ORGANOMETALLICS
Article

Organometallics **2010,** *29,* 125–133 125
DOI: 10.1021/om9008636

Activation of Terminal Alkynes by Frustrated Lewis Pairs

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Received October 5, 2009

The reactions of frustrated Lewis pairs (FLPs) derived from $B(C_6F_5)_3$ and the bulky Lewis bases 2,2,6,6-tetramethylpiperidine (**TMP**), tri-*tert*-butylphosphine, and lutidine (**Lut**) with terminal alkynes (acetylene, phenylacetylene, 3-ethynylthiophene) were investigated. The FLPs **TMP**$\cdots B(C_6F_5)_3$, *t*-$Bu_3P\cdots B(C_6F_5)_3$ and **Lut**$\cdots(C_6F_5)_3$ reacted with acetylene (HC≡CH) to yield the apparently thermodynamically more stable *E* isomers [**TMP**H][$(C_6F_5)_2B-C(C_6F_5)$=C(H)$B(C_6F_5)_3$] (**1-*E***), *t*-$Bu_3PC(H)$=C(H)$B(C_6F_5)_3$ (**2-*E***; 90%), and [*t*-Bu_3PH][$(C_6F_5)_2B-C(C_6F_5)$=C(H)$B(C_6F_5)_3$] (**3-*E***; 10%), and **Lut**C(H)=C(H)$B(C_6F_5)_3$ (**4-*E***), respectively. A mechanistic pathway for the reaction of acetylene is suggested to start with the formation of a weak $B(C_6F_5)_3$/acetylene adduct followed by a deprotonation of this species with any mentioned Lewis bases (LB), yielding the acetylide salts [LBH][$(C_6F_5)_3BC$≡CH]. Alternatively, nucleophilic addition of the LB to this adduct occurs to yield LBC(H)=C(H)$B(C_6F_5)_3$ compounds. Formation of **1** and **3-*E*** is explained by the reactions of [LBH][$B(C_6F_5)_3C$≡CH] salts with a second equivalent of $B(C_6F_5)_3$ to undergo electrophilic addition, forming the vinylidene adduct $(C_6F_5)_3B^-C^+$=C(H)$B(C_6F_5)_3$, which is subsequently stabilized by 1,2-migration of a C_6F_5 group to form [$(C_6F_5)_2BC(C_6F_5)$=C(H)$B(C_6F_5)_3$]. The reaction between $B(C_6F_5)_3$ and phenylacetylene yielded a mixture of (*Z*)- and (*E*)-PhC(H)=$C(C_6F_5)B(C_6F_5)_2$ (**11-*Z*** and **11-*E***), confirming that the reaction proceeds via an acetylene/vinylidene rearrangement and subsequent 1,2-shift of a C_6F_5 group to the carbenic center. The FLPs **TMP**$\cdots B(C_6F_5)_3$ and *t*$Bu_3P\cdots B(C_6F_5)_3$ were converted with phenylacetylene or 3-ethynylthiophene to yield the acetylide products [**TMP**H][PhC≡$CB(C_6F_5)_3$] (**5**), [**TMP**H][SC_4H_3C≡$CB(C_6F_5)_3$] (**6**), [*t*-Bu_3PH][PhC≡$CB(C_6F_5)_3$] (**7**), and [*t*-Bu_3PH][SC_4H_3C≡$CB(C_6F_5)_3$] (**8**), where **TMP** and *t*-Bu_3P acted as a base deprotonating the acetylenic proton. When the FLP **Lut**$\cdots B(C_6F_5)_3$ was reacted with phenylacetylene or 3-ethynylthiophene, the deprotonated product [**LutH**][PhC≡$CB(C_6F_5)_3$] (**9**; 47%) and the 1,2-addition compound **Lut**C(SC_4H_3C)=C(H)$B(C_6F_5)_3$ (**10**; 55%) were obtained. Compounds **1-*E***, **2-*E***, **5**, and **6** were characterized by X-ray diffraction studies.

I. Introduction

The strong Lewis acid tris(pentafluorophenyl)boron is capable of strongly polarizing hydrogen and preferential sp and sp^2 carbon centers, shaping them for further reactivities. In the realm of metallocene Ziegler-type polymerization catalysis metal−carbon bonds were seen to be heterolytically cleaved by $B(C_6F_5)_3$, leaving vacant sites behind. In addition, electrophilic carbon centers could be opened up by $B(C_6F_5)_3$ addition to coordinated or noncoordinated π systems.[1−5] Moreover, the Lewis acid $B(C_6F_5)_3$ was shown to be capable of inducing novel transformations[6,7] or was employed as a stoichiometric reagent to generate new types of organometallic and organic compounds.[8−10] More recently, Stephan et al. discovered that H_2 can be activated reversibly with heterolytic splitting by the "metal-free" internal Lewis pair [(2,4,6-$Me_3C_6H_2)_2PC_6F_4B(C_6F_5)_2$].[11] On the basis of this finding "metal-free" catalysts could be developed for the hydrogenation of bulky imines with the Lewis acid $B(C_6F_5)_3$.[12] This type of reactivity required the formation of encounter complexes called frustrated Lewis pairs (FLPs), consisting of sterically hindered Lewis bases in combination with sterically hindered Lewis acids and providing "unquenched" reactivity and prevention of Lewis pair

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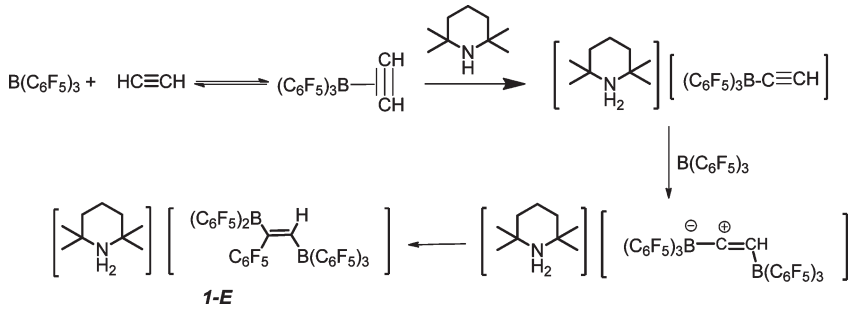
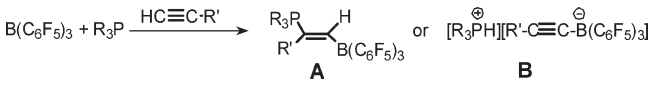
(1) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623.
(2) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.
(3) Karl, J.; Erker, G.; Fröhlich, R. *J. Am. Chem. Soc.* **1997**, *119*, 11165.
(4) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223.
(5) Piers, W. E. *Adv. Organomet. Chem.* **2005**, *52*, 1.
(6) Ishihara, K; Hananki, N.; Yamamoto, H. *Synlett* **1993**, 577.
(7) Nagata, T.; Toshihiro, T.; Yamada, T.; Imagawa, K.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 2614.
(8) Temme, B.; Erker, G.; Fröhlich, R.; Grehl, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1480.
(9) Erker, G.; Ahlers, W.; Fröhlich, R. *J. Am. Chem. Soc.* **1995**, *117*, 5853.
(10) Erker, G.; Schmuck, S.; Bendix, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1955.
(11) Welch, G. C.; Juan, R. R. S.; Masuda, J. D.; Stephan, D. W. *Science* **2006**, *314*, 1124.
(12) Chase, P. A.; Welch, G. C.; Jurca, T.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 8050.

Published on Web 12/11/2009

Scheme 1



formation. FLPs possess great potential in small-molecule chemistry.[13,14] $B(C_6F_5)_3$, because of its strong Lewis acidity and its bulkiness, was demonstrated to be an appropriate constituent of FLPs, and in combination with sterically hindered phosphines, amines, and carbenes, it allowed facile cleavage of H_2.[15−23] In addition to this H_2 splitting capability, ionic products were shown to serve as efficient catalysts for the hydrogenation of imines, nitriles, and aziridines, as well as enamine and silyl enol C=C double bonds.[24−26] In addition, FLPs with $B(C_6F_5)_3$ can undergo 1,2-addition to olefins together with the Lewis base,[16,17] open the THF ring in a bifunctional manner,[19,27] and activate B−H[28] and N−H bonds,[18] but only little has been reported about the reaction of such FLPs toward alkynes.[29,30] Stephan et al. have shown that FLPs can promote 1,2-addition reactions with substituted terminal alkynes to yield donor/acceptor substituted alkenes of type **A** or undergo C−H deprotonation to establish ionic products of type **B**.



In this article we describe reactions between various FLPs and acetylene or substituted terminal alkynes.

