Reaction of the Lewis Acid Tris(pentafluorophenyl)borane with a Phosphorus Ylide: Competition between Adduct Formation and Electrophilic and Nucleophilic Aromatic Substitution Pathways

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Treatment of the phosphorus ylide $Ph_3P=CH_2$ (**2a**) with $B(C_6F_5)_3$ (**1**) yields the adduct $Ph_3P^+-CH_2-B(C_6F_5)_3^-$ (**3a**), which was characterized by X-ray crystal structure analysis. The ylide $Ph_3P=CHPh$ (**2b**) reacts analogously with $B(C_6F_5)_3$ at 0 °C to form $Ph_3P^+-CHPh-B(C_6F_5)_3^-$ (**3b**), but this adduct formation is reversible. Increasing the temperature leads to the formation of $Ph_3P^+-CH_2-(p\text{-}C_6H_4)-B(C_6F_5)_3^-$ (**4**), which is formed by an electrophilic aromatic substitution reaction of the electron-deficient borane reagent at the ylidic phenyl group. Compound **4** is also cleaved upon prolonged thermolysis to eventually yield $Ph_3P^+-CHPh-(p\text{-}C_6F_4)-BF(C_6F_5)_2^-$ (**5**), which is the product of thermodynamic control in this series. Compound **5** arises from a nucleophilic aromatic substitution reaction of the nonstabilized phosphorus ylide at a $-C_6F_5$ ring of the $B(C_6F_5)_3$ reagent. Compound **5** was also characterized by an X-ray crystal structure analysis.

Introduction

Tris(pentafluorophenyl)borane (**1**) is a strong organometallic Lewis acid.[1] It was first synthesized by Stone, Massey, and Park, who described a few adducts of $B(C_6F_5)_3$.[2] Today there is a very widespread use of tris(pentafluorophenyl)borane as an activator component in homogeneous metallocene Ziegler catalyst formation. Mostly, the $B(C_6F_5)_3$ reagent is employed to abstract an alkyl carbanion equivalent from the respective dialkylmetallocene catalyst precursor to generate the catalytically active $[(R'Cp)_2M-R]^+$ cation and its corresponding $[RB(C_6F_5)_3]^-$ anion of a low nucleophilicity.[3] Also, $B(C_6F_5)_3$ has recently been used in addition reactions, e.g. to (butadiene)zirconocene, to generate very active homogeneous metallocene Ziegler catalysts of a dipolar betaine-type structure.[4] $B(C_6F_5)_3$ has been used in a few cases as a stoichiometric reagent to generate organometallic and organic compounds exhib-

iting novel structural types,[5] and it has, in a small number of cases, been employed as a Lewis acid catalyst in organic synthesis.[6] From this limited number of examples, it appeared to us that there might be synthetic potential in the use of the tris(pentafluorophenyl)borane reagent in organic and organometallic chemistry, beyond its well-established application as a Ziegler catalyst component,[3,7] that needed to be unveiled and developed. We have, therefore, begun to investigate the reaction courses followed when various types of organic or organometallic substrates were treated with this Lewis acid. An interesting cascade of competing reaction pathways was detected upon treatment of $B(C_6F_5)_3$ with simple nonstabilized phosphorus ylides. Some of the resulting products have phosphonium−borate betaine character and may, therefore, constitute interesting reagent systems themselves for future applications. The formation of such systems and their structural characterization is described here for a set of typical examples.

(1) The Lewis acidity of $B(C_6F_5)_3$ was determined NMR spectroscopically using the method introduced by R. F. Childs et al. On a relative scale (Lewis acidity BCl_3 (=1) > $SnCl_4$ (≈0.5)), $B(C_6F_5)_3$ is slightly less Lewis acidic (0.72) than BF_3 (0.77). For leading references concerning the applied method, see: Childs, R. F.; Mulholland, D. L. *Can. J. Chem.* **1982**, *60*, 801. Childs, R. F.; Mulholland, D. L. *Can. J. Chem.* **1982**, *60*, 809. Laszlo, P.; Teston, M. *J. Am. Chem. Soc.* **1990**, *112*, 8750.

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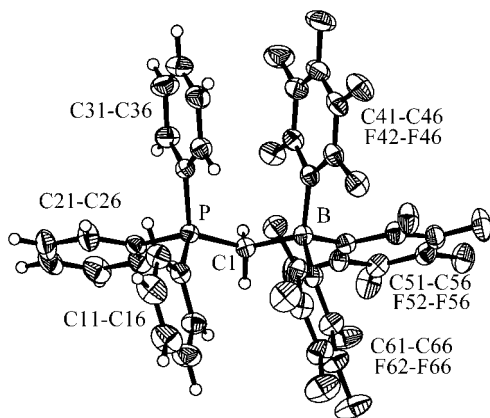
Figure 1. Molecular structure of **3a**. Selected bond lengths (Å) and angles (deg): P–C1 1.7919(14), P–C11 1.801(2), P–C21 1.810(2), P–C31 1.804(2), C1–B 1.675(2), B–C41 1.663(2), B–C51 1.664(2), B–C61 1.657(2); C1–P–C11 112.75(7), C1–P–C21 109.26(7), C1–P–C31 112.04(7), C11–P–C21 105.14(7), C11–P–C31 112.36(7), C21–P–C31 104.67(7), P–C1–B 123.38(10), C1–B–C41 111.63-(12), C1–B–C51 110.39(11), C1–B–C61 105.89(12), C41–B–C51 102.92(11), C41–B–C61 117.02(12), C51–B–C61 108.95(12).

