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Reactions of Boron Amidinates with CO_2 and CO and Other Small Molecules

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Abstract: Reaction of Piers' borane, $HB(C_6F_5)_2$, with either *tert*-butyl or isopropyl carbodiimide cleanly affords the boron amidinates $HC(RN)_2B(C_6F_5)_2$ [R = *i*Pr (**1**), *t*Bu (**2**)]. These species undergo a variety of insertion reactions. For example, treatment of **1** with CO_2 or excess carbodiimide gives $HC(i\text{PrN})_2(CO_2)B(C_6F_5)_2$ (**3**) or $HC(i\text{PrN})_2C(i\text{PrN})_2B(C_6F_5)_2$ (**4**), respectively. Similarly, exposure of **1** or **2** to 1 atm CO gives $HC(RN)_2(CO)B(C_6F_5)_2$ [R = *i*Pr (**5**), *t*Bu (**6**)], while reaction of **1** with CN*t*Bu gives $HC(RN)_2(CN\text{t}Bu)B(C_6F_5)_2$ [R = *i*Pr (**7**), *t*Bu (**8**)]. Compounds **1** and **2** also react with benzaldehyde, resulting in the formation of $HC(RN)_2(PhHCO)B(C_6F_5)_2$ [R = *i*Pr (**9**), *t*Bu (**10**)]. Compound **1** also reacts with MeCN to give $HC(i\text{PrN})_2(MeCN)B(C_6F_5)_2$ (**11**) and effects heterolytic C−H cleavage to afford $HC(i\text{PrN})(i\text{PrNH})(PhCC)B(C_6F_5)_2$ (**12**). In contrast, the species $PhC(i\text{PrN})_2B(C_6F_5)_2$ (**14**) derived from $PhC(i\text{PrN})_2BCl_2$ (**13**) failed to react with any of the above substrates. These data, in addition to the isolation of $HC(i\text{PrN})_2(C_6F_4)BF(C_6F_5)$ (**15**), the product of thermolysis of **1**, provide further support for the notion that the transient "open-chain" form of these amidinates is present in solution.

Introduction

The oxides of carbon are rather notorious molecules. Carbon monoxide, which is widely known for its toxicity, constitutes a major atmospheric pollutant derived from the exhaust of internal combustion engines. At the same time, the increasing levels of carbon dioxide in the atmosphere arising from the industrial revolution have contributed to global warming and climate change. Efforts to reduce the emissions of these gases have involved the development of more efficient combustion processes and the development of protocols for the sequestration of CO_2.[1] However, from a fundamental chemical perspective, the problem can be distilled to the limited reactivity known for these oxides.

While many studies have probed the reactivity of transition-metal species with CO and (to a lesser extent) CO_2, studies of the corresponding reactivity of main-group species have been rather limited. The combination of organolithium and Grignard reagents with CO to produce metal acyls has been well-documented.[2−5] Donor−acceptor adducts for the Al and Ga Lewis acids have been observed in matrix-isolation studies, while examples of CO insertion into B−B[6] and Al−C,[7−9] Ga−C,[10] and Ge−C[11] bonds have been reported. CO has also been shown to react with carbenes[12,13] and silylenes[14,15] to afford ketenes and silyl ketenes, respectively, although the analogous reactions with N-heterocyclic carbenes have not been observed.[16] Donor−acceptor adducts of CO such as $R_3B{\cdot}CO$ [R = H,[17] F, CF_3, C_6F_5, BX_2 (X = Cl, F)][18] are also known. The most well developed main-group chemistry involving CO involves reactions with organoboranes, which proceed via a transient adduct of CO and subsequent alkyl transfer to give aldehydes, ketones, and alcohols.[19,20] In a related sense, boron-bound CO has been shown to undergo nucleophilic attack by amines[21] or phosphines,[22] affording zwitterionic species of the form $R_3B(CO)ER'_3$ (E = N, P; R = CF_3; R′ = Me).[22]

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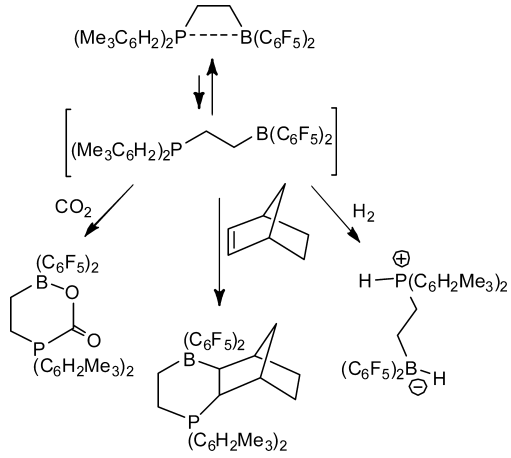
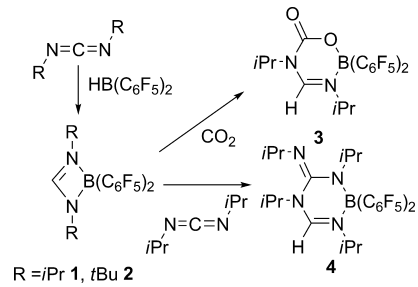
Scheme 1. Reactivity of the Four-Membered FLP with CO_2, Olefin, and H_2



On the other hand, CO_2 is known to react with amines to afford carbamic acids[23,24] and to insert into Al−C bonds[25] as well as N−E bonds of the amido complexes of P,[26] As, Si,[27] and B.[28] Phosphines and N-heterocyclic carbenes, both of which are strong main-group nucleophiles, can be used as catalysts in the fixation of CO_2 with propargyl alcohols to afford cyclic carbamates.[29] Recently, we developed phosphine−borane frustrated Lewis pair (FLP) systems[30−32] and showed that such inter- or intramolecular systems are capable of reversible CO_2 fixation.[33] In related work, O'Hare and co-workers[34] described the use of the FLP based on tetramethylpiperidine and $B(C_6F_5)_3$ to effect the stoichiometric reduction of CO_2 in the presence of H_2. In subsequent work, we described the formation of the CO_2-bound species $(C_6H_2Me_3)_3P(CO_2)(AlCl_3)_2$ and its stoichiometric reduction to methanol by treatment with NH_3BH_3 and water.[35]

In seeking new FLP systems that might also capture CO_2 and perhaps even CO, we took particular note of systems that react as FLPs and for which the Lewis acid−base adducts are accessible. One example is the FLP system pioneered by Erker and co-workers,[36] which is based on the phosphinoborane $(C_6H_2Me_3)_2PC_2H_4B(C_6F_5)_2$ (Scheme 1). This species exists in solution as an equilibrium mixture of the open-chain FLP form and the four-membered-ring P−B adduct. With this in mind,

Scheme 2. Syntheses of **1**−**4**



we focused on the potential reactivity of boron amidinates. While sterically bulky amidinate ligands have been exploited for polymerization catalysts[37−42] and the stabilization of reactive main-group species,[43−46] the reactivity of boron amidinates[38,47,48] has drawn little attention.[49] In this manuscript, we describe the synthesis and reactivity of new boron amidinates and demonstrate that although these species are isolated as four-membered chelate compounds, they are reactive. This affords new and rare examples of main-group species that react with a variety of small molecules, including CO_2 and CO.

Results and Discussion

Conventional syntheses of boron amidinates involve the metathetical treatment of BCl_3 with the Li salt of the ligand or the elimination of $ClSiMe_3$ from the silyl amidinate.[50] Alternatively, insertion of a carbodiimide into the B−N bond of R_2NBCl_2[51,49] or the B−C bond of $PhBCl_2$[47] has been employed. Herein we employed an approach based on hydroboration, using Piers' borane, $HB(C_6F_5)_2$.[52] This species reacts with isopropyl carbodiimide and with *tert*-butyl carbodiimide in CH_2Cl_2, affording the new products **1** and **2**, respectively, as colorless crystals (Scheme 2). These products were isolated in 80 and 84% yield, respectively. The ^{11}B NMR resonances of **1** and **2** were observed at 2.2 and 1.1 ppm, respectively, while the corresponding ^{19}F NMR spectra showed similar sets of signals at −133.8, −157.9, and −164.3 ppm and −131.9, −158.0, and −164.4 ppm. In both cases, these data reflect a four-coordinate B center. Both products exhibit an ^1H NMR singlet at 7.8 ppm consistent with the formation of an amidinate fragment, prompting the formulation of the products as $HC(RN)_2B(C_6F_5)_2$ [R = *i*Pr (**1**), *t*Bu (**2**)]. These formulations were subsequently confirmed via X-ray crystallographic studies (Figures 1 and 2). The

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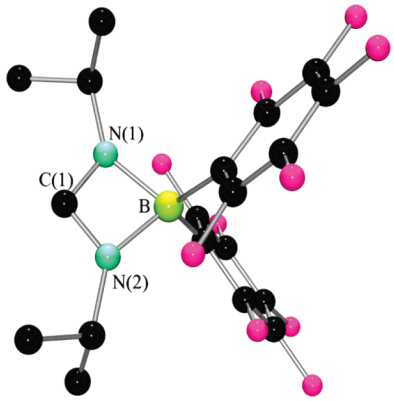

Figure 1. POV-ray depiction of **1**. Color code: C, black; F, pink; N, blue-green; B, yellow-green. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): N(1)−C(1), 1.310(3); N(1)−B, 1.590(3); N(2)−C(1), 1.318(3); N(2)−B, 1.583(3); C(8)−B, 1.623(3); C(14)−B, 1.613(3); C(1)−N(1)−B, 87.50(17); N(1)−C(1)−N(2), 103.7(2); C(1)−N(2)−B, 87.52(17); N(2)−B−N(1), 81.28(15).

