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Article

Addition of Enamines or Pyrroles and $B(C_6F_5)_3$ "Frustrated Lewis Pairs" to Alkynes

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Reaction of 1-morpholinocyclohexene with $B(C_6F_5)_3$ and phenylacetylene gave a mixture of two compounds, $[C_6H_{10}N(CH_2CH_2)_2O][PhCCB(C_6F_5)_3]$ (**1a**) and $C_6H_9(2\text{-}PhC{=}C(H)B(C_6F_5)_3)$-$(N(CH_2CH_2)_2O$ (**1b**). The analogous reaction with ethynylferrocene resulted in only the deprotonation product, the alkynyl-borate salt $[C_6H_{10}N(CH_2CH_2)_2O][CpFe(C_5H_4)CCB(C_6F_5)_3]$ (**2**). The related reactions of pyrrole, phenylacetylene, and $B(C_6F_5)_3$ led to the vinyl-borate addition product, $HNC_4H_4(2\text{-}PhC{=}C(H)B(C_6F_5)_3)$ (**3**). In a similar fashion, reaction of *N*-methylpyrrole, phenylacetylene, and $B(C_6F_5)_3$ gave a 3:2 ratio of the products $MeNC_4H_4(2\text{-}PhC{=}C(H)B(C_6F_5)_3)$ (**4a**) and $MeNC_4H_4(3\text{-}PhC{=}C(H)B(C_6F_5)_3)$ (**4b**), while the corresponding reaction of *N*-*tert*-butylpyrrole with phenylacetylene and $B(C_6F_5)_3$ provided a single product, tBuNC$_4$H$_4$(3-PhC=C(H)B(C$_6$F$_5$)$_3$) (**5a**). Variations in the aryl alkynes produced the corresponding addition complexes, tBuNC$_4$H$_4$-(3-ArC=C(H)B(C$_6$F$_5$)$_3$) (Ar = *p*-C$_6$H$_4$Br **5b**, *m*-C$_6$H$_4$Cl **5c**, *p*-C$_6$H$_4$CF$_3$ **5d**, CpFe(C$_5$H$_4$) **5e**). Similarly MeNC$_4$H$_2$(2,5-Me$_2$)(3-ArC=C(H)B(C$_6$F$_5$)$_3$) (Ar = Ph **6a**, *p*-C$_6$H$_4$Br **6b**, *m*-C$_6$H$_4$Cl **6c**, *p*-C$_6$H$_4$CF$_3$ **6d**, CpFe(C$_5$H$_4$) **6e**) were derived from 1,2,5-trimethylpyrrole. The species **5a** and **5b** were shown to rearrange to give tBuNC$_4$H$_3$(3-ArC=C(H)(C$_6$F$_5$)B(C$_6$F$_5$)$_2$) (Ar = Ph **7a**, CpFe(C$_5$H$_4$) **7b**). The related complexes RNC$_4$H$_3$(3-PhC=C(H)(C$_6$F$_5$)B(C$_6$F$_5$)$_2$) (R = SiMe$_3$ **8**, Ph **9**) and MeNC$_4$H-(2,5-Me$_2$)(3-PhC=C(H)(C$_6$F$_5$)B(C$_6$F$_5$)$_2$) (**10**) were derived directly from the corresponding reactions of the pyrrole, PhCCH, and $B(C_6F_5)_3$. In the case of the reaction of *N*-*tert*-butylpyrrole, phenylacetylene, and PhB(C$_6$F$_5$)$_2$, phenyl group migration was observed, affording exclusively the species tBuNC$_4$H$_3$(3-PhC=C(H)(Ph)B(C$_6$F$_5$)$_2$) (**11**). Reaction of **5a** or **4a/4b** and tBu$_3$P resulted in deprotonation and formation of the salts [tBu$_3$PH][RNC$_4$H$_3$(*X*-PhC=C(H)B(C$_6$F$_5$)$_3$)] (R = tBu, *X* = 3 **12**; R = Me *X* = 2 **13a**, 3 **13b**). Reaction of **5a**−**d** or **6a**−**d** with one equivalent of Et$_3$PO mediated proton transfer to generate a series of vinyl pyrroles tBuNC$_4$H$_3$(3-ArC=CH$_2$) (Ar = Ph **14a**, *p*-C$_6$H$_4$Br **14b**, *m*-C$_6$H$_4$Cl **14c**, *p*-C$_6$H$_4$CF$_3$ **14d**) and MeNC$_4$H$_2$(2,5-Me$_2$)(3-ArC=CH$_3$) (Ar = Ph **15a**, *p*-C$_6$H$_4$Br **15b**, *m*-C$_6$H$_4$Cl **15c**, *p*-C$_6$H$_4$CF$_3$ **15d**) and the byproduct Et$_3$PO·B(C$_6$F$_5$)$_3$.

Introduction

Since our initial reports of the activation of H_2 by sterically frustrated combinations of phosphines and boranes,[1] we have shown that such frustrated Lewis pairs (FLPs) activate B−H[2] and S−S bonds[3] and react with olefins,[4] dienes,[5] alkynes,[6] CO_2,[7] and N_2O.[8,9] While most of these early studies have focused on the FLPs derived from sterically encumbered phosphines and boranes, we believe this reactivity has some generality. Indeed, we and others have demonstrated FLP reactivity using carbenes,[10] amines,[11,12] and pyridines.[13] In the case of alkynes, we have shown that phosphines[6] and polyphosphines[14] in the presence of $B(C_6F_5)_3$ or $Al(C_6F_5)_3$ effect facile addition to the C−C triple bond. Berke and co-workers[15] have shown that similar reactions tolerate

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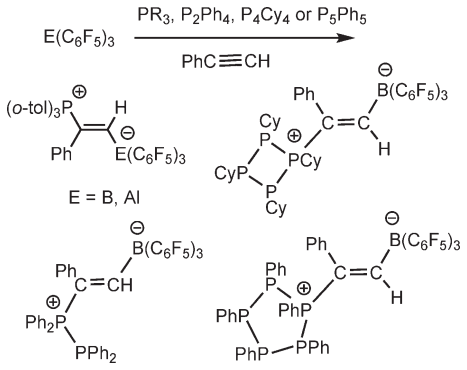
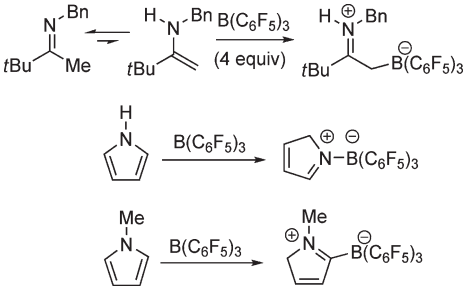
Scheme 1. Products of FLP−Alkyne Addition Reactions



Scheme 2. Reactions of an Enamine, Pyrrole, and *N*-Methylpyrrole with $B(C_6F_5)_3$



variability in the borane (Scheme 1). However, we were interested in probing the viability of C-based nucleophiles in conjunction with the Lewis acid $B(C_6F_5)_3$; these FLP−alkyne addition reactions could provide a route to new C−C bonds. To this end, we considered the possibility that enamines and pyrroles might act as suitable C-based nucleophiles in such reactions. We noted that the reactions of enamines[16,17] or pyrroles[18,19] and $B(C_6F_5)_3$ to give zwitterionic iminium-borates were sluggish. Resconi and co-workers showed that a Lewis acid−base adduct of pyrrole and $B(C_6F_5)_3$ forms readily;[20] however *N*-methylpyrrole reacts with $B(C_6F_5)_3$ over 4 days to form the zwitterion in which the borane is C-bound, $MeNC_4H_4(B(C_6F_5)_3)$ (Scheme 2).[18,21−23] In this paper, we exploit the slow direct reaction of enamines and pyrroles with $B(C_6F_5)_3$, to demonstrate the viability of such Lewis acid−base combinations in three-component reactions involving terminal alkynes. The nature of these products and their subsequent reactivity is also probed.

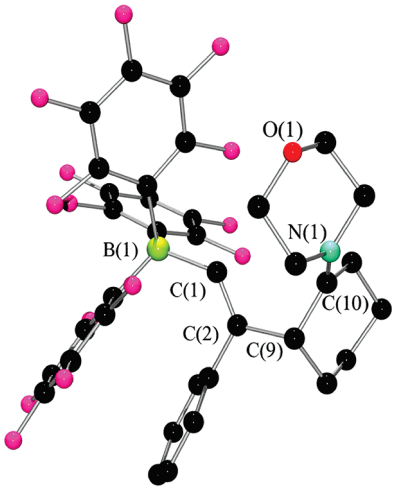
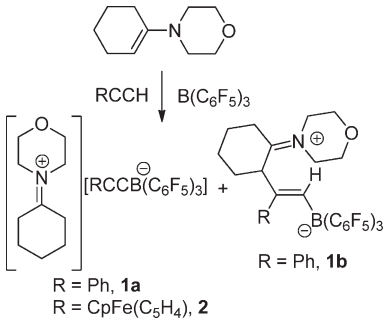


Figure 1. POV-Ray depiction of **1a**. C: black, F: pink, O: red, N: aquamarine, B: yellow-green. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): B(1)−C(1), 1.6354(16); C(1)−C(2), 1.3381(15); C(9)−C(10), 1.5040(16); N(1)−C(10), 1.3010(14); C(2)−C(1)−B(1), 132.24(10); C(1)−C(2)−C(9), 122.75(10).

Scheme 3. Synthesis of 1a,b and 2



Results and Discussion

The FLP-catalyzed hydrogenation of 1-morpholinocyclohexene has been reported,[24] implying that binding of the enamine or ether fragment to the Lewis acid is weak. As such, it was anticipated that 1-morpholinocyclohexene would be a suitable enamine for reaction with $B(C_6F_5)_3$ and terminal alkynes. Addition of $B(C_6F_5)_3$ to a solution of 1-morpholinocyclohexene with excess phenylacetylene in toluene resulted in the immediate formation of an immiscible layer. Subsequent workup afforded a microcrystalline solid. The ^{11}B NMR resonances at −16 and −20 ppm revealed this product was a mixture of two compounds (**1a** and **1b**, Scheme 3) and were characteristic of the borate center in a vinyl-borate zwitterion and an alkynylborate anion, respectively.[6] On the basis of further spectroscopic data these species were formulated as $[C_6H_{10}N(CH_2CH_2)_2O][PhCCB(C_6F_5)_3]$ (**1a**) and $C_6H_9(2\text{-}PhC{=}C(H)B(C_6F_5)_3)(N(CH_2CH_2)_2O$ (**1b**). Attempts to separate these complexes on the basis of differences in solubility were unsuccessful. Nevertheless, slow evaporation from dichloromethane afforded X-ray quality crystals of the addition product (Figure 1). The unsaturated *β*-carbon of the enamine is the site of addition on the nucleophile,

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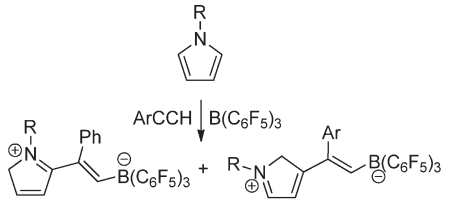
Scheme 4. Synthesis of 3, 4a−e, and 5a−e



resulting in an iminium-vinyl-borate zwitterion. The analogous reaction with ethynylferrocene resulted in only deprotonation to the corresponding alkynyl-borate salt, $[C_6H_{10}N(CH_2CH_2)_2O][CpFe(C_5H_4)CCB(C_6F_5)_3]$, **2** (Scheme 3). It is presumed that the steric demands of this terminal alkyne kinetically favor deprotonation over addition. As to the nature of the cation formed in the deprotonation pathway, 1-morpholinoenamine undergoes kinetic protonation at nitrogen, but tautomerizes to the thermodynamically favored iminium ion in solution.[25]