Results and Discussion

We first reacted the ylide methylene triphenylphosphorane (**2a**) with tris(pentafluorophenyl)borane. As expected, the 1:1 addition product **3a** forms easily at room temperature in toluene solution, eq 1.[8] It was

$$B(C_6F_5)_3 \ + \ Ph_3P{=}CH_2 \ \longrightarrow \ Ph_3\overset{\oplus}{P}{-}CH_2{-}\overset{\ominus}{B}(C_6F_5)_3 \quad (1)$$
$$\mathbf{1} \qquad\qquad \mathbf{2a} \qquad\qquad\qquad\qquad \mathbf{3a}$$

isolated as an air-stable colorless solid in 89% yield. Compound **3a** shows a typical phosphonium character (^{31}P NMR δ 30.3; ^1H NMR of the [P]–CH$_2$–[B] moiety δ 3.19). The borate ^{11}B NMR resonance of **3a** appears at δ –14.9 ppm. The ^{19}F NMR of **3a** is temperature invariant and shows the *o*-, *p*-, and *m*-C$_6$F$_5$ resonances at δ –132.2, –161.8, and –166.0 ppm.

The product **3a** was characterized by X-ray diffraction. Single crystals were obtained from benzene-*d$_6$* at ambient temperature. The X-ray crystal structure analysis (see Figure 1) shows the presence of a –CH$_2$– group bridging between a tetracoordinated phosphorus and a tetracoordinated boron center. The bonding angles at these centers are all close to tetrahedral. The average bond angle at phosphorus is 109.37° and at boron 109.47°. The P–C1–B angle amounts to 123.38-(10)°. Both the P–C1 (1.7919(14) Å) and the C1–B bond (1.675(2) Å) are in the range of C(sp^3)–X single bonds. Compound **3a** is a methylene-bridged phosphonium–borate betaine.

We next treated benzylidene triphenylphosphorane (**2b**) with B(C$_6$F$_5$)$_3$. Here, the situation is more compli-

cated because the primary product (**3b**) turned out to be thermally labile.[9] However, by carefully controlling the reaction conditions (see Experimental Section), the addition product **3b** was isolated as colorless crystals. The NMR data are as expected for the phosphonium–borate betaine structure (^{31}P NMR δ 31.8 ppm; ^1H NMR of the [P]–C*H*Ph–[B] unit δ 6.32 ($^2J_{PH}$ = 25 Hz); ^{11}B NMR δ –11 ppm). Complex **3b** exhibits temperature-dependent dynamic ^{19}F NMR spectra. At ambient temperature, a set of three ^{19}F NMR signals is observed (^{19}F NMR (toluene-*d$_8$*, 298 K) –129.5, –161.4, –166.3) corresponding to the *o*-, *p*-, and *m*-fluorine substituents at the –B(C$_6$F$_5$)$_3$ moiety. Upon lowering the temperature, these signals rapidly get broad and eventually split into a single set of 15 ^{19}F NMR resonances at 223 K (for details, see Experimental Section). This behavior indicates that the C–B rotation in **3b** becomes frozen at low temperature on the NMR time scale. If the (alkyl)triarylborate unit would then exhibit a chiral propeller geometry, the complex system **3b** should form two diastereoisomers, each of which would lead to a complete differentiation of ^{19}F NMR resonances. The fact that we have only observed a single set of 15 ^{19}F NMR signals for **3b** would, in principle, be consistent with the selective generation of only one specific diastereoisomer, but we regard it as more likely that the –BAr$_3$ unit in **3b** favors a prochiral rotational conformation under the low-temperature ^{19}F NMR conditions, which is, per se, characterized by a 2:1 differentiation of the C$_6$F$_5$ ligands at boron in solution. The adjacent chiral center at carbon then makes the pair of formerly symmetry-equivalent C$_6$F$_5$ groups diastereotopic. Consequently, we observe 15 ^{19}F NMR signals of **3b** and only a single set of ^1H, ^{13}C, and ^{11}B NMR spectra.

The X-ray crystal structure analysis of **3b** (see Figure 2) again shows pseudotetrahedral coordination geometries at phosphorus (average C–P–C bonding angle 109.3°), boron (mean C–B–C angle 109.5°), and the bridging carbon atom C1 (angles P–C1–B 126.3(1)°, P–C1–C41 108.3(1)°, B–C1–C41 112.9(2)°). The P–C1 (1.841(2) Å) and B–C1 bonds (1.717(3) Å) are even longer than in the related addition compound **3a**. The three C$_6$F$_5$ groups at boron are in different environments, as expected.

The adduct formation of the ylide **2b** with B(C$_6$F$_5$)$_3$ is apparently reversible (see below). Heating the solution of **3b** in toluene results in a complete disappearance of the starting material. A mixture of two rearrangement products **4** and **5** is formed (2:1 ratio after 24 h at 55 °C). The product **4** also turned out to be thermally labile. Prolonged thermolysis led to its complete disappearance with formation of the favored rearrangement product **5**. Compound **5** is the final product obtained, eventually, from the reaction of Ph$_3$P=CHPh with B(C$_6$F$_5$)$_3$ under thermodynamic control.