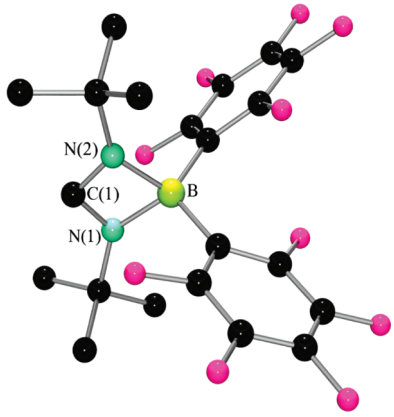

Figure 2. POV-ray depiction of **2**. Color code: C, black; F, pink; N, blue-green; B, yellow-green. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): N(1)−C(1), 1.321(2); N(1)−C(2), 1.4718(19); N(1)−B, 1.586(2); N(2)−C(1), 1.314(2); N(2)−B, 1.606(2); B−C(16), 1.626(2); B−C(10), 1.628(2); C(1)−N(1)−B, 87.97(11); C(1)−N(2)−B, 87.37(11); N(1)−C(1)−N(2), 103.70(13); N(1)−B−N(2), 80.95(10).

four-coordinate geometry about B gives rise to B−C and B−N distances in the ranges 1.613(3)−1.628(3) and 1.583(3)−1.606(2) Å, respectively, while the four-membered BNCN rings contain acute N−B−N angles of 81.28(15) and 80.95(10)° for **1** and **2**, respectively. These geometries are similar to those reported for $PhC(NSiMe_3)_2BX_2$ (X = Cl, Br),[50] $C_6H_4(C(NCy)_2BCl_2)_2$,[53] and $BuC(NtBu)_2BPh(Cl)$.[54] However, the B−N bond lengths in **1** and **2** are significantly longer than the ones found in those boron halide species [1.559(4) and 1.580(5) Å, respectively, for $PhC(NSiMe_3)_2BX_2$ (X = Cl, Br)[50] and 1.571(5) Å for $PhB(Cl)(NtBu)_2CBu$[54]]. This is perhaps unexpected, as the B centers in **1** and **2** are expected to be more Lewis acidic, but it appears that steric interactions between the N substituents and the C_6F_5 rings play a role. Further evidence of the steric congestion is provided by the short transannular B−C distances in **1** and **2** [2.015(3) and 2.028(3) Å, respectively].

As we had speculated that ring congestion and strain would provide access to the η^1 "open-chain" form of these amidinates,

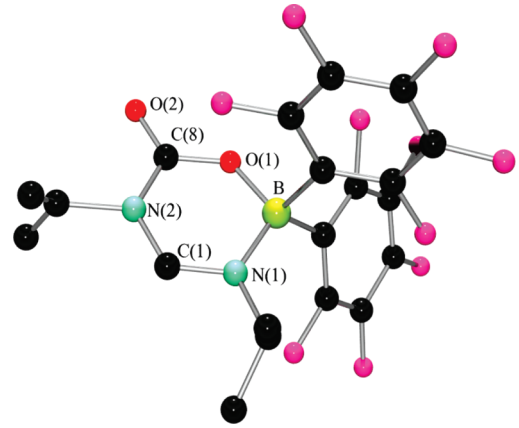

Figure 3. POV-ray depiction of **3**. Color code: C, black; F, pink; O, red; N, blue-green; B, yellow-green. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): O(1)−B, 1.493(5); O(1)−C(8), 1.292(5); O(2)−C(8), 1.208(5); N(1)−C(1), 1.293(5); N(1)−C(2), 1.509(6); N(1)−B, 1.544(6); N(2)−C(1), 1.327(6); C(8)−O(1)−B, 129.2(3); C(1)−N(1)−B, 119.6(3); C(1)−N(2)−C(8), 121.4(4); N(1)−C(1)−N(2), 125.9(4); O(2)−C(8)−O(1), 123.4(4); O(2)−C(8)−N(2), 121.0(4); O(1)−C(8)−N(2), 115.6(4); O(1)−B−N(1), 107.2(3).

efforts to observe these species by variable-temperature NMR spectroscopy were undertaken. At 80 °C in C_6D_5Br, no evidence of an "open-chain" form was observed. Despite the lack of evidence of access to an FLP-like form, the reactivity of **1** with CO_2 was probed. Placing a solution of **1** under an atmosphere of CO_2 for 16 h ultimately resulted in the formation of needlelike crystals of **3** in 96% yield (Scheme 2). This product exhibited a ^{11}B signal at 0.3 ppm and ^{19}F resonances at −134.9, −156.4, and −163.6 ppm. This species also exhibited a ^{13}C signal at 146.1 ppm attributable to the incorporation of CO_2. The corresponding CO IR stretching frequency was observed at 1742 cm^{-1}, giving rise to the formulation of **3** as $HC(iPrN)_2(CO_2)B(C_6F_5)_2$.

An X-ray structural study of **3** confirmed the insertion of the CO_2 fragment into the B−N bond, affording a six-membered heterocycle (Figure 3). The resulting B−N bond length is 1.544(6) Å, with a O−B−N angle of 107.2(3)°. The resulting B−O bond distance was determined to be 1.493(5) Å. This B−O bond distance in **3** is slightly shorter than those found in the P/B systems $tBu_3P(CO_2)B(C_6F_5)_3$ and $(C_6H_2Me_3)_2PC_2H_4B(C_6F_5)_2(CO_2)$ [1.5474(15) and 1.550(4) Å, respectively[33]], whereas the C═O and C−O bond lengths of 1.208(5) and 1.292(5) Å in **3** are similar to those seen in P/B−CO_2 complexes. Although the B center in **3** is expected to be less Lewis acidic those than in $B(C_6F_5)_3$ and $(C_6H_2Me_3)_2PC_2H_4B(C_6F_5)_2$, the stronger B−O bond implies greater donation from N to the CO_2 fragment.

The treatment of **1** (generated in situ) with excess carbodiimide was undertaken, as the N═C═N moiety in the latter is isoelectronic with CO_2. The formation of a new product, **4**, was evidenced by the shift in the ^{11}B resonance to −3.7 ppm and shifts in the ^{19}F signals to −132.4, −158.9, and −165.1 ppm. The ^1H NMR spectrum showed the amidinate-type CH proton at 7.5 ppm as well as isopropyl methine signals at 4.2, 3.7, 3.6,

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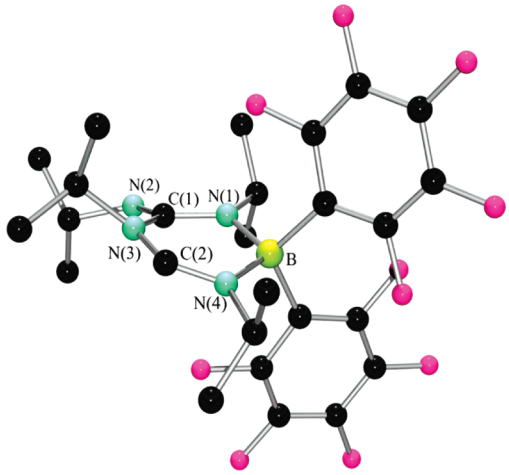


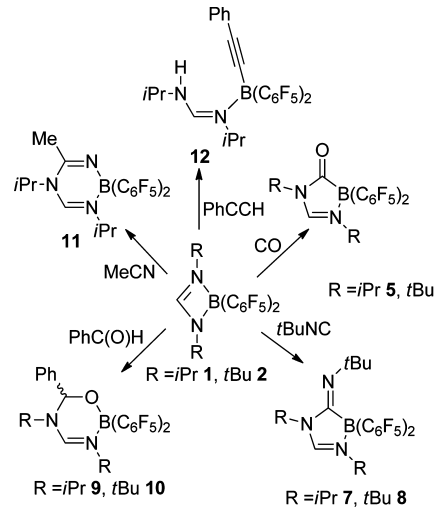
Figure 4. POV-ray depiction of **4**. Color code: C, black; F, pink; N, blue-green; B, yellow-green. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): B−N(1), 1.535(2); B−N(4), 1.573(2); N(1)−C(1), 1.3648(19); N(2)−C(1), 1.2674(19); N(3)−C(2), 1.326(2); N(4)−C(2), 1.2942(19); N(1)−B−N(4), 107.63(12); C(1)−N(1)−B, 125.02(12); C(2)−N(3)−C(1), 120.59(13); C(2)−N(4)−B, 120.84(13); N(1)−C(1)−N(3), 113.62(13); N(4)−C(2)−N(3), 125.49(14).

and 3.2 ppm. These data together with the remaining ^{1}H NMR resonances were consistent with the formulation of **4** as $HC(i\text{PrN})_2C(i\text{PrN})_2B(C_6F_5)_2$ (Scheme 2). A crystallographic study (Figure 4) revealed the nature of **4** as a six-membered ring formed by insertion of a carbodiimide fragment into one of the B−N bonds of **1**. The resulting B−N bond distances in **4** were found to be 1.535(2) and 1.573(2) Å, while the N−B−N angle was broadened to 107.63(12)°. The length of the exocyclic C═N bond was determined to be 1.2674(19) Å. This compound was often formed as a byproduct in the synthesis of **1**, especially in syntheses on a larger scale, reflective of the rapidity of this insertion.

It is noteworthy that the formation of **4** stands in marked contrast to the reported reaction of $(C_6H_2Me_3)_2PC_2H_4B(C_6F_5)_2$ with a carbodiimide, where a classical Lewis acid−base adduct between one of the imido N atoms and the B center is formed.[55] If it is assumed that a related adduct is formed as a transient species en route to **4**, it is reasonable to suggest that the greater basicity and steric accessibility result in nucleophilic attack of the central C by the pendant imido N atom, prompting ring closure.