Although the above alkyne addition pathway results in divergent reactivity, it was anticipated that steric bulk in weakly C-based nucleophiles could preclude adduct formation with the Lewis acid and facilitate addition. In this regard, we noted that substituted pyrroles were worthy of investigation, as they are less nucleophilic than 1-morpholinocyclohexene.[26,27] In addition, as the pK_a values of protonated pyrrole, *N*-methylpyrrole, and 1,2,3-trimethylpyrrole are −3.80, −2.90, and −0.24,[28] respectively, it is reasonable to assume that the deprotonation pathway will be less favored. To probe this hypothesis, a small-scale reaction of pyrrole, phenylacetylene, and $B(C_6F_5)_3$ was conducted in CD_2Cl_2. This led to the formation of a vinyl-borate addition product, $HNC_4H_4(2\text{-}PhC{=}C(H)B(C_6F_5)_3)$, **3** (Scheme 4), as evidenced by the characteristic, sharp ^{11}B NMR resonance (−16 ppm). However, upon standing, this signal vanished and was replaced with broad resonances at −3.6 and −4.2 ppm arising from unknown degradation products. In order to suppress the latter reaction pathway, the procedure was scaled up and the initial zwitterionic product **3** was precipitated out of solution by addition of a nonpolar solvent immediately following addition of the Lewis acid. Although this led to relatively low yields (57%), the ^{1}H NMR spectrum was consistent with alkyne addition at the α-position of the pyrrole. Electrophilic substitution at this position is usually typically favored over attack at the β-carbon of the pyrrole ring.[29] The alacrity of this reaction is evidenced by the absence of any byproducts despite the known reactions of $B(C_6F_5)_3$ and pyrrole,[20] and $B(C_6F_5)_3$ and phenyl acetylene.[15]

In a similar fashion, reaction of *N*-methylpyrrole, phenylacetylene, and $B(C_6F_5)_3$ was carried out. The ^{11}B NMR spectrum was comprised of a single resonance at −16 ppm. Duplicate *para*-fluorine resonances in the ^{19}F NMR spectrum as well as complex resonances in the ^{1}H NMR spectrum indicated the product was derived from addition to both the α- and β-carbons of the pyrrole. Integration of suitable ^{1}H resonances indicated a 3:2 ratio of the products $MeNC_4H_4(2\text{-}PhC{=}C(H)B(C_6F_5)_3)$ (**4a**) and $MeNC_4H_4(3\text{-}PhC{=}C(H)B(C_6F_5)_3)$ (**4b**), respectively (Scheme 4). Interestingly, a similar distribution of products was observed in the reaction of selenium-containing carbocations with *N*-methylpyrrole.[30] The species **4** are short-lived in CD_2Cl_2, degrading within 20 min of dissolution, as evidenced by the evolution of broad resonances at 3 and 2 ppm and a sharp resonance at *ca.* −8 ppm in the ^{11}B NMR spectrum. Hence spectroscopic characterization of **4** was conducted quickly. It is of note that the known zwitterion formed from direct reaction of *N*-methylpyrrole and $B(C_6F_5)_3$ was not observed as a byproduct, although this species was reportedly formed in reactions lasting 4−10 days.[18] Nonetheless, this indicates that pyrrole addition to alkyne is rapid. The analogous reaction of *N*-methylindole, phenylacetylene, and $B(C_6F_5)_3$ gave only the product $PhCH{=}C(C_6F_5)B(C_6F_5)_2$,[15] consistent with the view that *N*-methylpyrrole is a better nucleophile than the related indole.

The corresponding reaction of *N*-*tert*-butylpyrrole with phenylacetylene and $B(C_6F_5)_3$, followed by immediate precipitation with pentane, provided a single product, $tBuNC_4H_4(3\text{-}PhC{=}C(H)B(C_6F_5)_3)$ (**5a**, Scheme 4). This species, obtained in 86% yield, was a moisture-sensitive microcrystalline product. NMR data were consistent with exclusive β-carbon substitution, as is characteristic of electrophilic addition to sterically hindered, N-substituted pyrroles.[31] X-ray crystallographic characterization of **5a** (Figure 2) confirmed substitution at the β-position of the pyrrole and the regiochemistry about the former alkynyl fragment. This was consistent with nucleophilic attack at the more substituted carbon, congruent with the previous work with phosphines.[4,6] While the metrical parameters are not extraordinary, the C−C bond lengths within the pyrrole fragment indicate the acidic proton is localized on the carbon α to both the nitrogen and vinyl fragment, which allows for a contiguous π-system. The analogous reactions using a series of electron-deficient aryl alkynes, ArCCH (Ar = *p*-C_6H_4Br, *m*-C_6H_4Cl, *p*-$C_6H_4CF_3$, and $CpFe(C_5H_4)$), produced the corresponding addition complexes, $tBuNC_4H_4(3\text{-}ArC{=}C(H)B(C_6F_5)_3)$ (**5b**−**e**, Scheme 4). The solid-state molecular structure of the ferrocenyl-substituted complex (**5e**, Figure 2) was also determined and demonstrated similar structural parameters to those of **5a**. While this reaction appears to have some generality with electron-deficient alkynes, analogous reactions involving *N*-*tert*-butylpyrrole, $B(C_6F_5)_3$, with 1-hexene, 1-hexyne, or 3,3-dimethyl-1-butyne, or triphenylborane or $Et_2O{\cdot}BF_3$ with phenylacetylene and *N*-*tert*-butylpyrrole, did not afford similar products.

Using 1,2,5-trimethylpyrrole as a nucleophile, a similar series of complexes, $MeNC_4H_2(2,5\text{-}Me_2)(3\text{-}ArC{=}C(H)B(C_6F_5)_3)$ (Ar = Ph **6a**, *p*-C_6H_4Br **6b**, *m*-C_6H_4Cl **6c**, *p*-$C_6H_4CF_3$ **6d**, $CpFe(C_5H_4)$ **6e**), were synthesized (Scheme 5). As reaction at the α-position was blocked by the methyl

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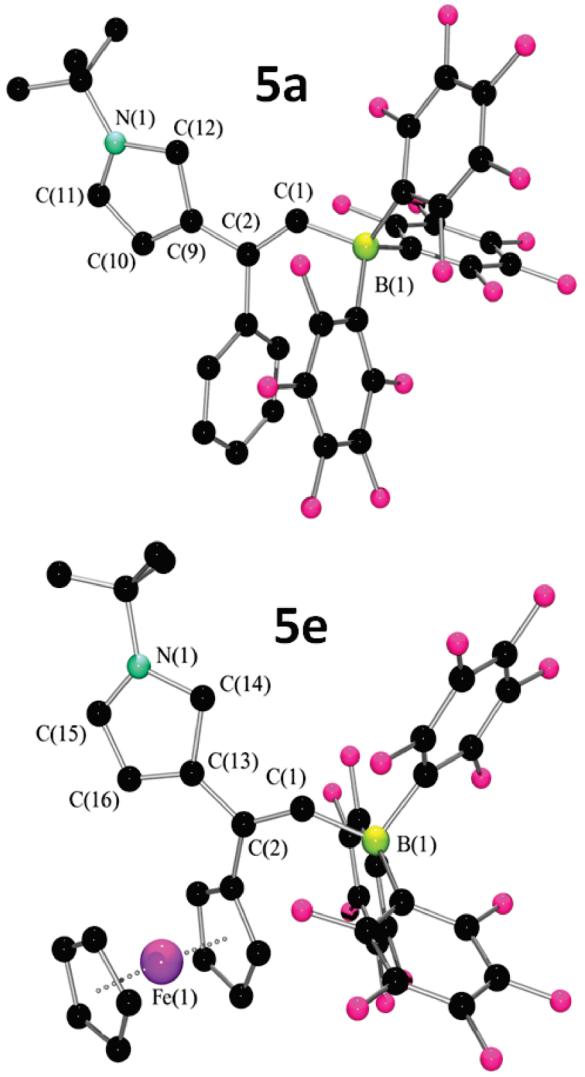
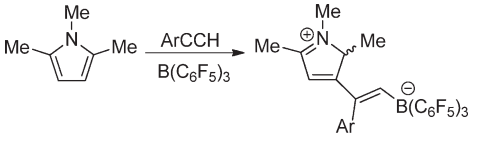


Figure 2. POV-Ray depiction of **5a** and **5e**. C: black, P: orange, F: pink, N: aquamarine, B: yellow-green, H: white. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): **5a**: C(1)−B(1), 1.629(4); C(1)−C(2), 1.345(4); C(2)−C(9), 1.454(4); C(9)−C(10), 1.354(4); C(10)−C(11), 1.416(4); N(1)−C(11), 1.295(4); N(1)−C(12), 1.473(3); C(9)−C(12), 1.501(4); C(11)−N(1)−C(12), 108.6(2); C(2)−C(1)−B(1), 130.0(2); C(1)−C(2)−C(9), 120.4(2). **5e**: C(1)−B(1), 1.641(3); C(1)−C(2), 1.350(3); C(2)−C(13), 1.460(3); C(2)−C(3), 1.479(3); C(9)−C(10), 1.424(4); C(10)−(C11), N(1)−C(15), 1.294(3); N(1)−C(14), 1.469(3); C(15)−N(1)−C(14), 109.25(19); C(1)−C(2)−C(3), 123.01(19); C(13)−C(2)−C(3), 118.09(19).

Scheme 5. Synthesis of 6a−e



Ar = Ph **6a**, *p*-C_6H_4Br **6b**, *m*-C_6H_4Cl **6c**, *p*-$C_6H_4CF_3$ **6d**, $CpFe(C_5H_4)$ **6e**

substituent, this reaction was also regioselective, although in this case a chiral center was generated. The molecular structure of **6a** was determined by X-ray crystallography (Figure 3), which revealed similar regiochemistry and

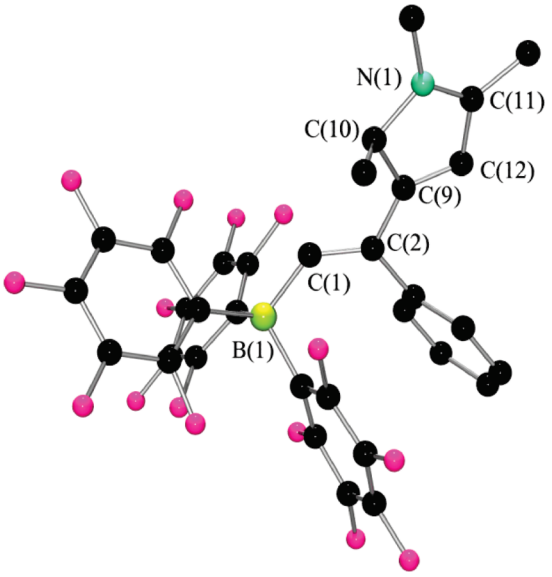


Figure 3. POV-Ray depiction of **6a**. C: black, P: orange, F: pink, N: aquamarine, B: yellow-green, H: white. Hydrogen atoms are omitted for clarity. **6a**: C(1)−B(1), 1.6259(17); C(1)−C(2), 1.3558(16); C(2)−C(9), 1.4575(16); C(9)−C(12), 1.3583(16); C(11)−C(12), 1.4324(18); C(11)−N(1), 1.3071(17); C(10)−N(1), 1.4705(15); C(9)−C(10), 1.5063(17); C(2)−C(1)−B(1), 131.37(11); C(1)−C(2)−C(9), 119.02(11); C(11)−N(1)−C(10), 110.82(10).

metrical parameters to **5a** and **5e**. Complexes **6a**−**e** were also very moisture sensitive, and although more robust in solution than **5a**−**e**, partial decomposition was observed over the course of 12 h by ^{19}F NMR spectroscopy.