(8) (a) Hawthorne, M. F. *J. Am. Chem. Soc.* **1958**, *80*, 3480. Hawthorne, M. F. *J. Am. Chem. Soc.* **1961**, *83*, 367. Seyferth, D.; Grim, S. O. *J. Am. Chem. Soc.* **1961**, *83*, 1613. Mathiason, D. R.; Miller, N. E. *Inorg. Chem.* **1968**, *7*, 709. Fluck, E.; Bayha, H.; Heckmann, G. *Z. Anorg. Allg. Chem.* **1976**, *421*, 1. Schmidbaur, H.; Müller, G.; Schubert, U. *Chem. Ber.* **1980**, *113*, 2575. See also: Bestmann, H. J.; Zimmermann, R. In Houben-Weyl. Methoden der Organischen Chemie; Regitz, M., Ed.; Thieme: Stuttgart, 1982; Vol. E 1, p 700 and references therein. (b) On the reversibility of adduct formation, see: Siebert, W. *Z. Naturforsch.* **1970**, *25b*, 314.

(9) Lability of ylide/BR$_3$ adducts due to rearrangement has been observed in a few specific cases; however, these usually involve formal transfer and insertion of the alkylidene unit into the B–C bond. See, e.g.: Köster, R.; Rickborn, B. *J. Am. Chem. Soc.* **1967**, *89*, 2782. For additional examples of reactions between phosphorus ylides and borane reagents, see, e.g.: Bestmann, H. J.; Sühs, K.; Röder, T. *Angew. Chem.* **1981**, *93*, 1098; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1038. Bestmann, H. J.; Arenz, T. *Angew. Chem.* **1984**, *96*, 363; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 381; *Angew. Chem.* **1986**, *98*, 571; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 559. See also: Köster, R. In Houben-Weyl. *Methoden der Organischen Chemie*; Thieme: Stuttgart, 1983; Vol. 13/3b, p 706–7 and references therein.
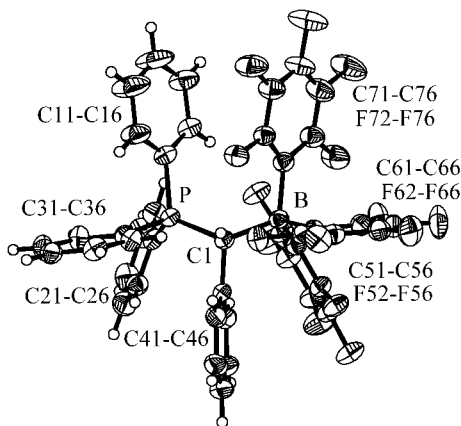
Figure 2. Molecular structure of **3b**. Selected bond lengths (Å) and angles (deg): P1−C1 1.841(2), P−C11 1.817(2), P−C21 1.812(2), P−C31 1.812(2), C1−C41 1.542(3), C1−B 1.717(3), B−C51 1.650(3), B−C61 1.674(3), B−C71 1.672(3); C1−P−C11 114.9(1), C1−P−C21 116.0(1), C1−P−C31 107.0(1), C11−P−C21 109.2(1), C11−P−C31 103.9(1), C21−P−C31 104.8(1), P−C1−B 126.3(1), P−C1−C41 108.3(1), B−C1−C41 112.9(2), C1−B−C51 106.2(2), C1−B−C61 110.7(2), C1−B−C71 115.4(2), C51−B−C61 112.2(2), C51−B−C71 114.4(2), C61−B−C71 97.8(2).

Figure 3. Molecular structure of **5**. Selected bond lengths (Å) and angles (deg): P−C1 1.841(9), P−C60 1.794(9), P−C70 1.794(10), P−C80 1.772(10), C1−C20 1.537(12), C1−C53 1.534(12), B−F 1.392(12), B−C30 1.633(15), B−C40 1.621(15), B−C50 1.659(14); C1−P−C60 110.2(4), C1−P−C70 101.7(4), C1−P−C80 114.5(4), C60−P−C70 108.8(4), C60−P−C80 110.0(5), C70−P−C80 111.3(4), P−C1−C53 118.2(6), P−C1−C20 113.1(6), C20−C1−C53 113.3(7), C1−C53−C52 119.1(8), C1−C53−C54 125.5(8), F−B−C30 106.2-(8), F−B−C40 106.6(8), F−B−C50 109.5(8), C30−B−C40 114.1(8), C30−B−C50 111.2(8), C40−B−C50 109.1(8).

The intermediate product was shown to have the structure **4** depicted in Scheme 1. It is apparently formed by attack of the electrophilic borane reagent at the electron-rich para position of the phenyl substituent at the ylide carbon atom. This leads to the formation of the product of an electrophilic aromatic substitution reaction.[10] Proton transfer from the intermediate (**6**) utilizes the ylide basicity. The resulting [P]−CH₂−Ar group is readily identified spectroscopically (^{31}P NMR δ 21.9 ppm; ^{1}H NMR δ 4.25 ($^{2}J_{PH}$ = 14.3 Hz); ^{13}C NMR δ 30.2 ($^{1}J_{PC}$ = 48 Hz)). The ^{11}B NMR resonance of **4** appears at δ −11.1 ppm.

