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Frustrated Lewis Pair Behavior of Intermolecular Amine/$B(C_6F_5)_3$ Pairs

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Supporting Information

ABSTRACT: Reactions of *N*,*N*-dimethylaniline, *N*-isopropylaniline, 1,4-$C_6H_4(CH_2NHtBu)_2$, and benzyldimethylamine with the Lewis acid $B(C_6F_5)_3$ have been studied. In the case of *N*,*N*-dimethylaniline the combination of the Lewis acid and base forms an almost completely noninteracting frustrated Lewis pair, while the corresponding reactions of *N*-isopropylaniline and benzyldimethylamine with $B(C_6F_5)_3$ afford the adducts $(PhNHiPr)B(C_6F_5)_3$ (**1**) and $PhCH_2NMe_2B(C_6F_5)_3$ (**2**), respectively. 1,4-$C_6H_4(CH_2NHtBu)_2$ reacts with 2 equiv of $B(C_6F_5)_3$ to give rise to an inseparable mixture of the mono- and bis-amine−borane adducts as well as an iminium salt derived from hydride abstraction from a benzylic carbon of the diamine. Subsequent selected reactions of the Lewis acid/base combinations with H_2 afforded $[PhNMe_2H][HB(C_6F_5)_3]$ (**3**), $[PhCH_2NMe_2H][HB(C_6F_5)_3]$ (**4**), and $[1,4\text{-}C_6H_4(CH_2NH_2tBu)_2][HB(C_6F_5)_3]_2$ (**5**). Reactions with CO_2 gave $PhCH_2NMe_2CO_2B(C_6F_5)_3$ (**6**), $[PhNiPrH_2][PhNiPrCO_2B(C_6F_5)_3]$ (**8**), $[1,4\text{-}C_6H_4(CH_2NH_2tBu)(CH_2NtBuCO_2B(C_6F_5)_3]$ (**9**), and $[C_5H_6Me_4NMeH]_2[1,4\text{-}C_6H_4(CH_2NtBuCO_2B(C_6F_5)_3)_2]$ (**10**). Interestingly, the species **4** also reacts with CO_2 to give $[PhCH_2NMe_2H][HCO_2B(C_6F_5)_3]$ (**7**). Species **8** reacts with $HSiEt_3$ to yield $[PhNiPrC(OSiEt_3)OB(C_6F_5)_3]$ (**11**). The adduct **2** also reacts with ethene, 2,4-hexadiyne, and the alkynes HC≡CR (R = *n*-Bu, Ph, *t*Bu, $SiMe_3$) to give the 1,2- addition products $PhCH_2NMe_2CH_2CH_2B(C_6F_5)_3$ (**12**), $PhCH_2NMe_2C(CCMe)=CMeB(C_6F_5)_3$ (**13**), and the ammonium alkynylborate salts $[PhCH_2NMe_2H][RCCB(C_6F_5)_3]$ (R = *n*-Bu (**14a**), Ph (**14b**), *t*Bu (**14c**), $SiMe_3$ (**14d**)). In contrast, the reaction of 1-hexyne with the Lewis pair $PhNMe_2$ and $B(C_6F_5)_3$ affords the trans-1,2-addition product $PhNMe_2C(C_4H_9)=CH(B(C_6F_5)_3)$ (**15**). This chemistry demonstrates the generality of such FLP chemistry, extending it to N-based Lewis bases and thereby expanding the scope for applications of FLP chemistry.

INTRODUCTION

The chemistry of frustrated Lewis pairs (FLPs) has seen significant development in recent years.[1] This has mostly been based on bulky phosphine−borane pairs, the later being predominantly derived from C_6F_5-substituted systems.[2] This has resulted in well-established pathways of metal-free heterolytic H_2 activation[2,3] and the catalytic hydrogenation of various polar substrates.[4] Phosphine-based FLPs have also been shown to heterolytically cleave B−H bonds[5] and disulfides,[6] ring open THF, cyclic ethers, and lactones,[7] and add to CO_2,[8] alkenes,[9] dienes,[10] alkynes,[11] conjugated enynes, diynes,[12] organic carbonyl compounds,[13] and azides[14] as well as CO,[15] N_2O,[16] and NO.[17] In contrast, the corresponding chemistry utilizing amine−borane FLP systems is less explored. The activation of H_2 by the combination of tetramethylpiperidine,[18] 1,4-diazabicyclo(2,2,2)octane,[19] or pyridines[20] with boranes has been demonstrated and employed in FLP-catalyzed hydrogenations of imines, enamines, and silyl enol ethers. In addition, these N/B FLPs have been employed to activate H_2 or silane and effect the reduction of CO_2 to methanol or methane, respectively.[8e] The utilization of smaller amines, especially those with α-C−H bonds, in FLP type reactivity appears to be more complicated than the more common P/B cases. Complications arise from competing reaction pathways that are specifically open to amines, such as α-C−H abstraction by the Lewis acid.[21] Indeed, this reaction has been shown to interfere with typical FLP chemistry in ferrocenophane-derived systems. While the small NMe_2 group of the ferrocenophanes and $B(C_6F_5)_3$ undergo cooperative FLP addition to the adjacent pendant alkenyl group at low temperatures, this reaction is reversed at higher temperatures, prompting formation of the corresponding iminium species.[22] In this paper, we describe studies of FLP chemistry employing several N/B pairs. These simple systems are shown to exhibit typical FLP chemistry, reacting with H_2, CO_2, olefins, alkynes, and diynes. This chemistry demonstrates the extension of FLP chemistry to N-based Lewis bases and thereby expanding the scope for applications.

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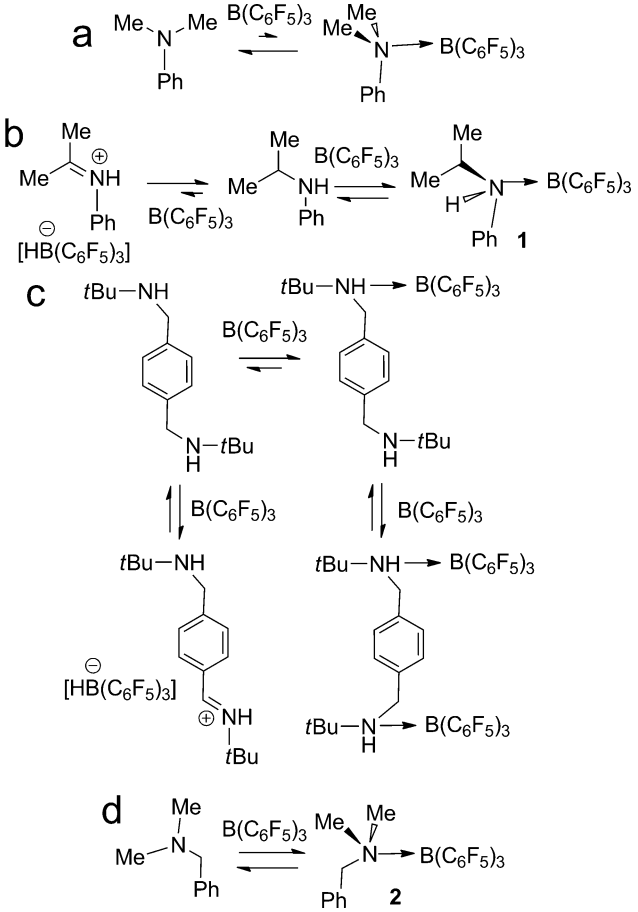
RESULTS AND DISCUSSION

Amine−Borane Adduct Formation. The reaction of *N*,*N*-dimethylaniline with $B(C_6F_5)_3$ has been previously studied. We found the same results as described in the literature;[21b] namely, formation of a product mixture characterized by ^{11}B NMR signals at ca. 63, −2, and −24 ppm, when $B(C_6F_5)_3$ was treated with the aniline derivative employed as purchased. In contrast, mixing of carefully purified *N*,*N*-dimethylaniline with $B(C_6F_5)_3$ under rigorous dry conditions did not lead to any appropriate reaction being observed. Monitoring the NMR features of the mixture of components in C_7D_8 revealed a broad ^{11}B NMR signal at ca. 60 ppm and ^{19}F NMR resonances at −128.8, −142.0, and −160.2 ppm (see the Supporting Information). It seems that $PhNMe_2$ and $B(C_6F_5)_3$ form an almost non-interacting FLP under these conditions (Scheme 1a).[23]

Scheme 1. Reactions of Amines with $B(C_6F_5)_3$



The corresponding reaction of *N*-isopropylaniline and $B(C_6F_5)_3$ in C_6D_5Br resulted in broad ^1H, ^{11}B, and ^{19}F NMR signals at 25 °C. On cooling to −80 °C, the mixture exhibited a ^{11}B NMR signal at ca. −3 ppm and the ^{19}F NMR spectrum exhibited 14 resonances consistent with inequivalent fluoroaryl groups (two *o*-F overlapping). The corresponding low-temperature ^1H NMR spectrum revealed inequivalent methyl resonances at 1.23 and 0.72 ppm. These data were consistent with the formation of the adduct $(PhNHiPr)B(C_6F_5)_3$ (**1**). Repetition of this reaction in pentane instantly yielded **1**, permitting its isolation. In the ^{11}B NMR spectrum, about 10% of the material gives rise to a signal at −23.6 ppm, consistent with the formation of the anion $[HB(C_6F_5)_3]^-$.[2b] This species is thought to arise from hydride abstraction from the amine, generating the salt $[PhNH{=}CMe_2][HB(C_6F_5)_3]$ by analogy to known systems (Scheme 1b).

In a similar sense, the corresponding reaction of 1,4-$C_6H_4(CH_2NHtBu)_2$ with 2 equiv of $B(C_6F_5)_3$ gave rise to an inseparable mixture of two species, as evidenced by two ^{11}B NMR signals. A broad signal at −3 ppm and a sharp doublet at −24 ppm appear in a 2:1 ratio. The chemical shift of the former signal is consistent with a mixture of mono- and bis-amine−borane adducts. The high-field signal is attributable to the anion $[HB(C_6F_5)_3]^-$ arising from the generation of [1,4-$C_6H_4(CH_2NHtBu)(CH{=}NHtBu)][HB(C_6F_5)_3]$ (Scheme 1c).

The reaction of the nucleophilic benzyldimethylamine with the Lewis acid $B(C_6F_5)_3$ results in the formation of the weak adduct **2** (Scheme 1d). This was evident from an upfield shift of the ^{11}B NMR signal to about 46 ppm (C_7D_8) as well as the ^{19}F NMR signals to −128.0, −145.7, and −161.0 ppm. Single crystals of adducts **1** and **2** were characterized by X-ray diffraction (Figure 1). The X-ray crystal structure analyses

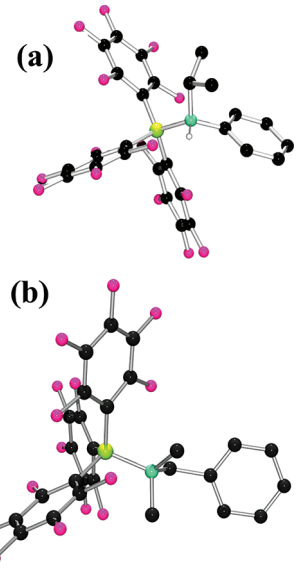


Figure 1. POV-ray depictions of (a) **1** and (b) **2**. Color codes: C, black; N, blue-green; B, yellow-green; F, pink; H, gray. Only the NH hydrogen atom is shown.

confirmed the formulations of these adducts. In the case of **1** the B−N bond distance was found to be 1.686(3) Å, whereas the B−N linkage in **2** is rather long at 1.807(3) Å,[20a,24] although the boron and the nitrogen atoms of both structures adopt pseudotetrahedral coordination geometries. The significant difference in the B−N distances is interesting, given that one might expect benzyldimethylamine to be more basic than *N*-isopropylaniline. Nonetheless, it is clear that the steric congestion about the tertiary amine center precludes a closer approach of N to B.

The above examples demonstrate the influence of both steric and electronic factors on the formation of classical Lewis adducts by amines and $B(C_6F_5)_3$. While such factors may "frustrate" the adduct formation, they provide equilibrium access to the free FLPs for subsequent reactivity. Moreover, the hydridophilic nature of the borane also generates the possibility of minor side products derived from hydride abstraction from the α-C to generate iminium salts.