II. Results and Discussion

IIa. Reactions of Acetylene with FLPs of $B(C_6F_5)_3$ and TMP, *t*-Bu_3P, and Lut. When dried HC≡CH was introduced into the toluene solution of FLP **TMP**···$B(C_6F_5)_3$, the reaction mixture turned orange and an oil separated at the bottom of the Young NMR tube after 30 min. Hexane was added to the oily residue to prompt precipitation of the ionic compound [**TMP**H][$(C_6F_5)_2$BC(C_6F_5)=C(H)B(C_6F_5)$_3$] (**1-*E***) (Scheme 1), which was isolated as an off-white solid in 56% yield. Multinuclear NMR in $CDCl_3$ showed that **1-*E*** exhibits a broad ^{1}H NMR resonance at 5.32 ppm attributable to the N*H* proton, as well as a resonance at 9.32 ppm assigned to the unique =C*H* proton. The ^{19}F NMR spectrum showed three sets of *o*-, *p*-, and *m*-C_6F_5 signals. One set of resonances at δ −140.60, −159.18, and −165.08 ppm was attributed to the carbon-bound C_6F_5 unit; the other two sets were detected at δ −132.14, −151.65, and −162.76 ppm and at δ −131.69, −162.31, and −167.05 ppm, in agreement with C_6F_5 residues bound to three-coordinate ($\Delta\delta_{p,m}$ = 11.11) and four-coordinate boron centers ($\Delta\delta_{p,m}$ = 4.74).[31,32] In the ^{11}B NMR spectrum one signal at −15.19 ppm was assigned to the four-coordinate boron moiety, but no signal was observed for the three-coordinate boron center of the anion. The X-ray crystallographic study confirmed the spectroscopically derived (*E*)-vinylidene structure of the anion of **1-*E***[33] 1,2-connected to the two different boron fragments −B(C_6F_5)$_3$ and −B(C_6F_5)$_2$ possessing a C=C distance of 1.363(3) Å (Figure 1). The electron-deficient boron center is in a trigonal arrangement deviating somewhat from planarity, in which the three B−C bond distances (B2−C2 = 1.532(3), B2−C27 = 1.589(3), B2−C33 = 1.577(3) Å) are longer than those in the pseudotetrahedral geometry of the $B(C_6F_5)_3$ substituent (B1−C1 = 1.634(3), B1−C3 = 1.674(3), B1−C9 = 1.648(3), B1−C15 = 1.650(3) Å). A very important structural feature of **1-*E*** is the parallel arrangement of the unique C-bound C_6F_5 group with one of the B−C_6F_5 groups, which is presumed to further stabilize the compound via π stacking of the aryl substituents. The ions are connected through multiple weak C−H···F hydrogen-bonding contacts.

A possible reaction mechanism for the formation of **1-*E*** would start from the presumably weak terminal alkyne/

(13) Stephan, D. W. *Org. Biomol. Chem.* **2008**, *6*, 1535.
(14) Stephan, D. W. *Dalton Trans.* **2009**, 3129.
(15) Welch, G. C.; Stephan, D. W. *J. Am. Chem. Soc.* **2007**, *129*, 1880.
(16) McCahill, J. S. J.; Welch, G. C.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 4968.
(17) Ullrich, M.; Seto, K. S.-H.; Lough, A. J.; Stephan, D. W. *Chem. Commun.* **2009**, 2335.
(18) Chase, P. A.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2008**, *47*, 7433.
(19) Holschunmacher, D.; Bannenberg, T.; Hrib, C. G.; Jones, P. G.; Tamm, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 7428.
(20) Sumerin, V.; Schulz, F.; Nieger, M.; Leskelä, M.; Repo, T.; Rieger, B. *Angew. Chem., Int. Ed.* **2008**, *47*, 6001.
(21) Huber, D. P.; Kehr, G.; Bergander, K.; Fröhlich, R.; Erker, G.; Tanino, S.; Ohki, Y.; Tatsumi, K. *Organometallics* **2008**, *27*, 5279.
(22) Ramos, A.; Lough, A. J.; Stephan, D. W. *Chem. Commun.* **2009**, 1118.
(23) Geier, S. J.; Stephan, D. W. *J. Am. Chem. Soc.* **2009**, *131*, 3476.
(24) Spies, P.; Schwendemann, S.; Lange, S.; Kehr, G.; Fröhlich, R.; Erker, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 7543.
(25) Sumerin, V.; Schulz, F.; Atsumi, M.; Wang, C.; Nieger, M.; Leskelä, M.; Repo, T.; Pyykkö, P.; Rieger, B. *J. Am. Chem. Soc.* **2008**, *130*, 14117.
(26) Wang, H.; Fröhlich, R.; Kehr, G.; Erker, G. *Chem. Commun.* **2008**, 5966.
(27) Welch, G. C.; Masuda, J. D.; Stephan, D. W. *Inorg. Chem.* **2006**, *45*, 478.
(28) Dureen, M. A.; Lough, A; Gilbert, T. M.; Stephan, D. W. *Chem. Commun.* **2008**, 4303.
(29) Dureen, M. A.; Stephan, D. W. *J. Am. Chem. Soc.* **2009**, *131*, 8396.
(30) Mömming, C. M.; Frömel, S.; Kehr, G.; Fröhlich, R.; Grimme, S.; Erker, G. *J. Am. Chem. Soc.* **2009**, *131*, 12280.
(31) Vagedes, D.; Erker, G.; Fröhlich, R. *Angew. Chem., Int. Ed.* **1999**, *38*, 3362.
(32) Spies, P.; Fröhlich, R.; Kehr, G.; Erker, G.; Grimme, S. *Chem. Eur. J.* **2008**, *14*, 779.
(33) Crystal data for **1-*E***: $C_{50}H_{24}B_2F_{30}N$, M_r = 1230.32, triclinic, $P\bar{1}$, a = 11.7619(4) Å, b = 11.9617(4) Å, c = 20.1408(7) Å, α = 84.658(3)°, β = 75.635(3)°, γ = 60.642(4)°, V = 2391.16(17) Å^3, Z = 2, D_c = 1.709 g cm^{-3}, μ = 0.181 mm^{-1}, λ = 0.710 73 Å, T = 183(2) K, 30 688 reflections collected, 9745 independent (R_{int} = 0.0567) and 5597 observed reflections ($I > 2\sigma(I)$), 749 refined parameters, R1 = 0.0410, wR2 = 0.08919. CCDC 748013.

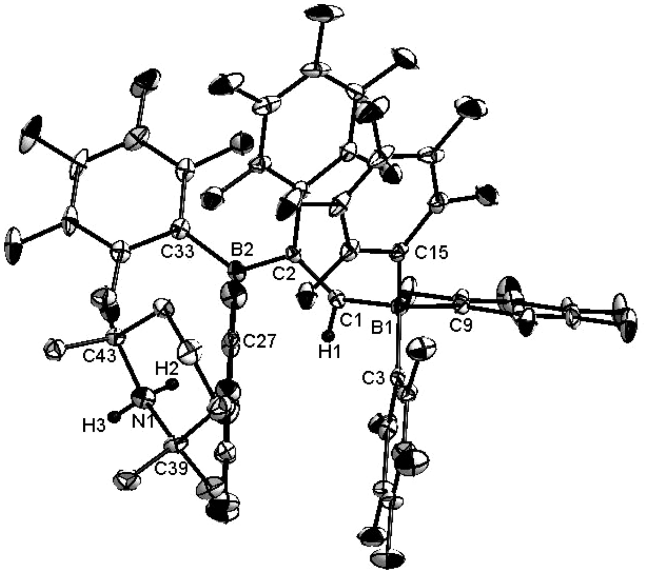


Figure 1. Molecular structure of **1-*E*** with 30% probability thermal ellipsoids. Hydrogen atoms, except for H_N and the H_{C1}, are omitted for clarity. Selected bond lengths (Å): C1−H1 = 0.958(17), N1−H3 = 0.90(2), N1−H2 = 0.93(2), N1−C39 = 1.537(3), N1−C43 = 1.540(3), B1−C1 = 1.634(3), B1−C3 = 1.674(3), B1−C9 = 1.648(3), B1−C15 = 1.650(3), B2−C2 = 1.532(3), B2−C27 = 1.589(3), B2−C33 = 1.577(3), C1−C2 = 1.363(3). Selected bond angles (deg): C39−N1−C43 = 121.27(15), C39−N1−H2 = 107.7(14), C43−N1−H2 = 103.5(13), C39−N1−H3 = 110.2(13), C43−N1−H3 = 107.6(14), H2−N1−H3 = 105.2(18), C1−B1−C9 = 109.92(15), C1−B1−C15 = 108.24(16), C9−B1−C15 = 114.67(16), C1−B1−C3 = 106.86(15), C9−B1−C3 = 104.96(15), C15−B1−C3 = 111.91(15), C2−B2−C33 = 127.65(17), C2−B2−C27 = 119.33(17), C33−B2−C27 = 113.00(16).

$B(C_6F_5)_3$ adduct, which thus gets polarized with an increase in the acidity of the acetylenic hydrogens. In the presence of **TMP** the acidic C−H bond of the terminal alkyne was deprotonated to form the σ-acetylide adduct $[B(C_6F_5)_3C{\equiv}CH]^-$. This anion behaves as a nucleophile at the β-position, adding $B(C_6F_5)_3$ to afford the vinylidene adduct $(C_6F_5)_3B^-C^+{=}C(H)B(C_6F_5)_3$. This zwitterionic species possesses a strongly electrophilic α-carbon center, triggering (similar to a Wagner−Meerwein rearrangement) a 1,2-shift of a perfluorophenyl group to the more stable **1-*E*** product. This perfluorophenyl group migration could also be found in the reaction of $B(C_6F_5)_3$ with phenylacetylene (vide infra, Scheme 5).