Compound **5** is the final product of thermodynamic control. It was characterized spectroscopically and identified by X-ray crystal structure analysis. Typical NMR spectroscopic features are observed to originate from the Ph₃P−CH(Ph) unit (^{31}P NMR δ 25.9 ppm; ^{1}H NMR δ 6.28 ($^{2}J_{PH}$ = 18.9 Hz); ^{13}C NMR δ 21.5 ppm) and the −BF unit (^{11}B NMR δ −1.2 ppm ($^{1}J_{BF}$ = 69 Hz); ^{19}F NMR δ −193.8 ppm). The C₆F₅ groups at boron are diastereotopic. This can be recognized by the small splitting of the respective o-C₆F₅ ^{19}F NMR signals. At ambient temperature, the −C₆F₄−BF moiety exhibits an AA′XX′Z ^{19}F NMR pattern (−C₆F₄− δ −133.5, −141.7 in dichloromethane-d_2 at 308 K). The ^{19}F NMR spectra of **5** are dynamic due to temperature-dependent freezing of the C−C(Ar) rotation on the NMR time scale. Broadening and then splitting into an ABCDZ pattern is observed upon lowering the monitoring temperature to eventually give rise to the observation of four −C₆F₄− signals at δ −134.2, −134.7, −136.0, and −145.8 ppm (in dichloromethane-d_2 at 193 K).

The X-ray crystal structure analysis (see Figure 3) confirms the structural assignment of **5**. It shows a pseudotetrahedral tris(aryl)BF unit with an average C(Ar)−B−C(Ar) angle of 111.5° and an average C(Ar)−
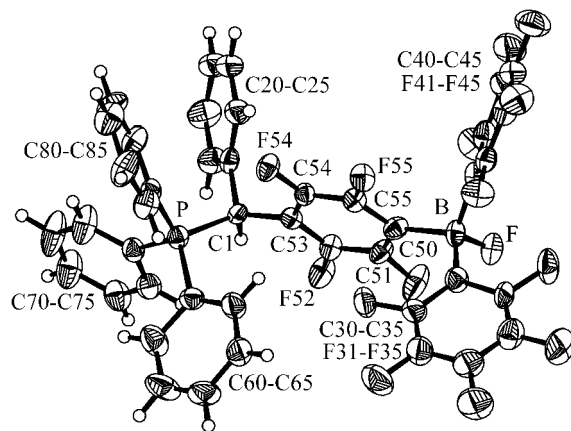
B−F angle of 107.4°. The B−F bond length is 1.392-(12) Å. The averaged C−P−C angle at phosphorus is close to tetrahedral (109.4°), and the corresponding angles at the sp³-hybridized carbon atom C1 are 113.1-(6)° (P−C1−C20), 113.3(7)° (C20−C1−C53), and 118.2-(6)° (P−C1−C53). The P−C1 bond is long (1.841(9) Å).
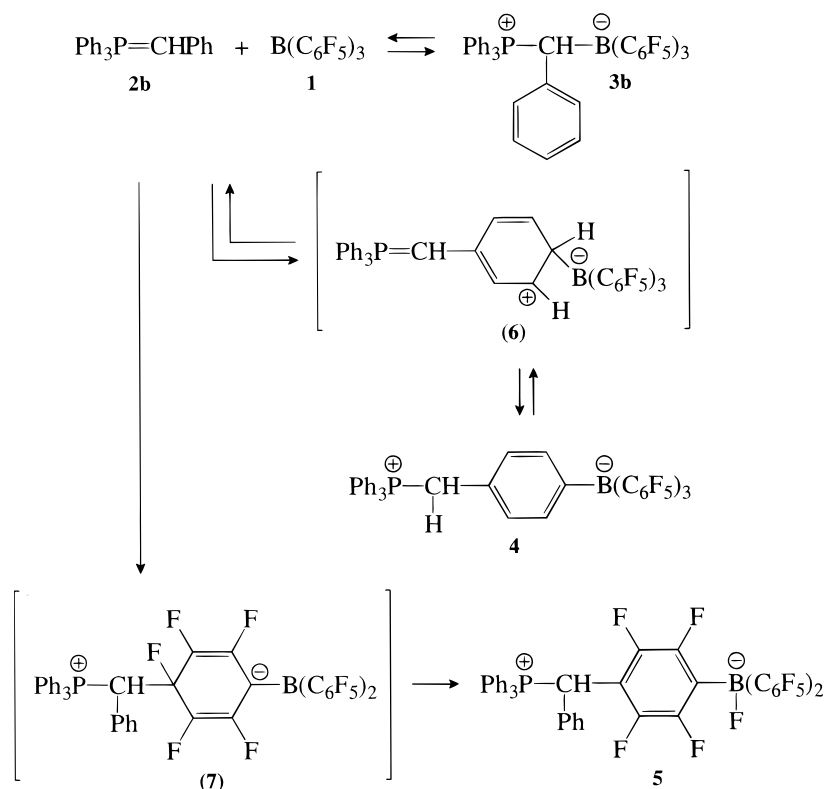
Apparently, the formation of the thermodynamic rearrangement product **5** is initiated by ylide attack at one of the −C₆F₅ ring systems. To achieve this, the reagents Ph₃P=CHPh and B(C₆F₅)₃ must be set free from the intermediately formed product **4**. Thus, it must be assumed that the electrophilic aromatic substitution process leading to the formation of **4** is reversible under the applied reaction conditions.[11,12] It appears that the combined influence of five fluorine substituents largely overcompensates the electron-releasing inductive effect of boron at the −C₆F₅ substituents at the B(C₆F₅)₃ reagent and makes this specific organometallic Lewis acid eventually sensitive to nucleophilic attack at the electron-deficient aromatic unit. Fluorine transfer from the resulting intermediate (**7**) then leads to the formation of the stable final product **5** directly. This sequence shows that the often used tris-(pentafluorophenyl)borane Lewis acid reagent does not only serve as a simple electrophilic borane but has a richer chemistry to offer that makes interesting new betaine systems available, which may be of use in organometallic synthesis. Potential applications of such systems, which are now easily available by the reaction sequence described in this paper, are currently being investigated in our laboratory.