In view of the ability of these boron amidinates to react with substrates that the P/B systems do not activate, the species **1** and **2** were exposed to ∼1 atm carbon monoxide, and spectroscopic monitoring revealed the slow formation of the products **5** and **6**, respectively (Scheme 3). In the case of **6**, the reaction was exceptionally slow, affording a yield of 97% after 3 weeks, whereas the reaction of **1** afforded **5** in 88% yield in 36 h. The ^{11}B NMR spectrum of **5** showed a signal at −11.0 ppm, and ^{19}F resonances appeared at −133.2, −158.0, and −164.2 ppm. Compound **6** exhibited similar shifts, and both compounds exhibited ^{1}H resonances consistent with inequivalent N substituents. Thus, the data are consistent with the formulations $HC(RN)_2(CO)B(C_6F_5)_2$ [R = *i*Pr (**5**), *t*Bu (**6**)]. IR spectra showed absorptions at 1714 and 1713 cm^{-1}, respectively, attributable to the expected C═O band. X-ray-quality crystals of **5** confirmed the formulation of the five-membered ring (Figure 5). The

Scheme 3. Syntheses of **5**−**12**



resulting B−C and B−N bond distances in the newly formed ring were 1.6365(14) and 1.5794(13) Å, respectively. The corresponding C−B−N angle was 97.57(7)°, while the C═O bond length was typical at 1.2169(12) Å. Although insertion of CO into B−C bonds of boranes is well-documented, the formation of **5** and **6** presents the first examples of insertion of CO into B−N bonds, to the best of our knowledge. It is noteworthy that no reports have described CO sequestration by FLPs.

This reactivity prompted an examination of the reactions of **1** and **2** with *tert*-butylisonitrile, a small molecule containing a C≡N moiety that is isoelectronic with CO. These reactions afforded the products **7** and **8** in 85 and 90% yield, respectively (Scheme 3), and the NMR spectral properties of these compounds were similar to those described for **5**, prompting their formulation as $HC(RN)_2(CN\text{tBu})B(C_6F_5)_2$ [R = *i*Pr (**7**), *t*Bu (**8**)]. X-ray-quality crystals of **7** afforded structural confirmation of this formulation (Figure 6). The C−B−N angle in **7** was determined to be 97.26(13)°, while the exocyclic C═N bond length was 1.255(2) Å. Once again, this observation stands in contrast to the corresponding reaction of $(C_6H_2Me_3)_2PC_2H_4B(C_6F_5)_2$, where a classical Lewis acid adduct is formed.[55]

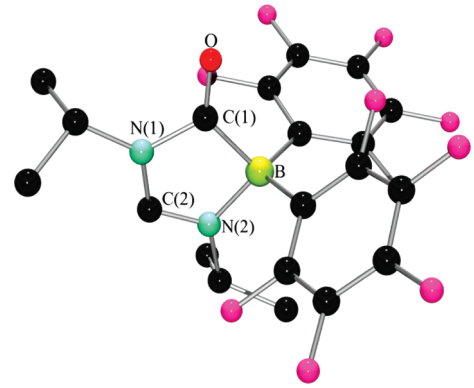


Figure 5. POV-ray depiction of **5**. Color code: C, black; F, pink; O, red; N, blue-green; B, yellow-green. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): O−C(1), 1.2169(12); N(1)−C(2), 1.3560(12); N(1)−C(1), 1.4229(12); N(2)−C(2), 1.2981(13); N(2)−B, 1.5794(13); C(1)−B, 1.6365(14); C(2)−N(1)−C(1), 109.99(8); C(2)−N(2)−B, 109.90(8); O−C(1)−N(1), 121.13(9); O(1)−C(1)−B, 132.82(9); N(1)−C(1)−B, 105.91(7); N(2)−C(2)−N(1), 116.02(8); N(2)−B−C(1), 97.57(7).

(55) Mömming, C. M.; Frömel, S.; Kehr, G.; Fröhlich, R.; Grimme, S.; Erker, G. *J. Am. Chem. Soc.* **2009**, *131*, 12280–12289.

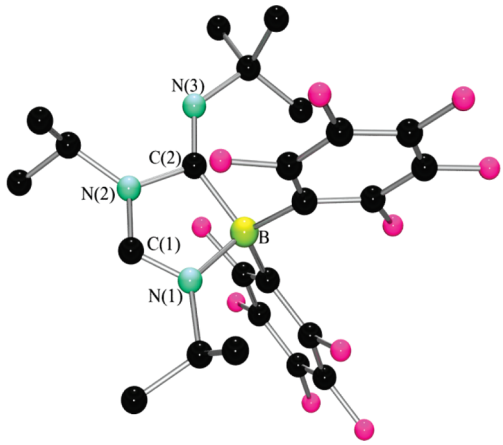


Figure 6. POV-ray depiction of **7**. Color code: C, black; F, pink; N, blue-green; B, yellow-green. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): N(1)−C(1), 1.293(2); N(1)−B, 1.603(2); N(3)−C(2), 1.255(2); N(2)−C(1), 1.325(2); N(2)−C(2), 1.455(2); N(3)−C(2), 1.255(2); B−C(2), 1.667(3); C(1)−N(1)−B, 109.91(14); C(1)−N(2)−C(2), 111.56(15); N(1)−B−C(2), 97.26(13); N(3)−C(2)−N(2), 113.12(16); N(3)−C(2)−B, 142.74(17); N(2)−C(2)−B, 103.97(14); N(1)−C(1)−N(2), 117.00(17).

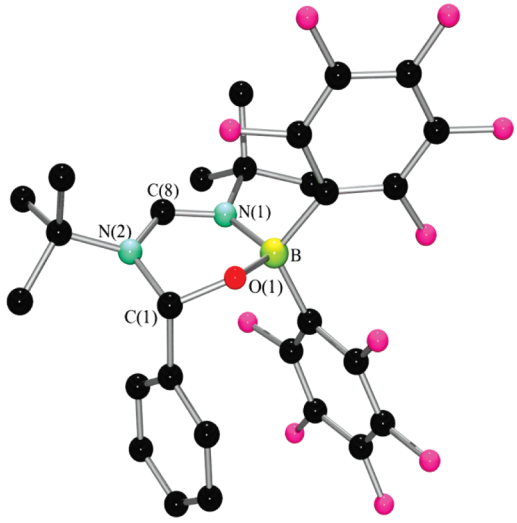


Figure 7. POV-ray depiction of **10**. Color code: C, black; F, pink; O, red; N, blue-green; B, yellow-green. Hydrogen atoms except for the NH proton have been omitted for clarity. Selected bond distances (Å) and angles (deg): O(1)−B, 1.4671(11); O(1)−C(1), 1.3955(10); N(1)−C(8), 1.3120(11); N(1)−B, 1.5962(11); N(2)−C(8), 1.3307(11); N(2)−C(1), 1.4779(11); C(1)−O(1)−B, 119.04(6); N(1)−C(8)−N(2), 126.29(8).

Compounds **1** and **2** also reacted with benzaldehyde, yielding the insertion products **9** and **10** in 82 and 70% yield, respectively. The products can be formulated as $HC(RN)_2(PhHCO)B(C_6F_5)_2$ [R = *i*Pr (**9**), *t*Bu (**10**)] (Scheme 3). The ^1H, ^{19}F, and ^{11}B NMR data were similar to those for the insertion products described above and are consistent with these formulations. In particular, the ^{19}F data show that the C_6F_5 rings are inequivalent (i.e., diastereotopic) as a result of the presence of the chiral (racemic) C atom upon incorporation of the carbonyl fragment. The formulation of **9** was unambiguously confirmed crystallographically (Figure 7).

Compound **1** also reacted with acetonitrile, affording the insertion product **11** in 70% yield. The product was formulated as $HC(iPrN)_2(MeCN)B(C_6F_5)_2$ (Scheme 3) on the basis of ^1H, ^{19}F and ^{11}B NMR data. The crystal structure of **11** (Figure 8) reveals B−N(3) and N(3)−C(8) distances of 1.5147(11) and 1.2551(11) Å, respectively. It is also the case that this reactivity is not observed in P/B FLP systems, where simple adduct formation with the borane is observed.

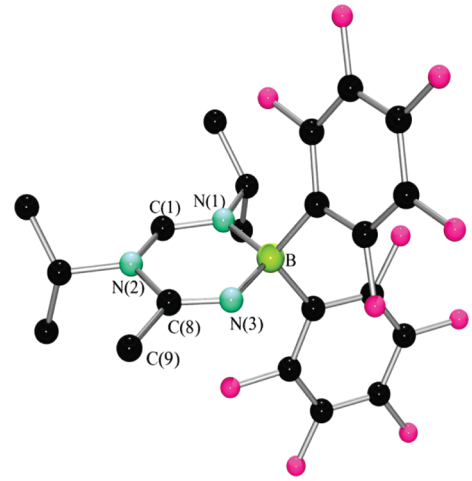


Figure 8. POV-ray depiction of **11**. Color code: C, black; F, pink; N, blue-green; B, yellow-green. Hydrogen atoms except for the NH proton have been omitted for clarity. Selected bond distances (Å) and angles (deg): N(1)−C(1), 1.2962(10); N(1)−B, 1.5831(12); N(2)−C(1), 1.3399(10); N(2)−C(8), 1.4464(11); N(3)−C(8), 1.2551(11); N(3)−B, 1.5147(11); C(8)−C(9), 1.5013(11); C(1)−N(1)−B, 120.19(7); C(1)−N(2)−C(8), 118.27(7); C(8)−N(3)−B, 124.57(7); N(3)−C(8)−N(2), 122.15(7).

To probe other FLP-type reactions of the boron amidinates, compounds **1** and **2** were exposed to 4 atm H_2. No reaction was observed, even upon heating to 60 °C. This observation is consistent with the results of previous efforts to activate H_2 using sterically demanding phosphines and aminoboranes of the form $R_2NB(C_6F_5)_2$, where no reaction occurred. This observation is consistent with the notion that a combined total Lewis acidity and basicity of the components of the FLP must reach a relatively high threshold to effect the heterolytic cleavage of H_2.