A solution of **5a** in CD_2Cl_2 was monitored by NMR spectroscopy. After 24 h the reaction revealed the clean and quantitative conversion to a new species with a sharp ^{11}B NMR resonance at −7 ppm. Concurrently, ^{19}F NMR spectroscopy revealed three inequivalent pentafluorophenyl rings. ^1H NMR data suggested the new compound **7a** contained an iminium fragment, but the resonance for the vinylic H *cis* to B had disappeared. A similar species, **7b**, was obtained from the analogous reaction with ethynylferrocene. X-ray crystallography was used to determine the molecular structures of these rearrangement products, confirming their formulation as the zwitterionic bicyclic species *t*$BuNC_4H_3$-(3-ArC=C(H)$(C_6F_5)B(C_6F_5)_2$) (Ar = Ph **7a**, $CpFe(C_5H_4)$ **7b**; Figure 4), with rings containing a borate or iminium centers. In both **7a** and **7b** the chiral centers are found to have hydrogen substituents that are *trans*-disposed with respect to each other in the solid state. However, the ^1H resonances arising from these H-substituents are quite broad, ostensibly an effect of proximity to boron, and thus it is unclear if a single diastereomer exists in solution.

The related complexes RNC_4H_3(3-PhC=C(H)(C_6F_5)-$B(C_6F_5)_2$) (R = $SiMe_3$ **8**, Ph **9**) were derived from the corresponding reactions of *N*-(trimethylsilyl)pyrrole and *N*-phenylpyrrole with PhCCH and $B(C_6F_5)_3$, respectively (Scheme 6). In these cases the intermediate species analogous to **5** were not observed. The analogous compound $MeNC_4H$-(2,5-Me_2)(3-PhC=C(H)$(C_6F_5)B(C_6F_5)_2$) (**10**) was obtained upon heating **6a** to 60 °C. This species was isolated as a mixture of diastereomers, as evidenced by inequivalent ^{11}B NMR resonances at −8.1 and −8.8 ppm. This was also supported by the solid-state molecular structure of **10**, where

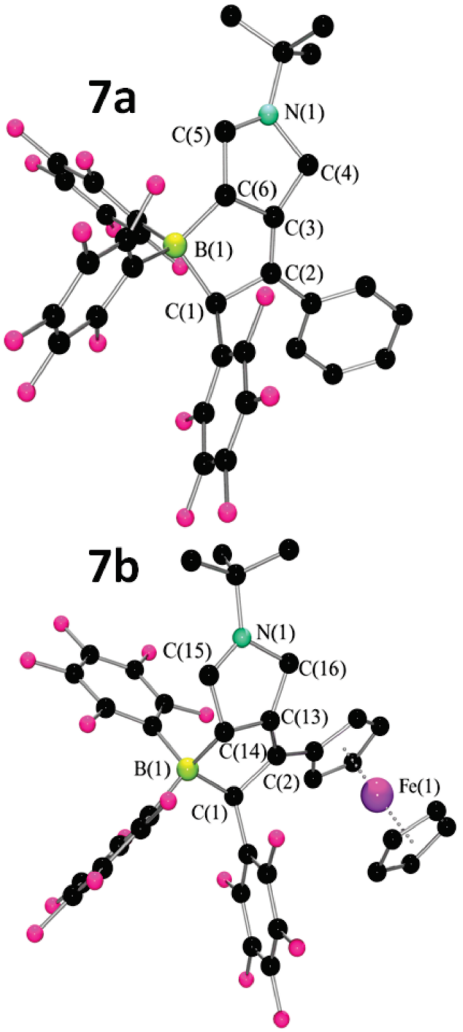


Figure 4. POV-Ray depictions of **7a** and **7b**. C: black, Fe: purple, F: pink, N: aquamarine, B: yellow-green. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): **7a**: B(1)−C(1), 1.706(5); C(1)−C(2), 1.548(5); C(2)−C(3), 1.346(5); C(3)−C(4), 1.513(5); N(1)−C(4), 1.508(4); N(1)−C(5), 1.295(4); C(5)−C(6), 1.470(5); B(1)−C(6), 1.671(5); C(5)−N(1)−C(4), 111.7(3); C(6)−B(1)−C(1), 99.2(2); C(2)−C(3)−C(4), 133.7(3). **7b**: C(1)−B(1), 1.690(4); C(1)−C(2), 1.533(4); C(2)−C(13), 1.342(4); C(13)−C(16), 1.497(4); N(1)−C(16), 1.511(4); N(1)−C(15), 1.291(4); C(14)−C(15), 1.460(4); C(14)−B(1), 1.669(4); C(15)−N(1)−C(16), 111.6(2); C(14)−B(1)−C(1), 98.9(2); C(2)−C(13)−C(16), 133.3(3).

the methyl group bound to the saturated C center was disordered (Figure 5).

The formation of these rearrangement products is thought to proceed via a 1,2-migration of one of the pentafluorophenyl groups followed by a ring-closing addition via the enamine fragment (Scheme 6). Such 1,2-migrations are common in the reactivity of borates and are involved in most of the utilitarian reactions of organoboranes,[32,33] and such C_6F_5 transfer reactions account for reactivity of terminal alkynes[15] with $B(C_6F_5)_3$ alone. Similar rearrangements were not observed from the α-addition products such as **3** and **4a**.

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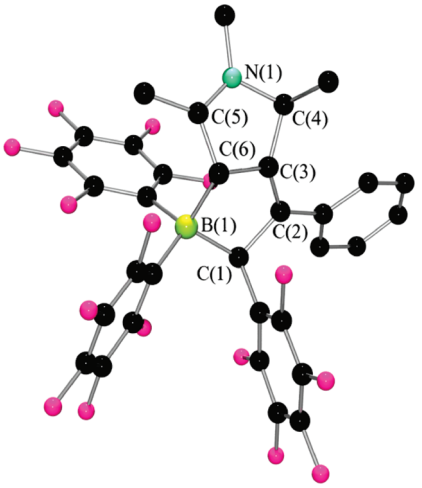
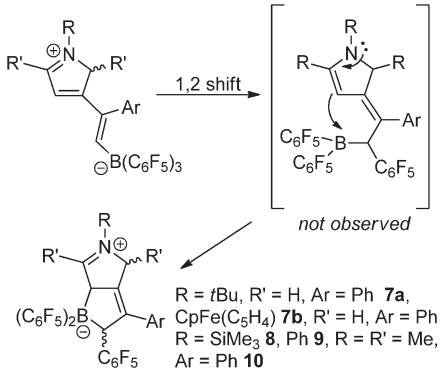


Figure 5. POV-Ray depiction of **10**. C: black, F: pink, N: aquamarine, B: yellow-green. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): B(1)−C(1), 1.690(4); C(1)−C(2), 1.528(4); C(2)−C(3), 1.345(4); C(3)−C(4), 1.518(4); N(1)−C(4), 1.491(4); N(1)−C(5), 1.293(4) C(6)−C(5), 1.478(4); B(1)−C(6), 1.680(4); C(6)−C(3), 1.502(4); C(6)−B(1)−C(1), 98.9(2); C(5)−N(1)−C(4), 114.2(3); C(2)−C(3)−C(4), 132.4(3).

Scheme 6. Synthesis of 7a,b and 8−10



However, the corresponding reaction of *N-tert*-butylpyrrole, phenylacetylene, and $PhB(C_6F_5)_2$ proceeded via this same process with phenyl group migration, exclusively leading to the species $tBuNC_4H_3(3\text{-}PhC{=}C(H)(Ph)B(C_6F_5)_2)$ (**11**), as evidenced by ^{19}F NMR spectroscopy. The same selectivity was not observed in the analogous reaction with $ClB(C_6F_5)_2$, where an inseparable mixture of products formed. These are presumed to arise from 1,2-migrations of either C_6F_5 or Cl.

In an effort to halt this rearrangement, tBu_3P was combined with **5a**, resulting in deprotonation of the pyrrole and formation of the salt $[tBu_3PH][tBuNC_4H_3(3\text{-}PhC{=}C(H)\text{-}B(C_6F_5)_3)]$ (**12**) (Scheme 7). This formulation was confirmed by an X-ray crystallographic study of **12** (Figure 6). The metrical parameters were unexceptional. In contrast to the precursor **5a**, this species **12** proved to be stable in solution for several weeks. Similar treatment of the mixture of **4a** and **4b** with tBu_3P afforded a mixture of the salts $[tBu_3PH]\text{-}[MeNC_4H_3(2\text{-}PhC{=}C(H)B(C_6F_5)_3)]$ (**13a**) and $[tBu_3PH]\text{-}[MeNC_4H_3(3\text{-}PhC{=}C(H)B(C_6F_5)_3)]$ (**13b**). In the case of **13a**, the molecular structure was confirmed crystallographically.

Employing a similar strategy, efforts to intercept the borane intermediate during the rearrangement process were undertaken by the addition of donor molecules. Treatment

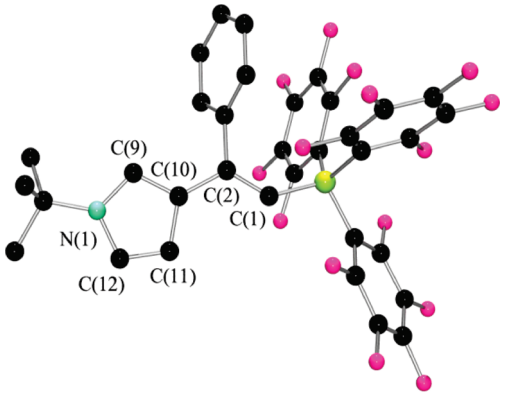


Figure 6. POV-Ray depiction of the cation of **12**. C: black, P: orange, F: pink, N: aquamarine, B: yellow-green, H: white. Most hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): B(1)−C(1), 1.634(5); C(1)−C(2), 1.343(4); C(2)−C(10), 1.479(4); C(9)−C(10), 1.373(5); N(1)−C(9), 1.382(4); N(1)−C(12), 1.375(4); C(11)−C(12), 1.362(5); C(1)−C(2)−C(10), 121.3(3); C(1)−C(2)−C(3), 123.3(3).

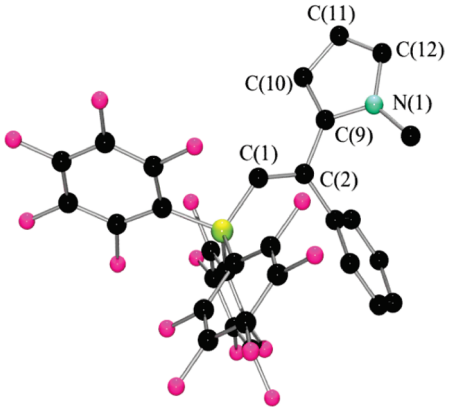
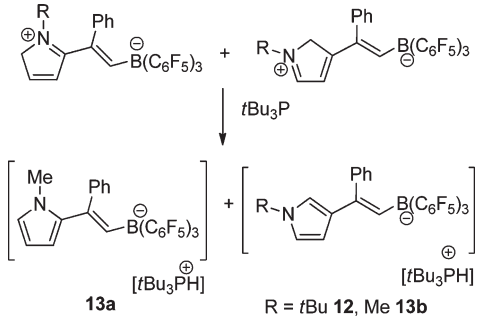


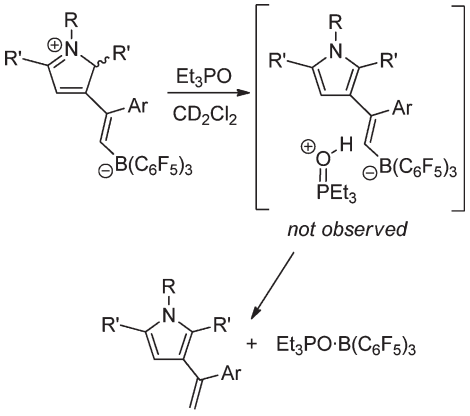
Figure 7. POV-Ray depiction of the cation of **13a**. C: black, P: orange, F: pink, N: aquamarine, B: yellow-green, H: white. Most hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): B(1)−C(1), 1.633(3); C(1)−C(2), 1.344(3); C(2)−C(9), 1.482(3); C(9)−C(10), 1.374(3); C(1)−C(2)−C(9), 119.55(19) C(10)−C(11), 1.416(4); C(11)−C(12), 1.352(5); N(1)−C(12), 1.367(4); N(1)−C(9), 1.379(3); C(1)−C(2)−C(3), 125.24(19); C(1)−C(2)−C(9), 119.55(19).