(10) For a related B(C₆F₅)₃ substitution reaction in metallocene chemistry, see, e.g.: Ruwwe, J.; Erker, G.; Fröhlich, R. *Angew. Chem.* **1996**, *108*, 108; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 80.

(11) For remotely related proton-transfer reactions of ylide adducts of group 4 metallocene complexes, see, e.g.: Erker, G.; Czisch, P.; Krüger, C.; Wallis, J. M. *Organometallics* **1985**, *4*, 2059. Erker, G.; Czisch, P.; Mynott, R.; Tsay, Y.-H.; Krüger, C. *Organometallics* **1985**, *4*, 1310. Erker, G.; Czisch, P.; Mynott, R. *Z. Naturforsch.* **1985**, *40b*, 1177.

(12) Electrophilic aromatic substitution at the phenyl rings of BPh₄⁻ is known: Hlatky, G. G.; Turner, H.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728.

Scheme 1

$$Ph_3P=CHPh \; + \; B(C_6F_5)_3 \; \rightleftharpoons \; Ph_3\overset{\oplus}{P}-CH-\overset{\ominus}{B}(C_6F_5)_3$$

2b   **1**   **3b**

(6)

4

(7)   5

Experimental Section

All reactions involving organometallic reagents or substrates were carried out in an inert atmosphere (argon) using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. The following instruments were used for physical characterization of the compounds. Bruker AC 200 P, Bruker ARX 300, and Varian Unity Plus 600 NMR spectrometers; Nicolet 5 DXC FT-IR spectrometer; DuPont 2910 (STA Instruments) DSC. Elemental analyses: Foss-Heraeus CHN-O-Rapid. X-ray crystal structure analyses: Enraf-Nonius CAD4 diffractometer (programs used include MolEN, SHELX 86, SHELX 93, and DIAMOND). Tris(pentafluorophenyl)borane (**1**)[2] and the ylides **2a**,**b**[13] were prepared according to literature procedures.

Preparation of the Methylene Triphenylphosphorane/ Tris(pentafluorophenyl)borane Adduct 3a. A solution of 0.72 g (2.60 mmol) of the ylide **2a** in 75 mL of toluene was added to a solution of 2.00 g (3.90 mmol) of $B(C_6F_5)_3$ (**1**) in 75 mL of toluene with stirring at ambient temperature. The yellow color disappeared over a period of ca. 30 min. The mixture was then stirred for an additional 6 h at 40 °C. Solvent was removed in vacuo. The remaining traces of toluene were removed by codistillation with pentane. The product **3a** was washed with several portions of ether and dried in vacuo. Yield: 1.81 g (89%). Mp: 251 °C (DSC). Anal. Calcd for $C_{37}H_{17}BF_{15}P$ (788.3): C, 56.38; H, 2.17. Found: C, 55.61; H, 2.67. IR (KBr): $\tilde{\nu}$ 3063, 2960, 1641, 1517, 1459, 1279, 1162, 1107, 1080, 982, 785, 692 cm^{-1}. ^{1}H NMR (chloroform-d_1, 200.1 MHz, 300 K): δ 7.68−7.62 and 7.52−7.25 (2m, 15H, PPh_3), 3.19 (m, 2H, P−CH_2) ppm. ^{13}C NMR (chloroform-d_1, 50.3 MHz, 300 K): δ 147.9 (d, $^1J_{CF}$ = 234 Hz, $B(C_6F_5)_3$ (*o*-*C*)), 138.7 (d, $^1J_{CF}$ = 237 Hz, $B(C_6F_5)_3$ (*p*-*C*)), 136.5 (d, $^1J_{CF}$ = 239 Hz, $B(C_6F_5)_3$ (*m*-*C*)), 133.7 (s, PPh_3 (*p*-*C*)), 133.1 (d, $^3J_{PC}$ = 10.0 Hz, PPh_3 (*m*-*C*)), 129.3 (d, $^2J_{PC}$ = 12 Hz, PPh_3 (*o*-*C*)), 122.0 (d, $^1J_{PC}$ = 84 Hz, PPh_3 (*ipso*-*C*) ppm; *ipso*-C of $B(C_6F_5)_3$ and CH_2

carbon resonance not observed. ^{31}P NMR (benzene-d_6, 81.0 MHz, 300 K): δ 30.3 ppm. ^{11}B NMR (benzene-d_6, 64.2 MHz, 300 K): δ −14.9 ppm. ^{19}F NMR (dichloromethane-d_2, 563.8 MHz, 298 K): δ −166.0 ($B(C_6F_5)_3$, *m*-F), −161.8 (*p*-F), −132.2 (*o*-F).