In contrast, heterolytic cleavage of the CH bond of a terminal alkyne was readily achieved. Combination of **1** with phenylacetylene resulted in the formation of the product **12** in 75% yield. This species exhibits a ^{11}B chemical shift of −12.9 ppm and ^{19}F resonances consistent with the formation of a four-coordinate boron center. The ^1H NMR spectrum shows inequivalent isopropyl fragments as well as single resonances corresponding to C−H and N−H fragments. These data, together with the ^{13}C resonances as well as crystallographic data, confirmed the formulation of **12** as $HC(iPrN)(iPrNH)(PhCC)B(C_6F_5)_2$ (Scheme 3 and Figure 9). The B−C bond length to the acetylide fragment is 1.581(3) Å, while the B−N bond distance is 1.589(3) Å. The B−N separation for the pendant N is 2.928 Å. Similar alkyne deprotonation reactions have been reported previously for phosphine/borane FLPs.[56]

Mechanistic Considerations. The above reactions demonstrate the remarkable reactivity of boron amidinates **1** and **2**. Moreover, these reactions suggest that the boron amidinates behave as FLPs, implying that the strained four-membered ring is in equilibrium with an "open-chain" form to some degree. In this latter form, where one of the N atoms dissociates from B, the unquenched Lewis acidity of the B center and the nucleophilicity of the pendant N atom allow for reactions with substrates. It is

(56) Dureen, M. A.; Stephan, D. W. *J. Am. Chem. Soc.* **2009**, *131*, 8396–8397.

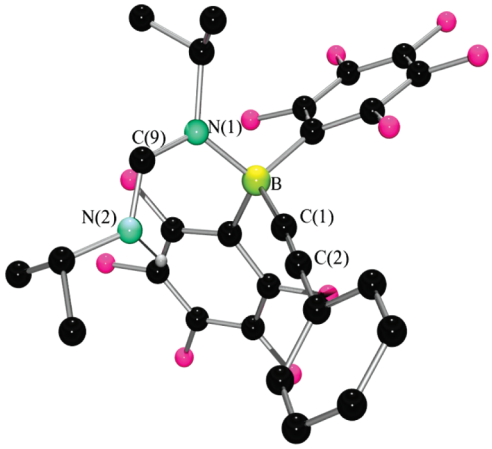


Figure 9. POV-ray depiction of **12**. Color code: C, black; F, pink; N, blue-green; B, yellow-green. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): N(1)−C(9), 1.298(3); N(2)−C(9), 1.309(3); N(1)−B, 1.589(3); C(1)−B, 1.581(3); C(1)−C(2), 1.199(3); C(9)−N(1)−B, 121.57(17); C(2)−C(1)−B, 172.4(2); N(1)−C(9)−N(2), 126.7(2).

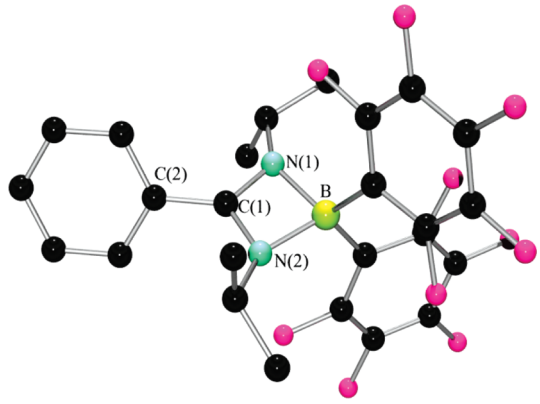


Figure 10. POV-ray depiction of **14**. Color code: C, black; F, pink; N, blue-green; B, yellow-green. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): N(1)−C(1), 1.3276(18); N(1)−B, 1.596(2); N(2)−C(1), 1.3319(19); N(2)−B, 1.597(2); C(1)−C(2), 1.476(2); C(14)−B, 1.633(2); C(20)−B, 1.624(2); C(1)−N(1)−B, 88.42(11); C(1)−N(2)−B, 88.20(11); N(1)−C(1)−N(2), 102.41(12); N(1)−B−N(2), 80.96(10).

reasonable to suggest that the activation of CO_2 or CO and their isoelectronic analogues may proceed via mechanisms involving an initial interaction with either the Lewis acidic B center or the pendant nucleophilic N or perhaps involving the concerted action of the acid and base, as with other FLPs.[33] Nonetheless, the precise details of these processes are not known. The postulate of FLP behavior is consistent with the observation that **2** undergoes insertion reactions much more slowly than **1**. Presumably, the enhanced basicity of the N atoms slows ring opening, and the additional steric crowding slows the reactions with substrates.

To evaluate the impact of steric demands on the reactivity, the species PhC(*i*PrN)$_2$BCl$_2$ (**13**) was prepared in a conventional fashion and converted to the boron amidinate PhC(*i*PrN)$_2$-B(C$_6$F$_5$)$_2$ (**14**). This species was isolated and characterized (Figure 10). In contrast to **1** and **2**, no reaction of **14** was observed in any of the efforts to effect insertion reactions with the variety of substrates described above. These observations further support the notion that steric crowding inhibits access to the "open-chain" form of the boron amidinate, thus precluding reactivity.

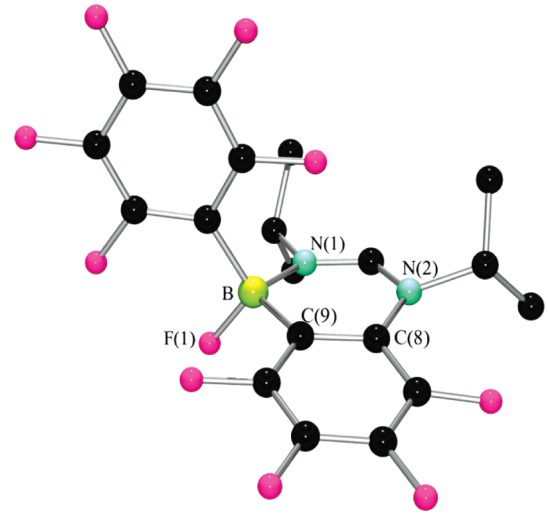
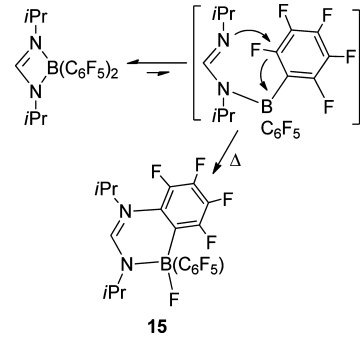


Figure 11. POV-ray depiction of **15** Color code: C, black; F, pink; N, blue-green; B, yellow-green. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): F(1)−B, 1.414(2); N(1)−B, 1.567(3); N(1)−C(1), 1.299(3); N(2)−C(1), 1.338(3); N(2)−C(8), 1.421(2); C(8)−C(9), 1.405(3); C(9)−B, 1.608(3); C(1)−N(1)−B, 123.41(17); C(1)−N(2)−C(8), 120.49(16); N(1)−C(1)−N(2), 125.76(18); C(8)−C(9)−B, 121.91(17); F(1)−B−N(1), 106.53(16); F(1)−B−C(9), 109.45(16); N(1)−B−C(9), 107.02(16).

Scheme 4. Synthesis of **15**



We also examined the thermolysis of **1** above 80 °C, which produced a new species, **15**, that did not revert to **1** upon cooling to room temperature. Spectroscopic studies of **15** revealed a ^{11}B NMR resonance at −0.6 ppm and ^{19}F NMR data that were consistent with the formation of BF and C_6F_4 fragments. These data, together with ^{1}H and ^{13}C NMR data, were consistent with the formulation of **15** as HC(*i*PrN)$_2$(C$_6$F$_4$)BF(C$_6$F$_5$). X-ray analysis confirmed the formation of a new species containing a six-membered ring in which one of the amidinate N atoms effects aromatic substitution at the ortho position of one of the B-bound C_6F_5 rings, with concurrent transfer of the F atom to B (Figure 11). The formation of **15** further supports the notion that a transient "open-chain" form of the amidinate is accessible, as this results in nucleophilic attack of an aromatic *o*-CF bond and subsequent F transfer to B to give **15** (Scheme 4). In a related sense, we recently reported an analogous *o*-CF bond attack by a pendant phosphine that led to the formation of C$_6$F$_4$B(C$_6$F$_5$)$_2$CH$_2$P*t*Bu$_2$, which contains a five-membered BCPC$_2$ ring.[57]

Conclusions

Herein we have described a new synthetic pathway to boron amidinates. These species react with CO_2, CO, carbodiimide, isocyanide, acetonitrile, and benzaldehyde to effect insertion

of these substrates into a B−N bond, affording new boron heterocycles. One boron amidinate also reacts with phenylacetylene to effect C−H activation, affording a boron acetylide species, while thermolysis of this boron amidinate results in ortho substitution of N on one of the B-bound fluoroarene rings. All of this reactivity points to reactions of the boron amidinates as masked FLPs. The general utility of boron amidinates as synthons for novel heterocycles continues to be of interest in our laboratories, with particular interest in the reactivity of the lighter dihalo analogues of these compounds.

Experimental Section

General Remarks. All manipulations were carried out under an atmosphere of dry, O_2-free N_2 employing an Innovative Technology glovebox and a Schlenk vacuum line. Solvents were purified with a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled Schlenk glass flasks equipped with Teflon-valve stopcocks (pentane, toluene, CH_2Cl_2) or dried over the appropriate agents and distilled into the same kind of storage flasks (C_6H_5Br). All of the solvents were thoroughly degassed after purification (repeated freeze−pump−thaw cycles). Deuterated solvents were dried over the appropriate agents, vacuum-transferred into storage flasks with Teflon stopcocks, and degassed accordingly (C_6D_5Br, CD_2Cl_2). Toluene and pentane were stored over potassium mirrors, while bromobenzene and dichloromethane were stored over 4 Å molecular sieves. ^{1}H, ^{11}B, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded at 25 °C on Varian 300 and 400 MHz and Bruker 400 MHz spectrometers. Chemical shifts are given relative to $SiMe_4$ and referenced to the residual solvent signal (^{1}H, ^{13}C) or relative to an external standard (^{11}B, $(Et_2O)BF_3$; ^{19}F, $CFCl_3$; ^{31}P, 85% H_3PO_4). Spectra were recorded in CD_2Cl_2 unless otherwise noted. In some instances, signal and/or coupling assignments were derived from two-dimensional NMR experiments. Chemical shifts are reported in parts per million and coupling constants as scalar values in hertz. Combustion analyses were performed in-house employing a PerkinElmer CHN analyzer. $HB(C_6F_5)_2$,[52] $Ph(iPrN)_2Li$,[58] and $PhMe\cdot Zn(C_6F_5)_2$[59] were synthesized via literature procedures. All of the other reagents were purchased from Aldrich; liquids were stored over 4 Å molecular sieves, and gases and solutions were used as received.