Scheme 7. Synthesis of 12 and 13a,b



of **5a** with thioethers, primary anilines, and triphenylphosphine sulfide had no effect on the rearrangement to **7a**. However, treatment of **5a** with one equivalent of Et_3PO rapidly afforded a mixture of the borane adduct $Et_3PO\cdot B(C_6F_5)_3$ and tBuNC$_4$H$_3$(3-PhC=CH$_2$) (**14a**). An independent synthesis of the adduct $Et_3PO\cdot B(C_6F_5)$ confirmed its formation in this reaction. Quantitative formation of the 3-vinylpyrrole **14a** is observed by ^{1}H NMR spectroscopy. The appearance of two characteristic doublets with chemical shifts between 5.5 and 5.0 ppm with geminal coupling constants of 1−2 Hz is consistent with known data for related 3-vinylpyrroles.[34] In a similar fashion treatment of **5b−d and 6a−d** afforded the series of vinyl pyrroles tBuNC$_4$H$_3$-(3-ArC=CH$_2$) (Ar = p-C$_6$H$_4$Br **14b**, m-C$_6$H$_4$Cl **14c**, p-C$_6$H$_4$-CF$_3$ **14d**) and MeNC$_4$H$_2$(2,5-Me$_2$)(3-ArC=CH$_3$) (Ar = Ph **15a**, p-C$_6$H$_4$Br **15b**, m-C$_6$H$_4$Cl **15c**, p-C$_6$H$_4$CF$_3$ **15d**) (Scheme 8). It is of note that the ferrocenyl complexes **5e** and **6e** did not react cleanly with Et_3PO, and it remains unclear whether the proton transfer reaction in this instance or the resulting vinyl products are more reactive. The formation of the vinyl pyrroles is thought to proceed via base-mediated proton shuttling to C with B−C bond cleavage and formation of the borane adduct. Similar reactivity was observed with the use of other bases such as Ph_3PO and Ph_3P, although Et_3PO proved to be the fastest and most selective reagent. While the vinyl pyrroles **14** and **15** were spectroscopically characterized,

Scheme 8. Generation of 14a−d and 15a−d



exhaustive efforts to isolate these species proved futile. Indeed, concentration of these species seemed to accelerate degradation to unidentified mixtures of products. This may be a result of the known ability of vinyl pyrroles to undergo [4+2] cycloadditions[35] or N-alkyl pyrroles to undergo Michael additions with electron-deficient alkenes.[36] Nonetheless, vinyl pyrroles are important synthons and intermediates in extensive synthetic chemistry,[29,34,37,38] and installation of a vinyl group at the β-position typically involves transformation of a formyl pyrrole,[39] direct vinylation via Michael-type additions[36] or transition metal catalyzed

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additions of activated alkyne.[40−42] As such reactions are often unselective due to the facility of electrophilic attack on pyrroles,[43] the present observation demonstrates that an FLP-alkyne addition approach to vinyl pyrroles is viable, although modifications are required to generate isolable vinyl pyrroles.

Conclusions. Herein the addition of FLPs to aryl-alkynes has been extended to enamines and pyrroles, providing the first instances of C−C bond formations in FLP systems. In the case of N-substituted pyrroles steric demands favor substitution at the β- rather than the α-position. The resulting zwitterions derived from β-substituted pyrrole/borane additions to alkynes are also shown to be reactive. These species undergo a 1,2 aryl-group shift from B to give bicyclic zwitterionic products. Deprotonation with a strong base gives robust salts, whereas weaker bases mediate proton shuttling to C, generating unstable vinyl pyrroles. The development of the other applications of FLP chemistry in the formation of new C−C bonds continues to be an area of interest in our laboratory.

Experimental Section

General Considerations. All manipulations were carried out under an atmosphere of dry, O_2-free N_2 employing a Vacuum Atmospheres 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 were dried over the appropriate agents and distilled into the same kind of storage flasks (C_6H_5Br). All 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. ^1H, ^{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 (^1H, ^{13}C) or relative to an external standard (^{11}B: $Et_2O\cdot BF_3$; ^{19}F: $CFCl_3$; ^{27}Al: $Al(NO_3)_3$; ^{31}P: 85% H_3PO_4). In some instances, signal and/or coupling assignment was derived from two-dimensional NMR experiments. Chemical shifts are reported in ppm, and coupling constants as scalar values in Hz. Combustion analyses were performed in-house employing a Perkin-Elmer CHN analyzer. *N-tert*-Butylpyrrole,[44] *N*-(trimethylsilyl)pyrrole,[45] and $PhB(C_6F_5)_2$[46] were synthesized via literature procedures; $B(C_6F_5)_3$ was generously donated by NOVA Chemicals Corporation; tri-*tert*-butylphosphine was purchased from Strem Chemicals; all other reagents were purchased from Aldrich. Phenyl acetylene was vacuum transferred from $CaCl_2$ and stored at −35 °C in the glovebox. Liquids were stored over 4 Å molecular sieves.

Synthesis of $[C_6H_{10}N(CH_2CH_2)_2O][PhCCB(C_6F_5)_3]$ (1a), C_6H_9(2-PhC=C(H)B$(C_6F_5)_3$)$(N(CH_2CH_2)_2O$ (1b), and $[C_6H_{10}N$-$(CH_2CH_2)_2O][CpFe(C_5H_4)CCB(C_6F_5)_3]$ (2). These compounds were synthesized via a similar procedure, and hence only one synthesis is described. **1a + 1b**: A solution of $B(C_6F_5)_3$ (100 mg, 0.2 mmol) in toluene (3 mL) was added to a mixture of 1-morpholinocyclohexene (34 mg, 0.2 mmol) and phenylacetylene (20 mg, 0.2 mmol) in toluene (3 mL) in one portion. A yellow layer immediately separated from the toluene layer, the latter layer was decanted, and the former was triturated and washed with pentane (3 × 5 mL) to afford a yellow solid (128 mg, 84%). The solid was determined from ^{11}B and ^{19}F NMR spectra to be a 50:50 mixture of the products resulting from deprotonation (**1a**) and addition (**1b**). ^1H NMR (CD_2Cl_2): 7.3 (dm, $^3J_{H-H}$ = 7 Hz), 7.3−7.1 (m), 7.0 (m), 6.8 (m), 6.3 (s), 4.4 (dm, J_{H-H} = 14 Hz), 4.2 (dm, J_{H-H} = 14 Hz), 4.4 (dt, J_{H-H} = 12 Hz, J_{H-H} = 3 Hz), 3.9 (m), 3.8 (m, br) 3.8 (m), 3.7 (m), 3.6 (m), 3.2 (m), 3.1 (m), 3.0 (m), 2.7 (t, $^3J_{H-H}$ = 6 Hz), 2.3 (t, $^3J_{H-H}$ = 6 Hz), 1.9−1.8 (m), 1.7 (m), 1.5 (m). ^{11}B NMR (CD_2Cl_2): −16.3 (s, addition), −20.9 (s, deprotonation). $^{13}C\{^1H\}$ NMR (CD_2Cl_2), partial: 198.1 (s), 194.7 (s), 148.7 (dm, $^1J_{C-F}$ = 238 Hz, *m*-C_6F_5), 141.2 (s), 139.0 (dm, $^1J_{C-F}$ = 247 Hz, *p*-C_6F_5), 131.7 (s), 128.9 (s), 128.2 (s), 127.3 (s), 127.2 (s), 127.1 (s), 67.0 (s), 66.7 (s), 64.1 (s), 53.9 (s), 53.6 (s), 52.1 (s), 45.9 (s), 42.6 (s), 34.0 (s), 31.4 (s), 29.5 (s), 27.6 (s), 27.5 (s), 25.4 (s), 24.8 (s), 23.6 (s), 19.01 (s), ^{19}F NMR (CD_2Cl_2): −132.6 (d, 6F addition, $^3J_{F-F}$ = 24 Hz, *o*-C_6F_5), −133.0 (d, 6F deprotonation, $^3J_{F-F}$ = 22 Hz, *o*-C_6F_5), −163.0 (t, 3F deprotonation, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −163.4 (t, 3F addition, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −166.8 (t, 6F deprotonation, $^3J_{F-F}$ = 22 Hz, *m*-C_6F_5), −167.3 (t, 6F addition, $^3J_{F-F}$ = 21 Hz, *m*-C_6F_5). Anal. Calcd for $C_{36}H_{23}BNOF_{15}$ (781.374): C, 55.34; H, 2.97; N, 1.79. Found: C, 55.03; H, 3.21; N, 1.76. X-ray quality crystals of the isomer resulting from addition were grown from a concentrated solution in dichloromethane.

2: purple powder, 122 mg, 70%. ^1H NMR (CD_2Cl_2): 5.1 (t, 1H, J_{H-H} = 2 Hz), 4.7 (s, br, 1H), 4.4 (s, 2H), 4.3 (t, 2H, J_{H-H} = 2 Hz, C*Cp*), 4.1 (s, 5H, *Cp*), 4.0 (t, 2H, J_{H-H} = 2 Hz, C*Cp*), 3.9 (m, 4H), 3.3 (m, 3H), 2.7 (t, 2H, $^3J_{H-H}$ = 7 Hz), 2.3 (t, 1H, J_{H-H} = 6 Hz), 2.0 (t, 1H, J_{H-H} = 6 Hz), 1.9 (pentet, 2H), 1.8−1.5 (m, 3H). ^{11}B NMR (CD_2Cl_2): −20.9 (s). $^{13}C\{^1H\}$ NMR (250 K, CD_2Cl_2), partial: 194.8 (s), 182.5 (s), 160 (s), 148.8 (dm, $^1J_{C-F}$ = 238 Hz, *o*-C_6F_5), 138.9 (dm, $^1J_{C-F}$ = 240 Hz, *p*-C_6F_5), 137.2 (dm, $^1J_{C-F}$ = 239 Hz, *m*-C_6F_5), 115.7 (s), 78.0 (s), 72.6 (s), 71.2 (s), 70.1 (s), 68.1 (s), 66.9 (s), 56.0 (s), 54.7 (s), 53.8 (s), 37.6 (s), 33.8 (s), 27.8 (s), 23.5 (s), ^{19}F NMR (CD_2Cl_2): −132.5 (d, 6F, $^3J_{F-F}$ = 23 Hz, *o*-C_6F_5), −163.6 (t, 3F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −167.2 (t, 6F, $^3J_{F-F}$ = 23 Hz, *m*-C_6F_5). Anal. Calcd for $C_{40}H_{27}BNOF_{15}Fe$ (889.295): C, 54.02; H, 3.06; N, 1.58. Found: C, 54.70; H, 3.39; N, 1.40.

Synthesis of HNC_4H_4(2-PhC=C(H)B$(C_6F_5)_3$) (3), $MeNC_4H_9$-(2-PhC=C(H)B$(C_6F_5)_3$) (4a), $MeNC_4H_4$(3-PhC=C(H)B$(C_6F_5)_3$) (4b), *t*$BuNC_4H_4$(3-ArC=C(H)B$(C_6F_5)_3$) (Ar = Ph 5a, *p*-C_6H_4Br 5b, *m*-C_6H_4Cl 5c, *p*-$C_6H_4CF_3$ 5d, CpFe(C_5H_4) 5e), and $MeNC_4H_2$(2,5-Me_2)(3-ArC=C(H)B$(C_6F_5)_3$) (Ar = Ph 6a, *p*-C_6H_4Br 6b, *m*-C_6H_4Cl 6c, *p*-$C_6H_4CF_3$ 6d, CpFe(C_5H_4) 6e). These compounds were synthesized via a similar procedure; therefore only one preparation is detailed. A solution of $B(C_6F_5)_3$ (123 mg, 0.24 mmol) in dichloromethane was cooled to −35 °C in a freezer. A solution of *N-tert*-butylpyrrole (29.6 mg, 0.24 mmol) in pentane (1.5 mL) was added in one portion followed by the dropwise addition of a solution of phenylacetylene (24.5 mg, 0.24 mmol) in pentane (1.5 mL). The solution was initially colorless and became more yellow over the course of the addition. After the phenylacetylene solution had been added, pentane (5 mL) was added in one portion to precipitate a yellow-white microcrystalline solid of **5a** with cocrystallized CH_2Cl_2 (153 mg, 86%).