The related reactions of the FLPs t-$Bu_3P\cdots B(C_6F_5)_3$ and **Lut**$\cdots B(C_6F_5)_3$ with acetylene were also investigated. Similar to the reaction to **1-*E***, after dried HC≡CH was introduced into the toluene solution of the t-$Bu_3P\cdots B(C_6F_5)_3$ FLP an oil separated at the bottom of the Young NMR tube after 30 min. The isolated off-white product was characterized as a mixture containing about 90% of (*E*)-t-$Bu_3PC(H){=}C(H)B(C_6F_5)_3$ (**2-*E***) and about 10% of $[t\text{-}Bu_3PH][(E)\text{-}(C_6F_5)_2BC(C_6F_5){=}C(H)B(C_6F_5)_3]$ (**3-*E***). The ^{1}H and ^{31}P NMR of **3-*E*** exhibit typical resonances for its cation, and the ^{19}F and ^{11}B NMR spectra are similar to those resonances seen for the $[B(C_6F_5)_2C(C_6F_5){=}C(H)B(C_6F_5)_3]^-$ anion of **1-*E***. In the ^{1}H NMR spectrum **2-*E*** features two triplet resonances at 8.24 ppm (t, J = 21 Hz) and 5.60 ppm (t, J = 21 Hz) for H_a and H_b (Scheme 2). The triplet splitting pattern is anticipated to be caused by similar H−H and H−P coupling constants (Figure 2). The ^{31}P NMR signal for **2-*E*** was found at 36.31 ppm and the ^{11}B NMR resonance at −14.25 ppm. The ^{19}F NMR spectrum of **2-*E*** showed signals at δ −132.82 (o-C_6F_5), −162.33 (p-C_6F_5), and −166.85 ppm (m-C_6F_5) originating from the four-coordinate boron atom. A single-crystal X-ray analysis confirms the formulation of **2-*E*** as (*E*)-t-$Bu_3PC(H){=}C(H)$-$B(C_6F_5)_3$ (Figure 3).[34] The distances of C1−C2 (1.333(3) Å) and C1−B (1.612(3) Å) are quite comparable to those in **1-*E***. The C2−P bond length was found to be 1.787(2) Å, which is unexceptionally long.

It should be pointed out that **TMP** and t-Bu_3P exhibit similar basicities (pK_a for t-Bu_3P is 11.4 and for **TMP** is 11.07),[35−37] so that the difference of the reaction paths of FLPs **TMP**$\cdots B(C_6F_5)_3$ and t-$Bu_3P\cdots B(C_6F_5)_3$ with acetylene are thought to originate from the difference in sterics of these Lewis bases. Enhanced steric congestion leads preferentially to deprotonation; less steric hindrance provokes 1,2-addition to the acetylenic moiety. In the case of compounds **2** and **3** there is apparently competition between deprotonation and 1,2-addition. However, t-Bu_3P may not be big enough to prevent attacking one carbon atom of acetylene; thus, the majority is 1,2-addition product, with only a small amount of C_{sp}−H deprotonated product in the mixture.

The reaction of lutidine (**Lut**) and $B(C_6F_5)_3$ leads first of all to a classical Lewis acid−base adduct, which was however found to display FLP behavior in the activation of H_2.[23] In toluene solution an equilibrium is established; in the ^{1}H NMR spectra at room temperature both the Lewis adduct and the free Lewis acid and base are observed. When the reaction mixture was purged with acetylene at 80 °C for 20 h, only the 1,2-addition product **Lut**$C(H){=}C(H)B(C_6F_5)_3$ (**4-*E***) could be isolated, which like **2-*E*** could be envisaged to form by nucleophilic addition of **Lut** to a weak σ or π $B(C_6F_5)_3$/acetylene adduct. **4-*E*** was isolated in 34% yield. **4-*E*** features ^{1}H NMR resonances at 6.66 (d, J = 15 Hz) and 6.18 ppm (d, J = 15 Hz) for H_a and H_b (Scheme 2). The ^{19}F NMR signals are located at δ −133.11 (o-C_6F_5), −163.75 (p-C_6F_5), and −168.00 ppm (m-C_6F_5) and are quite similar to those found for compound **4-*E***. This observation would support the view that the less sterically hindered Lewis bases favor the formation of 1,2-addition products in reactions of their FLPs with acetylene.

The reaction of phenylacetylene (PhC≡CH) or 3-ethynylthiophene ($SC_4H_3C{\equiv}CH$) with the **TMP**$\cdots B(C_6F_5)_3$ or t-$Bu_3P\cdots B(C_6F_5)_3$ FLPs proceeded exclusively along the deprotonation pathway, forming the respective salts [**TMP**H]-$[PhC{\equiv}CB(C_6F_5)_3]$ (**5**), [**TMP**H]$[SC_4H_3C{\equiv}CB(C_6F_5)_3]$ (**6**), $[t\text{-}Bu_3PH][PhC{\equiv}CB(C_6F_5)_3]$ (**7**), and $[t\text{-}Bu_3PH][SC_4H_3C{\equiv}CB(C_6F_5)_3]$ (**8**) (see Scheme 3).

(34) Crystal data for **2-*E***: $C_{39}H_{37}BF_{15}P$, M_r = 832.47, monoclinic, $P2_1/c$, a = 12.3469(2) Å, b = 18.0538(2) Å, c = 17.8463(2) Å, β = 104.935(2)°, V = 3843.71(9) Å^3, Z = 4, D_c = 1.439 g cm^{-3}, μ = 0.173 mm^{-1}, λ = 0.710 73 Å, T = 183(2) K, 33 277 reflections collected, 7864 independent (R_{int} = 0.026) and 5618 observed reflections ($I > 2\sigma(I)$), 523 refined parameters, R1 = 0.050, wR2 = 0.134. CCDC 748014.

(35) Streuli, C. A. *Anal. Chem.* **1960**, *32*, 985.

(36) Bush, R. C.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 681.

(37) Graton, J.; Berthelot, M.; Laurence, C. *J. Chem. Soc., Perkin Trans.* **2001**, 2130.

(38) Crystal data for **5**: $C_{35}H_{25}BF_{15}N$, M_r = 755.37, triclinic, $P\bar{1}$, a = 10.2056(11) Å, b = 12.2576(8) Å, c = 14.6323(8) Å, α = 70.676(3)°, β = 87.904(3)°, γ = 68.808(4)°, V = 1603.3(2) Å^3, Z = 2, D_c = 1.565 g cm^{-3}, μ = 0.152 mm^{-1}, λ = 0.710 73 Å, T = 183(2) K, 20 184 reflections collected, 7943 independent (R_{int} = 0.0320) and 5663 observed reflections ($I > 2\sigma(I)$), 481 refined parameters, R1 = 0.0388, wR2 = 0.0904. CCDC 748015.

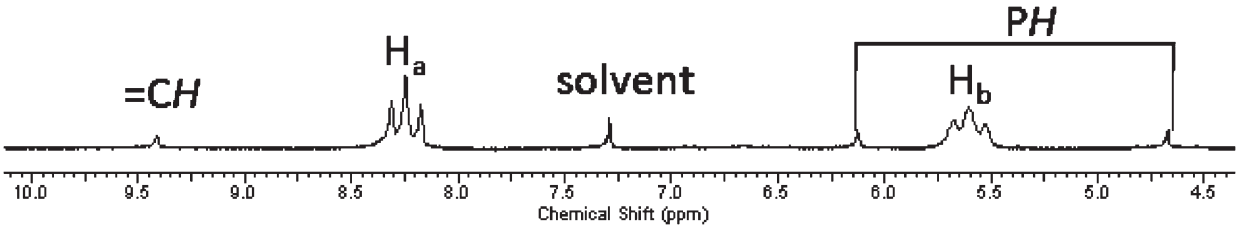
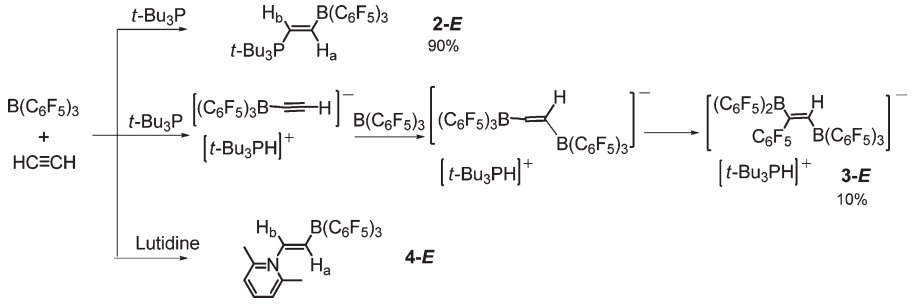


Figure 2. ^{1}H NMR spectrum of the mixture of **2-*E*** and **3-*E*** in $CDCl_3$.