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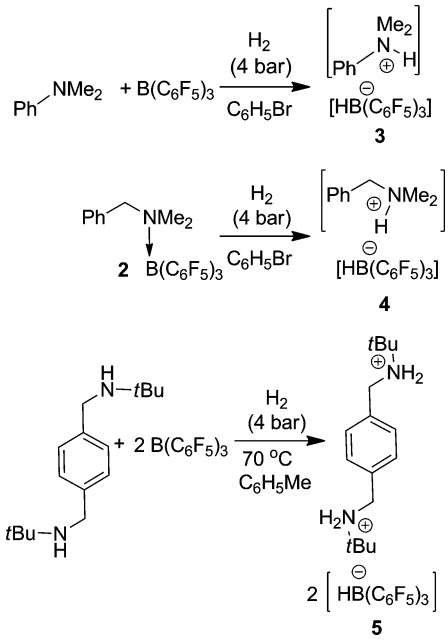
Reactions with Dihydrogen. The *N*,*N*-dimethylaniline–$B(C_6F_5)_3$ Lewis pair reacted rapidly with H_2 (4 atm) at 25 °C, despite the low basicity of the Lewis base component, to effect the heterolytic cleavage of H_2 and yield the ammonium–hydridoborate salt $[PhNMe_2H][HB(C_6F_5)_3]$ (**3**) (Scheme 2).

Scheme 2. Reactions of Amine–$B(C_6F_5)_3$ with H_2



Product **3** was subsequently isolated in near-quantitative yield, and crystals were obtained from pentane–dichloromethane at −32 °C. The metric parameters were unexceptional, and typical pseudotetrahedral geometries about N and B were observed (Figure 2a). The ^{11}B, ^{1}H, and ^{19}F NMR spectra confirm the formation of the hydridoborate anion.[2b] The corresponding $[PhNMe_2H]^+$ cation shows a sharp ^{1}H NMR resonance at 8.60 ppm attributable to the NH proton as well as a singlet at 2.72 ppm attributable to two N-bound methyl groups. The corresponding IR bands for **3** are observed at ν_{NH} 3060 cm^{-1} and ν_{BH} 2311 cm^{-1}. The same reaction with D_2 afforded **3-*d*$_2$**, as evidenced by the observation of ^{2}H NMR resonances attributable to the ND and BD moieties. In addition, some deuteration of the aromatic ring of the $[PhNMe_2D]^+$ cation was also observed (see the Supporting Information).

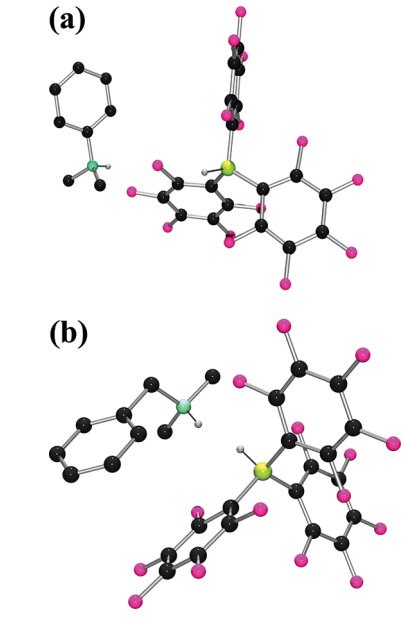


Figure 2. POV-ray depictions of (a) **3** and (b) **4**. Color code: C, black; N, blue-green; B, yellow-green; F, pink; H, gray. Only the BH and NH hydrogen atoms are shown.

In C_6D_5Br, adduct **2** reacts slowly at 25 °C with H_2 (4 atm) to give the salt $[PhCH_2NMe_2H][HB(C_6F_5)_3]$ (**4**) (Scheme 2 and Figure 2). The reaction was complete on standing for 3 days to afford **4** in 88% isolated yield. This species gives rise to typical NMR features of the anion, while the cation shows a methylene ^{1}H NMR resonance at 3.52 ppm and a methyl singlet at 2.25 ppm. The corresponding experiment with D_2 gave the analogous salt **4-*d*$_2$**, which exhibited ^{2}H NMR signals at 7.35 ppm (ND) and 3.23 ppm (BD). The formulation of **4** was also confirmed by X-ray diffraction (Figure 2b).

In the case of the diamine 1,4-$C_6H_4(CH_2NHtBu)_2$, treatment with 2 equiv of $B(C_6F_5)_3$ in toluene and exposure to H_2 (4 atm) resulted in the formation of a precipitate at 25 °C. Subsequent isolation of the residue afforded a quantitative yield of the salt $[1,4\text{-}C_6H_4(CH_2NH_2tBu)_2][HB(C_6F_5)_3]_2$ (**5**). The ^{1}H NMR spectrum of **5** showed a broad signal at 5.95 ppm attributable to the NH_2 fragment, while the ^{1}H, ^{19}F, and ^{11}B NMR spectra confirmed the presence of the borate anion. The formulation of **5** was confirmed unambiguously by X-ray diffraction (Figure 3). The metric parameters are unexceptional.

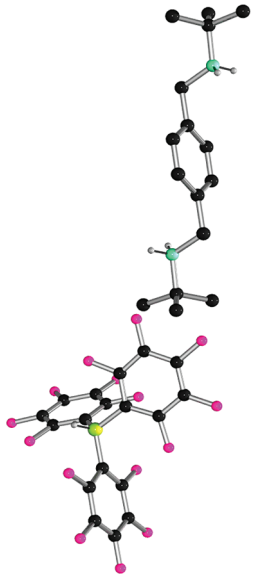


Figure 3. POV-ray depiction of **5**. Color code: C, black; N, blue-green; B, yellow-green; F, pink; H, gray. Only one of borate anions and only the BH and NH hydrogen atoms are shown.

Reactions with Carbon Dioxide. We have previously shown that P-based FLPs react with carbon dioxide to yield the respective addition products in which P and B add to a C–O bond in CO_2. In this fashion, $tBu_3PCO_2B(C_6F_5)_3$ and $Mes_2P(CO_2)CH_2CH_2B(C_6F_5)_2$ were characterized.[8a] Subsequently, we also described a series of related P/B-FLP-CO_2 species.[8e] In all cases, these species were shown to be thermally labile, liberating CO_2 rapidly at temperatures between −20 and

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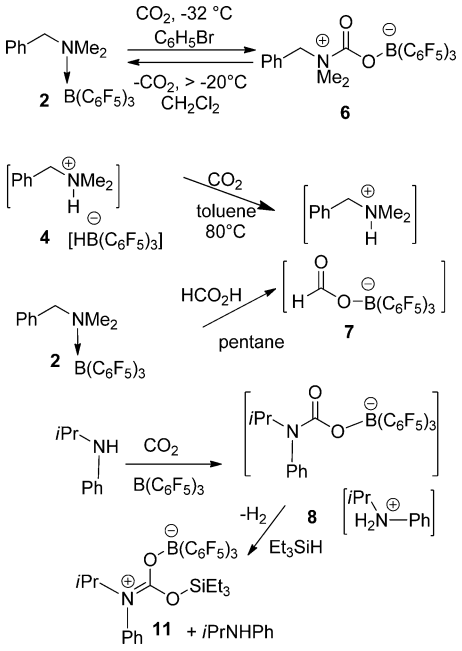
+80 °C in solution. In a similar fashion, the reactions of amine−borane species were probed. While primary and secondary amines are known to react with CO_2 to generate carbamates,[25] $PhCH_2NMe_2$ appears to be unreactive with CO_2.[26] However, the mixture of $PhCH_2NMe_2$ with $B(C_6F_5)_3$ (i.e., **2**) reacted slowly with CO_2 in C_6H_5Br or toluene solution at low temperature (−32 °C) over a period of 12 h to yield the thermolabile addition product **6** (Scheme 3). While this system

Scheme 3. Reactions with CO_2



releases CO_2 rapidly in solution (CH_2Cl_2) above ca. −20 °C, the product **6** was isolable in 54% yield at low temperature. Single-crystal X-ray diffraction of compound **6** revealed amine N binding to the C of CO_2 with O binding to $B(C_6F_5)_3$ (Figure 4). The N−C and B−O bond lengths were found to be

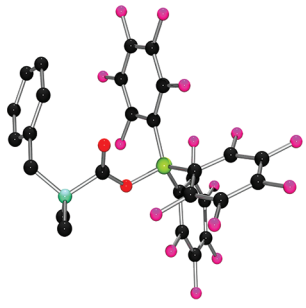


Figure 4. POV-ray depiction of **6**. Color code: C, black; N, blue-green; B, yellow-green; O, red; F, pink. Hydrogen atoms are not shown.

1.545(2) and 1.550(2) Å, respectively. The carbamate-like core of the molecule features a trigonal-planar carbon atom with pertinent bond angles of 133.06(18)° (O−C−O) and 118.04(17) and 108.85(16)° (N−C−O). The C−O−B angle is 121.54(15)°, while the angles about N are typical of a pseudotetrahedral coordination geometry.

The C═O bond in the adduct **6** is short (C−O = 1.193(3) Å); indeed markedly shorter than those observed in the related and previously reported P/B-FLP adducts.[8a] This corresponds with the observed ^{13}C NMR carbonyl resonance of **6** (150.1 ppm), which has shifted upfield by about 10 ppm toward the value for free CO_2 (125 ppm), suggesting a stronger C═O bond in **6**. This is also consistent with the observed increase of the IR ν(C═O) stretching band in **6** (1822 cm^{-1}), which is markedly closer to the asymmetric stretching band of CO_2 (2345 cm^{-1}) than the C═O groups in related P/B CO_2 derivatives.[8a]

The species **4** also reacts with CO_2 at 80 °C to give the ammonium borylformate salt **7**, which was isolated as a white solid from the reaction mixture in 90% yield (Scheme 3). The presence of the formate moiety is evidenced by the signal at 8.29 ppm in the ^1H NMR spectrum and at 170.2 ppm in the ^{13}C NMR spectrum. This anion gives rise to a ^{11}B NMR signal at −2.2 ppm and ^{19}F NMR resonances at −134.2, −157.9, and −164.3 ppm as well as an IR ν(C═O) stretching band at 1621 cm^{-1}. Compound **7** was independently synthesized by treatment of the FLP adduct **2** with formic acid and characterized by X-ray diffraction (Figure 5). Compound **7**

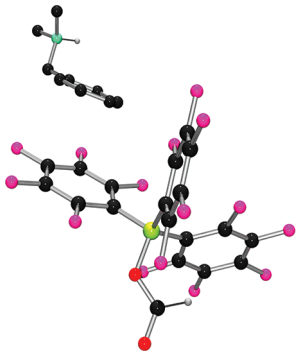


Figure 5. POV-ray depiction of **7**. Color code: C, black; N, blue-green; B, yellow-green; O, red; F, pink; H, gray. Only COH and NH hydrogen atoms are shown.

features a B−O bond length of 1.535(3) Å and a C═O double bond of 1.213(5) Å, which are both slightly shorter than the respective bonds in the related system $[C_5H_6Me_4NH_2][HCO_2B(C_6F_5)_3]$ (B−O = 1.546(3) Å, C═O = 1.236(3) Å).[27−29]

Following a similar reaction strategy, a mixture of *N*-isopropylaniline and $B(C_6F_5)_3$ was exposed to $^{13}CO_2$ (1 atm). After the mixture was stirred at 25 °C for 2 days, workup led to the isolation of the product **8** as a white powder in 95% yield. The ^1H NMR spectrum of **8** shows a resonance at 7.55 ppm attributable to an NH_2 fragment as well as two sets of resonances for isopropyl groups. These data, in addition to the ^{19}F and ^{11}B NMR spectra, were consistent with the formation of a borate, while the ^{13}C NMR signal at 159.4 ppm was attributed to the N-bound CO_2 moiety. In addition to these NMR features, the IR absorption at 1646 cm^{-1} (using $^{13}CO_2$) was consistent with the formulation of **8** as $[PhNiPrH_2][PhNiPrCO_2B(C_6F_5)_3]$. This was confirmed crystallographically (Figure 6). The N−C and B−O bond distances associated with the NCO_2B fragment **8** were found to be 1.355(3) and 1.508(3) Å, respectively.