X-ray Crystal Structure Analysis of 3a. Single crystals were obtained from a reaction mixture of 32.0 mg (0.12 mmol) of **2a** with 60.0 mg (0.12 mmol) of $B(C_6F_5)_3$ (**1**) in 1 mL of benzene-d_6 after 2 days at room temperature; formula $C_{37}H_{17}$-$BF_{15}P \cdot 1.5C_6H_6$, M = 905.45, 0.7 × 0.5 × 0.5 mm, a = 12.515-(1) Å, b = 12.894(1) Å, c = 13.313(1) Å, α = 104.70(1)°, β = 98.75(1)°, γ = 103.03(1)°, V = 1973.9(3) Å^3, ρ_{calc} = 1.523 g cm^{-3}, μ = 15.75 cm^{-1}, empirical absorption correction via φ scan data (0.934 ≤ C ≤ 0.999), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.541 78 Å, T = 223 K, $\omega/2\theta$ scans, 8420 reflections collected (+h, ±k, ±l), [(sin θ)/λ] = 0.62 Å^{-1}, 8037 independent and 7801 observed reflections [$I \geq 2\sigma(I)$], 569 refined parameters, R = 0.040, wR^2 = 0.111, maximum residual electron density 0.34 (−0.23) e Å^{-3}, hydrogens calculated and riding.

Reaction of Benzylidene Triphenylphosphorane (2b) with $B(C_6F_5)_3$. (a) Formation of the Adduct 3b. Pentane was allowed to diffuse from the gas phase into a reaction mixture containing 200 mg (0.56 mmol) of the ylide **2b** and 291 mg of $B(C_6F_5)_3$ (**1**) in 10 mL of toluene at 0 °C. During a period of 2 weeks at 0 °C, crystals of the colorless product **3b** had formed, which were collected and dried in vacuo. Yield of **3b**: 353 mg (72%). Amorphous **3b** was obtained on a larger scale as follows: 1.00 g (1.95 mmol) of $B(C_6F_5)_3$ was dissolved in 50 mL of toluene and cooled to −10 °C. A solution of the ylide **2b** (688 mg, 1.95 mmol) in 50 mL of toluene was added with stirring. A clear colorless solution was obtained. After 1 h of stirring, 200 mL of cold pentane (−10 °C) was added. The precipitation was completed by keeping the mixture for 2 h at −30 °C. The product was collected by filtration. It was washed with cold pentane (2 × 50 mL) and dried in vacuo to give 1.24 g (74%) of **3b**, mp 137 °C (decomp.). Anal. Calcd

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for $C_{43}H_{21}BF_{15}P$ (864.4): C, 59.75; H, 2.45. Found: C, 59.72; H, 3.63. ^{1}H NMR (toluene-d_8, 599.9 MHz, 298 K): δ 7.21 (m, 6H), 6.88 (m, 3H), 6.73 (m, 6H, PPh$_3$), 6.71 (m, 2H), 6.66 (m, 1H), 6.55 (m, 2H, Ph), 6.32 (bd, 1H, $^2J_{PH}$ = 25 Hz, P–CH–Ph) ppm. ^{13}C NMR (toluene-d_8, 150.7 MHz, 298 K): δ 148.9 (d, $^1J_{CF}$ = 249 Hz, B(C$_6$F$_5$)$_3$ (o-C), 139.5 (d, $^1J_{CF}$ = 246 Hz, B(C$_6$F$_5$)$_3$ (p-C), 137.2 (d, $^1J_{CF}$ = 261 Hz, B(C$_6$F$_5$)$_3$ (m-C), 134.7 (d, $^3J_{PC}$ = 8 Hz, PPh$_3$ (m-C), 133.3 (d, $^4J_{PC}$ = 2 Hz, PPh$_3$ (p-C), 130.8 (d, $^2J_{PC}$ = 12 Hz, PPh$_3$ (o-C), 129.0 (d, $^2J_{PC}$ = 6 Hz, Ph (o-C), 128.2 (d, $^3J_{PC}$ = 10 Hz, Ph (m-C), 127.0 (d, $^4J_{PC}$ = 3 Hz, Ph (p-C), 125.3 (d, $^1J_{PC}$ = 85 Hz, Ph (ipso-C), 122.5 (d, $^1J_{PC}$ = 80 Hz, PPh$_3$ (ipso-C), 35.5 (br, PCH) ppm; ipso-C of B(C$_6$F$_5$)$_3$ not observed. ^{31}P NMR (benzene-d_6, 81.0 MHz, 300 K): δ 31.8 ppm. ^{11}B NMR (benzene-d_6, 64.2 MHz, 300 K): δ –11.0 ppm. ^{19}F NMR (toluene-d_8, 563.8 MHz, 298 K): δ –129.5 (6F, o-C$_6$F$_5$), –161.4 (3F, $^3J_{FF}$ = 21 Hz, p-C$_6$F$_5$), –166.3 (6F, m-C$_6$F$_5$). ^{19}F NMR (toluene-d_8, 563.8 MHz, 223 K): δ –127.8 (1F), –129.9 (2F), –130.3 (1F), –131.4 (1F), –132.4 (1F, o-C$_6$F$_5$), –160.1 (1F), –161.0 (2F, p-C$_6$F$_5$), –164.7, –165.1, –165.3, –165.6, –166.1, –167.4 (1F each, m-C$_6$F$_5$).