Scheme 2



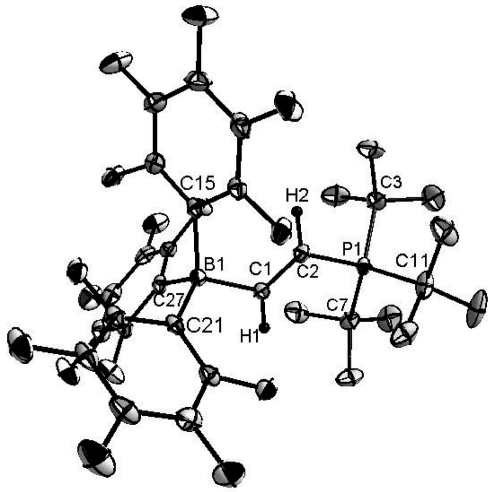
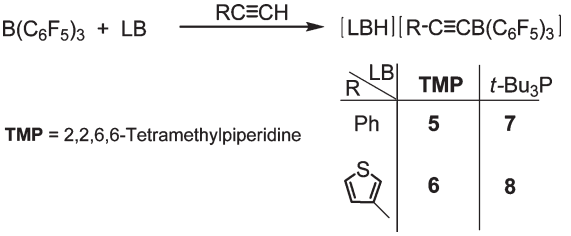


Figure 3. Molecular structure of **2-*E*** with 30% probability thermal ellipsoids. Hydrogen atoms, except for H_{C1} and H_{C2}, are omitted for clarity. Selected bond lengths (Å): C1−C2 = 1.333(3), C1−B1 = 1.612(3), C1−H1 = 0.90(2), C2−P1 = 1.787(2), C2−H2 = 1.01(3), C3−P1 = 1.887(3), C7−P1 = 1.888(2), C11−P1 = 1.887(2), C15−B1 = 1.659(3), C21−B1 = 1.654(3), C27−B1 = 1.656(3). Selected bond angles (deg): C2−P1−C11 = 105.77(10), C2−P1−C3 = 104.61(11), C11−P1−C3 = 112.35(13), C2−P1−C7 = 109.97(11), C11−P1−C7 = 112.23(11), C3−P1−C7 = 111.45(12), C1−B1−C21 = 113.90(17), C1−B1−C27 = 100.92(16), C21−B1−C27 = 112.81(17), C1−B1−C15 = 110.86(17), C21−B1−C15 = 105.02(16), C27−B1−C15 = 113.61(17).

In the ^{1}H NMR spectra of **5** and **6** broad H_N resonances appear at δ 4.04 and 4.13 ppm, evidencing the presence of ammonium cations. The ^{19}F and ^{11}B NMR spectra are quite similar for **5** (^{19}F NMR δ −133.89, −164.13, −168.20 ppm; ^{11}B NMR δ −18.57 ppm) and **6** (^{19}F NMR δ −133.92, −164.15, −168.21; ^{11}B NMR δ −18.53 ppm), pointing to the structural similarities of these compounds. Compounds **7** and **8** exhibit the same ^{19}F and ^{11}B NMR resonances as those

Scheme 3



R \ LB	TMP	*t*-Bu$_3$P
Ph	5	7
	6	8

in **5** and **6**. Also, the cations of **7** and **8** show the typical resonances in the ^{1}H and ^{31}P NMR spectra. The X-ray structural analysis of **5** shows that the boron atom adopts a pseudotetrahedral geometry with a B−C(sp) bond distance of 1.5934(19) Å, much shorter than the other three B−C(sp^2) bond distances (B1−C9 = 1.653(2); B1−C15 = 1.644(2); B1−C21 = 1.6676(19) Å) (Figure 4).[38] The ions are connected through a weak N−H···F hydrogen bond; the separation between H1 and F15 is 2.21 Å. A crystallographic study of **6** (Figure 5) revealed a structure related to **5** with the counterions also connected through weak N−H···F hydrogen bonding of H1−F11 at a distance of 2.22 Å.[39] The B−C(sp) and N−H bond lengths of 1.5969 (17) and 0.864 Å are comparable to those in **5**.

We suppose that at higher temperatures the **Lut**−$B(C_6F_5)_3$ adduct dissociates with formation of a **Lut**···$B(C_6F_5)_3$ FLP in concentrations sufficient for subsequent reactivity. Indeed, phenylacetylene (PhC≡CH) and 3-ethynylthiophene (SC_4H_3C≡CH) were sought to be transformed in the presence of **Lut** and $B(C_6F_5)_3$. We reckoned that the lower basicity of **Lut** in comparison with **TMP** or *t*-Bu_3P would cause the deprotonation pathway to be less preferred and

(39) Crystal data for **6**: $C_{33}H_{23}BF_{15}NS$, M_r = 761.40, triclinic, $P\bar{1}$, a = 11.0873(2) Å, b = 12.1753(2) Å, c = 12.7089(2) Å, α = 100.776(2)°, β = 101.541(2)°, γ = 103.953(2)°, V = 1580.61(5) Å^3, Z = 2, D_c = 1.600 g cm^{-3}, μ = 0.218 mm^{-1}, λ = 0.710 73 Å, T = 183(2) K, 39 687 reflections collected, 9654 independent (R_{int} = 0.0241) and 7111 observed reflections ($I > 2\sigma(I)$), 473 refined parameters, R1 = 0.0401, wR2 = 0.1114. CCDC 748016.

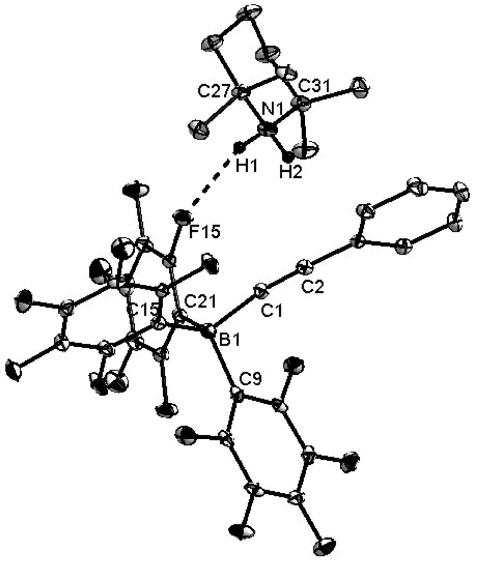


Figure 4. Molecular structure of **5** with 30% probability thermal ellipsoids. Hydrogen atoms, except for the H_N atom, are omitted for clarity. Selected bond lengths (Å): N1−H1 = 0.881(16), N1−H2 = 0.914(17), N1−C27 = 1.5387(17), N1−C31 = 1.5371(18), B1−C9 = 1.653(2), B1−C15 = 1.644(2), B1−C21 = 1.6676(19), B1−C1 = 1.5934(19). Selected bond angles (deg): H1−N1−H2 = 103.5(14), H1−N1−C27 = 105.6(10), H1−N1−C31 = 106.1(10), H2−N1−C27 = 108.5(10), H2−N1−C31 = 110.2(10), C31−N1−C27 = 121.37(10), C1−B−C15 = 112.78(10), C1−B1−C9 = 102.93(11), C15−B1−C9 = 114.36(11), C1−B1−C21 = 109.37(11), C15−B1−C21 = 106.67(10), C9−B1−C21 = 110.71(10).

that **Lut** would mainly react as a Lewis base. The reaction between $SC_4H_3C{\equiv}CH$ proceeded sluggishly, producing [**LutH**][$PhC{\equiv}CB(C_6F_5)_3$] (**9**) (47%) and **Lut**$C(SC_4H_3C){=}C(H)B(C_6F_5)_3$ (**10**; 55%) (Scheme 4). The ^{1}H NMR spectrum of **9** showed a broad signal attributable to the H_N nucleus at 12.30 ppm. The ^{19}F and ^{11}B NMR spectrum of **9** were found to be quite similar to those of **5** or **6**. The ^{1}H NMR signal for the vinyl proton of **10** is located at 6.74 ppm. One set of ^{19}F NMR signals for the aryl substituents (δ −132.84, −163.72, −168.08 ppm) and one ^{11}B NMR signal (δ −16.39 ppm) are in agreement with a four-coordinate boron.

IIb. Reactions of Phenylacetylene (PhC≡CH) and 3-Ethynylthiophene ($SC_4H_3C{\equiv}CH$) with $B(C_6F_5)_3$. Further studies were carried out in the absence of a Lewis base, which caused another reaction pathway to become prevalent. A 1:1 mixture of $B(C_6F_5)_3$ and PhC≡CH turned deep red in toluene solution, and according to the ^{1}H and ^{19}F NMR spectra two products were identified as the isomers (*Z*)- and (*E*)-$PhC(H){=}C(C_6F_5)B(C_6F_5)_2$ (**11-*Z*** and **11-*E***; near 1:1 in ratio) (Scheme 5). The ^{1}H NMR spectra exhibited resonances at 7.73 and 7.59 ppm, respectively. The ^{19}F NMR spectra revealed several sets of signals attributable to both a carbon-bound $-C_6F_5$ unit (**11-*E*** −144.43, −156.19, −162.59 ppm; **11-*Z*** −140.78, −156.61, −162.59 ppm) and two boron-bound $-C_6F_5$ units (**11-*E*** −130.63, −147.35, −163.79 ppm; **11-*Z*** −131.88, −148.46, −163.79 ppm). It is reasonable to assume that an acetylene/vinylidene rearrangement had taken place and that related to a Wagner−Meerwein rearrangement[40,41] the highly electrophilic α-carbon center of the

(40) Hanson, J. R. *Comp. Org. Syn.* **1991**, *3*, 705.
(41) Olah, G. A. *Accts.Chem. Res.* **1976**, *9*, 41.