The closely related product $[1,4\text{-}C_6H_4(CH_2NH_2tBu)(CH_2NtBuCO_2B(C_6F_5)_3)]$ (**9**) was derived from the corresponding reaction of the diamine $1,4\text{-}C_6H_4(CH_2NHtBu)_2$ with $B(C_6F_5)_3$ and CO_2 (Scheme 4). This zwitterionic salt was isolated in 88% yield and exhibited spectral parameters

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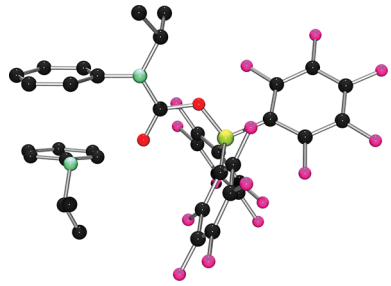
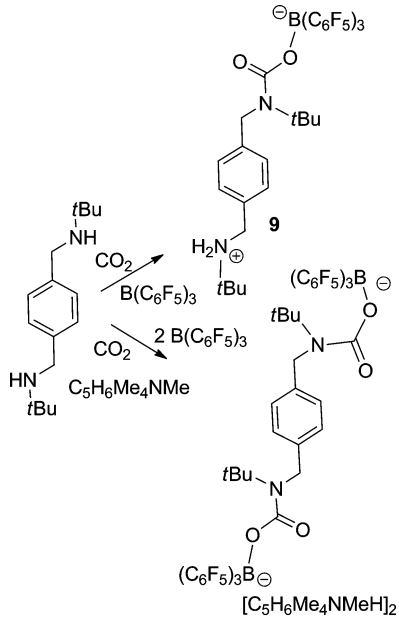


Figure 6. POV-ray depiction of **8**. Color code: C, black; N, blue-green; B, yellow-green; F, pink; O, red. Hydrogen atoms are not shown.

Scheme 4. Reactions of Diamine with CO_2 and $B(C_6F_5)_3$



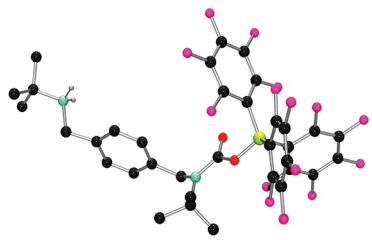


Figure 7. POV-ray depiction of **9**. Color code: C, black; N, blue-green; B, yellow-green; F, pink; O, red; H, gray. Only the NH hydrogen atom is shown.

analogous to those of **8**. The nature of this species was also confirmed crystallographically (Figure 7). The N−C and B−O distances associated with the NCO_2B fragment were found to average 1.364(6) and 1.496(6) Å, respectively. Repetition of this reaction in the presence of 2 equiv of 1,2,2,6,6-pentamethylpiperidine resulted in isolation of the salt $[C_5H_6Me_4NMeH]_2[1,4\text{-}C_6H_4(CH_2NtBuCO_2B(C_6F_5)_3)_2]$ (**10**). Both amine fragments of the precursor diamine have reacted with CO_2 and the borane forms the dianion, while the more basic pentamethylpiperidine forms the corresponding cations. The structure of **10** was determined crystallographically (Scheme 4 and Figure 8). The N−C and B−O distances of the

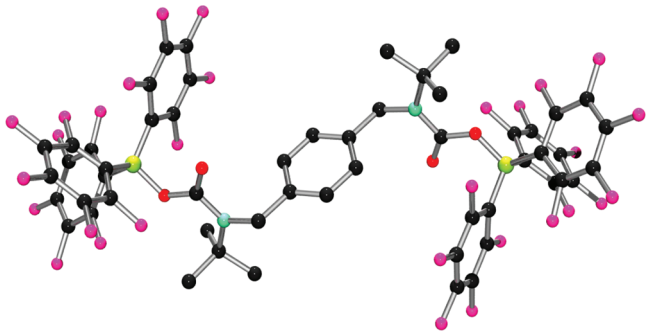


Figure 8. POV-ray depiction of the dianion of **10**. Color code: C, black; N, blue-green; B, yellow-green; F, pink; O, red. Hydrogen atoms are not shown.

NCO_2B fragment are in the range of those for **8** and **10** (N−C = 1.380(5) Å, B−O = 1.508(5) Å).

Piers and co-workers have previously shown that the formatoborate salt $[TMPH][HC(O)OB(C_6F_5)_3]$ reacts with silane, ultimately giving CH_4, with $(Et_3Si)_2O$.[27b] For comparison, species **8** was reacted with $HSiEt_3$, giving rise to the new species **11**, which was isolated in 64% yield (Scheme 3). The ^1H NMR spectrum of **11** was consistent with the loss of the NH_2 protons of the cation of **8** and showed the presence of the $SiEt_3$ fragment. The ^{19}F and ^{11}B NMR spectra revealed signals at −135.0, −160.0, −165.3, and −3.98 ppm, respectively. The ^{13}C NMR resonance at 156.4 ppm was consistent with the incorporation of $^{13}CO_2$. Collectively, these data were consistent with the formulation of **11** as $[PhNiPrC(OSiEt_3)OB(C_6F_5)_3]$ and the concurrent evolution of H_2. Compound **11** was subsequently confirmed crystallographically (Figure 9). The

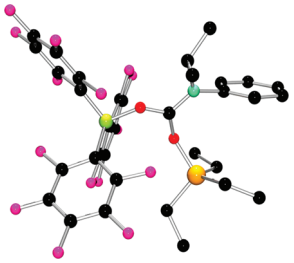


Figure 9. POV-ray depiction of **11**. Color code: C, black; N, blue-green; B, yellow-green; F, pink; O, red; Si, orange. Hydrogen atoms are not shown.

N−C distance in **11** was found to be 1.327(3) Å, similar to that in **8**−**10**, while the B−O distance is elongated slightly to 1.557(3) Å and the Si−O distance to 1.706(2) Å. Interestingly, efforts to effect similar reactions of **9** with $HSiEt_3$ were unsuccessful. At 25 °C, multinuclear NMR data revealed no reaction between $HSiEt_3$ and **9**, whereas heating to 80 °C resulted only in the liberation of CO_2. The differing reactivities of **8** and **9** are attributed to increased steric congestion adjacent to the CO_2 fragment and the decreased acidity of the ammonium fragment in **9**, which combine to preclude silylation and evolution of H_2.

Reactions with Alkenes and Alkynes. We have previously demonstrated that P/B FLPs add to alkenyl or alkynyl fragments. Amine-based FLPs have been shown to exhibit intramolecular additions of amines to alkenyl or alkynyl substituents in the presence of $B(C_6F_5)_3$.[30] The adduct **2** reacts slowly with ethene (2 atm) in pentane at 25 °C to yield the 1,2-

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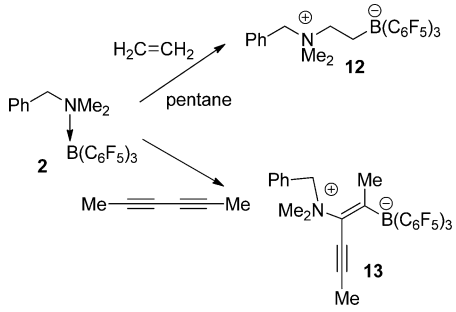
FLP addition product $PhCH_2NMe_2CH_2CH_2B(C_6F_5)_3$ (**12**). This product was isolated in 57% yield (Scheme 5). The X-ray

Scheme 5. Reactions of 2 with Ethene and Diyne



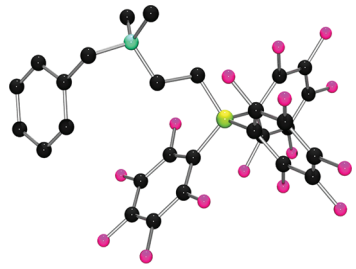


Figure 10. POV-ray depiction of **12**. Color code: C, black; N, blue-green; B, yellow-green; F, pink. Hydrogen atoms are not shown.

crystal structure analysis of **12** (Figure 10) confirmed the addition reaction and revealed the new N−C and B−C bond lengths of 1.518(3) and 1.666(4) Å, respectively. This zwitterionic product adopts an antiperiplanar conformation of the core atoms with a B1−C1−C2−N3 dihedral angle of 172.92(5)° and a C1−C2 bond length of 1.514(3) Å. In C_6D_6, compound **12** exhibits ^{1}H NMR signals for the methylene groups at 2.31 (NCH_2) and 1.55 (CH_2B) ppm, while the corresponding ^{13}C NMR resonances were seen at 68.9 (NCH_2) and 15.6 (CH_2B) ppm. The ^{11}B NMR signal at −14.4 ppm is typical of a borate, as is the $\Delta\delta(^{19}F_{p,m})$ of 4.2 ppm for the ^{19}F NMR resonances.

The N/B-FLP **2** reacts with the reagent 2,4-hexadiyne to undergo regioselective addition, affording the *trans*-1,2-addition product $PhCH_2NMe_2C(CCMe)=CMeB(C_6F_5)_3$ (**13**), which was isolated in 52% yield as a white solid (Scheme 5). The ^{13}C NMR spectrum of **13** shows a 1:1:1:1 quartet resonance at 156.6 ppm with a C−B coupling of about 52 Hz. This signal is indicative of boron substitution at C2. The adjacent olefinic carbon atom C3 gives rise to a ^{13}C NMR resonance at 126.7 ppm, while the acetylenic carbons give rise to signals at 74.4 and 97.2 ppm. The corresponding ^{11}B NMR resonance is seen at −12.1 ppm. The observation of a total of 15 inequivalent ^{19}F NMR resonances at ambient temperature is consistent with the hindered rotation around the B−C σ bonds. This conformational chirality results in diastereomeric environments for the methyl groups and methylene hydrogens adjacent to nitrogen. As a consequence, the methylene group gives rise to two ^{1}H NMR resonances at 4.59 and 4.46 ppm with a two-bond H, H coupling constant of 13.1 Hz. The methyl groups on nitrogen are inequivalent and show two signals at 3.36 and 3.27 ppm. This reactivity with diyne stands in contrast to the corresponding reaction of the intramolecular P/B-FLP $Mes_2PCH_2CH_2B(C_6F_5)_2$, which results in 1,4-addition, yielding a heterocyclic eight-membered 1,2,3-butatriene derivative.[12] The X-ray crystal structure analysis of **13** (Figure 11)

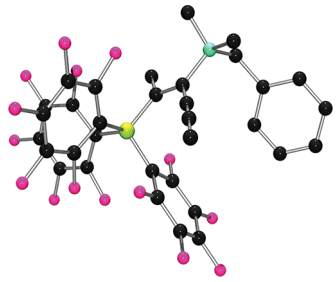
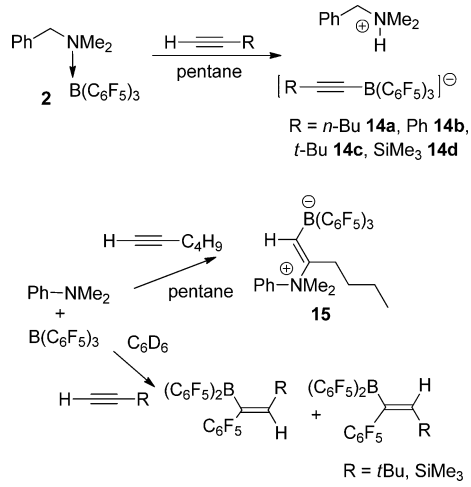


Figure 11. POV-ray depiction of **13**. Color code: C, black; N, blue-green; B, yellow-green; F, pink. Hydrogen atoms are not shown.

confirmed the regioselective *trans*-1,2-addition of the N/B-FLP **2** to one of the carbon−carbon triple bonds, giving rise to the tetrasubstituted *Z*-configured olefinic subunit with a C−C bond length of 1.345(3) Å.