3: off-white powder, 38 mg, 57%. ^1H NMR (CD_2Cl_2): 9.4 (s, 1H, C=C*H*), 9.0 (s, br, 1H, N*H*), 7.8 (d, 1H, $^3J_{H-H}$ = 8 Hz, C*H*=CH), 7.6 (d, 1H, $^3J_{H-H}$ = 8 Hz, C*H*=CH), 7.3 (m, 3H, *Ph*), 6.9 (d, 2H, $^3J_{H-H}$ = 7 Hz, *o-Ph*), 4.7 (s, 2H, CH_2). ^{11}B NMR (CD_2Cl_2): −16.1 (s). ^{19}F NMR (CD_2Cl_2): −131.6 (d, 6F, $^3J_{F-F}$ = 22 Hz, *o*-C_6F_5), −162.2 (t, 3F, $^3J_{F-F}$ = 19 Hz,

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Table 1. Selected Crystallographic Data

	1b	5a·CH_2Cl_2	5e·½CH_2Cl_2	6a	7a	7b	10	12	13a
Formula	$C_{36}H_{23}BF_{15}NO$	$C_{34}H_{19}BF_{15}N\cdot CH_2Cl_2$	$C_{38}H_{23}BNF_{15}Fe\cdot \frac{1}{2}CH_2Cl_2$	$C_{31}H_{17}BNF_{15}\cdot CH_2Cl_2$	$C_{34}H_{19}BF_{15}N$	$C_{38}H_{23}BNF_{15}Fe\cdot \frac{1}{2}CH_2Cl_2$	$C_{33}H_{17}BNF_{15}$	$C_{46}H_{41}BF_{15}NP\cdot CH_2Cl_2$	$C_{43}H_{30}BF_{15}NP\cdot CH_2Cl_2$
Formula wt	781.36	822.24	930.16	782.18	737.31	971.62	723.29	1023.54	982.47
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	P-1	$P2_1/n$	C2/c	$P2_1/c$	P-1	$P2_1/n$
a(A)	10.0570(5)	9.2434(4)	10.5618(4)	9.6323(4)	19.031(2)	25.6744(10)	14.767(3)	11.9237(4)	12.4988(3)
b(A)	19.7317(11)	18.8844(9)	21.7397(9)	12.9229(5)	13.5891(16)	15.7733(6)	12.815(2)	13.1835(5)	14.4454(4)
c(A)	16.1914(9)	19.6905(10)	17.3339(7)	14.0863(7)	24.744(3)	19.4148(8)	15.639(3)	16.4600(5)	24.9410(6)
α(deg)	90	90	90	91.893(3)	90	90	90	78.235(2)	90
β(deg)	98.613(3)	99.296(3)	106.472(2)	101.946(2)	105.483(6)	103.157(2)	94.286(6)	74.475(2)	103.228(1)
γ(deg)	90	90	90	101.373(2)	90	90	90	74.673(2)	90
V(A^3)	3176.8(3)	3392.0(3)	3816.7(3)	1676.77(13)	6167.05	7656.0(5)	2951.1(9)	2379.56(14)	4383.62(19)
Z	4	4	4	2	8	4	4	2	4
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
d(calc) gcm^{-3}	1.634	1.610	1.619	1.549	1.588	1.686	1.628	1.429	1.489
μ, mm^{-1}	0.159	0.303	0.640	0.302	0.156	0.710	0.161	0.263	0.283
Data collected	111208	46956	120747	91334	103918	78457	42286	48012	53228
R_{int}	0.0812	0.0483	0.0759	0.0323	0.1354	0.0571	0.0465	0.0508	0.0460
Data used	9552	5497	8812	12191	10845	9996	6682	11231	14811
Variables	487	491	592	481	919	554	462	623	591
R ($>2\sigma$)	0.0370	0.0465	0.0420	0.0468	0.0535	0.0587	0.0669	0.0742	0.0623
wR_2	0.0993	0.1162	0.1146	0.1235	0.1524	0.1804	0.1403	0.2162	0.1854
GOF	1.032	1.022	1.017	1.039	0.975	1.031	1.138	1.101	1.038

p-C_6F_5), −166.8 (t, 6F, $^3J_{F-F}$ = 21 Hz, *m*-C_6F_5). Anal. Calcd for $C_{30}H_{11}BNF_{15}$ (681.213): C, 52.90; H, 2.60; N, 1.90. Found: C, 52.39; H, 1.89; N, 2.18.

4a + 4b: white microcrystalline solid, 706 mg, 87%. Ratio of major (2-vinyl) to minor (3-vinyl) isomer (3:2). ^{1}H NMR (CD_2Cl_2): 8.3 (s, 1H major isomer), 8.3 (s, 1H minor isomer), 8.2 (s, 1H minor isomer), 7.5 (d, 1H major isomer, J_{H-H} = 6 Hz), 7.2−7.0 (m), 6.9 (d, 2H, J_{H-H} = 7 Hz), 6.8 (m, 2H), 5.8 (s, 1H), 5.2 (s, 2H, minor isomer), 4.8 (s, 2H, major isomer), 3.7 (s, 3H minor isomer), 3.4 (s, 3H major isomer). ^{11}B NMR (CD_2Cl_2): −16.2 (s, br). ^{19}F NMR (CD_2Cl_2): −131.9 (d, 6F minor and major isomers, $^3J_{F-F}$ = 22 Hz, *o*-C_6F_5), −162.5 (t, 3F, major isomer, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −163.1 (t, 3F minor isomer, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −166.9 (t, 6F major isomer, $^3J_{F-F}$ = 21 Hz, *m*-C_6F_5), −167.2 (t, 6F minor isomer, $^3J_{F-F}$ = 21 Hz, *m*-C_6F_5). Anal. Calcd $C_{31}H_{13}BNF_{15}$ (695.240): C, 53.55; H, 1.88; N, 2.01. Found: C, 53.69; H 1.94; N, 2.01.

5a: yellow-white microcrystalline solid of **5a** with cocrystallized CH_2Cl_2 (153 mg, 86%). ^{1}H NMR (CD_2Cl_2): 8.3 (dd, 1H, $^3J_{H-H}$ = 7 Hz, $^4J_{H-H}$ = 2 Hz, C*H*═N), 8.2 (s, 1H, C═C-*H*), 7.1−7.0 (m, 3H, *Ph*), 6.8 (dm, 2H, $^3J_{H-H}$ = 7 Hz, *o*-Ph), 5.8 (d, 1H, $^3J_{H-H}$ = 2 Hz, C*H*CH═N), 5.2 (d, 2H, $^4J_{H-H}$ = 2 Hz, NCH_2), 1.6 (s, 9H, ^{t}*Bu*). ^{11}B NMR (CD_2Cl_2): −16.2 (s). ^{13}C{^{1}H} NMR (250 K, CD_2Cl_2), partial: 167.3 (s), 168.9 (s), 128.3(s), 127.9 (s), 126.8 (s), 117.8 (s), 62.4 (s), 60.7 (s), 29.6(s). ^{19}F NMR (CD_2Cl_2): −131.9 (d, 6F, $^3J_{F-F}$ = 22 Hz, *o*-C_6F_5), −162.8 (t, 3F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −167.0 (t, 6F, $^3J_{F-F}$ = 21 Hz, *m*-C_6F_5). Anal. Calcd for $C_{34}H_{19}BNF_{15}\cdot CH_2Cl_2$ (822.253): C, 51.13; H, 2.57; N, 1.70. Found: C, 51.35; H, 2.74; N, 1.83. X-ray quality crystals were grown from a concentrated solution in dichloromethane.

5b: yellow powder, 153 mg, 96%. ^{1}H NMR (CD_2Cl_2): 8.3 (m, 1H, C*H*═N), 8.25 (s, 1H, C═C*H*), 7.2 (d, 2H, $^3J_{H-H}$=8 Hz), 6.7 (d, 2H, $^3J_{H-H}$=8 Hz), 5.9 (d, 1H, $^3J_{H-H}$=2 Hz, C*H*CH═N), 5.2 (d, 2H, $^4J_{H-H}$ = 2 Hz, NCH_2), 1.6 (s, 9H, ^{t}*Bu*). ^{11}B NMR (CD_2Cl_2): −16.3 (s). ^{19}F NMR (CD_2Cl_2): −131.8 (d, 6F, $^3J_{F-F}$= 23 Hz, *o*-C_6F_5), −162.8 (t, 3F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −167.0 (t, 6F, $^3J_{F-F}$=21 Hz, *m*-C_6F_5). Anal. Calcd for $C_{34}H_{18}BNF_{15}Br$ (816.216): C, 50.03; H, 2.22; N, 1.72. Found: C, 49.86; H, 2.33; N, 1.74.

5c: yellow powder, 111 mg, 74%. ^{1}H NMR (CD_2Cl_2): 8.3 (m, 1H, C*H*═N), 8.26 (s, 1H, C═C*H*), 7.1 (dm, 1H, $^3J_{H-H}$ = 8 Hz), 7.06 (t, 1H, $^3J_{H-H}$ = 8 Hz), 6.8 (dm, 1H, $^3J_{H-H}$ = 8 Hz), 6.7 (m, 1H), 5.9 (d, 1H, $^3J_{H-H}$ = 2 Hz, C*H*CH═N), 5.2 (d, 2H, $^4J_{H-H}$ = 2 Hz, NCH_2), 1.6 (s, 9H, ^{t}*Bu*). ^{11}B NMR (CD_2Cl_2): −16.3 (s). ^{19}F NMR (CD_2Cl_2): −131.7 (d, 6F, $^3J_{F-F}$ = 23 Hz, *o*-C_6F_5), −162.5 (t, 3F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −167.0 (t, 6F, $^3J_{F-F}$ = 21 Hz, *m*-C_6F_5). Anal. Calcd for $C_{34}H_{18}BNF_{15}Cl$ (771.765): C, 52.92; H, 2.35; N, 1.81. Found: C, 52.79; H, 2.44; N, 1.93.

5d: yellow powder, 145 mg, 90%. ^{1}H NMR (CD_2Cl_2): 8.33 (m, 1H, C*H*═N), 8.29 (s, 1H, C═C*H*), 7.4 (d, 2H, $^3J_{H-H}$ = 8 Hz), 7.0 (d, 2H, $^3J_{H-H}$ = 8 Hz), 5.8 (d, 1H, $^3J_{H-H}$ = 2 Hz, C*H*CH═N), 5.2 (d, 2H, $^4J_{H-H}$ = 2 Hz, NCH_2), 1.6 (s, 9H, ^{t}*Bu*). ^{11}B NMR (CD_2Cl_2): −16.3 (s). ^{19}F NMR (CD_2Cl_2): −63.2 (s, 3F, CF_3), −131.8 (d, 6F, $^3J_{F-F}$ = 22 Hz, *o*-C_6F_5), −162.3 (t, 3F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −166.9 (t, 6F, $^3J_{F-F}$ = 21 Hz, *m*-C_6F_5). Anal. Calcd for $C_{35}H_{18}BNF_{18}$ (805.319): C, 52.20; H, 2.25; N, 1.34. Found: C, 53.03; H, 2.87; N, 1.74.