Synthesis of $HC(RN)_2B(C_6F_5)_2$ [R = *i*Pr (1), *t*Bu (2)]. These compounds were prepared in a similar fashion, and thus, only the preparation of **2** is detailed. $HB(C_6F_5)_2$ (100 mg, 0.3 mmol) was dissolved in dichloromethane (8 mL), and *tert*-butyl carbodiimide (44.5 mg, 0.3 mmol) in dichloromethane (1 mL) was added dropwise. The reaction mixture was stirred for 30 min, after which the solvent was removed under reduced pressure. The resultant white solid was recrystallized from pentane to afford colorless crystals of **2**.

Data for **1**: Colorless crystals, 281 mg, 84%. ^{1}H NMR: δ 7.8 (s, 1H, *H*C═N), 3.8 (septet, 2H, $^3J_{H-H}$ = 7 Hz, C*H*$(CH_3)_2$), 1.2 (d, 12H, $^3J_{H-H}$ = 7 Hz, CH(C*H*$_3)_2$). ^{11}B NMR: δ 2.2 (s). ^{13}C{^{1}H} NMR, partial: δ 159.4 (s, N═*C*(H)−N), 148.1 (dm, $^1J_{C-F}$ = 240 Hz, *o*-C_6F_5), 140.5 (dm, $^1J_{C-F}$ = 260 Hz, *p*-C_6F_5), 137.8 (dm, $^1J_{C-F}$ = 260 Hz, *m*-C_6F_5), 47.2 (s, *C*H$(CH_3)_2$), 23.4 (s, CH(*C*H$_3)_2$). ^{19}F NMR: δ −133.8 (d, 4F, $^3J_{F-F}$ = 23 Hz, *o*-C_6F_5), −157.9 (tm, 2F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −164.3 (m, 4F, $^3J_{F-F}$ = 19 Hz, *m*-C_6F_5). Anal. Calcd for $C_{19}H_{15}BN_2F_{10}$ (472.138): C, 48.34; H, 3.20; N, 5.93. Found: C, 48.15; H, 3.23; N, 6.01. X-ray-quality crystals were grown from slow cooling of a solution in pentane.

Data for **2**: Yield: 116 mg, 80%. ^{1}H NMR: δ 7.8 (s, 1H, *H*C═N), 1.1 (s, 18H, ^{t}Bu). ^{11}B NMR: δ 1.1 (s). ^{13}C{^{1}H} NMR, partial: δ 158.7 (s, N═*C*(H)−N), 148.8 (dm, $^1J_{C-F}$ = 250 Hz, *o*-C_6F_5), 140.6 (dm, $^1J_{C-F}$ = 253 Hz, *p*-C_6F_5), 138.6 (dm, $^1J_{C-F}$ = 257 Hz, *m*-C_6F_5), 53.4 (s, *C*$(CH_3)_3$), 29.7 (s, C(*C*H$_3)_3$). ^{19}F NMR: δ −131.9 (dd, 4F, $^3J_{F-F}$ = 24 Hz, $^4J_{F-F}$ = 9 Hz, *o*-C_6F_5), −158.0 (tm, 2F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −164.4 (m, 4F, $^3J_{F-F}$ = 19 Hz, *m*-C_6F_5). Anal. Calcd for $C_{21}H_{19}BN_2F_{10}$ (500.192): C, 50.43; H, 3.83; N, 5.60. Found: C, 50.21; H, 4.11; N, 5.80. X-ray-quality crystals were grown from slow cooling of a solution in pentane.

Synthesis of $HC(iPrN)_2(CO_2)B(C_6F_5)_2$ (3). A solution of **1** (20 mg, 0.04 mmol) in CD_2Cl_2 (∼0.8 mL) in a Teflon-sealed NMR tube was degassed via the freeze−pump−thaw technique and pressurized with ∼1 atm CO_2. The solution was left for 16 h, at which point ^{1}H, ^{11}B, and ^{19}F spectra revealed the reaction to be complete and quantitative. The reaction mixture was transferred to a tared vial, and pentane (3 mL) was added and the reaction mixture cooled to −35 °C. After the formation of fine needlelike crystals, the supernatant was decanted, and the crystals were dried in vacuo (21 mg, 96%). ^{1}H NMR: δ 7.8 (s, 1H, *H*C═N), 4.7 (septet, 1H, $^3J_{H-H}$ = 6 Hz, C*H*$(CH_3)_2$), 3.8 (septet, 1H, $^3J_{H-H}$ = 6 Hz, C*H*$(CH_3)_2$), 1.4 (d, 6H, $^3J_{H-H}$ = 6 Hz, CH(C*H*$_3)_2$), 1.2 (d, 6H, $^3J_{H-H}$ = 6 Hz, CH(C*H*$_3)_2$). ^{11}B NMR: δ 0.3 (s). ^{3}C{^{1}H} NMR, partial: δ 152.1 (s, N═*C*(H)−N), 148.2 (dm, $^1J_{C-F}$ = 245 Hz, *o*-C_6F_5), 146.1 (s, *C*O_2), 140.6 (dm, $^1J_{C-F}$ = 255 Hz, *p*-C_6F_5), 137.2 (dm, $^1J_{C-F}$ = 250 Hz, *m*-C_6F_5), 52.5 (s, *C*H$(CH_3)_2$), 50.5 (s, *C*H$(CH_3)_2$), 22.9 (s, CH(*C*H$_3)_2$), 21.5 CH(*C*H$_3)_2$). ^{19}F NMR: δ −134.9 (dd, 4F, $^3J_{F-F}$ = 24 Hz, $^4J_{F-F}$ = 9 Hz, *o*-C_6F_5), −156.4 (t, 2F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −163.6 (m, 4F, *m*-C_6F_5). Anal. Calcd for $C_{20}H_{15}BN_2O_2F_{10}$ (516.147): C, 46.54; H, 2.92; N, 5.42. Found: C, 46.49; H, 3.04; N, 5.55. X-ray-quality crystals were grown from slow cooling of a solution in 3:1 pentane/dichloromethane.

Synthesis of $HC(iPrN)_2C(iPrN)_2B(C_6F_5)_2$ (4). $HB(C_6F_5)_2$ (69 mg, 0.2 mmol) was dissolved in dichloromethane (8 mL), and isopropyl carbodiimide (51 mg, 0.4 mmol) in dichloromethane (1 mL) was added. The reaction mixture was stirred for 48 min, after which the solvent was concentrated to ∼1 mL under reduced pressure. Pentane (2 mL) was added, and subsequent cooling to −35 °C afforded colorless crystals (92 mg, 79%). ^{1}H NMR: δ 7.5 (s, 1H, *H*C═N), 4.2 (m, br, 1H, C*H*$(CH_3)_2$), 3.7 (septet, 1H, $^3J_{H-H}$ = 6 Hz, C*H*$(CH_3)_2$), 3.6 (septet, 1H, $^3J_{H-H}$ = 6 Hz, C*H*$(CH_3)_2$), 3.2 (m, 1H, $^3J_{H-H}$ = 7 Hz, C*H*$(CH_3)_2$), 1.4 (d, 6H, $^3J_{H-H}$ = 7 Hz, CH(C*H*$_3)_2$), 1.1 (d, 6H, $^3J_{H-H}$ = 7 Hz, CH(C*H*$_3)_2$), 1.05 (d, 6H, $^3J_{H-H}$ = 7 Hz, CH(C*H*$_3)_2$), 1.0 (d, 6H, CH(C*H*$_3)_2$). ^{11}B NMR: δ −3.7 (s). ^{13}C{^{1}H} NMR, partial: δ 150.8 (s, N═*C*(H)−N), 149.6 (dm, $^1J_{C-F}$ = 240 Hz, *o*-C_6F_5), 140.3 (dm, $^1J_{C-F}$ = 250 Hz, *p*-C_6F_5), 138.8 (s, N−*C*(N)═N), 137.7 (dm, $^1J_{C-F}$ = 245 Hz, *m*-C_6F_5), 54.1 (s, *C*H$(CH_3)_2$), 50.2 (s, *C*H$(CH_3)_2$), 49.3 (s, *C*H$(CH_3)_2$), 49.2 (s, *C*H$(CH_3)_2$), 25.6 (s, CH(*C*H$_3)_2$), 23.5 (s, CH(*C*H$_3)_2$), 22.9 (s, CH(*C*H$_3)_2$), 20.2 (s, CH(*C*H$_3)_2$). ^{19}F NMR: δ −132.4 (s, br, 4F, *o*-C_6F_5), −158.9 (tm, 2F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −165.1 (dd, 4F, $^3J_{F-F}$ = 23 Hz, $^4J_{F-F}$ = 4 Hz, *m*-C_6F_5). Anal. Calcd for $C_{26}H_{29}BN_4F_{10}$ (598.340): C, 52.19; H, 4.89; N, 9.36. Found: C, 51.88; H, 5.11; N, 9.60. The crystalline product was suitable for X-ray analysis.

Synthesis of $HC(RN)_2(CO)B(C_6F_5)_2$ [R = *i*Pr (5), *t*Bu (6)]. These compounds were prepared in a similar fashion, and thus, only the preparation of **5** is detailed. A solution of **1** (22 mg, 0.04 mmol) in CD_2Cl_2 (∼ 0.8 mL) in a Teflon-sealed NMR tube was degassed via the freeze−pump−thaw technique and pressurized with ∼1 atm CO. The solution was left for 36 h, at which point ^{1}H, ^{11}B, and ^{19}F spectra revealed the reaction to be complete and quantitative. The reaction mixture was transferred to a tared vial, and pentane (3 mL) was added. After the formation of fine needlelike crystals, the supernatant was decanted, and the crystals were dried in vacuo (20 mg, 88%).