X-ray Crystal Structure Analysis of 3b. Single crystals were obtained by allowing pentane to diffuse through the gas phase into a solution of 20.0 mg (56 μmol) of the ylide **2b** and 30.0 mg (57 μmol) of B(C$_6$F$_5$)$_3$ (**1**) in 1 mL of toluene at 0 °C; formula $C_{43}H_{21}BF_{15}P$, M = 864.38, 0.1 × 0.1 × 0.1 mm, a = 13.273(1) Å, b = 14.665(1) Å, c = 19.250(2) Å, β = 101.84(1)°, V = 3667.3(5) Å^3, ρ_{calc} = 1.566 g cm^{-3}, μ = 16.66 cm^{-1}, empirical absorption correction via φ scan data (0.941 $\leq$ C $\leq$ 0.999), Z = 4, monoclinic, space group P2$_1$/c (No. 14), λ = 1.541 78 Å, T = 223 K, $\omega/2\theta$ scans, 15 267 reflections collected (+h, ±k, ±l), [(sin θ)/λ] = 0.62 Å^{-1}, 7464 independent and 4924 observed reflections [$I \geq 2\sigma(I)$], 541 refined parameters, R = 0.046, wR^2 = 0.116, maximum residual electron density 0.27 (–0.47) e Å^{-3}, hydrogens calculated and riding.

(b) Formation of the Mixture of Isomers 4 and 5. A 200 mg (0.56 mmol) amount of the ylide **2b** and 291 mg (0.57 mmol) of B(C$_6$F$_5$)$_3$ (**1**) were dissolved in 50 mL of toluene and kept for 24 h at 55 °C. The solution turned dark red during this period of time. The progress of the reaction was checked by ^{31}P NMR spectroscopy. The NMR data of **4** were obtained from a 2:1 mixture of **4** and **5** obtained by reacting **1** (30 mg) with **2b** (21 mg) in benzene-d_6, as described above. Compound **4**: ^{1}H NMR (benzene-d_6, 599.9 MHz, 298 K) δ 7.27–6.96 and 6.92–6.76 (2m, Σ 17H, Ph (m-H) and PPh$_3$), 6.58 (m, 2H, $^3J_{HH}$ = 7.23 Hz, Ph (o-H)), 4.25 (d, 2H, $^2J_{PH}$ = 14.3 Hz, P–CH_2) ppm; ^{13}C NMR (benzene-d_6, 150.8 MHz, 298 K) δ 148.9 (d, $^1J_{CF}$ = 234 Hz, B(C$_6$F$_5$)$_3$ (o-C), 141.9 (d, $^1J_{CF}$ = 221 Hz, B(C$_6$F$_5$)$_3$ (p-C), 139.7 (d, $^1J_{CF}$ = 246 Hz, B(C$_6$F$_5$)$_3$ (m-C), 135.1 (d, $^4J_{PC}$ = 3 Hz, PPh$_3$ (p-C), 134.2 (d, $^3J_{PC}$ = 9 Hz, PPh$_3$ (m-C), 133.8 (d, $^2J_{PC}$ = 10 Hz, PPh$_3$ (o-C), 130.9 (d, $^3J_{PC}$ = 6 Hz, Ph (o-C), 129.0 (d, $^4J_{PC}$ = 12 Hz, Ph (m-C), 127.0 (d, $^2J_{PC}$ = 9 Hz, Ph (ipso-C), 117.1 (d, $^1J_{PC}$ = 86 Hz, PPh$_3$ (ipso-C), 30.2 (d, $^1J_{PC}$ = 48 Hz, P–CH$_2$) ppm, ipso-carbon resonances of –C$_6$F$_5$ and of the phenylene ring adjacent to [B] were not located; ^{31}P NMR (benzene-d_6, 242.8 MHz, 298 K) δ 21.9 ppm; ^{11}B NMR (benzene-d_6, 64.2 MHz, 298 K) δ –11.1 ppm; GHSQC^{14} (benzene-d_6, 599.9 MHz, 298 K) δ 30.2/4.25 (CH$_2$) ppm; GHMBC^{14} (C,H) NMR (benzene-d_6, 599.9 MHz, 298 K) δ 130.9 (C$_6$H$_4$ (o-C)/6.58 (C$_6$H$_4$ (o-H)), 130.9 (C$_6$H$_4$ (o-C)/4.25 (CH$_2$), 129.0 (C$_6$H$_4$ (m-C)/6.58 (C$_6$H$_4$ (o-H)), 127.0 (C$_6$H$_4$ (ipso-C)/4.25 (CH$_2$), 117.1 (PPh$_3$ (ipso-C)/4.25 (CH$_2$), 30.2 (CH$_2$)/6.58 (C$_6$H$_4$ (o-H)) ppm; GHMBC^{14} (P,H) NMR (benzene-d_6, 599.9 MHz, 298 K) δ 21.9 (P–CH$_2$)/6.58 (C$_6$H$_4$ (o-H)), 21.9 (P–CH$_2$)/4.25 (P–CH_2) ppm.