The analogous reaction of **2** with the terminal alkynes HC≡CR (R = *n*-Bu, Ph, *t*Bu, $SiMe_3$) resulted in deprotonation of the alkynes, affording the corresponding ammonium alkynylborate salts $[PhCH_2NMe_2H][RCCB(C_6F_5)_3]$ (R = *n*-Bu (**14a**), Ph (**14b**), *t*Bu (**14c**), $SiMe_3$ (**14d**)) (Scheme 6). Spectroscopically,

Scheme 6. Reactions with Terminal Alkynes



these species are similar. For example, **14a** exhibits characteristic ^{13}C NMR resonances for the acetylenic carbon atoms at 101.3 and 96.1 ppm, with the former exhibiting typical coupling of ca. 70 Hz to the adjacent boron atom, while the latter exhibits a much smaller coupling value. The product **14a** was characterized by X-ray diffraction (Figure 12). This species showed a new B−C bond length of 1.605(3) Å and alkynyl C−C bond length of 1.199(4) Å (for **14a**); otherwise, the metric parameters are unexceptional. Such deprotonation of terminal alkynes has been previously reported for basic phosphines.[11a−d,31]

The analogous reaction of 1-hexyne with the $PhNMe_2$/$B(C_6F_5)_3$ mixture in pentane at 25 °C overnight gave the regioselective *trans*-1,2-addition product $[PhNMe_2C(C_4H_9)=CH(B(C_6F_5)_3]$ (**15**), which was isolated in 50% yield after recrystallization from dichloromethane/pentane at −32 °C. It

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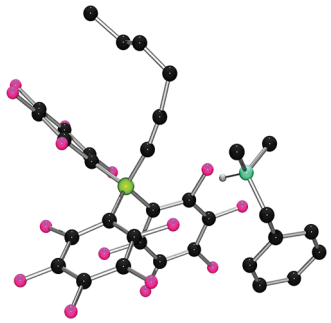

Figure 12. POV-ray depiction of **14a**. Color code: C, black; N, blue-green; B, yellow-green; F, pink; H, gray. Only NH hydrogen atoms are shown.

features ^{13}C NMR signals of the trisubstituted alkenyl moiety at 141.1 and 146.4 ppm, respectively, and a ^{11}B NMR signal at ca. −16 ppm. The X-ray crystal structure analysis of compound **15** (Figure 13) shows the transoid disposition of the $B(C_6F_5)_3$ and

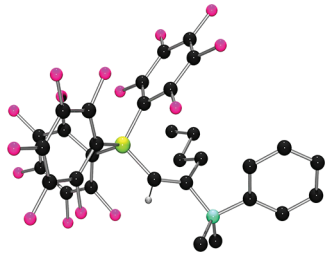

Figure 13. POV-ray depiction of **15**. Color code: C, black; N, blue-green; B, yellow-green; F, pink; H, gray. Only alkene CH hydrogen atoms are shown.

$PhNMe_2$ substituents about the terminal olefinic bond. The corresponding B−C distance is 1.647(5) Å, while the olefinic C−C bond length is 1.320(5) Å.

The contrasting behavior of the aniline derivative based FLP is attributed to the reduced basicity of $PhNMe_2$ in comparison to $PhCH_2NMe_2$. The impact of this reduced basicity was further illustrated in efforts to react $PhNMe_2/B(C_6F_5)_3$ with either *t*BuCCH or Me_3SiCCH. Apparently, the aniline derivative is not sufficiently basic to abstract a proton from these acetylenes, nor does 1,2-N/B-FLP addition occur; presumably this is a result of increased steric hindrance. Rather, the reaction between $B(C_6F_5)_3$ and the 1-alkyne derivatives occurs to give the products of 1,1-carboboration of the alkyne.[32] These products have been previously detailed, and the nature of the products was confirmed by independent synthesis in the absence of the amine.

CONCLUSION

The above chemistry demonstrates the ability of amines to partake in FLP chemistry. While in some cases formation of classical Lewis adducts are seen, it is still possible for such systems to engage in subsequent reactivity with other substrates. Herein, reactions with H_2, CO_2, olefins, alkynes, and diynes have been demonstrated for amine−borane combinations. This work serves to demonstrate that the notion of FLP chemistry extends broadly beyond sterically demanding phosphine−borane combinations, thus establishing some generality of such reactivity. Moreover, this chemistry offers new synthetic strategies based on amines in FLP chemistry. We are continuing to develop and apply the unique reactivity of FLPs in synthetic chemistry and catalysis.

EXPERIMENTAL SECTION

General Considerations. All reactions involving air- and/or moisture-sensitive compounds were carried out under an inert gas atmosphere (Münster, argon purchased from Westfalen AG; Toronto, nitrogen) using Schlenk-type glassware and a glovebox (Münster, Glovebox 150 B-G II from *MBraun*; Toronto, glovebox from Innovative Technology). All other manipulations were performed on a double-manifold N_2 (H_2)/vacuum line with Schlenk-type glassware or in an N_2-filled inert-atmosphere glovebox. The N_2 and H_2 gases were dried by passage through a Dririte column. Solvents (Aldrich) were dried using an Innovative Technologies solvent system (toluene, hexanes, pentane, CH_2Cl_2). NMR spectra were obtained on a Bruker ARX 300 spectrometer (^1H, 300 MHz; ^{13}C, 75 MHz), a Bruker Avance 400 MHz spectrometer, or a Varian Inova 500 spectrometer (^1H, 500 MHz; ^{13}C, 126 MHz; ^{19}F, 470 MHz; ^{11}B, 160 MHz). For ^1H NMR and ^{13}C NMR, chemical shifts (δ) are given relative to TMS and referenced to the solvent signal (^{19}F relative to external $CFCl_3$; ^{11}B relative to external $BF_3{\cdot}Et_2O$). NMR assignments were supported by additional 1D and 2D NMR experiments. NMR spectra were recorded at 25 °C unless otherwise stated, and chemical shifts are reported in ppm. NMR solvents were purchased from Cambridge Isotopes, dried over CaH_2 (CD_2Cl_2, C_6D_5Br, and $CDCl_3$), vacuum-distilled prior to use, and stored over 4 Å molecular sieves in the glovebox. Elemental analyses were performed on a Elementar Vario El III instrument. IR spectra were recorded on a Varian 3100 FT-IR spectrometer (Excalibur Series). Melting points were obtained with a DSC Q20 (TA Instruments). The synthesis of *N,N′*-(1,4-phenylenebis(methylene))bis(*tert*-butylamine) was achieved by the literature method of Tilley and Sayigh.[33] $B(C_6F_5)_3$ was purified by two successive sublimations (Toronto) or freshly prepared and precipitated from pentane (Münster).

Reaction of $PhNMe_2$ and $B(C_6F_5)_3$. *N,N*-Dimethylaniline (10.0 mg, 0.083 mmol) and $B(C_6F_5)_3$ (42.2 mg, 0.083 mmol) were dissolved in C_7D_8 (0.5 mL) to yield a reaction solution which was characterized by NMR spectroscopy. ^1H NMR (600 MHz, C_7D_8, 298 K): δ 7.11 (m, 2H, *m*-C_6H_5); 6.67 (m, 1H, *p*-C_6H_5); 6.51 (m, 2H, *o*-C_6H_4); 2.47 (s, 6H, NMe_2). ^{19}F NMR (564 MHz, C_7D_8, 298 K): δ −128.8 (m, 2F, *o*-C_6F_5); −142.0 (m, 1F, *p*-C_6F_5); −160.2 (m, 2F, *m*-C_6F_5) ($\Delta\delta(^{19}F_{p,m})$ = 18.2). $^{11}B\{^1H\}$ NMR (192 MHz, C_7D_8, 298 K): δ 59.9 (br, $\nu_{1/2} \approx$ 950 Hz).

Synthesis of PhNH(*i*Pr)($B(C_6F_5)_3$) (1). In a glovebox, a 20 mL vial equipped with a magnetic stir bar was charged with $B(C_6F_5)_3$ (176 mg, 0.344 mmol) and *N*-isopropylaniline (46.5 mg, 0.344 mmol) in toluene (4 mL). All volatiles were removed, and the crude oil was washed with hexanes (2 mL). The hexanes portion was reduced in volume and placed in a −40 °C freezer. Colorless crystals of **1** were obtained (122 mg, 0.192 mmol, 55%). ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.84 (br s, 1H, NH), 7.37 (m, 3H, *o,p*-Ar), 7.05 (m, 2H, *m*-Ar), 3.68 (m, 1 H, $^3J_{H-H}$ = 6.1 Hz, $CH(CH_3)_2$), 1.23 ppm (d, 6H, $^3J_{H-H}$ = 6.5 Hz, $CH(CH_3)_2$). ^{13}C NMR (101 MHz, CD_2Cl_2, 298 K): δ 147.8 (dm, $^1J_{C-F} \approx$ 246 Hz, C_6F_5), 139.0 (dm, $^1J_{C-F} \approx$ 242 Hz, C_6F_5), 136.5 (dm, $^1J_{C-F} \approx$ 236 Hz, C_6F_5), 132.8 (*i*-Ar), 130.1 (*o*-Ar), 129.5 (*p*-Ar), 122.7 (*m*-Ar), 55.6 (CH), 19.5 ppm (CH_3). ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): δ −134.6 (d, 2F, $^3J_{F-F}$ = 25 Hz, *o*-C_6F_5), −160.9 (t, 1F, $^3J_{F-F}$ = 42 Hz, *p*-C_6F_5), −165.6 (m, 2F, *m*-C_6F_5). ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): δ −2.19 (s). Anal. Calcd for $C_{27}H_{13}BF_{15}N$: C, 50.11; H, 2.02; N, 2.16. Found: C 49.61; H, 2.46; N, 2.09. X-ray: $C_{27}H_{13}BF_{15}N$, M = 647.19, a = 11.6228(4) Å, b = 18.1284(7) Å, c = 23.6578(9) Å, V = 4984.8(3) Å^3, Z = 8, orthorhombic, $P2_12_12_1$, data (λ = 0.710 69 Å, T = 150 K), 8773 (R_{int} = 0.030) and 7798 reflections ($I \geq 2\sigma(I)$), 798 parameters, R1 = 0.032, wR2 = 0.076, GOF = 1.021.

Synthesis of $PhCH_2NMe_2(B(C_6F_5)_3)$ (2). *N,N*-Dimethylbenzylamine (10.0 mg, 0.074 mmol) and $B(C_6F_5)_3$ (38.2 mg, 0.074 mmol) were dissolved in C_6D_5Br (0.5 mL) and C_7D_8 (0.5 mL), respectively, and mixed to yield a solution which was characterized by NMR

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spectroscopy. ^{1}H NMR (400 MHz, C_6D_5Br, 298 K): δ 7.19 (m, 5H, C_6H_5); 3.63 (br s, 2H, CH_2N); 2.21 (s, 6H, NCH_3). ^{1}H NMR (600 MHz, C_7D_8, 298 K): δ 7.08, 7.04, 7.02 (m, $\sum$5H, C_6H_5); 3.36 (br s, 2H, CH_2N); 2.00 (s, 6H, NCH_3). ^{19}F NMR (377 MHz, C_6D_5Br, 298 K): δ −126.3 (br, 2F, *o*-C_6F_5); −147.9 (br, 1F, *p*-C_6F_5); −160.6 (br, 2F, *m*-C_6F_5), ($\Delta\delta(^{19}F_{p,m})$ = 12.7). ^{19}F NMR (564 MHz, C_7D_8, 298 K): δ −128.0 (br, 2F, *o*-C_6F_5); −145.7 (br, 1F, *p*-C_6F_5); −161.0 (br, 2F, *m*-C_6F_5), ($\Delta\delta(^{19}F_{p,m})$ = 15.3). ^{11}B{^{1}H} NMR (128 MHz, C_6D_5Br, 298 K): δ 30.3 ($\nu_{1/2} \approx$ 1200 Hz). ^{11}B{^{1}H} NMR (192 MHz, C_7D_8, 298 K): δ 46.3 ($\nu_{1/2} \approx$ 800 Hz). X-ray: $C_{27}H_{13}BF_{15}N{\cdot}CH_2Cl_2$, M = 732.12, a = 9.9870(5) Å, b = 10.6730(5) Å, c = 14.3150(7) Å, α = 71.935(2)°, β = 80.851(2)°, γ = 81.259(2)°, V = 1423.59(12) Å^3, Z = 2, triclinic, $P\bar{1}$, data (λ = 1.541 78 Å, T = 223 K) 4868 (R_{int} = 0.040) and 4417 reflections ($I \geq 2\sigma(I)$), 426 parameters, R1 = 0.047, wR2 = 0.126, GOF = 1.035.