Data for **5**: Yield: 20 mg, 88%. ^{1}H NMR (CD_2Cl_2): δ 8.3 (s, 1H, *H*C═N), 4.4 (septet, 1H, $^3J_{H-H}$ = 6 Hz, C*H*$(CH_3)_2$), 3.8 (septet, 1H, $^3J_{H-H}$ = 6 Hz, C*H*$(CH_3)_2$), 1.3 (d, 6H, $^3J_{H-H}$ = 6 Hz,

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CH(CH_3)$_2$), 1.2 (d, 6H, $^3J_{H-H}$ = 6 Hz, CH(CH_3)$_2$). ^{11}B NMR (CD_2Cl_2): δ −11.0 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2), partial: δ 157.7 (s, N=*C*(H)−N), 148.6 (dm, $^1J_{C-F}$ = 248 Hz, *o*-C_6F_5), 140.6 (dm, $^1J_{C-F}$ = 266 Hz, *p*-C_6F_5), 137.8 (dm, $^1J_{C-F}$ = 255 Hz, *m*-C_6F_5), 51.6 (s, *C*H(CH$_3$)$_2$), 43.6 (s, *C*H(CH$_3$)$_2$), 23.3 (s, CH(*C*H$_3$)$_2$), 22.2 (s, CH(*C*H$_3$)$_2$). ^{19}F NMR (CD_2Cl_2): δ −133.2 (m, 4F, *o*-C_6F_5), −158.0 (t, 2F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −164.2 (m, 4F, *m*-C_6F_5). Anal. Calcd for $C_{20}H_{15}BN_2OF_{10}$ (500.148): C, 48.03; H, 3.02; N, 5.60. Found: C, 47.85; H, 2.63; N, 5.89. X-ray-quality crystals were grown from slow diffusion of pentane into a solution in dichloromethane.

Data for **6**: The reaction was complete after 3 weeks under ∼1 atm CO. Microcrystalline solid, 5 mg, 97%. ^{1}H NMR: δ 8.4 (s, 1H, *H*C=N), 1.5 (s, 9H, C(C*H*$_3$)$_3$), 1.3 (s, 9H, C(C*H*$_3$)$_3$). ^{11}B NMR: δ −11.5 (s). ^{13}C{^{1}H} NMR, partial: δ 159.5 (s, N=*C*(H)−N), 148.8 (dm, $^1J_{C-F}$ = 239 Hz, *o*-C_6F_5), 140.5 (dm, $^1J_{C-F}$ = 261 Hz, *p*-C_6F_5), 138.0 (dm, $^1J_{C-F}$ = 257 Hz, *m*-C_6F_5), 59.2 (s, *C*(CH$_3$)$_3$), 57.5 (s, *C*(CH$_3$)$_3$), 30.1 (s, C(*C*H$_3$)$_3$), 28.7 (s, C(*C*H$_3$)$_3$). ^{19}F NMR: δ −132.1 (s, br, 4F, *o*-C_6F_5), −157.9 (t, 2F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −164.1 (td, 4F, $^3J_{F-F}$ = 20 Hz, $^4J_{F-F}$ = 6 Hz, *m*-C_6F_5). Anal. Calcd for $C_{22}H_{19}BN_2OF_{10}$ (528.202): C, 50.03; H, 3.63; N, 5.30. Found: C, 50.15; H, 3.44; N, 5.01.

Synthesis of HC(RN)$_2$(CN*t*Bu)B(C$_6$F$_5$)$_2$ [R = *i*Pr (7), *t*Bu (8)]. These compounds were prepared in a similar fashion, and thus, only the preparation of **7** is detailed. A solution of *tert*-butylisonitrile (8.8 mg, 0.11 mmol) in pentane (1 mL) was added in one portion to a solution of **1** (50 mg, 0.11 mmol) in bromobenzene (2 mL). The solvent was removed under reduced pressure and the residue recrystallized from pentane to afford clear, colorless crystals (50 mg, 85%).

Data for **7**: ^{1}H NMR: δ 7.9 (s, 1H, *H*C=N), 4.8 (septet, 1H, $^3J_{H-H}$ = 7 Hz, C*H*(CH$_3$)$_2$), 3.8 (septet, 1H, $^3J_{H-H}$ = 6 Hz, C*H*(CH$_3$)$_2$), 1.3 (d, 6H, $^3J_{H-H}$ = 7 Hz, CH(C*H*$_3$)$_2$), 1.1 (d, 6H, $^3J_{H-H}$ = 6 Hz, CH(C*H*$_3$)$_2$), 0.9 (s, 9H, C(C*H*$_3$)$_3$). ^{11}B NMR: δ −10.0 (s). ^{13}C{^{1}H} NMR, partial: δ 153.8 (s, N=*C*(H)−N), 149.2 (dm, $^1J_{C-F}$ = 232 Hz, *o*-C_6F_5), 140.2 (dm, $^1J_{C-F}$ = 260 Hz, *p*-C_6F_5), 138.0 (dm, $^1J_{C-F}$ = 273 Hz, *m*-C_6F_5), 54.8 (s, *C*(CH$_3$)$_3$), 47.9 (s, *C*H(CH$_3$)$_2$), 43.2 (s, *C*H(CH$_3$)$_2$), 30.7 (s, C(*C*H$_3$)$_3$), 23.8 (s, CH(*C*H$_3$)$_2$), 22.4 (s, CH(*C*H$_3$)$_2$). ^{19}F NMR: δ −129.9 (s, br, 4F, *o*-C_6F_5), −158.5 (tm, 2F, $^3J_{F-F}$ = 18 Hz, *p*-C_6F_5), −164.6 (td, 4F, $^3J_{F-F}$ = 20 Hz, $^4J_{F-F}$ = 6 Hz, *m*-C_6F_5). Anal. Calcd for $C_{24}H_{24}BN_3F_{10}$ (555.272): C, 51.92; H, 4.36; N, 7.57. Found: C, 52.05; H, 4.62; N, 7.52. X-ray-quality crystals were grown from slow cooling of a solution in pentane.

Data for **8**: Colorless microcrystalline solid, 21 mg, 90%. ^{1}H NMR: δ 8.1 (s, 1H, *H*C=N), 1.6 (s, 9H, C(C*H*$_3$)$_3$), 1.1 (s, 9H, C(C*H*$_3$)$_3$), 0.9 (s, 9H, C(C*H*$_3$)$_3$). ^{11}B NMR: δ −10.07 (s). ^{13}C{^{1}H} NMR, partial: δ 156.2 (s, N=*C*(H)−N), 149.0 (dm, $^1J_{C-F}$ = 241 Hz, *o*-C_6F_5), 140.6 (dm, $^1J_{C-F}$ = 245 Hz, *p*-C_6F_5), 137.9 (dm, $^1J_{C-F}$ = 260 Hz, *m*-C_6F_5), 58.2 (s, *C*(CH$_3$)$_3$), 58.0 (s, *C*(CH$_3$)$_3$), 55.2 (s, *C*(CH$_3$)$_3$), 30.8 (s, C(*C*H$_3$)$_3$), 30.7 (s, C(*C*H$_3$)$_3$), 29.3 (s, C(*C*H$_3$)$_3$). ^{19}F NMR: δ −128.3 (s, br, 4F, *o*-C_6F_5), −158.8 (t, 2F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −164.9 (m, 4F, *m*-C_6F_5). Anal. Calcd for $C_{26}H_{28}BN_3F_{10}$ (583.326): C, 53.54; H, 4.84; N, 7.20. Found: C, 53.84; H, 4.92; N, 7.10.

Synthesis of HC(RN)$_2$(PhHCO)B(C$_6$F$_5$)$_2$ [R = *i*Pr (9), *t*Bu (10)]. These compounds were prepared in a similar fashion, and thus, only the preparation of **9** is detailed. A solution of benzaldehyde (6.5 mg, 0.05 mmol) in pentane (1 mL) was added in one portion to a solution of **1** (29 mg, 0.05 mmol) in toluene (2 mL). The solvent was removed under reduced pressure, and the residue was washed with pentane (2 mL) and dried in vacuo to afford a white powder (29 mg, 82%).

Data for **9**: ^{1}H NMR: δ 7.8 (s, 1H, *H*C=N), 7.4−7.3 (m, 5H, *Ph*), 5.5 (s, 1H, C*H*(Ph)) 3.5 (septet, 1H, $^3J_{H-H}$ = 7 Hz, C*H*(CH$_3$)$_2$), 3.3 (septet, 1H, $^3J_{H-H}$ = 7 Hz, C*H*(CH$_3$)$_2$), 1.3 (d, 3H, $^3J_{H-H}$ = 7 Hz, CH(C*H*$_3$)$_2$), 1.2 (d, 3H, $^3J_{H-H}$ = 7 Hz, CH(C*H*$_3$)$_2$), 1.15 (d, 3H, $^3J_{H-H}$ = 7 Hz, CH(C*H*$_3$)$_2$), 1.05 (d, 3H, $^3J_{H-H}$ = 7 Hz, CH(C*H*$_3$)$_2$). ^{11}B NMR: δ −1.5 (s). ^{13}C{^{1}H} NMR, partial: δ 150.4 (s, N=*C*(H)−N), 148.2 (dm, $^1J_{C-F}$ = 249 Hz, *o*-C_6F_5), 138.6 (dm, $^1J_{C-F}$ = 256 Hz, *p*-C_6F_5), 138.1 (s), 137.4 (dm, $^1J_{C-F}$ = 252 Hz, *m*-C_6F_5), 129.3 (s), 128.5 (s), 127.6 (s), 84.6 (s, C*H*(Ph)), 50.5 (s, *C*H(CH$_3$)$_2$), 50.3 (s, *C*H(CH$_3$)$_2$), 23.7 (s, CH(*C*H$_3$)$_2$), 22.7 (s, CH(*C*H$_3$)$_2$), 21.9 (s, CH(*C*H$_3$)$_2$), 20.9 (s, CH(*C*H$_3$)$_2$). ^{19}F NMR: δ −132.4 (m, 2F, *o*-C_6F_5), −135.3 (s, br, 2F, *o*-C_6F_5), −158.9 (t, 1F, $^3J_{F-F}$ = 18 Hz, *p*-C_6F_5), −159.1 (t, 1F, $^3J_{F-F}$ = 19 Hz, *p*-C_6F_5), −164.8 (m, 2F, *m*-C_6F_5), −165.1 (m, 2F, *m*-C_6F_5). Anal. Calcd for $C_{26}H_{21}BN_2OF_{10}$ (578.262): C, 54.00; H, 3.66; N, 4.84. Found: C, 53.89; H, 3.77; N, 4.59.