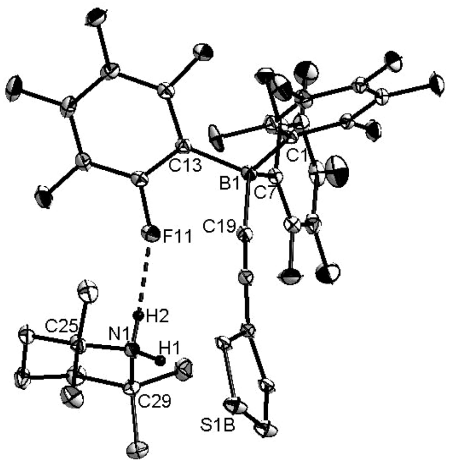
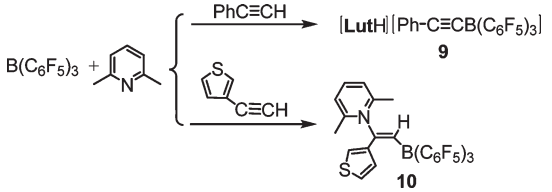
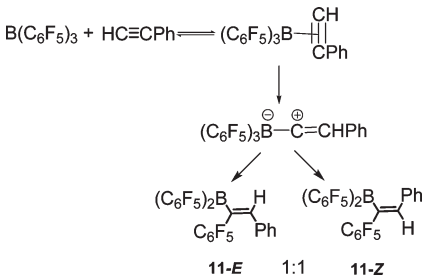


Figure 5. Molecular structure of **6** with 30% probability thermal ellipsoids. Hydrogen atoms, except for the H_N atom, are omitted for clarity. Selected bond lengths (Å): N1−H1 = 0.874(16), N1−H2 = 0.852(17), N1−C25 = 1.5398(16), N1−C29 = 1.5394(15), B1−C1 = 1.6479(18), B1−C7 = 1.6440(18), B1−C13 = 1.6609(17), B1−C19 = 1.5969(17). Selected bond angles (deg): H1−N1−H2 = 108.9(14), H1−N1−C29 = 108.1(9), H1−N1−C25 = 107.2(10), H2−N1−C29 = 107.0(11), H2−N1−C25 = 104.4(11), C29−N1−C25 = 120.84(9), C1−B1−C7 = 112.76(9), C1−B1−C13 = 113.41(9), C19−B1−C7 = 113.22(10), C1−B1−C19 = 102.86(9), C19−B1−C13 = 109.23(9), C7−B1−C13 = 105.53(9).

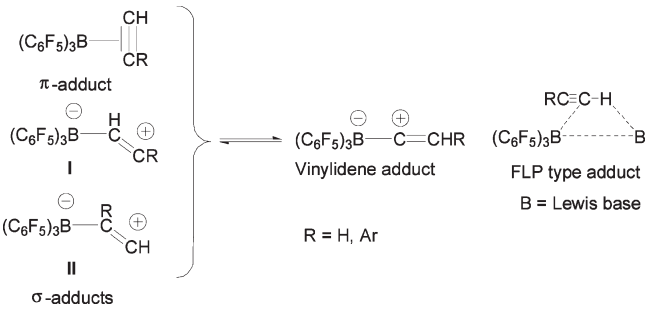
Scheme 4



Scheme 5



Scheme 6



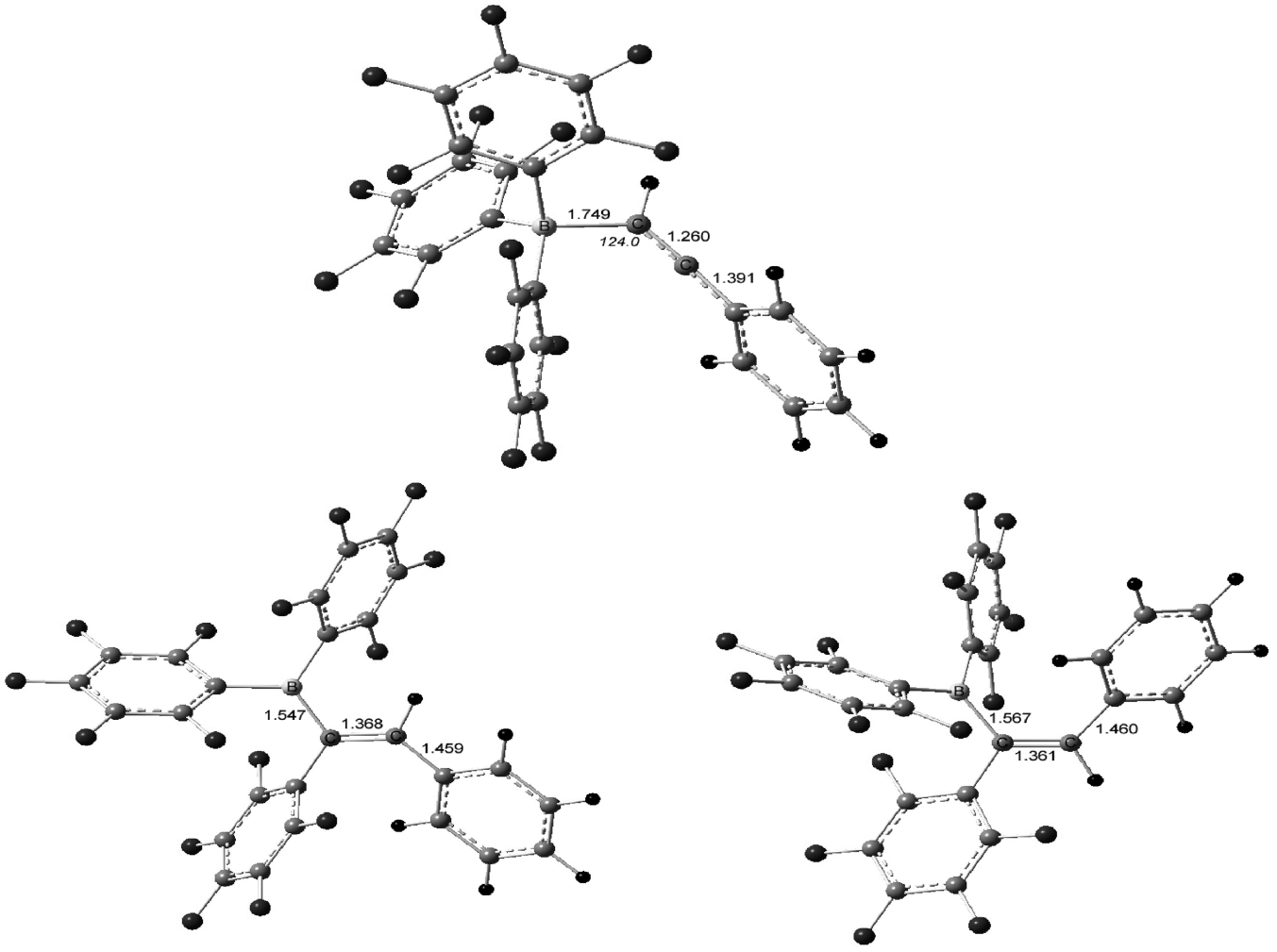


Figure 6. Optimized geometries and selected bond distances (Å) and angles (deg) of **11-*E*** (bottom left), **11-*Z*** (bottom right), and a possible σ-type intermediate (top) during the reaction of $B(C_6F_5)_3$ with phenylacetylene, calculated at the B3PW91/6-31+g(d) level.

formed vinylidene intermediate $[(C_6F_5)_3B^-C^+{=}C(H)Ph]$ became saturated by a boron to carbon C_6F_5-1,2-shift. The reaction between $B(C_6F_5)_3$ and PhC≡CH was very fast, which made it impossible to trace intermediates.[42,43] Furthermore, the *Z* and *E* isomers of $PhC(H){=}C(C_6F_5)$-$B(C_6F_5)_2$ were found to be inert toward bulky Lewis bases so that products other than **11-*E*** and **11-*Z*** could not be found.

Unlike the reaction between $B(C_6F_5)_3$ and PhC≡CH, the reaction of a 1:1 mixture of $SC_4H_3C{\equiv}CH$ and $B(C_6F_5)_3$ could not be driven to completion and most of the $B(C_6F_5)_3$ Lewis acid remained unreacted, even after prolonged reaction times at room temperatures. Only a trace amount of $SC_4H_3CH{=}C^+B^-(C_6F_5)_3$ was formed, exhibiting a set of ^{19}F NMR signals at δ −129.79, −160.68, and −165.67 ppm. On the basis of a signal at 8.07 ppm in the ^1H NMR spectrum a $S\cdots H$ hydrogen-bonding contact seemed to be present. Presumably the $S_{thiophene}$ atom acts as a Lewis base and prevents proper contact between the Lewis acid and the acetylenic π-bond of the $SC_4H_3C{\equiv}CH$ molecule. The very low concentration of this complex seemed sufficient, however, for a deprotonation with strong Lewis base or for 1,2-addition with weak Lewis base so that compounds **6**, **8**, and **10** could be formed.

IIc. DFT Calculations. It became evident from Schemes 1−5 that the activation of acetylenes by $B(C_6F_5)_3$ could be envisaged by primary weak interactions of both reaction partners, which could be established in the form of a σ or a π complex (Scheme 6). In the additional presence of a base (Lewis base) we could envisage stepwise activation with initial formation of the σ or π adducts and their subsequent deprotonation. Alternatively, bifunctional activation through a four-centered FLP type arrangement could occur, transferring the acetylide unit to the Lewis acid $B(C_6F_5)_3$ and the proton to the base (Lewis base) in a more or less concerted fashion (Scheme 6).

The acetylene/vinylidene rearrangement is anticipated to be base-mediated, proceeding with a deprotonation/protonation sequence, or could simply operate on the basis of a proton shift, preferably via a σ adduct.