Synthesis of [PhNMe$_2$H][HB(C$_6$F$_5$)$_3$] (3) and [PhNMe$_2$D][DB(C$_6$F$_5$)$_3$] (3-*d*$_2$). These compounds were prepared in a similar fashion. A solution of $B(C_6F_5)_3$ (42.2 mg, 0.083 mmol) and *N*,*N*-dimethylaniline (10.0 mg, 0.083 mmol) in C_6D_5Br (2 mL) was subjected to three freeze−pump−thaw cycles and back-filled with H_2 (∼4 atm) at −196 °C. The solution was stored overnight at 25 °C, and all volatiles were removed *in vacuo*. Upon addition of dichloromethane (0.5 mL) and pentane (5 mL), a white precipitate was formed, which was collected and dried to finally give the ammonium salt **3** (48.0 mg, 0.076 mmol, 92%). Data for **3** are as follows. ^{1}H NMR (400 MHz, C_6D_5Br, 298 K): δ 8.60 (s, 1H, NH); 7.07 (m, 3H, C_6H_5); 6.89 (m, 2H, C_6H_5); 3.50 (br, 1:1:1:1 q, $^1J_{BH} \approx$ 80 Hz, 1H, BH); 2.72 (s, 6H, NCH_3). ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ 8.88 (s, 1H, NH); 7.56 (m, 3H, C_6H_5); 7.37 (m, 2H, C_6H_5); 3.46 (br, 1:1:1:1 q, $^1J_{BH} \approx$ 78 Hz, 1H, BH); 3.39 (s, 6H, NCH_3). ^{13}C{^{1}H} NMR (101 MHz, C_6D_5Br, 298 K): δ 148.3 (dm, $^1J_{C-F} \approx$ 230 Hz, C_6F_5); 140.7 (*i*-C_6H_5); 138.7 (dm, $^1J_{C-F} \approx$ 251 Hz, C_6F_5); 136.8 (dm, $^1J_{C-F} \approx$ 247 Hz, C_6F_5); 131.0, 130.8, 118.9 (C_6H_5); 47.2 (NCH_3); n.o. (*i*-C_6F_5). ^{19}F NMR (377 MHz, C_6D_5Br, 298 K): δ −133.9 (m, 2F, *o*-C_6F_5); −160.4 (m, 1F, *p*-C_6F_5); −164.3 (m, 2F, *m*-C_6F_5), ($\Delta\delta(^{19}F_{p,m})$ = 4.1). ^{11}B NMR (128 MHz, C_6D_5Br, 298 K): δ −24.0 (d, $^1J_{BH} \approx$ 80 Hz). ^{11}B{^{1}H} NMR (128 MHz, C_6D_5Br, 298 K): −24.0 (s, $\nu_{1/2} \approx$ 50 Hz). IR: ν_{NH} 3060 cm^{-1} and ν_{BH} 2311 cm^{-1}. Anal. Calcd for $C_{26}H_{13}BF_{15}N$: C, 49.16; H, 2.06; N, 2.21. Found: C, 49.24; H, 2.25; N, 2.11. Data for **3-*d*$_2$** are as follows. ^{2}H NMR (77 MHz, CD_2Cl_2, 298 K): δ 8.81 (br s, ND); 7.63, 7.41 (each br, C_6H_4D); 3.45 (br m, BD). ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 298 K): δ −24.3 (s, $\nu_{1/2} \approx$ 60 Hz). ^{11}B NMR (160 MHz, CD_2Cl_2, 298 K): −24.3 (s, $\nu_{1/2} \approx$ 50 Hz). X-ray: $C_{27}H_{15}BF_{15}N$, M = 635.18, a = 9.9101(4) Å, b = 16.3709(14) Å, c = 15.6368(10) Å, β = 94.644(4)°, V = 2528.5(3) Å^3, Z = 4, monoclinic, $P2_1/n$, data (λ = 1.541 78 Å, T = 223 K) 4294 (R_{int} = 0.058) and 3080 reflections ($I \geq 2\sigma(I)$), 396 parameters, R1 = 0.049, wR2 = 0.128, GOF = 1.015.

Synthesis of [PhCH$_2$NMe$_2$H][HB(C$_6$F$_5$)$_3$] (4) and [PhCH$_2$NMe$_2$D][DB(C$_6$F$_5$)$_3$] (4-*d*$_2$). These compounds were prepared in a similar fashion: a solution of $B(C_6F_5)_3$ (37.9 mg, 0.074 mmol) and *N*,*N*-dimethylbenzylamine (10.0 mg, 0.074 mmol) in C_6D_5Br (1 mL) was subjected to three freeze−pump−thaw cycles and back-filled with H_2 at −196 °C (∼4 atm). After the mixture was stirred at 25 °C for 30 min, dichloromethane (0.1 mL) was added and the resulting solution was layered with hexane (5 mL). Storing at 25 °C for 3 days yielded white crystals (42.4 mg, 0.065 mmol, 88%). Data for **4** are as follows. ^{1}H NMR (400 MHz, C_6D_5Br, 295 K): δ 7.36 (NH), 7.19 (m, 1H, *p*-C_6H_5); 7.09 (m, 2H, *m*-C_6H_5); 6.86 (m, 2H, *o*-C_6H_5); 3.52 (s, 2H, CH_2N); 3.31 (br q, $^1J_{HB} \approx$ 83 Hz, BH); 2.25 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (101 MHz, C_6D_5Br, 297 K): δ 130.6 (*p*-C_6H_5); 130.1 (*o*-C_6H_5); 129.4 (*m*-C_6H_5); 127.5 (*i*-C_6H_5); 62.7 (CH_2N); 42.8 (NCH_3) [C_6F_5 not listed]. ^{19}F NMR (377 MHz, C_6D_5Br, 295 K): δ −133.9 (m, 2F, *o*-C_6F_5); −160.7 (t, $^3J_{FF}$ = 20.1 Hz, 1F, *p*-C_6F_5); −164.5 (m, 2F, *m*-C_6F_5), ($\Delta\delta(^{19}F_{p,m})$ = 3.8). ^{11}B NMR (128 MHz, C_6D_5Br, 295 K): δ −24.3 (d, $^1J_{BH} \sim$ 84 Hz). ^{11}B{^{1}H} NMR (128 MHz, C_6D_5Br, 295 K): −24.3 (s, $\nu_{1/2} \approx$ 60 Hz). Anal. Calcd for $C_{27}H_{15}BF_{15}N$: C, 49.95; H, 2.33; N, 2.16. Found: C, 49.79; H, 2.39; N, 2.20. Data for **4-*d*$_2$** are as follows. ^{2}H NMR (77 MHz, CD_2Cl_2, 298 K): δ 7.35 (br, ND); 4.27 (br, CHDN); 3.23 (br, BD). ^{11}B NMR (160 MHz, CD_2Cl_2, 298 K): δ −24.6 (ca. 50%, br d, $^1J_{BH} \approx$ 88 Hz, BH); −24.8 (ca. 50%, br, BD). ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 298 K): −24.6 (BH); −24.8 (br, BD). X-ray: $C_{27}H_{15}BF_{15}N$, M = 649.21, a = 10.1853(3) Å, b = 13.3147(8) Å, c = 21.7805(7) Å, α = 86.615(4)°, β = 73.671(3)°, γ = 68.525(3)°, V = 2634.6(2) Å^3, Z = 4, triclinic, $P\bar{1}$, data (λ = 1.541 78 Å, T = 223 K), 9134 (R_{int} = 0.042) and 7448 reflections ($I \geq 2\sigma(I)$), 810 parameters, R1 = 0.056, wR2 = 0.150, GOF = 1061.

Synthesis of [1,4-C$_6$H$_4$(CH$_2$NH$_2$*t*Bu)$_2$][HB(C$_6$F$_5$)$_3$]$_2$ (5). In a glovebox, a 100 mL glass bomb equipped with a magnetic stir bar and Teflon screw cap was charged with a solution of $B(C_6F_5)_3$ (304 mg, 0.594 mmol) and 1,4-$C_6H_4(CH_2NHtBu)_2$ (72.5 mg, 0.297 mmol) in toluene (4 mL). The reaction was degassed three times with a freeze−pump−thaw cycle on the vacuum/H_2 line. The reaction flask was cooled to −196 °C and filled with H_2 (4 atm). At 25 °C, immediate precipitation of a white solid was observed. The reaction mixture was stirred overnight at 70 °C. Pentane (10 mL) was added, after which the supernatant was decanted. The residue was washed with pentane (2 × 2 mL) and dried in vacuo to afford **5** as a white powder (374 mg, 0.297 mmol, 100%). Crystals suitable for X-ray crystal structure analyses were obtained from a concentrated solution in C_6D_5Br at 25 °C. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.27 (s, 4H, Ar); 5.95 (br s, 4H, NH_2); 4.38 (s, 4H, CH_2); 3.39 (q, $^1J_{H-B}$ = 83 Hz, B*H*); 1.62 ppm (s, 18H, $C(CH_3)_3$). ^{13}C{^{1}H} NMR (101 MHz, d_8-THF, 298 K): δ 149.3 (dm, $^1J_{C-F} \approx$ 236 Hz, C_6F_5); 146.1 (*i*-Ar); 138.5 (dm, $^1J_{C-F} \approx$ 243 Hz, C_6F_5); 137.4 (dm, $^1J_{C-F} \approx$ 246 Hz, C_6F_5); 134.5 (br, *i*-C_6F_5); 131.4 (Ar); 59.5 ($C(CH_3)_3$); 46.1 (CH_2); 25.9 ppm ($C(CH_3)_3$). ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): δ −134.9 (d, 2F, $^3J_{F-F}$ = 23 Hz, *o*-C_6F_5); −163.5 (t, 1F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5); −167.0 ppm (m, 2F, *m*-C_6F_5). ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): δ −24.3 ppm (d, $^1J_{B-H}$ = 94 Hz, BH). Anal. Calcd for $C_{52}H_{32}B_2F_{30}N_2$: C, 48.93; H, 2.53; N, 2.19. Found: C, 48.82; H, 2.69; N, 2.52. X-ray: $C_{52}H_{32}B_2F_{30}N_2{\cdot}C_6H_5Br$, M = 1432.42, a = 9.3616(18) Å, b = 11.479(2) Å, c = 15.046(3) Å, α = 73.474(9)°, β = 85.102(9)°, γ = 67.335(6)°, V = 1429.9(5) Å^3, Z = 1, triclinic, $P\bar{1}$, data (λ = 0.710 69 Å, T = 150 K), 4780 (R_{int} = 0.059) and 2984 reflections ($I \geq 2\sigma(I)$), 424 parameters, R1 = 0.060, wR2 = 0.163, GOF = 1.081.

Synthesis of [PhCH$_2$NMe$_2$CO$_2$B(C$_6$F$_5$)$_3$] (6). *N*,*N*-Dimethylbenzylamine (150 mg, 1.11 mmol) and $B(C_6F_5)_3$ (570 mg, 1.11 mmol) were dissolved in C_6H_5Br (10 mL), and the solution was subjected to two freeze−pump−thaw cycles. At 25 °C the reaction flask was filled with an atmosphere of CO_2 and left at −32 °C for 12 h. Then pentane (10 mL) was added, and the resulting white precipitate was filtered off and dried *in vacuo* at −10 °C to yield 390 mg (54%, 0.600 mmol) of the carbon dioxide containing compound. Crystals suitable for diffraction were grown from a C_6H_5Br solution that was stored under an atmosphere of CO_2 at −32 °C for several days. ^{1}H NMR (500 MHz, CD_2Cl_2, 218 K): δ 7.54 (m, 1H, *p*-C_6H_5); 7.42 (m, 2H, *m*-C_6H_5); 7.25 (m, 2H, *o*-C_6H_5); 4.46 (s, 2H, CH_2N); 3.08 (s, 6H, NCH_3). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 218 K): δ 150.1 (CO); 147.4 (dm, $^1J_{C-F} \approx$ 238 Hz, C_6F_5); 139.1 (dm, $^1J_{C-F} \approx$ 246 Hz, C_6F_5); 136.2 (dm, $^1J_{C-F} \approx$ 246 Hz, C_6F_5); 132.4 (*o*-C_6H_5); 131.1 (*p*-C_6H_5); 129.3 (*m*-C_6H_5); 125.5 (*i*-C_6H_5); 117.5 (br, *i*-C_6F_5); 66.8 (CH_2N); 48.0 (NCH_3). ^{19}F NMR (470 MHz, CD_2Cl_2, 218 K): δ −135.6 (m, 2F, *o*-C_6F_5); −158.9 (br t, $^3J_{FF} \approx$ 20 Hz, 1F, *p*-C_6F_5); −164.7 (m, 2F, *m*-C_6F_5) ($\Delta\delta(^{19}F_{p,m})$ = 5.8). IR (KBr/cm^{-1}): ν 1822 (m). Anal. Calcd for $C_{28}H_{13}BF_{15}NO_2$: C, 48.65; H, 1.90; N, 2.03. Found: C, 48.52; H, 1.99; N, 1.97. X-ray: $C_{28}H_{13}BF_{15}NO_2$, M = 691.20, a = 14.309(3) Å, b = 12.160(2) Å, c = 15.471(3) Å, β = 92.833(7)°, V = 2688.6(9) Å^3, Z = 4, monoclinic, $P2_1/n$, data (λ = 0.710 69 Å, T = 150 K), 6176 (R_{int} = 0.036) and 4293 reflections ($I \geq 2\sigma(I)$), 424 parameters, R1 = 0.045, wR2 = 0.115, GOF = 1016.