5e: green powder, 194 mg, 76%. ^{1}H NMR (CD_2Cl_2): 8.5 (m, 1H, C*H*═N), 8.0 (s, 1H, C═C*H*), 7.6 (d, 2H, $^3J_{H-H}$ = 2 Hz, C*H*CH═N), 5.2 (d, 2H, $^4J_{H-H}$ = 2 Hz, NCH_2), 4.1 (t, 2H, $^3J_{H-H}$ = 2 Hz, C*Cp*′), 4.05 (s, 5H, *Cp*), 4.0 (t, 2H, $^3J_{H-H}$ = 2 Hz, C*Cp*′), 1.7 (s, 9H, ^{t}*Bu*). ^{11}B NMR (CD_2Cl_2): −16.0 (s). ^{19}F NMR (CD_2Cl_2): −131.1 (d, 6F, $^3J_{F-F}$ = 22 Hz, *o*-C_6F_5), −163.1 (t, 3F, $^3J_{F-F}$ = 22 Hz, *p*-C_6F_5), −167.2 (t, 6F, $^3J_{F-F}$ = 23 Hz, *m*-C_6F_5). Anal. Calcd for $C_{38}H_{23}BNF_{15}Fe\cdot 1/2CH_2Cl_2$ (881.703): C, 51.76; H, 2.74; N, 1.59. Found: C, 51.71; H, 3.09; N, 1.71. X-ray quality crystals were grown by layering of a solution in dichloromethane with pentane.

6a: white powder, 140 mg, 97%. ^{1}H NMR (CD_2Cl_2): 7.9 (s, 1H, C=C*H*), 7.1−7.0 (m, 3H, *Ph*), 6.8 (d, 2H, $^3J_{H-H}$ = 7 Hz, *o*-Ph), 5.7 (s, 1H, C*H*CMe=N), 5.1 (m, 1H, NC*H*Me), 3.5 (s, 3H, N-*Me*), 2.4 (d, 3H, J_{H-H} = 2 Hz, C*Me*=N), 1.8 (d, 3H, $^3J_{H-H}$ = 8 Hz, NCH*Me*). ^{11}B NMR (CD_2Cl_2): −16.3 (s). ^{19}F NMR (CD_2Cl_2): −131.8 (d, 6F, $^3J_{F-F}$ = 23 Hz, *o*-C_6F_5), −163.3 (t, 3F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −167.3 (t, 6F, $^3J_{F-F}$ = 22 Hz, *m*-C_6F_5). Anal. Calcd for $C_{33}H_{17}BNF_{15}$ (723.293): C, 54.80; H, 2.37; N, 1.94. Found: C, 54.54; H, 2.76; N, 2.04. X-ray quality crystals were grown by slow cooling of a solution in dichloromethane.

6b: yellow powder, 151 mg, 96%. ^{1}H NMR (CD_2Cl_2): 8.0 (s, 1H, C=C*H*), 7.3 (d, 2H, $^3J_{H-H}$ = 8 Hz), 6.7 (d, 2H, $^3J_{H-H}$ = 8 Hz), 5.7 (s, 1H, C*H*CMe=N), 5.1 (m, 1H, NC*H*Me), 3.6 (s, 3H, N-*Me*), 2.4 (d, 3H, J_{H-H} = 2 Hz, C*Me*=N), 1.8 (d, 3H, $^3J_{H-H}$ = 8 Hz, NCH*Me*). ^{11}B NMR (CD_2Cl_2): −16.4 (s). ^{19}F NMR (CD_2Cl_2): −131.8 (d, 6F, $^3J_{F-F}$ = 23 Hz, *o*-C_6F_5), −162.9 (t, 3F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −167.0 (t, 6F, $^3J_{F-F}$ = 22 Hz, *m*-C_6F_5). Anal. Calcd for $C_{33}H_{16}BNF_{15}Br$ (802.189): C, 49.14; H, 2.01; N, 1.75. Found: C, 49.24; H, 2.29; N, 1.77.

6c: yellow powder, 145 mg, 98%. ^{1}H NMR (CD_2Cl_2): 7.9 (s, 1H, C=C*H*), 7.1 (dm, 1H, $^3J_{H-H}$ = 8 Hz), 7.06 (t, 1H, $^3J_{H-H}$ = 8 Hz), 6.8 (dm, 1H, $^3J_{H-H}$ = 8 Hz), 6.6 (m, 1H), 5.7 (s, 1H, C*H*-CMe=N), 5.1 (m, 1H, NC*H*Me), 3.5 (s, 3H, N*Me*), 2.4 (d, 3H, J_{H-H} = 2 Hz, C*Me*=N), 1.8 (d, 3H, $^3J_{H-H}$ = 8 Hz, NCH*Me*). ^{11}B NMR (CD_2Cl_2): −16.4 (s). ^{19}F NMR (CD_2Cl_2): −131.8 (d, 6F, $^3J_{F-F}$ = 22 Hz, *o*-C_6F_5), −162.7 (t, 3F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −167.1 (t, 6F, $^3J_{F-F}$ = 23 Hz, *m*-C_6F_5). Anal. Calcd for $C_{33}H_{16}BNF_{15}Cl$ (757.738): C, 52.31; H, 2.13; N, 1.85. Found: C, 52.20; H, 2.39; N, 1.88.

6d: yellow powder: 149 mg, 96%. ^{1}H NMR (CD_2Cl_2): 8.0 (s, 1H, C=C*H*), 7.3 (d, 2H, $^3J_{H-H}$ = 8 Hz), 6.9 (d, 2H, $^3J_{H-H}$ = 8 Hz), 5.7 (s, 1H, C*H*CMe=N), 5.1 (m, 1H, NC*H*Me), 3.6 (s, 3H, N*Me*), 2.4 (d, 3H, J_{H-H} = 2 Hz, C*Me*=N), 1.8 (d, 3H, $^3J_{H-H}$ = 8 Hz, NCH*Me*). ^{11}B NMR (CD_2Cl_2): −16.4 (s). ^{19}F NMR (CD_2Cl_2): −63.2 (s, 3F, CF_3), −131.8 (d, 6F, $^3J_{F-F}$ = 22 Hz, *o*-C_6F_5), −162.8 (t, 3F, $^3J_{F-F}$ = 22 Hz, *p*-C_6F_5), −167.0 (t, 6F, $^3J_{F-F}$ = 22 Hz, *m*-C_6F_5). Anal. Calcd for $C_{34}H_{16}BNF_{18}$ (791.292): C, 51.61; H, 2.04; N, 1.77. Found: C, 51.46; H, 2.32; N, 1.77.

6e: purple-copper powder, 153 mg, 94%. ^{1}H NMR (CD_2Cl_2): 7.7 (s, 1H, C=C*H*), 7.3 (s, 1H, C*H*CMe=N), 5.1 (5.1 (m, 1H, NC*H*Me), 4.1 (s, 2H, C*Cp*′), 4.0 (s, 5H, *Cp*), 3.95 (s, 2H, C*Cp*′), 3.6 (s, 3H, N*Me*), 2.6 (s, 3H, C*Me*=N), 1.7 (d, 3H, $^3J_{H-H}$ = 7 Hz, NCH*Me*). ^{11}B NMR (CD_2Cl_2): −16.1 (s). ^{19}F NMR (CD_2Cl_2): −131.9 (d, 6F, $^3J_{F-F}$ = 23 Hz, *o*-C_6F_5), −163.2 (t, 3F, $^3J_{F-F}$ = 22 Hz, *p*-C_6F_5), −167.3 (t, 6F, $^3J_{F-F}$ = 21 Hz, *m*-C_6F_5). Anal. Calcd for $C_{37}H_{21}BNF_{15}Fe$ (831.215): C, 53.46; H, 2.55; N, 1.69. Found: C, 53.78; H, 3.04; N, 169.

Synthesis of *t*BuNC$_4$H$_3$(3-ArC=C(H)(C$_6$F$_5$)B(C$_6$F$_5$)$_2$) (Ar = Ph 7a, CpFe(C$_5$H$_4$) 7b). These compounds were generated in a similar fashion; therefore only one synthesis is specified. **7a**: A solution of **5a** (50 mg, 0.07 mmol) in dichloromethane (5 mL) was left at room temperature for 36 h, at which point it was layered with pentane (5 mL) and cooled to −35 °C for 12 h. The supernatant liquid was decanted, and the resulting colorless crystals were dried *in vacuo* (28 mg, 56%). ^{1}H NMR (CD_2Cl_2): 8.6 (s, 1H, C*H*=N), 7.5−7.4 (m, 4H, *Ph*), 6.8 (tm, 1H, $^3J_{H-H}$ = 7 Hz, *p*-Ph), 5.5 (s, br, 1H), 5.1 (m, br, 1H), 4.9 (d, 1H, $^2J_{H-H}$ = 17 Hz, NC*H*H′), 4.7 (d, 1H, $^2J_{H-H}$ = 17 Hz, NCH*H*′), 1.4 (s, 9H, *tBu*). ^{11}B NMR (CD_2Cl_2): −6.8 (s). ^{13}C NMR (CD_2Cl_2): 186.2 (s, *C*=N), 148.6 (dm, $^1J_{C-F}$ = 240 Hz, *o*-BC_6F_5), 148.2 (dm, $^1J_{C-F}$ = 240 Hz, *o*-BC_6F_5), 143.1 (s), 139.1 (dm, $^1J_{C-F}$ = 250 Hz), 137.4 (dm, $^1J_{C-F}$ = 247 Hz), 136.5 (s), 135.0 (s), 129.3 (s), 128.5 (s), 127.9 (s), 62.9 (s), 61.7 (m, br, *C*B), 57.2 (s), 38.4 (m, br, *C*B), 28.6 (s, C*Me*$_3$). ^{19}F NMR (CD_2Cl_2): −133.4 (m, 2F, *o*-C_6F_5), −134.2 (m, 2F, *o*-C_6F_5), −142.4 (s, br, 1F, *o*-C_6F_5), −142.8 (s, br, 1F, *o*-C_6F_5), −160.0 (t, 1F, $^3J_{F-F}$ = 22 Hz, *p*-C_6F_5), −160.9 (t, 1F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −161.5 (t, 3F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −164.3 (m, 2F, *m*-C_6F_5), −164.6 (s, br, 1F, *m*-C_6F_5), −165.6 (m, 3F, *m*-C_6F_5). Anal. Calcd for $C_{34}H_{19}BNF_{15}$ (737.321): C, 55.39; H, 2.60; N, 1.90. Found: C, 54.92; H, 2.92; N, 1.58. The product crystals were suitable for X-ray diffraction.

7b: red crystals, 32 mg, 52%. ^{1}H NMR (CD_2Cl_2): 8.6 (s, 1H, C*H*=N), 5.1 (s, br, 1H), 4.9 (m, br, 1H), 4.7 (d, 1H, $^2J_{H-H}$ = 17 Hz, NC*H*H′), 4.6 (d, 1H, $^2J_{H-H}$ = 17 Hz, NCH*H*′), 4.4 (s, 1H, *Cp*CC), 4.35 (s, 1H, *Cp*CC), 4.3 (s, 1H, *Cp*CC), 4.25 (s, 1H, *Cp*CC), 3.8 (s, 5H, *Cp*), 1.4 (s, 9H, *tBu*). ^{11}B NMR (CD_2Cl_2): −6.3 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2): 186.4 (s, *C*=N), 69.9 (s, *Cp*CC), 69.5 (s, *Cp*CC), 69.2 (s, *Cp*), 68.8 (s, *Cp*CC), 66.2 (s), 62.7 (s), 56.7 (s), 54.4 (s, N*C*HH′), 34.7 (s, *C*Me$_3$), 28.7 (s, C*Me*$_3$). ^{19}F NMR (CD_2Cl_2): −133.0 (d, 2F, $^3J_{F-F}$ = 23 Hz, *o*-C_6F_5), −134.4 (m, 2F, *o*-C_6F_5), −141.1 (s, br, 1F, *o*-C_6F_5), −141.8 (s, br, 1F, *o*-C_6F_5), −160.1 (t, 1F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −160.9 (t, 1F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −161.2 (t, 3F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −164.4 (m, 3F, *m*-C_6F_5), −165.5 (m, 3F, *m*-C_6F_5). Anal. Calcd for $C_{48}H_{23}BNF_{15}Fe$ (845.252): C, 54.00; H, 2.74; N, 1.66. Found: C, 53.63; H, 2.97; N, 1.37. The product crystals were suitable for X-ray diffraction.