Data for **10**: Colorless microcrystalline solid, 17 mg, 70%. ^{1}H NMR: δ 8.3 (s, 1H, *H*C=N), 7.1−7.0 (m, 5H, *Ph*), 6.2 (s, 1H, C*H*(Ph)), 1.5 (s, 9H, C(C*H*$_3$)$_3$), 1.3 (s, 9H, C(C*H*$_3$)$_3$). ^{11}B NMR: δ −3.1 (s). ^{13}C{^{1}H} NMR, partial: δ 153.5 (s, N=*C*(H)−N), 138.6 (s), 1838.5 (s), 127.9 (s, br), 81.3 (s, C*H*(Ph)), 59.95 (s, *C*(CH$_3$)$_3$), 59.4 (s, *C*(CH$_3$)$_3$), 30.5 (s, C(*C*H$_3$)$_3$), 29.3 (s, C(*C*H$_3$)$_3$). ^{19}F NMR: δ −132.3 (dd, 1F, $^3J_{F-F}$ = 26 Hz, $^4J_{F-F}$ = 8 Hz, *o*-C_6F_5), −133.3 (d, 1F, $^3J_{F-F}$ = 24 Hz, *o*-C_6F_5), −133.6 (d, 1F, $^3J_{F-F}$ = 22 Hz, *o*-C_6F_5), −132.4 (dd, 1F, $^3J_{F-F}$ = 24 Hz, $^4J_{F-F}$ = 8 Hz, *o*-C_6F_5), −159.7 (t, 1F, $^3J_{F-F}$ = 19 Hz, *p*-C_6F_5), −162.0 (t, 1F, $^3J_{F-F}$ = 24 Hz, *p*-C_6F_5), −165.6 (m, 2F, *m*-C_6F_5), −167.5 (m, 1F, *m*-C_6F_5), −167.7 (m, 1F, *m*-C_6F_5). Anal. Calcd for $C_{28}H_{25}BN_2OF_{10}$ (606.316): C, 55.47; H, 4.16; N, 4.62. Found: C, 55.52; H, 4.33; N, 4.73. X-ray-quality crystals were grown from slow diffusion of pentane into a solution in dichloromethane.

Synthesis of HC(*i*PrN)$_2$(MeCN)B(C$_6$F$_5$)$_2$ (11). Acetonitrile (20 mg, 0.05 mmol) in pentane (1 mL) was added in one portion to a solution of **1** (25 mg, 0.05 mmol) in dichloromethane (2 mL). The solvent was removed under reduced pressure and the residue washed with cold pentane (0.5 mL) to afford a white powder (25 mg, 87%). ^{1}H NMR: δ 7.6 (s, 1H, *H*C=N), 4.2 (septet, 1H, $^3J_{H-H}$ = 7 Hz, C*H*(CH$_3$)$_2$), 3.6 (septet, 1H, $^3J_{H-H}$ = 7 Hz, C*H*(CH$_3$)$_2$), 2.1 (s, 3H, *Me*), 1.4 (d, 6H, $^3J_{H-H}$ = 7 Hz, CH(C*H*$_3$)$_2$), 1.1 (d, 6H, $^3J_{F-F}$ = 7 Hz, CH(C*H*$_3$)$_2$). ^{11}B NMR: δ −4.4 (s). ^{13}C{^{1}H} NMR, partial: δ 150.2 (s, N=*C*(H)−N), 149.6 (dm, $^1J_{C-F}$ = 240 Hz, *o*-C_6F_5), 141 0.4 (s, Me*C*) 140.2 (dm, $^1J_{C-F}$ = 245 Hz, *p*-C_6F_5), 137.6 (dm, $^1J_{C-F}$ = 260 Hz, *m*-C_6F_5), 52.1 (s, *C*H(CH$_3$)$_2$), 51.0 (s, *C*H(CH$_3$)$_2$), 23.5 (s, CH(*C*H$_3$)$_2$), 23.3 (s, CH(*C*H$_3$)$_2$), 23.0 (s, *C*H$_3$). ^{19}F NMR: δ −135.3 (dd, 4F, $^3J_{F-F}$ = 24 Hz, $^4J_{F-F}$ = 8 Hz, *o*-C_6F_5), −159.8 (t, 2F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −165.1 (m, 4F, *m*-C_6F_5). Anal. Calcd for $C_{21}H_{18}BN_3F_{10}$ (519.19): C, 49.15; H, 3.54; N, 8.19. Found: C, 48.81; H, 3.96; N, 7.87. X-ray-quality crystals were grown from diffusion of pentane into a solution in dichloromethane.

Synthesis of HC(*i*PrN)(*i*PrNH)B(C$_6$F$_5$)$_2$(CCPh) (12). Phenylacetylene (0.1 mL, 0.9 mmol) was added in one portion to a solution of **1** (11 mg, 0.02 mmol) in CD_2Cl_2 (0.8 mL). The reaction was monitored by ^{11}B NMR spectroscopy and appeared to reach ∼80% completion after 1 week, at which point pentane (1 mL) was added and the reaction mixture cooled to −35 °C overnight to afford colorless crystals (10 mg, 75%). ^{1}H NMR: δ 7.4 (d, 1H, *HC* = NH), 7.3 (m, 2H, Ph), 7.3−7.2 (m, 3H, Ph), 7.0 (m, br, =N*H*), 3.93 (septet, 1H, $^3J_{H-H}$ = 6 Hz, C*H*(CH$_3$)$_2$), 3.6 (m, 1H, C*H*(CH$_3$)$_2$), 1.3 (d, 6H, $^3J_{H-H}$ = 7 Hz, CH(C*H*$_3$)$_2$), 1.2 (d, 6H, $^3J_{H-H}$ = 7 Hz, CH(C*H*$_3$)$_2$). ^{11}B NMR: δ −12.9 (s). ^{13}C{^{1}H} NMR, partial: δ 154.2 (s, N=*C*(H)−N), 148.3 (dm, $^1J_{C-F}$ = 240 Hz, *o*-C_6F_5), 140.0 (dm, $^1J_{C-F}$ = 248 Hz, *p*-C_6F_5), 137.9 (dm, $^1J_{C-F}$ = 250 Hz, *m*-C_6F_5), 131.7 (s), 128.8 (s), 128.0 (s), 125.5(s), 50.9 (s, *C*H(CH$_3$)$_2$), 23.9 (s, CH(*C*H$_3$)$_2$), 23.8 (s, CH(*C*H$_3$)$_2$). ^{19}F NMR: δ −133.4 (dd, 4F, $^3J_{F-F}$ = 23 Hz, $^4J_{F-F}$ = 7 Hz, *o*-C_6F_5), −159.4 (t, 2F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −165.0 (m, 4F, *m*-C_6F_5). Anal. Calcd for $C_{27}H_{21}BN_2F_{10}$ (574.274): C, 56.47; H, 3.69; N, 4.88. Found: C, 56.35; H, 4.05; N, 5.01. X-ray-quality crystals were grown from slow diffusion of pentane into a solution in dichloromethane.

Synthesis of PhC(*i*PrN)$_2$BCl$_2$ (13). A solution of PhC(*i*PrN)$_2$Li (432 mg, 2.2 mmol) in toluene (8 mL) was cooled to −35 °C, at which point boron trichloride (2.2 mL, 1.0 M in heptane, 2.2 mmol) was added in one portion. The reaction mixture was stirred for 5 min, after which the solvent was removed under reduced pressure. The residue was extracted into pentane (15 mL) and filtered through

Table 1. Crystallographic Data

	1	**2**	**3**·$^1/_2CH_2Cl_2$	**4**	**5**	**7**
formula	$C_{19}H_{15}BN_2F_{10}$	$C_{21}H_{19}BN_2F_{10}$	$C_{20.5}H_{16}BN_2O_2F_{10}Cl$	$C_{26}H_{29}BN_4F_{10}$	$C_{20}H_{15}BN_2OF_{10}$	$C_{24}H_{24}BN_3F_{10}$
formula weight	472.14	500.19	558.11	598.34	500.15	555.27
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$C2/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	13.2107(10)	11.4966(6)	34.510(3)	11.2343(5)	16.1775(8)	10.3891(4)
b (Å)	11.2408(9)	11.8061(6)	11.4156(10)	16.3811(7)	9.8189(5)	11.6890(4)
c (Å)	13.749(1)	16.2558(9)	12.7933(11)	15.2027(7)	12.9563(6)	21.6116(7)
α (deg)	90	90	90	90	90	90
β (deg)	91.133(2)	101.241(3)	109.377(8)	97.190(2)	95.769(1)	96.453(1)
γ (deg)	90	90	90	90	90	90
V (Å^3)	2041.3(3)	2164.1(2)	4754.5(7)	2775.8(2)	2047.62(17)	2607.85(16)
Z	4	4	8	4	4	4
T (K)	150(2)	150(2)	150(2)	170(2)	150(2)	150(2)
d_{calc} (g/cm^3)	1.536	1.535	1.559	1.432	1.622	1.414
abs. coeff, Γ (mm^{-1})	0.155	0.150	0.261	0.132	0.163	0.134
data collected	16705	19726	48727	44638	50738	74894
R_{int}	0.0447	0.0365	0.1114	0.0587	0.0369	0.0381
data used	4105	4988	5561	6373	6751	5995
variables	297	307	331	370	311	0.134
R (>2σ)	0.0425	0.0388	0.0686	0.0396	0.0358	0.0453
wR_2	0.1135	0.0944	0.2653	0.0989	0.1005	0.1359
GOF	0.997	1.016	0.968	1.011	1.026	1.029