Synthesis of [PhCH$_2$NHMe$_2$][HCO$_2$B(C$_6$F$_5$)$_3$] (7). Compound **4** (100 mg, 0.154 mmol) was dissolved in toluene (4 mL). After two freeze−pump−thaw cycles, the solution was pressurized with CO_2 (1.5 atm) and then heated to 80 °C overnight. The solvent was removed under reduced pressure, and pentane (10 mL) was added. Drying *in vacuo* yielded 96.0 mg (0.139 mmol, 90%) of the formic acid adduct **7**. ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 8.29 (s, 1H, CHO); 6.98 (m, 3H, *m*,*p*-C_6H_5); 6.75 (m, 2H, *o*-C_6H_5); 2.84 (s, 2H, CH_2N); 1.46 (s, 6H, NCH_3), n.o. (NH). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ 170.2 (CHO); 148.6 (dm, $^1J_{C-F} \approx$ 243 Hz, C_6F_5); 140.2 (dm, $^1J_{C-F} \approx$

247 Hz, C_6F_5); 137.6 (dm, $^1J_{C-F} \approx 251$ Hz, C_6F_5); 130.5 (*p*-C_6H_5), 130.4 (*o*-C_6H_5); 129.4 (*m*-C_6H_5); 128.0 (*i*-C_6H_5); 120.6 (br, *i*-C_6F_5); 60.8 (CH_2N); 40.9 (NCH_3). ^{19}F NMR (470 MHz, C_6D_6, 298 K): δ −134.2 (m, 2F, *o*-C_6F_5); −157.9 (t, 1F, $^3J_{FF} \approx 21$ Hz, *p*-C_6F_5); −164.3 (m, 2F, *m*-C_6F_5) ($\Delta\delta(^{19}F_{p,m}) = 6.4$). $^{11}B\{^1H\}$ NMR (160 MHz, C_6D_6, 298 K): δ −2.2 ($\nu_{1/2} \approx 200$ Hz). IR (KBr/cm^{-1}): ν 1621 (m). Anal. Calcd for $C_{28}H_{15}BF_{15}NO_2$: C, 48.51; H, 2.18; N, 2.02. Found: C, 48.33; H, 2.49; N, 2.36. X-ray: $C_{28}H_{15}BF_{15}NO_2$, *M* = 693.22, *a* = 7.5203(3) Å, *b* = 18.6531(8) Å, *c* = 19.9816(10) Å, *V* = 2803.0(2) Å^3, *Z* = 4, orthorhombic, $P2_12_12_1$, data (λ = 1.541 78 Å, *T* = 223 K) 4454 (R_{int} = 0.064) and 3270 reflections ($I \geq 2\sigma(I)$), 432 parameters, R1 = 0.043, wR2 = 0.102, Flack parameter −0.09(17), GOF = 1.035.

Synthesis of [PhN*i*PrH$_2$][PhN*i*PrCO$_2$B(C$_6$F$_5$)$_3$] (8). In a glovebox, a 50 mL glass bomb equipped with a magnetic stir bar and Teflon screw tap was charged with a solution of $B(C_6F_5)_3$ (500 mg, 0.978 mmol) and *N*-isopropylaniline (264 mg, 1.95 mmol) in toluene (7 mL). The reaction was degassed three times with a freeze−pump−thaw cycle on the vacuum/CO_2 line. The reaction flask was cooled to −196 °C and filled with $^{13}CO_2$ (1 atm). The reaction mixture was stirred at 25 °C for 2 days. All volatiles were then removed *in vacuo*; the residue was dissolved in a minimum amount of dichloromethane, and the product was precipitated as a white powder using hexanes. The product was washed with hexanes (2 × 2 mL) and dried *in vacuo* to yield **8** (769 mg, 0.930 mmol, 95%). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.55 (br s, NH_2); 7.48−7.33 (m, 6H, *m*,*p*-Ar); 7.10 (d, 2H, *o*-Ar); 6.68 (br d, 2H, *o*-Ar); 4.78 (m, 1H, C*H*); 3.09 (br s, 1H, C*H*); 1.12 (d, 6H, CH(CH_3)$_2$); 0.91 ppm (br s, 6H, CH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 298 K): δ 159.4 (s, NCO_2); 147.9 (dm, $^1J_{C-F} \approx 240$ Hz, C_6F_5); 140.3 (s, *i*-Ar); 138.7 (dm, $^1J_{C-F} \approx 243$ Hz, C_6F_5); 136.5 (dm, $^1J_{C-F} \approx 239$ Hz, C_6F_5); 132.1 (s, *o*-Ar); 129.8 (br, *i*-C_6F_5); 129.6 (s, *m*-Ar); 127.5 (s, *p*-Ar); 122.2 (br, *o*-Ar); 49.0 (s, CH); 21.2 (s, CH(CH_3)$_2$); 19.2 ppm (br, CH(CH_3)$_2$).^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): δ −134.7 (d, 2F, $^3J_{F-F}$ = 22 Hz, *o*-C_6F_5); −162.3 (t, 1F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5); −166.8 ppm (m, 2F, *m*-C_6F_5). ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): δ −3.95 ppm (s). IR: ν(C═O) 1646 cm^{-1}. Anal. Calcd for $C_{75}H_{50}B_2Cl_2F_{30}N_4O_4$: C, 51.96; H, 2.91; N, 3.23. Found: C, 51.63; H, 3.28; N, 3.29. X-ray: $C_{37}H_{24}BF_{15}N_2O_2 \cdot {}^1/_2CH_2Cl_2$, *M* = 866.86, *a* = 11.2336(4) Å, *b* = 14.9889(6) Å, *c* = 44.3937(16) Å, β = 90.618(2)°, *V* = 7474.5(5) Å^3, *Z* = 8, monoclinic, $P2_1/c$, data (λ = 0.710 69 Å, *T* = 150 K), 13 157 (R_{int} = 0.048) and 10 517 reflections ($I \geq 2\sigma(I)$), 1072 parameters, R1 = 0.053, wR2 = 0.127, GOF = 1.051.

Synthesis of [1,4-C$_6$H$_4$(CH$_2$NH$_2$*t*Bu)(CH$_2$N*t*BuCO$_2$B(C$_6$F$_5$)$_3$)] (9). In a glovebox, a 50 mL glass bomb equipped with a magnetic stir bar and Teflon screw tap was charged with a solution of $B(C_6F_5)_3$ (154 mg, 0.300 mmol) and *N*,*N*′-(1,4-phenylenebis(methylene))bis-(*tert*-butylamine) (73.3 mg, 0.300 mmol) in toluene (5 mL). The reaction was degassed three times with a freeze−pump−thaw cycle on the vacuum/CO_2 line. The reaction flask was cooled to −196 °C and filled with $^{13}CO_2$ (1 atm). Upon warming to 25 °C, precipitate was observed in the reaction flask. The mixture was stirred overnight at 50 °C. Pentane (3 mL) was added, after which the supernatant was decanted. The product was washed with pentane (3 × 2 mL) and dried *in vacuo* to afford **9** as a white powder (212 mg, 0.263 mmol, 88%). Crystals suitable for X-ray crystal structure analyses were obtained by recrystallization from a standing solution in C_6H_5Br at 25 °C. ^{1}H NMR (400 MHz, d_8-THF, 298 K): δ 7.88 (br, 2H, NH_2); 7.34 (br, 2H, Ar); 7.21 (br d, 2H, Ar); 4.67 (br, 2H, CH_2); 4.20 (br m, 2H, NH_2CH_2); 1.48 (s, 9H, CH_3); 1.30 ppm (br, 9H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, d_8-THF, 298 K): δ 157.6 (NCO_2); 148.1 (dm, $^1J_{C-F} \approx 246$ Hz, C_6F_5); 145.7 (*i*-Ar); 138.1 (dm, $^1J_{C-F} \approx 246$ Hz, C_6F_5); 136.0 (dm, $^1J_{C-F} \approx 242$ Hz, C_6F_5); 128.7 (*o*-Ar); 128.6 (*i*-Ar); 127.6 (*o*-Ar); 124.3 (br, *i*-C_6F_5); 57.9 (C(CH_3)$_3$); 54.9 (C(CH_3)$_3$); 47.9 (CH_2); 45.7 (CH_2); 29.0 (br, CH_3); 25.4 ppm (CH_3) ^{19}F NMR (377 MHz, d_8-THF, 298 K): δ −134.9 (br, 2F, *o*-F); −162.7 (br, 1F, *p*-F); −167.8 ppm (br, 2F, *m*-F). ^{11}B NMR (128 MHz, d_8-THF, 298 K): δ −4.24 (s) ppm. IR: ν(C═O) 1645 cm^{-1}. Anal. Calcd for $C_{35}H_{28}BF_{15}N_2O_2 \cdot$THF: C, 53.44; H, 4.14; N, 3.20. Found: C, 53.89; H, 4.63; N, 3.16. X-ray: $C_{35}H_{28}BF_{15}N_2O_2 \cdot CH_2Cl_2 \cdot$THF, *M* = 961.43, *a* = 11.8169(9) Å, *b* = 14.2528(10) Å, c = 25.8313(18) Å, α = 92.291(4)°, β = 101.983(4)°, γ = 94.629(4)°, *V* = 4234.7(5) Å^3, *Z* = 4, triclinic, $P\bar{1}$, data (λ = 0.710 69 Å, *T* = 150 K), 14 788 (R_{int} = 0.043) and 8568 reflections ($I \geq 2\sigma(I)$), 1135 parameters, R1 = 0.085, wR2 = 0.271, GOF = 1.031.

Synthesis of [C$_5$H$_6$Me$_4$NMeH]$_2$[1,4-C$_6$H$_4$(CH$_2$N*t*BuCO$_2$B-(C$_6$F$_5$)$_3$)$_2$] (10). In a glovebox, a 50 mL glass bomb equipped with a magnetic stir bar was charged with $B(C_6F_5)_3$ (206 mg, 0.402 mmol), *N*,*N*′-(1,4-phenylenebis(methylene))bis(*tert*-butylamine) (50.0 mg, 0.201 mmol), and 1,2,2,6,6-pentamethylpiperidine (62.4 mg, 0.402 mmol) in toluene (5 mL). The reaction was degassed three times with a freeze−pump−thaw cycle on the vacuum/CO_2 line. The reaction flask was cooled to −196 °C and filled with CO_2 (1 atm). The reaction mixture was stirred at 25 °C overnight. Over this reaction time precipitate was observed in the reaction vessel. Pentane (3 mL) was added, after which the supernatant was decanted. The product was washed with pentane (3 × 2 mL) and dried *in vacuo* to afford the product as a white crystalline material (153 mg, 46%). Colorless crystals suitable for X-ray crystal structure analyses were obtained by recrystallization from a THF solution layered with hexanes in a −40 °C freezer. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.07 (s, 4H, C_6H_4); 7.04 (br, 2H, NH); 4.61 (br, 4H, CH_2); 2.63 (s, 6H, NCH_3); 1.72−1.58 (br m, 12H, *m*,*p*-CH_2); 1.37 (br, 18H, ^{t}Bu); 1.28 ppm (s, 24H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 298 K): δ 158.7 (NCO_2); 148.0 (dm, $^1J_{C-F} \approx 240$ Hz, C_6F_5); 138.2 (dm, $^1J_{C-F} \approx 246$ Hz, C_6F_5); 136.2 (dm, $^1J_{C-F} \approx 246$ Hz, C_6F_5); 128.8 (*i*-Ar); 125.9 (Ar); 124.2 (*i*-C_6F_5); 64.8 (C(CH_3)$_2$); 54.9 (C(CH_3)$_3$); 48.3 (amine-CH_2); 38.1 (PMP *m*-CH_2); 29.5 (^{t}Bu); 29.0 (NCH_3); 28.5 (PMP-CH_3); 18.8 (PMP-CH_3); 15.4 ppm (PMP-*p*-CH_2). ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): δ −133.6 (br, 2F, *o*-C_6F_5); −164.8 (br, 1F, *p*-C_6F_5); −168.6 ppm (br, 2F, *m*-C_6F_5). ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): δ −4.70 ppm (s). IR (KBr): ν 1693 cm^{-1} (vs, C═O). Anal. Calcd for $C_{74}H_{70}B_2F_{30}N_4O_4$: C, 53.19; H, 4.22; N, 3.35. Found: C, 53.03; H, 4.38; N, 3.39. X-ray: $C_{37}H_{35}BF_{15}N_2O_2$, *M* = 835.48, *a* = 15.0642(17) Å, *b* = 12.3370(14) Å, *c* = 21.279(2) Å, β = 109.498(7)°, *V* = 3727.8(7) Å^3, *Z* = 4, monoclinic, $P2_1/c$, data (λ = 0.710 69 Å, *T* = 150 K), 8566 (R_{int} = 0.129) and 3321 reflections ($I \geq 2\sigma(I)$), 526 parameters, R1 = 0.068, wR2 = 0.221, GOF = 0.965.

