm (s, *CH*); ^{13}C NMR (CD_2Cl_2) (partial): δ = 13.9, 24.4, 64.0, 122.5, 137.7 (dm, $^1J_{C-F}$=252 Hz, C*F*), 140.3, 148.1 (dm, $^1J_{C-F}$=252 Hz, C*F*), 162.1, 168.3 (m); ^{19}F NMR (CD_2Cl_2): δ = −131.5 (br d, $^3J_{F-F}$=17 Hz, 6F, *ortho*-C_6F_5), −150.5 (br s, 3F, *para*-C_6F_5), −162.9 ppm (br s, 6F, *meta*-C_6F_5); ^{11}B NMR (CD_2Cl_2): δ = 42.2 ppm (br s, *B*O); elemental analysis calcd (%) for $C_{31}H_{17}BF_{15}NO_4$: C 48.78, H 2.24, N 1.84; found: C 48.59, H 2.17, N 1.85.

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 N2 stream, thus maintaining a dry, O_2-free environment for each crystal. The data were collected on a Bruker Apex II diffractometer. 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 multi-scan method (SADABS).

Structure solution and refinement: Non-hydrogen atomic scattering factors were taken from the literature tabulations.[24] 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 $\omega(F_o-F_c)^2$ 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 the residual electron densities in each case were of no chemical significance. Additional details are provided in Table 2 and the Supporting Information.

Table 2. Crystallographic data.

Crystal	**2a**	**4c**	**3e**	**6c**
formula	$C_{32}H_{21}BF_{15}NO_4$	$C_{31}H_{19}BF_{15}NO_4$	$C_{29}H_{15}BF_{15}NO_2$	$C_{31}H_{17}BF_{15}NO_4$
formula weight	780.35	765.28	705.23	763.27
crystal system	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a [Å]	9.7091(9)	13.7038(3)	15.7452(13)	11.4131(2)
b [Å]	12.2814(12)	27.7497(5)	24.0777(18)	18.7242(3)
c [Å]	14.0010(14)	18.4929(3)	20.9825(18)	15.061(2)
α [°]	78.055	90.00	90.00	90.00
β [°]	82.764(1)	97.925(1)	109.924(2)	108.4620(10)
γ [°]	86.857(1)	90.00	90.00	90.00
V [Å^3]	1619.6(3)	6965.2(2)	7478.5(11)	3052.72(8)
Z	2	8	8	4
ρ_{calcd} [g cm^{-1}]	1.598	1.460	1.253	1.661
μ [cm^{-1}]	0.162	0.149	0.129	0.170
data: total (indep)	6337	13625	14587	5983
data $F_o^2>3\sigma(F_o^2)$	5062	7111	6244	4479
variables	494	904	871	473
R[a]	0.0374	0.0576	0.0616	0.0357
R_w[b]	0.1013	0.1652	0.1747	0.0856
goodness of fit	1.036	0.933	0.819	1.006

[a] $R=\Sigma(F_o-F_c)/\Sigma F_o$. [b] $R_w=(\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o)^2])^{1/2}$.

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