Synthesis of RNC$_4$H$_3$(3-PhC=C(H)(C$_6$F$_5$)B(C$_6$F$_5$)$_2$) (R = SiMe$_3$ 8, Ph 9). These compounds were generated in a similar fashion; therefore only one synthesis is specified. **8**: A solution of *N*-trimethylsilylpyrrole (14 mg, 0.1 mmol) and phenylacetylene (10 mg, 0.1 mmol) in dichloromethane (2 mL) was cooled to −35 °C, at which point B(C_6F_5)$_3$ (51 mg, 0.1 mmol) in dichloromethane (1 mL) was added. The solution was allowed to warm to room temperature over the course of 20 min, after which pentane (10 mL) was added and the reaction mixture cooled to −35 °C. The supernatant liquid was decanted, and the resulting white powder dried *in vacuo* (60 mg, 80%). ^{1}H NMR (CD_2Cl_2): 8.8 (s, 1H, C*H*=N), 7.5−7.4 (m, 4H, *Ph*), 7.3 (tm, 1H, $^3J_{H-H}$ = 7 Hz, *p*-Ph), 5.5 (s, br, 1H), 5.3 (m, br, 1H), 4.8 (d, 1H, $^2J_{H-H}$ = 18 Hz, NC*H*H′−), 4.6 (d, 1H, $^2J_{H-H}$ = 18 Hz, NCH*H*′−), 0.4 (s, 9H, Si*Me*$_3$). ^{11}B NMR (CD_2Cl_2): −6.4 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2), partial: 199.1 (s, *C*=N), 148.8 (dm, $^1J_{C-F}$ = 241 Hz, *o*-BC_6F_5), 142.7 (s), 139.5 (dm, $^1J_{C-F}$ = 235 Hz, *p*-BC_6F_5), 136.2 (dm, $^1J_{C-F}$ = 250 Hz, *m*-BC_6F_5), 136.7 (s), 136.5 (s), 129.3 (s), 128.4 (s), 127.9 (s), 58.9 (s), 54.4 (s), 34.8 (s), 22.9 (s), 14.4 (s), −1.5 (s, Si*Me*$_3$). ^{19}F NMR (CD_2Cl_2): −133.4 (m, 2F, *o*-C_6F_5), −134.4 (d, 2F, $^3J_{F-F}$ = 20 Hz,*o*-C_6F_5), −142.3 (s, br, 1F, *o*-C_6F_5), −142.7 (s, br, 1F, *o*-C_6F_5), −160.3 (t, 1F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −161.0 (t, 1F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −161.6 (t, 3F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −164.5 (m, 2F, *m*-C_6F_5), −164.6 (s, br, 1F, *m*-C_6F_5), −165.6 (m, 3F, *m*-C_6F_5). Anal. Calcd for $C_{33}H_{19}BNF_{15}Si$ (753.395): C, 52.61; H, 2.54; N, 1.86. Found: C, 51.91; H, 2.90; N, 1.92.

9: white powder, 75 mg, 50%. ^{1}H NMR (CD_2Cl_2): 8.7 (s, 1H, C*H*=N), 7.6 (d, 2H, $^3J_{H-H}$ = 7 Hz, *o*-Ph), 7.5 (d, 2H, $^3J_{H-H}$ = 7 Hz, *o*-Ph), 7.4 (t, 2H, $^3J_{H-H}$ = 7 Hz), 7.3−7.2 (m, 4H), 5.6 (s, br, 1H), 5.5 (d, 1H, $^2J_{H-H}$ = 17 Hz, NCH*H*′), 5.1 (d, 1H, $^2J_{H-H}$ = 17 Hz, NCH*H*′), 5.1 (s, br, 1H). ^{11}B NMR (CD_2Cl_2): −6.1 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2), partial: 188.9 (s, *C*=N), 148.4 (dm, $^1J_{C-F}$ = 241 Hz, *o*-BC_6F_5), 147.4 (dm, $^1J_{C-F}$ = 241 Hz, *o*-BC_6F_5), 143.8 (s), 137.6 (dm, $^1J_{C-F}$ = 250 Hz, *m*-BC_6F_5), 137.6 (s), 136.3 (s), 134.0 (s), 132.2 (s), 131.2 (s), 129.3 (s), 129 0.1 (s), 128.7 (s), 127.9 (s), 122.7 (s), 121.5 (s), 64.4 (s, br, *C*-B), 62.1 (s), 37.1 (s, br, *C*-B). ^{19}F NMR (CD_2Cl_2): −133.4 (d, 2F, $^3J_{F-F}$ = 20 Hz, *o*-C_6F_5), −134.4 (d, 2F, $^3J_{F-F}$ = 22 Hz, *o*-C_6F_5), −142.2 (s, br, 1F, *o*-C_6F_5), −142.5 (s, br, 1F, *o*-C_6F_5), −159.8 (t, 1F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −160.7 (t, 1F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −161.3 (t, 3F, $^3J_{F-F}$ = 22 Hz, *p*-C_6F_5), −164.1 (m, 2F, *m*-C_6F_5), −164.5 (s, br, 1F, *m*-C_6F_5), −165.4 (m, 3F, *m*-C_6F_5). Anal. Calcd for $C_{36}H_{15}BNF_{15}$ (757.311): C, 57.10; H, 2.00; N, 1.85. Found: C, 56.57; H, 2.36; N, 1.86.

Synthesis of MeNC$_4$H(2,5-Me$_2$)(3-PhC=C(H)(C$_6$F$_5$)B(C$_6$F$_5$)$_2$) (10) and *t*BuNC$_4$H$_3$(3-PhC=C(H)(Ph)B(C$_6$F$_5$)$_2$) (11). These compounds were generated in a similar fashion; therefore only one synthesis is specified. A solution of **6a** (38 mg, 0.05 mmol) in

bromobenzene (1 mL) was heated to 60 °C for 3 h. The solution was cooled to room temperature and layered with pentane (2 mL). Block-like crystals formed upon diffusion, the supernatant was then decanted, and the crystals were dried under reduced pressure (14 mg, 37%). The product was a mixture of diastereomers in a ratio of 4 to 1. ^{1}H NMR (CD_2Cl_2): 7.4−7.1 (m, major + minor isomers, *Ph*), 5.2 (s, br, 1H major + minor isomer), 5.1 (m, br, 1H minor isomer), 4.9 (s, br, 1H major isomer), 4.7 (q, 1H major + minor isomer, $^3J_{H-H}$ = 7 Hz, NC*H*Me), 3.2 (d, 3H major isomer, $^4J_{H-H}$ = 2 Hz, N*Me*), 3.18 (d, 3H minor isomer, $^4J_{H-H}$ = 3 Hz, N*Me*), 2.3 (s, 3H minor isomer, −C(*Me*)=N), 2.2 (s, 3H major isomer, C*Me*=N), 1.7 (d, 3H major isomer, $^3J_{H-H}$ = 7 Hz, NC*H*Me), (d, 3H minor isomer, $^3J_{H-H}$ = 7 Hz, NC*H*Me), ^{11}B NMR (CD_2Cl_2): −8.1 (s, major isomer), −8.8 (s, minor isomer). ^{19}F NMR (CD_2Cl_2): −129.3 (d, 2F, $^3J_{F-F}$ = 20 Hz, *o*-C_6F_5), −129.7 (s, br, 2F minor isomer, *o*-C_6F_5), −134.0 (s, br, 2F major isomer, *o*-C_6F_5), −134.3 (s, br, 2F minor isomer, *o*-C_6F_5), −141.7 (dd, 1F major isomer, $^3J_{F-F}$ = 23 Hz, $^4J_{F-F}$ = 6 Hz, *o*-C_6F_5), −143.2 (m, major + minor isomer, *o*-C_6F_5), −160.2 (t, 1F major isomer, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −160.6 (t, 1F minor isomer, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −161.3 (t, 1F major isomer, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −161.4 (t, 1F minor isomer, $^3J_{F-F}$ = 19 Hz, *p*-C_6F_5), −161.6 (t, 1F minor isomer, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −161.65 (t, 1F major isomer, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −164.2 (m, major + minor isomer, *m*-C_6F_5), −164.8 (tm, 1F major isomer, $^3J_{F-F}$ = 22 Hz, *m*-C_6F_5), −165.7 (m, major + minor isomer, *m*-C_6F_5), −166.1 (m, major + minor isomer, *m*-C_6F_5). Anal. Calcd for $C_{33}H_{17}BNF_{15}$ (723.294): C, 54.80; H, 2.37; N, 1.94. Found: C, 54.35; H, 2.61; N, 1.48.

11: white powder, 200 mg, 62%. ^{1}H NMR (CD_2Cl_2): 9.0 (s, 1H, C*H*=N), 7.5 (d, 2H, $^3J_{H-H}$ = 8 Hz, *o*-Ph), 7.4 (t, 2H, $^3J_{H-H}$ = 8 Hz, *m*-Ph), 7.3 (t, 1H, $^3J_{H-H}$ = 8 Hz, *p*-Ph), 7.1 (d, 2H, $^3J_{H-H}$ = 8 Hz, *o*-Ph), 7.0 (t, 2H, $^3J_{H-H}$ = 8 Hz, *m*-Ph), 6.9 (t, 1H, $^3J_{H-H}$ = 7 Hz, *p*-Ph), 5.0 (d, 1H, $^2J_{H-H}$ = 17 Hz, NCH*H*′), 4.8 (m, br, 2H), 4.7 (s, br, 1H), 1.4 (s, 9H, *t*Bu). ^{11}B NMR (CD_2Cl_2): −3.7 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2), partial: 187.0 (s, *C*=N), 148.7 (dm, $^1J_{C-F}$ = 238 Hz, *o*-BC_6F_5), 147.9 (dm, $^1J_{C-F}$ = 238 Hz, *o*-BC_6F_5), 145.6 (s), 145.1 (s), 138.8 (dm, $^1J_{C-F}$ = 240 Hz), 137.2 (dm, $^1J_{C-F}$ = 247 Hz), 136.9 (s), 133.4 (s), 129.1 (s), 128.2 (s), 128.0 (s), 127.98 (s), 127.4 (s), 124.3 (s), 62.4 (s), 61.1 (m, br, *C*B), 57.0(s), 49.8 (m, br, *C*B), 28.6 (s, C*Me*$_3$). ^{19}F NMR (CD_2Cl_2): −132.8 (dd, 2F, $^3J_{F-F}$ = 25 Hz, $^3J_{F-F}$ = 9 Hz, *o*-C_6F_5), −134.1 (s, br, 2F, *o*-C_6F_5), −160.7 (t, 1F, $^3J_{F-F}$ = 23 Hz, *p*-C_6F_5), −162.0 (t, 1F, $^3J_{F-F}$ = 22 Hz, *p*-C_6F_5), −164.9 (m, 2F, *m*-C_6F_5), −166.1(m, 2F, *m*-C_6F_5). Anal. Calcd for $C_{34}H_{24}BNF_{10}$ (647.368): C, 63.08; H, 374; N, 2.16. Found: C, 62.73; H, 3.79; N, 2.30.