Synthesis of [PhN*i*PrC(OSiEt$_3$)OB(C$_6$F$_5$)$_3$] (11). In a glovebox, compound **8** (68.4 mg, 0.0827 mmol) was weighed into a 20 mL vial and dissolved in toluene (3 mL). To this solution, $HSiEt_3$ (13.3 μL, 0.0835 mmol) was added via syringe. The reaction mixture was mixed overnight at 25 °C. All volatiles were removed, and the crude oil was dissolved in a minimum amount of pentane and placed in a −40 °C freezer overnight. Colorless crystals of **11** were obtained (42.6 mg, 0.0529 mmol, 64%). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.56 (m, 3H, *m*,*p*-Ar); 7.15 (m, 2H, *o*-Ar); 4.77 (m, 1H, $^3J_{H-H}$ = 6.6 Hz, C*H*); 1.15 (d, 6H, $^3J_{H-H}$ = 6.6 Hz, CH(CH_3)$_2$); 0.64 (t, 9H, $^3J_{H-H}$ = 8 Hz, Si(CH_2CH_3)$_3$, 0.10 (q, 6H, $^3J_{H-H}$ = 8 Hz, Si(CH_2CH_3)$_3$. $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 298 K): δ 156.4 (NCO_2); 148.3 (dm, $^1J_{C-F} \approx 249$ Hz, C_6F_5); 137.5 (dm, $^1J_{C-F} \approx 250$ Hz, C_6F_5); 136.5 (dm, $^1J_{C-F} \approx 242$ Hz, *m*-C_6F_5); 134.8 (*i*-Ar); 130.7 (*p*-Ar); 130.2 (*m*-Ar); 130.1 (*o*-Ar); 129.4 (br, *i*-C_6F_5); 53.7 (NCH); 20.7 (CH(CH_3)$_2$); 6.07 (Si(CH_2CH_3)$_3$); 4.31 ppm (Si(CH_2CH_3)$_3$). ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): δ −135.0 (br, 2F, *o*-C_6F_5); −160.0 (br, 1F, *p*-C_6F_5); −165.3 (br, 2F, *p*-C_6F_5) ppm. ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): δ −3.98 ppm (s). Anal. Calcd for $C_{34}H_{27}BF_{15}NO_2Si$: C, 50.70; H, 3.38; N, 1.74. Found: C, 50.85; H, 3.54; N, 1.84. X-ray: $C_{34}H_{27}BF_{15}NO_2Si$, *M* = 805.47, *a* = 10.0980(8) Å, *b* = 11.9201(9) Å, *c* = 15.5418(13) Å, α = 88.808(4)°, β = 80.396(5)°, γ = 69.131(4)°, *V* = 1722.0(2) Å^3, *Z* = 2, triclinic, $P\bar{1}$, data (λ = 0.710 69 Å, *T* = 150 K), 6044 (R_{int} = 0.053) and 4109 reflections ($I \geq 2\sigma(I)$), 487 parameters, R1 = 0.042, wR2 = 0.108, GOF = 1.012.

Synthesis of PhCH$_2$NMe$_2$CH$_2$CH$_2$B(C$_6$F$_5$)$_3$ (12). A solution of *N*,*N*-dimethylbenzylamine (30.0 mg, 0.222 mmol) and $B(C_6F_5)_3$ (114 mg, 0.222 mmol) in pentane (5 mL) was degassed carefully and pressurized with ethylene (2 atm), upon which a white solid started to precipitate. Stirring was continued for 2 days, and then the precipitate was filtered off. After crystallization of the solid from dichloromethane/pentane at −32 °C, the product was obtained (57%, 85.6 mg, 0.126 mmol). ^{1}H NMR (600 MHz, C_6D_6, 298 K): δ 6.96 (m, 1H, *p*-C_6H_5); 6.91 (m, 2H, *m*-C_6H_5); 6.21 (m, 2H, *o*-C_6H_5); 2.48 (s, 2H,

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$^{Ph}CH_2N$); 2.31 (m, 2H, NCH_2); 1.55 (br, 2H, CH_2B); 1.20 (s, 6H, NCH_3). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298 K): δ 148.9 (dm, $^1J_{C-F} \approx 241$ Hz, C_6F_5); 139.0 (dm, $^1J_{C-F} \approx 253$ Hz, C_6F_5); 137.4 (dm, $^1J_{C-F} \approx 239$ Hz, C_6F_5); 132.0 (*o*-C_6H_5); 131.0 (*p*-C_6H_5); 129.0 (*m*-C_6H_5); 125.9 (*i*-C_6H_5); n.o. (*i*-C_6F_5); 68.9 (NCH_2); 67.2 ($^{Ph}CH_2N$); 47.8 (NCH_3); 15.6 (br, CH_2B). ^{19}F NMR (564 MHz, C_6D_6, 298 K): δ −132.7 (m, 2F, *o*-C_6F_5); −160.8 (t, ^3J = 20.2 Hz, 1F, *p*-C_6F_5); −165.0 (m, 2F, *m*-C_6F_5) ($\Delta\delta(^{19}F_{p,m})$ = 4.2). $^{11}B\{^1H\}$ NMR (160 MHz, C_6D_6, 298 K): δ −14.4 ($\nu_{1/2} \approx 30$ Hz). Anal. Calcd for $C_{29}H_{17}BF_{15}N{\cdot}0.3CH_2Cl_2$: C, 50.20; H, 2.51; N, 2.00. Found: C, 50.06; H, 2.17; N, 1.90. X-ray: $C_{29}H_{17}BF_{15}N{\cdot}^1/_2CH_2Cl_2$, M = 717.71, a = 13.2426(3) Å, b = 13.7868(3) Å, c = 18.2798(5) Å, α = 111.590(2)°, β = 99.707(2)°, γ = 101.426(1)°, V = 2933.02(12) Å^3, Z = 4, triclinic, $P\bar{1}$, data (λ = 1.541 78 Å, T = 223 K), 10 000 (R_{int} = 0.052) and 7942 parameters ($I \geq 2\sigma(I)$), 872 parameters, R1 = 0.048, wR2 = 0.124, GOF = 1.051.

Synthesis of $PhCH_2NMe_2C(CCMe)$=$CMeB(C_6F_5)_3$ (13). 2,4-Hexadiyne (11.5 mg, 0.148 mmol) was added to a solution of *N*,*N*-dimethylbenzylamine (20.0 mg, 0.148 mmol) and $B(C_6F_5)_3$ (75.8 mg, 0.148 mmol) in pentane (5 mL). After the mixture was stirred overnight at 25 °C, the obtained precipitate was filtered off and dried under reduced pressure to yield the product **13** (52%, 55.8 mg, 0.077 mmol). ^1H NMR (500 MHz, CD_2Cl_2, 298 K): δ 7.50 (m, 1H, *p*-C_6H_5); 7.38 (m, 2H, *m*-C_6H_5); 7.22 (m, 2H, *o*-C_6H_5); 4.59 (d, $^2J_{HH}$ = 13.1 Hz, 1H, CH_2N); 4.46 (d, $^2J_{HH}$ = 13.1 Hz, 1H, CH_2N); 3.36 (s, 3H, NCH_3); 3.27 (s, 3H, NCH_3); 2.00 (br s, 3H, 1-H); 1.63 (s, 3H, 6-H). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 298 K): δ 156.6 (1:1:1:1 q, $^1J_{CB} \approx 52$ Hz, C-2); 132.4 (*o*-C_6H_5); 131.4 (*p*-C_6H_5); 129.5 (*m*-C_6H_5); 127.7 (*i*-C_6H_5); 126.7 (br, C-3); 97.2 (C-5); 74.7 (br, C-4); 69.2 (CH_2N); 56.0, 53.3 (NCH_3); 22.2 (br, C-1); 4.1 (C-6) [C_6F_5 not listed]. ^{19}F NMR (470 MHz, CD_2Cl_2, 298 K): δ −129.5 (m, 1F, *o*-$C_6F_5^A$); −129.6 (m, 1F, *o*-$C_6F_5^C$); −129.9 (m, 1F, *o*-$C_6F_5^C$); −130.5 (m, 1F, *o*-$C_6F_5^B$); −131.9 (m, 1F, *o*-$C_6F_5^B$); −133.1 (m, 1F, *o*-$C_6F_5^A$); −162.2 (t, ^3J = 20.5 Hz, 1F, *p*-$C_6F_5^A$); −163.1 (t, ^3J = 21.6 Hz, 1F, *p*-$C_6F_5^C$); −163.5 (t, ^3J = 20.6 Hz, 1F, *p*-$C_6F_5^B$); −165.9 (m, 1F, *m*-$C_6F_5^A$); −166.5 (m, 1F, *m*-$C_6F_5^A$); −167.3 (m, 2F, *m*-$C_6F_5^C$); −167.4 (m, 2F, *m*-$C_6F_5^B$); −168.0 (m, 1F, *m*-$C_6F_5^C$); −168.2 (m, 1F, *m*-$C_6F_5^B$). $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 298 K): δ −12.1 ($\nu_{1/2} \approx$ 20 Hz). Anal. Calcd for $C_{33}H_{19}BF_{15}N$: C, 54.65; H, 2.64; N, 1.93. Found: C, 54.69; H, 3.00; N, 1.93. X-ray: $C_{33}H_{19}BF_{15}N{\cdot}^1/_2C_5H_{12}$, M = 761.38, a = 10.3487(3) Å, b = 13.2156(8) Å, c = 13.9427(10) Å, α = 97.316(3)°, β = 107.850(5)°, γ = 109.846(3)°, V = 1649.26(14) Å^3, Z = 2, triclinic, $P\bar{1}$, data (λ = 1.541 78 Å, T = 223 K), 5717 (R_{int} = 0.042) and 4943 reflections ($I \geq 2\sigma(I)$), 471 parameters, R1 = 0.058, wR2 = 0.175, maximum GOF = 1.064.

Synthesis of $[PhCH_2NMe_2H][RC{\equiv}CB(C_6F_5)_3]$ (R = *n*-Bu (14a), Ph (14b), *t*Bu (14c), $SiMe_3$ (14d)). These compounds were prepared in a general way. A representative example: a solution of *N*,*N*-dimethylbenzylamine (50.0 mg, 0.370 mmol) and $B(C_6F_5)_3$ (190 mg, 0.370 mmol) in pentane (10 mL) was treated with 1-hexyne (30.5 mg, 0.370 mmol) and the reaction mixture was stirred vigorously overnight. The resulting white solid was filtered off, washed with pentane, and dried *in vacuo* to yield the zwitterionic compound **14a** (190 mg, 0.26 mmol, 70%).