(c) Preparation of Rearrangement Product 5. The dark red reaction mixture, prepared as described above, in toluene was stirred for 2 days at room temperature. During this period of time, the solution decolorized and the product precipitated as a colorless solid. It was collected by filtration, washed twice with pentane (10 mL), and dried in vacuo to yield 430 mg (89%) of **5**. Mp: 158 °C (DSC). Anal. Calcd for $C_{43}H_{21}$-BF$_{15}$P (864.4): C, 59.75; H, 2.45. Found: C, 61.90; H, 3.04. IR (KBr): $\tilde{\nu}$ 3064, 3031, 2919, 1643, 1514, 1463, 1273, 1241, 1095, 965, 785, 693, 526 cm^{-1}. ^{1}H NMR (dichloromethane-d_2, 599.3 MHz, 298 K): δ 7.82 (m, 3H), 7.61 (m, 6H), 7.40 (m, 6H, PPh$_3$), 7.36 (t, 1H), 7.25 (t, 2H), 7.06 (d, 2H, Ph), 6.26 (d, 1H, $^2J_{PH}$ = 18.6 Hz, P–CH) ppm. ^{13}C NMR (dichloromethane-d_2, 50.3 MHz, 300 K, J_{PC} determined at 150.7 MHz): δ 148.6 (d, $^1J_{CF}$ = 210 Hz, B(C$_6$F$_5$)$_2$ (o-C) and –(C$_6$F$_4$)B (o-C)), 139.2 (d, $^1J_{CF}$ = 245 Hz, B(C$_6$F$_5$)$_2$ (p-C)), 139.7 (B(C$_6$F$_5$)$_2$ (m-C) and –(C$_6$F$_4$)B (m-C)), 136.0 ($^4J_{PC}$ = 3.2 Hz), 134.8 ($^2J_{PC}$ = 9.6 Hz), 130.7 ($^3J_{PC}$ = 12.5 Hz, p-, o-, m-PPh$_3$), 130.3 ($^3J_{PC}$ = 5.3 Hz), 130.1 ($^5J_{PC}$ = 2.4 Hz), 130.0 ($^4J_{PC}$ = 1.6 Hz, o-, p-, m-Ph), 118.5 (Ph (ipso-C)), 117.7 ($^1J_{PC}$ = 83 Hz, ipso-C of PPh$_3$), 42.1 ($^1J_{PC}$ = 48 Hz) ppm; ipso-carbons adjacent to boron not observed. ^{31}P NMR (dichloromethane-d_2, 81.0 MHz, 300 K): δ 25.9 ppm. ^{11}B NMR (dichloromethane-d_2, 64.2 MHz, 300 K): δ –1.2 ($^1J_{BF}$ = 69 Hz) ppm. ^{19}F NMR (dichloromethane-d_2, 564.3 MHz, 298 K): δ –193.8 (B–F), –168.1 (t, $^3J_{FF}$ = 21 Hz, 4F, B(C$_6$F$_5$)$_2$ (m-F)), –163.4 (t, $^3J_{FF}$ = 21 Hz, 2F, B(C$_6$F$_5$)$_2$ (p-F)), –141.7 (br, 2F, (C$_6$F$_4$)B (m-F)), –136.7 (d, $^3J_{FF}$ = 23 Hz, 2F, B(C$_6$F$_5$)$_2$ (o-F)), –133.7 (m, $^3J_{FF}$ = 20 Hz, $^4J_{FF}$ = 13.6 Hz, 4F, (C$_6$F$_4$)B (o-F)) ppm. ^{19}F NMR (dichloromethane-d_2, 563.8 MHz, 193 K): δ –193.5 (BF), –166.8 (4F, B(C$_6$F$_5$)$_2$ (m-F)), –161.9 (2F, B(C$_6$F$_5$)$_2$ (p-F)), –136.8 and –137.2 (each one F, B(C$_6$F$_5$)$_2$, (o-F)), –145.8, –136.0, –134.7, –134.2 (each 1F, ABXY of –C$_6$F$_4$–).

X-ray Crystal Structure Analysis of 5. Single crystals of **5** were obtained by allowing pentane to diffuse through the gas phase into a solution of **5** in benzene-d_6; formula $C_{43}H_{21}$-BF$_{15}$P, M = 864.38, 0.3 × 0.2 × 0.1 mm, a = 11.749(1) Å, b = 12.156(1) Å, c = 17.021(2) Å, α = 108.96(1)°, β = 94.78(1)°, γ = 101.91(1)°, V = 2074.2(3) Å^3, ρ_{calc} = 1.384 g cm^{-3}, μ = 1.64 cm^{-1}, no absorption correction (0.983 $\leq$ C $\leq$ 0.999), Z = 2, triclinic, space group P$\bar{1}$ (No. 2), λ = 0.710 73 Å, T = 223 K, $\omega/2\theta$ scans, 7675 reflections collected (±h, +k, ±l), [(sin θ)/λ] = 0.59 Å^{-1}, 7301 independent and 3907 observed reflections [$I \geq 2 \sigma(I)$], 541 refined parameters, R = 0.145, wR^2 = 0.412, maximum residual electron density 3.98 (–0.53) e Å^{-3}, hydrogens calculated and riding. The remaining electron density is concentrated around 0.4,0,0 and 0.4,0,0.5, indicating solvent molecules. Filling in the highest peaks led to a strong decrease in the R-value, but it was not possible to find a chemically reasonable description of the electron density. Therefore this was not taken into account in the final refinement.

Supporting Information Available: Further details af the X-ray crystal structure analyses of the compounds **3a**, **3b,** and **5** including tables of atomic coordinates, thermal parameters, bond lengths and angles, and spectroscopic features of **3b** and **5** (46 pages). Ordering information is given on any current masthead page.

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