	10	**11**	**12**	**14**	**15**
formula	$C_{28}H_{25}BN_2OF_{10}$	$C_{21}H_{18}BN_3F_{10}$	$C_{27}H_{21}BF_{10}N_2$	$C_{25}H_{19}BN_2F_{10}$	$C_{19}H_{15}BF_{10}N_2$
formula weight	606.31	519.19	574.27	548.23	472.14
crystal system	monoclinic	triclinic	triclinic	orthorhombic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$Pcba$	$P\bar{1}$
a (Å)	9.7338(3)	8.2916(12)	8.4288(2)	14.6255(12)	14.3554(2)
b (Å)	14.8731(4)	10.6546(15)	9.3068(4)	16.4744(16)	15.9382(2)
c (Å)	18.2826(5)	12.5718(18)	17.6394(8)	20.2803(18)	20.1115(4)
α (deg)	90	100.759(7)	76.475(2)	90	89.5980(10)
β (deg)	93.477(2)	98.769(7)	85.958(2)	90	74.1920(10)
γ (deg)	90	101.432(7)	89.111(2)	90	64.3460(10)
V (Å^3)	2641.93(13)	1048.6(3)	1342.00(10)	4886.5(8)	3958.26(14)
Z	4	2	2	8	8
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)
d_{calc} (g/cm^3)	1.524	1.625	1.421	1.490	1.585
abs. coeff, Γ (mm^{-1})	0.141	0.159	0.132	0.141	0.159
data collected	68526	10708	25676	82565	103071
R_{int}	0.0424	0.0306	0.0286	0.0584	0.0517
data used	12607	7464	6154	5598	21261
variables	385	321	369	348	1169
R (>2σ)	0.0405	0.0429	0.0531	0.0374	0.0517
wR_2 (>2σ)	0.1176	0.1282	0.1387	0.0875	0.0947
GOF	1.026	1.027	1.014	0.966	1.025

Celite. The reaction mixture was concentrated to ∼1 mL in vacuo and cooled to −35 °C to afford colorless crystals (351 mg, 56%). ^{1}H NMR: δ 7.7−7.6 (m, 3H, *Ph*), 7.5 (m, 2H, *Ph*) 3.9 (m, 2H, $^3J_{H-H}$ = 7 Hz, C*H*(CH$_3$)$_2$), 1.3 (d, 12H, $^3J_{H-H}$ = 7 Hz, CH(C*H*$_3$)$_2$). ^{11}B NMR: δ 6.0 (s). ^{13}C{^{1}H} NMR, partial: δ 174.0 (s, br, N=*C*(Ph)−N), 132.8(s), 129.9 (s), 128.3(s), 125.9 (s, br), 46.9 (s, *C*H(CH$_3$)$_2$), 22.9 (s, CH(*C*H$_3$)$_2$). Anal. Calcd for $C_{13}H_{19}BN_2Cl_2$ (285.025): C, 54.78; H, 6.72; N, 9.83. Found: C, 54.53; H, 6.64; N, 9.81.

Synthesis of PhC(*i*PrN)$_2$B(C$_6$F$_5$)$_2$ (14). A solution of **13** (351 mg, 1.2 mmol) was dissolved in dichloromethane (5 mL) and cooled to −35 °C, after which a solution of PhMe·Zn(C$_6$F$_5$)$_2$ (605 mg, 1.2 mmol) in dichloromethane (3 mL) was added, resulting in the immediate formation of a white precipitate. After the reaction mixture was warmed to ambient temperature, the solvent was removed under reduced pressure, and the residue was extracted into pentane (10 mL) and filtered through Celite. The solution was concentrated to ∼2 mL and cooled to −35 °C to afford colorless crystals (635 mg, 94%). ^{1}H NMR: δ 7.7−7.6 (m, 5H, *Ph*), 3.8 (septet, 2H, $^3J_{H-H}$ = 7 Hz, C*H*(CH$_3$)$_2$), 0.9 (d, 12H, $^3J_{H-H}$ = 7 Hz, CH(C*H*$_3$)$_2$). ^{11}B NMR: δ 1.1 (s). ^{13}C{^{1}H} NMR, partial: δ 171.6 (s, N=*C*(Ph)−N), 148.1 (dm, $^1J_{C-F}$ = 245 Hz, *o*-C$_6$F$_5$), 139.9 (dm, $^1J_{C-F}$ = 251 Hz, *p*-C$_6$F$_5$), 137.3 (dm, $^1J_{C-F}$ = 251 Hz, *m*-C$_6$F$_5$), 131.4 (s), 129.1 (s), 127.7 (s), 127.5 (s), 46.2 (s, *C*H(CH$_3$)$_2$), 22.2 (s, CH(*C*H$_3$)$_2$). ^{19}F NMR: δ −132.5 (dd, 4F, $^3J_{F-F}$ = 24 Hz, $^4J_{F-F}$ = 9 Hz, *o*-C$_6$F$_5$), −158.2 (t, 2F, $^3J_{F-F}$ = 21 Hz, *p*-C$_6$F$_5$), −164.4 (m, 4F, $^3J_{F-F}$ = 19 Hz, *m*-C$_6$F$_5$). Anal. Calcd for $C_{25}H_{19}BN_2F_{10}$ (548.256): C, 54.77; H, 3.49; N, 5.11. Found: C, 54.69; H, 3.53; N, 5.29. X-ray-quality crystals were grown from slow cooling of a solution in pentane.

Synthesis of HC(*i*PrN)$_2$(C$_6$F$_4$)BF(C$_6$F$_5$) (15). A solution of **1** (15 mg, 0.026 mmol) in C$_6$D$_5$Br (0.8 mL) was heated to 120 °C for 5 min and then cooled to room temperature. The reaction did not proceed below 80 °C according to ^{1}H NMR analysis. Pentane (2 mL) was added and the reaction mixture cooled to −35 °C overnight to afford colorless crystals that were then dried under reduced pressure (10 mg, 67%). ^{1}H NMR: δ 7.8 (d, 1H, $^4J_{H-H}$ = 2 Hz, *H*C=N), 4.9 (septet of doublets, 1H, $^3J_{H-H}$ = 7 Hz, $^4J_{H-H}$ = 2 Hz, C*H*(CH$_3$)$_2$), 4.0 (septet, 1H, $^3J_{H-H}$ = 7 Hz, C*H*(CH$_3$)$_2$), 1.6 (d, 3H, $^3J_{H-H}$ = 7 Hz, CH(C*H*$_3$)$_2$), 1.5 (d, 3H, $^3J_{H-H}$ = 7 Hz, CH(C*H*$_3$)$_2$), 1.4 (d, 3H, $^3J_{H-H}$ = 7 Hz, CH(C*H*$_3$)$_2$), 1.2 (d, 6H, $^3J_{H-H}$ = 7 Hz, CH(C*H*$_3$)$_2$). ^{11}B NMR: δ −0.6 (d, $^1J_{B-F}$ = 59 Hz). ^{13}C{^{1}H} NMR, partial: δ 148.4 (dm, $^1J_{C-F}$ = 241 Hz, *o*-C$_6$F$_5$), 148.3 (s, N=*C*(H)−N), 141.4 (dm, $^1J_{C-F}$ = 249 Hz), 140.6 (dm, $^1J_{C-F}$ =

249 Hz), 138.3 (dm, $^1J_{C-F} = 251$ Hz), 137.7 (dm, $^1J_{C-F} = 248$ Hz), 122.3 (d, $^2J_{C-F} = 12$ Hz, N−C_{Ar}), 119.3 (s, br, B−*C*), 55.4 (s, *C*H(CH$_3$)$_2$), 55.2 (s, *C*H(CH$_3$)$_2$), 51.4 (s, *C*H(CH$_3$)$_2$), 25.1 (s, CH(*C*H$_3$)$_2$), 24.1 (s, CH(*C*H$_3$)$_2$), 23.0 (s, CH(*C*H$_3$)$_2$), 22.96 (s, CH(*C*H$_3$)$_2$). ^{19}F NMR: δ −134.4 (m, 1F), −135.3 (td, 2F, $^3J_{F-F} =$ 23 Hz, $^4J_{F-F} = 9$ Hz, *o*-C$_6$F$_5$), 148.3 (t, 1F, $J_{F-F} = 14$ Hz), 157.5 (t, $J_{F-F} = 18$ Hz), −158.7 (t, 1F, $^3J_{F-F} = 21$ Hz, *p*-C$_6$F$_5$), −159.7 (dd, 1F, $J_{F-F} = 23$ Hz, $J_{F-F} = 21$ Hz), −165.0 (m, 4F, *m*-C$_6$F$_5$), 169.3 (m, br, B−*F*). Anal. Calcd for $C_{19}H_{15}BN_2F_{10}$ (472.138): C, 48.33; H, 3.20; N, 5.93. Found: C, 47.83; H, 3.42; N, 5.82. X-ray-quality crystals were grown from slow diffusion of pentane into a solution in dichloromethane.

X-ray Data Collection and Reduction. Crystals were coated in Paratone-N oil in the glovebox, mounted on a MiTegen Micromount, and placed under a N_2 stream, thus maintaining a dry, O_2-free environment for each crystal. The data were collected on a Bruker Apex II diffractometer employing Mo Kα radiation ($\lambda =$ 0.71073 Å). Data collection strategies were determined using Bruker Apex software and optimized to provide >99.5% complete data to a 2θ value of at least 55°. The data were collected at 150 ± 2 K for all of the crystals except **4**, for which the data were collected at 170 K. 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 Solution and Refinement. Non-hydrogen atomic scattering factors were taken from literature tabulations.[60] 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 using full-matrix least-squares techniques on F, minimizing the function $w(F_o - F_c)^2$, where the weight w is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all of the 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 were 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 were 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. The results of the crystallographic analyses are shown in Table 1.

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Supporting Information Available: Crystallographic data (CIF) for compounds **1**−**5**, **7**, **10**−**12**, **14**, and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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