Data for **14a** are as follows. ^1H NMR (500 MHz, C_6D_6, 298 K): δ 7.00 (m, 1H, *p*-C_6H_5); 6.95 (m, 2H, *m*-C_6H_5); 6.62 (m, 2H, *o*-C_6H_5); 2.83 (s, 2H, CH_2N); 1.59 (m, 2H, 3-H); 1.46 (s, 6H, NCH_3); 1.43 (m, 2H, 4-H); 1.31 (m, 2H, 5-H); 0.84 (t, $^3J_{HH}$ = 7.3 Hz, 3H, 6-H); n.o. (NH). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298 K): δ 148.9 (dm, $^1J_{C-F} \approx$ 238 Hz, C_6F_5); 139.3 (dm, $^1J_{C-F} \approx 245$ Hz, C_6F_5); 137.3 (dm, $^1J_{C-F} \approx$ 249 Hz, C_6F_5); 131.1 (*p*-C_6H_5); 130.7 (*o*-C_6H_5); 129.6 (*m*-C_6H_5); 126.5 (*i*-C_6H_5); 124.6 (br m, *i*-C_6F_5); 101.3 (1:1:1:1 q, $^1J_{CB}$ = 71.1 Hz, C-1); 96.1 (1:1:1:1 q, $^2J_{CB}$ = 14.4 Hz, C-2); 61.9 (CH_2N); 41.8 (NCH_3); 31.9 (C-4); 22.0 (C-5); 20.7 (C-3); 13.6 (C-6). ^{19}F NMR (470 MHz, C_6D_6, 298 K): δ −132.1 (m, 2F, *o*-C_6F_5); −161.3 (t, ^3J = 22.2 Hz, 1F, *p*-C_6F_5); −165.6 (m, 2F, *m*-C_6F_5), ($\Delta\delta(^{19}F_{p,m})$ = 4.3). $^{11}B\{^1H\}$ NMR (160 MHz, C_6D_6, 298 K): δ −20.6 (s, $\nu_{1/2} \approx$ 20 Hz). Anal. Calcd for: $C_{33}H_{23}BF_{15}N$: C, 54.34; H, 3.18; N, 1.92. Found: C, 53.84; H, 3.13; N, 2.07. X-ray: $C_{33}H_{23}BF_{15}N$, M = 729.33, a = 10.0966(4) Å, b = 10.4671(6) Å, c = 16.6994(5) Å, α = 73.407(4)°, β = 73.953(2)°, γ = 72.449(6)°, V = 1577.24(12) Å^3, Z = 2, triclinic, $P\bar{1}$, data (λ = 1.541 78 Å, T = 223 K) 5412 (R_{int} = 0.040) and 4657 reflections ($I \geq 2\sigma(I)$), 471 parameters, R1 = 0.053, wR2 = 0.151, GOF = 1.024.

Data for **14b** are as follows. ^1H NMR (500 MHz, C_6D_6, 298 K): δ 7.22 (m, 2H, 4-H); 7.01 (m, 1H, *p*-C_6H_5); 6.94 (m, 2H, *m*-C_6H_5); 6.83 (m, 3H, 5,6-H); 6.49 (m, 2H, *o*-C_6H_5); 2.75 (s, 2H, CH_2N); 1.34 (s, 2H, NCH_3). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298 K): δ 149.0 (dm, $^1J_{C-F} \approx 239$ Hz, C_6F_5); 139.2 (dm, $^1J_{C-F} \approx 221$ Hz, C_6F_5); 137.3 (dm, $^1J_{C-F} \approx 226$ Hz, C_6F_5); 131.7 (C-4); 131.1 (*p*-C_6H_5); 130.5 (*o*-C_6H_5); 129.6 (*m*-C_6H_5); 128.8 (C-5); 127.3 (C-6); 126.3 (C-3); 126.2 (*i*-C_6H_5); 124.1 (br m, *i*-C_6F_5); 111.9 (1:1:1:1 q, $^1J_{CB} \approx 70$ Hz, C-1); 94.9 (1:1:1:1 q, $^2J_{CB} \approx 15$ Hz,, C-2); 61.9 (CH_2N); 42.0 (NCH_3). ^{19}F NMR (470 MHz, C_6D_6, 298 K): δ −132.3 (m, 2F, *o*-C_6F_5); −161.2 (t, $^3J_{FF}$ = 21.1 Hz, 1F, *p*-C_6F_5); −165.5 (m, 2F, *m*-C_6F_5), ($\Delta\delta(^{19}F_{p,m})$ = 4.3). $^{11}B\{^1H\}$ NMR (160 MHz, C_6D_6, 298 K): δ −20.3 ($\nu_{1/2} \approx$ 20 Hz). Anal. Calcd for $C_{35}H_{19}BF_{15}N$: C, 56.10; H, 2.56; N, 1.87. Found: C, 55.24; H, 2.56; N, 2.17.

Data for **14c** are as follows. ^1H NMR (500 MHz, C_6D_6, 298 K): δ 7.05 (m, 1H, *p*-C_6H_5); 7.00 (m, 2H, *m*-C_6H_5); 6.56 (m, 2H, *o*-C_6H_5); 2.81 (s, 2H, CH_2N); 1.42 (s, 6H, NCH_3); 1.27 (s, 9H, *t*Bu). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298 K): δ 149.0 (dm, $^1J_{C-F} \approx 240$ Hz, C_6F_5); 138.8 (dm, $^1J_{C-F} \approx 243$ Hz, C_6F_5); 137.3 (dm, $^1J_{C-F} \approx 247$ Hz, C_6F_5); 131.2 (*p*-C_6H_5); 130.5 (*o*-C_6H_5); 129.7 (*m*-C_6H_5); 126.4 (*i*-C_6H_5); 104.4 (br, C-2); 61.8 (CH_2N); 42.0 (NCH_3); 31.9 (*t*Bu); 28.7 (*t*Bu), n.o. (*i*-C_6F_5); n.o. (C-1). ^{19}F NMR (470 MHz, C_6D_6, 298 K): δ −131.7 (m, 2F, *o*-C_6F_5); −162.4 (t, $^3J_{FF}$ = 20.4 Hz, 1F, *p*-C_6F_5); −166.3 (m, 2F, *m*-C_6F_5), ($\Delta\delta(^{19}F_{p,m})$ = 3.9). $^{11}B\{^1H\}$ NMR (160 MHz, C_6D_6, 298 K): δ −20.3 ($\nu_{1/2} \approx$ 25 Hz). Anal. Calcd for $C_{33}H_{23}BF_{15}N$: C, 54.34; H, 3.18; N, 1.92. Found: C, 54.62; H, 3.21; N, 1.89.

Data for **14d** are as follows. ^1H NMR (500 MHz, C_6D_6, 298 K): δ 7.01 (m, 1H, *p*-C_6H_5); 6.95 (m, 2H, *m*-C_6H_5); 6.60 (m, 2H, *o*-C_6H_5); 2.87 (br s, 2H, CH_2N); 1.45 (br s, 6H, NCH_3); 0.04 (s, $^2J_{SiH}$ = 6.9 Hz, 9H, $SiCH_3$). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298 K): δ 148.9 (dm, $^1J_{C-F} \approx 244$ Hz, C_6F_5); 139.4 (dm, $^1J_{C-F} \approx 235$ Hz, C_6F_5); 137.4 (dm, $^1J_{C-F} \approx 245$ Hz, C_6F_5); 131.1 (*p*-C_6H_5); 130.7 (*o*-C_6H_5); 129.6 (*m*-C_6H_5); 126.3 (*i*-C_6H_5); 101.2 (m, C-2); 61.4 (CH_2N); 41.6 (NCH_3); 0.78 ($SiCH_3$), n.o. (*i*-C_6F_5); n.o. (C-1). ^{19}F NMR (470 MHz, C_6D_6, 298 K): δ −131.8 (m, 2F, *o*-C_6F_5); −160.6 (t, ^3J = 21.1 Hz, 1F, *p*-C_6F_5); −165.3 (m, 2F, *m*-C_6F_5), ($\Delta\delta(^{19}F_{p,m})$ = 4.7). $^{11}B\{^1H\}$ NMR (160 MHz, C_6D_6, 298 K): δ −20.9 ($\nu_{1/2} \approx$ 20 Hz). ^{29}Si DEPT NMR (99 MHz, C_6D_6, 298 K): δ −19.3 ($\nu_{1/2} \approx$ 5 Hz). Anal. Calcd for $C_{32}H_{23}BF_{15}NSi$: C, 51.56; H, 3.11; N, 1.88. Found: C, 51.27; H, 3.29; N, 1.91.

Synthesis of $[PhNMe_2C(C_4H_9){=}CH(B(C_6F_5)_3)]$ (15). *N*,*N*-Dimethylaniline (40.0 mg, 0.330 mmol), $B(C_6F_5)_3$ (170 mg, 0.332 mmol), and 1-hexyne (27.1 mg, 0.330 mmol) were dissolved in pentane (5 mL), and the mixture was stirred at 25 °C overnight. The solvent was removed under reduced pressure to yield a yellow oil, which was purified by fractional crystallization from dichloromethane/pentane at −32 °C. Compound **15** was isolated in 50% yield (118 mg, 0.165 mmol). ^1H NMR (600 MHz, C_6D_6, 298 K): δ 6.71 (m, 3H, *m*-,*p*-Ph); 6.70 (m, 1H, 1-H); 6.48 (m, 2H, *o*-Ph); 1.98 (s, 6H, NCH_3); 1.53 (m, 2H, 3-H); 0.70 (m, 2H, 5-H); 0.49 (t, $^3J_{HH}$ = 7.1 Hz, 3H, 6-H); 0.30 (m, 2H, 4-H). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6, 298 K): δ 146.4 (C-2); 141.1 (br, C-1); 130.1 (*p*-Ph); 129.9 (*m*-Ph), 120.1 (*o*-Ph); n.o. (*i*-Ph); 53.7 (NCH_3); 30.6 (C-4); 30.0 (C-3); 23.1 (C-5); 13.4 (C-6) [C_6F_5 not listed]. ^{19}F NMR (564 MHz, C_6D_6, 298 K): δ −132.2 (m, 2F, *o*-C_6F_5); −160.6 (t, ^3J = 20.4 Hz, 1F, *p*-C_6F_5); −165.2 (m, 2F, *m*-C_6F_5), ($\Delta\delta(^{19}F_{p,m})$ = 4.6). $^{11}B\{^1H\}$ NMR (192 MHz, C_6D_6, 298 K): δ −16.3 ($\nu_{1/2} \approx$ 20 Hz). Anal. Calcd for $C_{33}H_{19}BF_{15}N{\cdot}0.25CH_2Cl_2$: C, 53.50; H, 2.61; N, 1.87. Found: C, 53.22; H, 2.97; N, 2.28. X-ray: $C_{32}H_{21}BF_{15}N{\cdot}CH_2Cl_2$, M = 800.23, a = 9.5086(6) Å, b = 11.9158(7) Å, c = 15.6879(10) Å, α = 94.247(5)°, β = 97.456(4)°, γ = 106.783(3)°, V = 1675.69(18) Å^3, Z = 2, triclinic, $P\bar{1}$, data (λ = 1.54178 Å, T = 223 K) 5741 (R_{int} = 0.058) and 4440 reflections ($I \geq 2\sigma(I)$), 472 parameters, R1 = 0.068, wR2 = 0.192, GOF = 1.030.

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X-ray Data Collection and Reduction (Toronto). 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 diffractometer with Mo Kα radiation (λ = 0.710 69 Å). The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multiscan method (SADABS).

X-ray Data Collection and Reduction (Münster). Crystals were coated in FOMBLIN Y oil, mounted on a glass fiber, and placed under an N_2 stream, thus maintaining a dry, O_2-free environment for each crystal. The data were collected on Nonius KappaCCD diffractometers, both with APEXII detectors; in the case of Mo radiation a rotating anode generator equipped with Montel mirrors was used. The frames were integrated with the DENZO-SMN software package[34] including absorption corrections[35] using the empirical multiscan method.

Structure Solution and Refinement (Toronto). Non-hydrogen atomic scattering factors were taken from the literature tabulations.[36] The heavy-atom positions were determined using direct methods employing the SHELXTL direct methods routine.[37] 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^2, 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 1.10 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 the Supporting Information.

Structure Solution and Refinement (Münster). Non-hydrogen atomic scattering factors were taken from the literature tabulations.[36] The heavy-atom positions were determined using direct or Patterson methods employing the SHELXS routine.[37] 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^2 employing the SHELXL routine. 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 C−H bond lengths between 0.94 and 0.99 Å, depending on the type of carbon atom. H atom temperature factors were fixed at 1.20 or 1.50 times the isotropic temperature factor of the C atom to which they are bonded. 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 data for the structural studies have been deposited with the Cambridge Crystallographic Database.

■ ASSOCIATED CONTENT

Supporting Information

Text, figures, and CIF files giving synthetic, experimental, and crystallographic details. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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