The calculations revealed no stabilized form of interaction with acetylene of the kinds sketched in Scheme 6, since no prominent local minima were found on the energy hypersurface during the optimization process. This might be due to deficiencies to the DFT calculational procedures not representing well polar structures with considerable charge separation of the σ or π type. For the interaction of $B(C_6F_5)_3$ with phenylacetylene, however, a local minimum could be

(42) Dierker, G.; Ugolotti, J.; Kehr, G.; Fröhlich, R.; Erker, G. *Adv. Synth. Catal.* **2009**, *351*, 1080.
(43) (a) Wrackmeyer, B. *Coord. Chem. Rew.* **1995**, *145*, 125. (b) Venkatesan, K.; Blacque, O.; Fox, T.; Alfonso, M.; Schmalle, H. W.; Berke, H. *Organometallics* **2004**, *23*, 1183. (c) Selegue, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 5921.

localized for the σ adduct **I** (Figure 6). The formation of this σ-type adduct is slightly endothermic (7.1 kcal/mol) with respect to the starting materials. Its potential energy would still be in a range to be easily reached by thermal activation. The isomeric σ adduct **II** was calculated to be unstable, and it was not possible to find a local minimum for it.

In both cases of R = H, Ph the DFT optimization processes to establish vinylidene adducts did not converge to a definite local minimum structure, but still we have to assume its transient existence, since it would ascribe the only topological alternative to eventually reach **11-*E*** and **11-*Z*** with a consecutive 1,2-C_6F_5 shift. **11-*E*** and **11-*Z*** were calculated to possess high thermodynamic driving forces in their formations (−42.5 vs −41.1 kcal/mol, respectively) with respect to the energetic level of free $B(C_6F_5)_3$ and acetylene. The slight energetic preference for **11-*E*** agrees with the observation that this isomer is prevailing under experimental circumstances.

III. Conclusion

In summary, we have applied the frustrated Lewis pairs LB···LA (**TMP**···$B(C_6F_5)_3$ *t*-Bu_3P···$B(C_6F_5)_3$, and **Lut**-$B(C_6F_5)_3$) for the activation of terminal alkynes, which furnished two different initial pathways: (a) a deprotonation pathway and (b) a 1,2-addition pathway.

The deprotonation pathway (a) proceeded with deprotonation of any of the initial $(C_6F_5)_3B(\sigma\text{-},\pi\text{-HC}{\equiv}\text{CR})$ complexes with the Lewis base acting as a base or with "bifunctional" heterolysis of the ≡C−H bond (Scheme 6). This bifunctional heterolysis would involve a four-centered transition state of the ≡C−H bond and the FLP encounter complex. For any of these mechanistic alternatives the primary products are the $[B(C_6F_5)_3C{\equiv}CR][LBH]$ ion pairs (R = H, Ar). However, neither the experimental nor the theoretical studies provided definite clues on the type of intermediate appearing in the reactions of Schemes 1−5.

Along pathway (b) the Lewis pairs could be envisaged to undergo 1,2-additions to the alkynes to generate LBC(R)=C(H)$B(C_6F_5)_3$ structures. Initially, we anticipate for this case again a primary interaction of the Lewis acid $B(C_6F_5)_3$ with the acetylenes via σ and π complexes (Scheme 6). The final step of nucleophilic addition of the LB should naturally depend on the nucleophilic character of the base, as seen for *t*-Bu_3P and **LUT**. The regioselectivity of **LUT** addition to the higher substituted end of the $B(C_6F_5)_3$ adduct with $SC_4H_3C{\equiv}CH$ points to the involvement of the σ complex of type **I** or of the π complex (Scheme 6).

Boron to carbon C_6F_5-1,2-migrations were also seen to be an important feature of this chemistry. They appeared as follow-up reactions of initially formed $[B(C_6F_5)_3C{\equiv}CH]^-$ anions of **1-*E*** and **3-*E***, which then underwent $B(C_6F_5)_3$ addition. Subsequently this anion was transformed via C_6F_5 migration to an (*E*)-$[(C_6F_5)_2BC(C_6F_5){=}C(H)\text{-}B(C_6F_5)_3]^-$ product. The reaction of phenylacetylene with $B(C_6F_5)_3$ could be viewed as a related 1,2-carboboration case[42] where the electrophilic carbon of the initially formed $(C_6F_5)_3B^-C^+{=}C(H)R$ vinylidene species became saturated by the same migrational step to yield (*E*)- and (*Z*)-RC(H)=$C(C_6F_5)B(C_6F_5)_2$ compounds.[43]

IV. Experimental Section

IVa. General Considerations. All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques or in a glovebox (M. Braun 150B-G-II) filled with dry nitrogen. Solvents were freshly distilled under N_2 by employing standard procedures and were degassed by freeze−thaw cycles prior to use. $B(C_6F_5)_3$ was synthesized according to the literature.[44] All other organic reagents were purchased from Aldrich and used without further purification. ^{1}H NMR, ^{19}F NMR, $^{31}P\{^1H\}$ NMR, and $^{11}B\{^1H\}$ NMR data were recorded on a Varian Gemini-200 or 300 spectrometer. Chemical shifts are expressed in parts per million (ppm) referenced to deuterated solvent used. ^{19}F, ^{11}B, and ^{31}P NMR were referenced to $CFCl_3$, $BF_3{\cdot}OEt_2$, and 85% H_3PO_4, respectively. Microanalyses were carried out at Anorganisch-Chemisches Institut of the University of Zürich.

Crystallographic data were collected at 183(2) K on an Oxford Xcalibur diffractometer (four-circle κ platform, Ruby CCD detector, and a single-wavelength Enhance X-ray source with Mo Kα radiation, λ = 0.710 73 Å).[45] The selected suitable single crystals were mounted using polybutene oil on the top of a glass fiber fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, face-indexing analytical absorption correction,[46] and data reduction were performed with the Oxford program suite *CrysAlisPro*.[47] The structures were solved with direct methods and were refined by full-matrix least-squares methods on F^2 with SHELXL-97.[48] All programs used during the crystal structure determination process are included in the WINGX software.[49] The program PLATON[50] was used to check the results of the X-ray studies and to analyze the hydrogen-bonding systems.

Calculations were carried out at the DFT level of theory with the Gaussian03 program package[51] using the hybrid functional B3PW91[52,53] and the standard Pople 6-31G+(d) basis set.[54] Geometry optimizations were carried out without any symmetry restrictions, and the nature of the optimized minima was evaluated by computations of harmonic vibrational frequencies at the same theory level. The relative energies were calculated by correcting the B3LYP/6-31+G(d) total energies for zero-point vibrational energies (ZPE).

IVb. [TMPH][$(C_6F_5)_2BC(C_6F_5){=}C(H)B(C_6F_5)_3$] (1-*E*). In a Young NMR tube, $B(C_6F_5)_3$ (0.0768 g, 0.15 mmol) and 2,2,6,6-tetramethylpiperidine (**TMP**; 0.0212 g, 0.15 mmol) were dissolved in 1 mL of toluene. Dried HC≡CH (1000 mbar, ca. 0.15

(44) Lancaster, S. *SyntheticPage* **2003**, 215.
(45) *Xcalibur CCD System*; Oxford Diffraction Ltd, Abingdon, Oxfordshire, England, 2007.
(46) Clark, R. C.; Reid, J. S. *Acta Crystallogr.* **1995**, *A51*, 887–897.
(47) *CrysAlisPro* (Versions 1.171.32/33), Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
(48) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.
(49) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.
(50) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7–13.
(51) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision C.01*; Gaussian, Inc., Wallingford, CT, 2004.
(52) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(53) Burke, K., Perdew, J. P. Yang, W. *Electronic Density Functional Theory: Recent Progress and New Directions*; Dobson, J. F., Vignale, G., Das, M. P., Eds.; Plenum: New York, 1998.
(54) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

mmol) was then filled into the NMR tube and shaken. A brown oil formed at the bottom of the NMR tube 30 min later at room temperature. Hexane was then added to the oil to induce precipitation. The mixture was filtered, washed with hexane, and dried in vacuo. The product was collected as an off-white solid. Yield: 56%. Crystals were obtained from a mixture of benzene and hexane at 25 °C. Anal. Calcd for $C_{47}H_{21}B_2F_{30}N$: C, 47.39; H, 1.78; N, 1.18. Found: C, 47.20; H, 1.53; N, 1.43. ^{1}H NMR ($CDCl_3$, 300 MHz, 293 K): δ 1.49 (s, 12H, $-CH_3$), 1.82 (m, 4H, CH_2), 1.89 (m, 2H, CH_2), 5.32 (br, 2H, NH_2), 9.36 ppm (s, 1H, C*H*). ^{11}B{^{1}H} NMR ($CDCl_3$, 96 MHz, 293 K): δ −15.19 ppm (s). ^{19}F NMR ($CDCl_3$, 282 MHz, 293 K): δ −131.69 (d, 6F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), −132.14 (d, 4F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), −140.60 (d, 2F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), −151.65 (t, 2F, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5), −159.18 (t, 1F, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5), −162.31 (t, 3F, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5), −162.76 (t, 4F, $^3J_{FF}$ = 23 Hz, *m*-C_6F_5), −165.08 (t, 2F, $^3J_{FF}$ = 23 Hz, *m*-C_6F_5), −167.05 ppm (t, 6F, $^3J_{FF}$ = 23 Hz, *m*-C_6F_5). The solubility of **1** was too low to permit C_6F_5 resonances of low intensity to be observed in the ^{13}C NMR spectrum.