Synthesis of [*t*Bu$_3$PH][*t*BuNC$_4$H$_3$(3-PhC=C(H)B(C$_6$F$_5$)$_3$)] (12), [*t*Bu$_3$PH][MeNC$_4$H$_3$(2-PhC=C(H)B(C$_6$F$_5$)$_3$)] (13a), and [*t*Bu$_3$PH][MeNC$_4$H$_3$(3-PhC=C(H)B(C$_6$F$_5$)$_3$)] (13b). These compounds were generated in a similar fashion; therefore only one preparation is described. **12**: Dichloromethane (5 mL) was added to an intimate mixture of **5a** (80 mg, 0.1 mmol) and *t*Bu$_3$P (22 mg, 0.1 mmol) to afford a clear, colorless solution. Removal of solvent under reduced pressure and subsequent trituration and washing with pentane (2 × 3 mL) afforded 93 mg of a white powder (91%). ^{1}H NMR (CD_2Cl_2): 7.0 (s, br, s, 1H, C=C*H*B-(C_6F_5)$_3$), 6.9 (m, 3H, *Ph*), 6.9 (m, 2H, Ph), 6.7 (t, 1H, J_{H-H} = 3 Hz, pyrrole), 6.2 (m, 2H, pyrrole), 5.1 (d, 1H, $^1J_{H-P}$ = 428 Hz, P*H*), 1.6 (d, 27H, $^3J_{H-P}$ = 16 Hz, P^t*Bu*), 1.4 (s, 9H, ^{t}*Bu*). ^{11}B NMR (CD_2Cl_2): −15.9 (s). ^{19}F NMR (CD_2Cl_2): −131.5 (d, 6F, $^3J_{F-F}$ = 21 Hz, *o*-C_6F_5), −165.4 (t, 3F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −168.3 (t, 6F, $^3J_{F-F}$ = 21 Hz, *m*-C_6F_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): 61.2 (s). Anal. Calcd for $C_{46}H_{46}BNF_{15}P$ (939.642): C, 58.80; H, 4.93; N, 1.49. Found: C, 58.52; H, 5.0; N, 1.79. X-ray quality crystals were grown by layering a solution in dichloromethane with pentane.

13a + 13b: white powder, 93 mg, 90%. Ratio of major (2-vinyl) to minor (3-vinyl) isomer: 2:1. ^{1}H NMR (CD_2Cl_2): 7.0 (s, 1H minor isomer, C=C*H*B(C_6F_5)$_3$), 6.9−6.8 (m), 6.8 (s, major isomer C=C*H*B(C_6F_5)$_3$), 6.4 (m, 1H major isomer and 1H minor isomer), 6.1 (t, 1H minor isomer J_{H-H} = 3 Hz), 5.9 (m, 1H major isomer and 1H minor isomer), 5.7 (dd, 1H major isomer J_{H-H} = 4 Hz, J_{H-H} = 2 Hz,), 5.1 (d, 1H, $^1J_{H-P}$ = 428 Hz, P*H*), 3.5 (s, 3H minor isomer, N*Me*), 3.3 (s, 3H minor isomer, N*Me*), 1.6 (d, 27H, $^3J_{H-P}$ = 16 Hz, P^t*Bu*). ^{11}B NMR (CD_2Cl_2): −16.1 (s, br). ^{19}F NMR (CD_2Cl_2): −131.6 (d, 6F minor isomer, $^3J_{F-F}$ = 22 Hz, *o*-C_6F_5), −131.7 (d, 6F minor isomer, $^3J_{F-F}$ = 22 Hz, *o*-C_6F_5), −165.0 (t, 3F major isomer, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −165.5 (t, 3F minor isomer, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −168.0−168.5 (t, 6F major isomer + 6F minor isomer, *m*-C_6F_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): 61.3 (s). Anal. Calcd for $C_{43}H_{40}BNF_{15}P$ (897.561): C, 57.54; H, 4.49; N, 1.56. Found: C, 57.00; H, 4.44; N, 1.43.

***In Situ* Generation of *t*BuNC$_4$H$_3$(3-ArC=CH$_2$) (Ar = Ph 14a *p*-C$_6$H$_4$Br 14b, *m*-C$_6$H$_4$Cl 14c, *p*-C$_6$H$_4$CF$_3$ 14d) and MeNC$_4$H$_2$-(2,5-Me$_2$)(3-ArC=CH$_3$) (Ar = Ph 15a, *p*-C$_6$H$_4$Br 15b, *m*-C$_6$H$_4$-Cl 15c, *p*-C$_6$H$_4$CF$_3$ 15d).** These compounds were generated in a similar fashion; therefore only one preparation is described (**15a**). NMR data were collected within 30 min for all samples. **14a**: ^{1}H NMR (CD_2Cl_2): 7.5 (dd, 2H, $^3J_{H-H}$ = 8 Hz, $^4J_{H-H}$ = 2 Hz, *o*-Ph), 7.4−7.3 (m, 3H, *m*-Ph and *p*-Ph), 6.8 (t, 1H, $^3J_{H-H}$ = 3 Hz, CH=C*H*N), 6.7 (m, 1H, CR=C*H*N), 6.2 (m, 1H, C*H*=CHN), 5.3 (d, 1H, $^2J_{H-H}$ = 2 Hz, C*H*H′), 5.0 (d, 1H, $^2J_{H-H}$ = 2 Hz, CH*H*′), 1.5 (s, 9H, *t*Bu).

14b: ^{1}H NMR (CD_2Cl_2): 7.5 (d, 2H, $^3J_{H-H}$ = 8 Hz), 7.3 (d, 2H, $^3J_{H-H}$ = 8 Hz), 6.8 (t, 1H, $^3J_{H-H}$ = 3 Hz, CH=C*H*N), 6.7 (t, 1H, $^4J_{H-H}$ = 2 Hz, CR=C*H*N), 6.2 (dd, 1H, $^3J_{H-H}$ = 3 Hz, $^4J_{H-H}$ = 2 Hz, C*H*=CHN), 5.3 (d, 1H, $^2J_{H-H}$ = 2 Hz, C*H*H′), 5.0 (d, 1H, $^2J_{H-H}$ = 2 Hz, CH*H*′), 1.5 (s, 9H, *t*Bu).

14c: ^{1}H NMR (CD_2Cl_2): 7.4 (m, 1H), 7.4−7.35 (m, 1H), 7.3 (m, 2H), 6.8 (t, 1H, $^3J_{H-H}$ = 3 Hz, CH=C*H*N), 6.7 (t, 1H, $^4J_{H-H}$ = 2 Hz, CR=C*H*N), 6.2 (dd, 1H, $^3J_{H-H}$ = 3 Hz, $^4J_{H-H}$ = 2 Hz, C*H*=CHN), 5.4 (d, 1H, $^2J_{H-H}$ = 2 Hz, C*H*H′), 5.0 (d, 1H, $^2J_{H-H}$ = 2 Hz, CH*H*′), 1.5 (s, 9H, *t*Bu).

14d: ^{1}H NMR (CD_2Cl_2): 7.6−7.5 (m, 4H), 6.8 (t, 1H, $^3J_{H-H}$ = 3 Hz, CH=C*H*N), 6.7 (m, 1H, CR=C*H*N), 6.2 (m, 1H, C*H*=CHN), 5.4 (d, 1H, $^2J_{H-H}$ = 1 Hz, C*H*H′), 5.0 (d, 1H, $^2J_{H-H}$ = 1 Hz, CH*H*′), 1.5 (s, 9H, *t*Bu). ^{19}F NMR (CD_2Cl_2): −63.7 (s, 3F, C*F*$_3$).

15a: To an intimate mixture of **6a** (14.4 mg, 0.02 mmol) and triethylphosphine oxide (2.7 mg, 0.02 mmol) was added CD_2Cl_2 (0.8 mL). The reaction mixture went from a clear yellow solution to a very pale orange solution within a few seconds and was transferred to an NMR tube. ^{1}H NMR (CD_2Cl_2): 7.4 (dd, 2H, $^3J_{H-H}$ = 8 Hz, $^4J_{H-H}$ = 2 Hz, *o*-Ph), 7.3−7.2 (m, 3H, *m*-Ph and *p*-Ph), 5.7 (s, 1H, C*H*=CMe), 5.3 (d, 1H, $^2J_{H-H}$ = 2 Hz, C*H*H′), 5.1 (d, 1H, $^2J_{H-H}$ = 2 Hz, CH*H*′), 3.4 (s, 3H, N*Me*), 2.2 (s, 3H, C*Me*), 2.0 (s, 3H, C*Me*).

15b: ^{1}H NMR (CD_2Cl_2): 7.4 (d, 2H, $^3J_{H-H}$ = 8 Hz), 7.3 (d, 2H, $^3J_{H-H}$ = 8 Hz), 5.7 (s, 1H, C*H*=CMe), 5.3 (d, 1H, $^2J_{H-H}$ = 2 Hz, C*H*H′), 5.1 (d, 1H, $^2J_{H-H}$ = 2 Hz, CH*H*′), 3.4 (s, 3H, N*Me*), 2.2 (s, 3H, C*Me*), 2.0 (s, 3H, C*Me*).

15c: ^{1}H NMR (CD_2Cl_2): 7.4 (m, 1H), 7.3−7.2 (m, 3H,), 5.7 (s, 1H, C(*H*)=C(Me)), 5.3 (d, 1H, $^2J_{H-H}$ = 2 Hz, C*H*H′), 5.1 (d, 1H, $^2J_{H-H}$ = 2 Hz, CH*H*′), 3.4 (s, 3H, N*Me*), 2.2 (s, 3H, C*Me*), 2.0 (s, 3H, C*Me*).

15d: ^{1}H NMR (CD_2Cl_2): 7.6 (d, 2H, $^3J_{H-H}$ = 8 Hz), 7.5 (d, 2H, $^3J_{H-H}$ = 8 Hz), 5.7 (s, 1H, C*H*=CMe), 5.4 (d, 1H, $^2J_{H-H}$ = 2 Hz, C*H*H′), 5.2 (d, 1H, $^2J_{H-H}$ = 2 Hz, CH*H*′), 3.4 (s, 3H, N*Me*), 2.2 (s, 3H, C*Me*), 2.0 (s, 3H, C*Me*). ^{19}F NMR (CD_2Cl_2): −63.6 (s, 3F, C*F*$_3$),

Synthesis of Et$_3$PO·B(C$_6$F$_5$)$_3$. To a solution of B(C_6F_5)$_3$ (47 mg, 0.092 mmol) in pentane (2 mL) was added Et_3P=O (20 mg, 0.15 mmol) in one portion, which instantly afforded a white precipitate (40 mg, 68%). ^{1}H NMR (CD_2Cl_2): 2.0 (dq, 6H, $^2J_{H-P}$ = 12 Hz, $^3J_{H-H}$ = 7 Hz, CH_2CH$_3$), 1.1 (dq, 9H, $^2J_{H-P}$ = 18 Hz, $^3J_{H-H}$ = 7 Hz, CH$_2$CH_3). ^{11}B NMR (CD_2Cl_2): −2.7 (s, br). ^{19}F NMR (CD_2Cl_2): −134.4 (m, 6F, *o*-C_6F_5), −159.1 (t, 3F,

$^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −165.0 (m, 6F, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 78.1 (s). Anal. Calcd for $C_{24}H_{15}BOF_{15}P$ (646.145): C, 44.61; H, 2.34. Found: C, 44.12; H, 2.82.

X-ray Crystallography. Crystals were coated in Paratone-N oil in the glovebox, mounted on a MiTegen Micromount, and placed under an N_2 stream, thus maintaining a dry, O_2-free environment for each crystal. The data were collected on a Bruker Apex II diffractometer employing Mo Kα radiation (λ = 0.71073 Å). Data collection strategies were determined using Bruker Apex software and optimized to provide > 99.5% complete data to a 2θ value of at least 55°. The data were collected at 150(±2) K for all crystals. 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). Non-hydrogen atomic scattering factors were taken from the literature tabulations.[47] The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on *F*, minimizing the function $w(F_o - F_c)^2$ where the weight *w* is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases atoms were treated isotropically. C−H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C−H bond length of 0.95 Å. H atom temperature factors were fixed at 1.20 times the isotropic temperature factor of the C atom to which they are bonded. The H atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance.

(47) Cromer, D. T.; Waber, J. T. *Int. Tables X-Ray Crystallogr.* **1974**, *4*, 71–147.

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