IVc. *t*-$Bu_3PC(H)$=$C(H)B(C_6F_5)_3$ (2-*E*) and [*t*-Bu_3PH][-(C_6F_5)$_2$BC(C_6F_5)=C(H)B(C_6F_5)$_3$] (3-*E*). In a Young NMR tube, $B(C_6F_5)_3$ (0.0768 g, 0.15 mmol) and tri-*tert*-butylphosphine (0.03 g, 0.15 mmol) were dissolved in 1 mL of toluene. Dried HC≡CH (1000 mbar, ca. 0.15 mmol) was then filled into the NMR tube and shaken. A brown oil formed at the bottom of the NMR tube 30 min later at room temperature. Hexane was then added to the oil to induce precipitation. The mixture was filtered, washed with hexane, and dried in vacuo. The product was collected as an off-white solid which contained about 90% of **2-*E*** and 10% of **3-*E***. Yield: 56%. Crystals of **2-*E*** were obtained from a mixture of toluene and hexane at 25 °C. Data for **2-*E*** are as follows. ^{1}H NMR ($CDCl_3$, 300 MHz, 293 K): δ 1.55 (d, 27H, $^3J_{H-P}$ = 12 Hz, P{C(CH_3)$_3$}$_3$), 5.60 (t, overlap, *J* = 21 Hz, =C*H*), 8.24 ppm (t, overlap, *J* = 21 Hz, =C*H*). ^{11}B{^{1}H} NMR ($CDCl_3$, 96 MHz, 293 K): δ −14.25 ppm (s). ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz, 293 K): δ 36.31 ppm (s). ^{19}F NMR ($CDCl_3$, 282 MHz, 293 K): δ −132.82 (d, 6F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), −162.33 (t, 3F, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5), −166.85 ppm (t, 6F, $^3J_{FF}$ = 20 Hz, *m*-C_6F_5). ^{13}C{^{1}H} NMR ($CDCl_3$, 282 MHz, 293 K): δ 147.91 (dm, $^1J_{C-F}$ = 238 Hz, *o*-C_6F_5), 138.62 (dm, $^1J_{C-F}$ = 230 Hz, *p*-C_6F_5), 136.51 (dm, $^1J_{C-F}$ = 238 Hz, *m*-C_6F_5), 101.85, 101.08 (=*C*H), 39.62 (d, $^1J_{C-P}$ = 32 Hz, P{*C*-(CH_3)$_3$}$_3$), 30.02 ppm (s, P{C(*C*H_3)$_3$}$_3$). Data for **3-*E*** are as follows. ^{1}H NMR ($CDCl_3$, 300 MHz, 293 K): δ 1.67 (d, 27H, $^3J_{H-P}$ = 15 Hz, P{C(CH_3)$_3$}$_3$), 5.4 (d, 1H, $^1J_{H-P}$ = 440 Hz, P*H*), 9.41 ppm (s, 1H, =C*H*). ^{11}B{^{1}H} NMR ($CDCl_3$, 96 MHz, 293 K): δ −15.14 ppm (s). ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz, 293 K): δ 58.11 ppm (s).

IVd. Lut$C(H)$=$C(H)B(C_6F_5)_3$ (4). In a Young NMR tube, $B(C_6F_5)_3$ (0.0768 g, 0.15 mmol) and Lutidine (**Lut**) (0.016 g, 0.15 mmol) were dissolved in 1 mL of toluene. Dried HC≡CH (1000 mbar, ca. 0.15 mmol) was filled into the NMR tube, and the NMR tube was kept at 80 °C for 20 h. Hexane was then added to the mixture solution to induce precipitation. The mixture was filtered, washed with hexane and ethyl ether, and dried in vacuo. The product was collected as a white solid. Yield: 34%. Anal. Calcd for $C_{27}H_{11}BF_{15}N$: C, 50.26; H, 1.72; N, 2.17. Found: C, 50.17; H, 1.68; N, 2.19. ^{1}H NMR (CD_3CN, 300 MHz, 293 K): δ 2.52 (s, 6H, $-CH_3$), 6.18 (d, 1H, $^3J_{H-H}$ = 18 Hz, =C*H*), 6.66 (d, 1H, $^3J_{H-H}$ = 18 Hz, =C*H*), 7.62 (d, 2H, $^3J_{H-H}$ = 6 Hz, *m*-C_5H_3N), 8.10 ppm (t, 1H, $^3J_{H-H}$ = 6 Hz, *p*-C_5H_3N). ^{11}B{^{1}H} NMR (CD_3CN, 96 MHz, 293 K): δ −15.88 ppm (s). ^{19}F NMR (CD_3CN, 282 MHz, 293 K): δ −133.11 (d, 6F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), −163.75 (t, 3F, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5), −168.00 ppm (t, 2F, $^3J_{FF}$ = 20 Hz, *m*-C_6F_5). ^{13}C{^{1}H} NMR (CD_3CN, 75 MHz, 293 K) (partial): 157.20, 144.89, 127.17, 21.86 ppm.

IVe. [TMPH][PhC≡$CB(C_6F_5)_3$] (5). $B(C_6F_5)_3$ (0.1024 g, 0.2 mmol), 2,2,6,6-tetramethylpiperidine (**TMP**; 0.0283 g, 0.2 mmol), and phenylacetylene (0.021 g, 0.2 mmol) were dissolved in 2 mL of toluene, and the orange solution was stirred at room temperature for 30 min. The reaction mixture was then concentrated to half of its original volume, and hexane (5 mL) was added to promote precipitation. The mixture was filtered, washed with hexane, and dried in vacuo. The product was collected as a white solid. Yield: 87%. Crystals were obtained from a mixture of toluene and hexane at 25 °C. Anal. Calcd for $C_{35}H_{25}BF_{15}N$: C, 55.65; H, 3.34; N, 1.85. Found: C, 55.54; H, 3.41; N, 1.83. ^{1}H NMR (toluene-d_8, 300 MHz, 293 K): δ 0.41 (s, 12H, $-CH_3$), 0.55 (m, 4H, CH_2), 0.59 (m, 2H, CH_2), 4.04 (br, 2H, NH_2), 6.80 (d, 2H, $^3J_{HH}$ = 1.8 Hz, Ph *H*), 6.82 (d, 1H, $^3J_{HH}$ = 2.1 Hz, Ph *H*), 7.14 ppm (m, 2H, Ph *H*). ^{11}B{^{1}H} NMR (toluene-d_8, 96 MHz, 293 K): δ −18.57 ppm (s). ^{19}F NMR (toluene-d_8, 282 MHz, 293 K): δ −133.89 (d, 6F, $^3J_{FF}$ = 25 Hz, *o*-C_6F_5), −164.13 (t, 3F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), −168.20 ppm (t, 6F, $^3J_{FF}$ = 20 Hz, *m*-C_6F_5). ^{13}C{^{1}H} NMR (toluene-d_8, 75 MHz, 293 K): δ 149.45 (dm, $^1J_{C-F}$ = 240 Hz, *o*-C_6F_5), 139.65 (dm, $^1J_{C-F}$ = 227 Hz, *p*-C_6F_5), 137.70 (dm, $^1J_{C-F}$ = 256 Hz, *m*-C_6F_5), 132.67 (*o*-Ph), 132.26 (*p*-Ph), 127.37 (*m*-Ph), 84.02 (Ph−*C*CB), 77.67 (Ph−C*C*B), 54.16 (*o*-C_5H_7N), 36.50 (*m*-C_5H_7N), 29.51 (CH_3), 16.88 ppm (*p*-C_5H_7N).

IVf. [TMPH][C_4H_3SC≡$CB(C_6F_5)_3$] (6). $B(C_6F_5)_3$ (0.1024 g, 0.2 mmol), 2,2,6,6-tetramethylpiperidine (**TMP**; 0.0283 g, 0.2 mmol), and 3-ethynylthiophene (0.022 g, 0.2 mmol) were dissolved in 2 mL of toluene, forming a deep red solution that was stirred at room temperature for 30 min. The reaction mixture was then concentrated to half of its original volume, and hexane (5 mL) was added to prompt precipitation. The mixture was filtered, washed with hexane, and dried in vacuo. The product was collected as a light brown solid. Yield: 86%. Crystals were obtained from a mixture of toluene and hexane at 25 °C. Anal. Calcd for $C_{33}H_{23}BF_{15}NS$: C, 52.06; H, 3.04; N, 1.84. Found: C, 52.21; H, 3.08; N, 1.82. ^{1}H NMR (toluene-d_8, 300 MHz, 293 K): δ 0.47 (s, 12H, CH_3), 0.64 (m, 4H, $-CH_2$), 0.71 (m, 2H, CH_2), 4.13 (br, 2H, NH_2), 6.60 (m, 1H, C_4H_3S), 6.66 (m, 1H, C_4H_3S), 6.69 ppm (dd, 1H, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, C_4H_3S). ^{11}B{^{1}H} NMR (toluene-d_8, 96 MHz, 293 K): δ −18.53 ppm (s). ^{19}F NMR (toluene-d_8, 282 MHz, 293 K): δ −133.92 (d, 6F, $^3J_{FF}$ = 25 Hz, *o*-C_6F_5), −164.15 (t, 3F, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5), −168.21 ppm (t, 6F, $^3J_{FF}$ = 20 Hz, *m*-C_6F_5). ^{13}C{^{1}H} NMR (toluene-d_8, 75 MHz, 293 K): δ 149.47 (dm, $^1J_{C-F}$ = 238 Hz, *o*-C_6F_5), 139.83 (dm, $^1J_{C-F}$ = 230 Hz, *p*-C_6F_5), 137.69 (dm, $^1J_{C-F}$ = 245 Hz, *m*-C_6F_5), 131.13 (C_4H_3S), 130.42 (C_4H_3S), 126.31 (C_4H_3S), 77.35 (*CC*B), 53.94 (*o*-C_5H_7N), 36.52 (*m*-C_5H_7N), 29.48 (CH_3), 16.91 (*p*-C_5H_7N).

IVg. [*t*-Bu_3PH][C_4H_3SC≡$CB(C_6F_5)_3$] (8). $B(C_6F_5)_3$ (0.1024 g, 0.2 mmol), tri-*tert*-butylphosphine (0.0405 g, 0.2 mmol), and 3-ethynylthiophene (0.022 g, 0.2 mmol) were dissolved in 2 mL of toluene, forming a brown solution that was stirred at room temperature for 30 min. The reaction mixture was then concentrated to half of its original volume, and hexane (5 mL) was added to prompt precipitation. The mixture was filtered, washed with hexane, and dried in vacuo. The product was collected as a light brown solid. Yield: 82%. Anal. Calcd for $C_{36}H_{31}BF_{15}PS$: C, 52.57; H, 3.80. Found: C, 52.32; H, 3.72. ^{1}H NMR (CD_3CN, 300 MHz, 293 K): δ 1.6 (d, 27H, $^3J_{H-P}$ = 15 Hz, P{C(CH_3)$_3$}$_3$), 5.36 (d, 1H, $^1J_{H-P}$ = 444 Hz, P*H*), 1H, C_4H_3S), 6.90 (dd, 1H, *J* = 6 Hz, 2 Hz, C_4H_3S), 7.25 (d, 1H, *J* = 6 Hz, C_4H_3S), 7.28 (d, 1H, *J* = 6 Hz, C_4H_3S). ^{11}B{^{1}H} NMR (CD_3CN, 96 MHz, 293 K): δ −21.11 ppm (s). ^{31}P{^{1}H} NMR (CD_3CN, 121 MHz, 293 K): δ 56.97 ppm (s). ^{19}F NMR (CD_3CN, 282 MHz, 293 K): δ −133.91 (d, 6F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), −164.49 (t, 3F, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5), −168.62 ppm (t, 6F, $^3J_{FF}$ = 20 Hz, *m*-C_6F_5). ^{13}C{^{1}H} NMR (CD_3CN, 75 MHz, 293 K; partial): δ 149.02 (dm, $^1J_{C-F}$ = 240 Hz, *o*-C_6F_5), 139.52 (dm, $^1J_{C-F}$ = 230 Hz, *p*-C_6F_5), 137.77 (dm, $^1J_{C-F}$ = 242 Hz, *m*-C_6F_5), 130.82 (C_4H_3S), 130.60 (C_4H_3S), 125.92 (C_4H_3S), 38.16 (d, $^1J_{C-P}$ = 28 Hz, P{*C*(CH_3)$_3$}$_3$), 30.07 ppm (s, P{C(*C*H_3)$_3$}$_3$).

IVh. [LutH][PhC≡CB(C_6F_5)$_3$] (9). $B(C_6F_5)_3$ (0.1024 g, 0.2 mmol), Lutidine (**Lut**; 0.021 g, 0.2 mmol), and phenylacetylene (0.021 g, 0.2 mmol) were dissolved in 2 mL of toluene, and the yellow solution was stirred at 80 °C for 8 h. The reaction mixture was then concentrated to half of its original volume, and hexane (5 mL) was added to promote precipitation. The mixture was filtered, washed with hexane, and dried in vacuo. The product was collected as a yellow solid. Yield: 37%. Anal. Calcd for $C_{33}H_{15}BF_{15}N$: C, 54.95; H, 2.10; N, 1.94. Found: C, 54.71; H, 2.08; N, 1.82. ^{1}H NMR (CD_3CN, 300 MHz, 293 K): δ 2.58 (s, 6H, $-CH_3$), 7.22 (m, 5H, Ph *H*), 7.44 (d, 2H, $^3J_{H-H}$ = 6 Hz, *m*-C_5H_3N), 8.02 (t, 1H, $^3J_{H-H}$ = 6 Hz, *p*-C_5H_3N), 12.30 ppm (br, 1H, N*H*). $^{11}B\{^1H\}$ NMR (CD_3CN, 96 MHz, 293 K): δ −20.89 ppm (s). ^{19}F NMR (CD_3CN, 282 MHz, 293 K): δ −133.93 (d, 6F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), −164.50 (t, 3F, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5), −168.63 ppm (t, 2F, $^3J_{FF}$ = 23 Hz, *m*-C_6F_5). $^{13}C\{^1H\}$ NMR (CD_3CN, 75 MHz, 293 K) (partial): 155.43, 149.41 (dm, $^1J_{C-F}$ = 246 Hz, *o*-C_6F_5), 144.21, 139.17 (dm, $^1J_{C-F}$ = 243 Hz, *p*-C_6F_5), 137.42 (dm, $^1J_{C-F}$ = 245 Hz, *m*-C_6F_5), 131.55, 129.03, 127.02, 124.33, 20.74 ppm.

IVi. [Lut(C_4H_3S)C═C(H)B(C_6F_5)$_3$] (10). $B(C_6F_5)_3$ (0.1024 g, 0.2 mmol), Lutidine (**Lut**; 0.021 g, 0.2 mmol), and 3-ethynylthiophene (0.022 g, 0.2 mmol) were dissolved in 2 mL of toluene, and the orange solution was stirred at 80 °C for 8 h. The reaction mixture was then concentrated to half of its original volume, and hexane (5 mL) was added to promote precipitation. The mixture was filtered, washed with hexane, and dried in vacuo. The product was collected as a brown solid. Yield: 45%. Anal. Calcd for $C_{31}H_{13}BF_{15}NS$: C, 51.19; H, 1.80; N, 1.93. Found: C, 51.15; H, 1.85; N, 1.98. ^{1}H NMR (CD_3CN, 300 MHz, 293 K): δ 2.59 (s, 6H, $-CH_3$), 6.74 (s, 1H, ═C*H*), 6.82 (m, 1H, C_4H_3S), 7.16 (d, 1H, *J* = 6 Hz, C_4H_3S), 7.19 (d, 1H, *J* = 6 Hz, C_4H_3S), 7.70 (d, 2H, $^3J_{H-H}$ = 6 Hz, *m*-C_5H_3N), 8.19 (t, 1H, $^3J_{H-H}$ = 6 Hz, *p*-C_5H_3N). $^{11}B\{^1H\}$ NMR (CD_3CN, 96 MHz, 293 K): δ −16.39 ppm (s). ^{19}F NMR (CD_3CN, 282 MHz, 293 K): δ −132.84 (d, 6F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), −163.72 (t, 3F, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5), −168.08 ppm (t, 2F, $^3J_{FF}$ = 23 Hz, *m*-C_6F_5). $^{13}C\{^1H\}$ NMR (CD_3CN, 75 MHz, 293 K; partial): δ 157.12, 149.25 (dm, $^1J_{C-F}$ = 240 Hz, *o*-C_6F_5), 145.39, 139.36 (dm, $^1J_{C-F}$ = 243 Hz, *p*-C_6F_5), 137.40 (dm, $^1J_{C-F}$ = 245 Hz, *m*-C_6F_5), 129.12, 128.33, 126.92, 124.33, 21.44 ppm.

IVj. (*Z*)- and (*E*)-PhC(H)═C(C_6F_5)B(C_6F_5)$_2$ (11-*Z* and 11-*E*). $B(C_6F_5)_3$ (0.0128 g, 0.025 mmol) and PhC≡CH (0.0026 g, 0.025 mmol) were dissolved in 0.5 mL of benzene-d_6 in a NMR tube, and the solution turned red. ^{1}H NMR (benzene-d_6, 300 MHz, 293 K): δ 7.73 (s, 1H, ═C*H*, 10-*Z*), 7.59 (s, 1H, ═C*H*, **11-*E***), 6.87−6.72 (m, 10H, Ph *H*, 10-***Z*** and **11-*E***). ^{19}F NMR (benzene-d_6, 282 MHz, 293 K): δ −130.63 (d, 4F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5, **11-*E*** $B(C_6F_5)_2$), −131.88 (d, 4F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5, **11-*Z*** $B(C_6F_5)_2$), −140.78 (d, 2F, $^3J_{FF}$ = 21 Hz, *o*-C_6F_5, **11-*Z*** C_6F_5), −144.43 (d, 2F, $^3J_{FF}$ = 21 Hz, *o*-C_6F_5, **11-*E*** C_6F_5), −147.35 (t, 2F, $^3J_{FF}$ = 23 Hz, *p*-C_6F_5, **11-*E*** $B(C_6F_5)_2$), −148.46 (t, 2F, $^3J_{FF}$ = 23 Hz, *p*-C_6F_5, **11-*Z*** $B(C_6F_5)_2$), −156.19 (t, 1F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5, **11-*E*** C_6F_5), −156.61 (t, 1F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5, **11-*Z*** C_6F_5), 162.59 (m, 4F, *m*-C_6F_5, **11-*Z*** and **11-*E*** C_6F_5), 163.79 (m, 8F, *m*-C_6F_5, **11-*Z*** and **11-*E*** $B(C_6F_5)_2$).

Acknowledgment. Support from the Swiss National Science Foundation and the Funds of the University of Zurich are gratefully acknowledged.

Supporting Information Available: CIF files giving details of the X-ray crystal structure analyses for **1-*E***, **2-*E***, **5**, and **6** and tables giving the energies and Cartesian coordinates of the DFT optimized molecules. This material is available free of charge via the Internet at http://pubs.acs.org.