JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

ARTICLE

pubs.acs.org/JACS

P−C Bond Activation Chemistry: Evidence for 1,1-Carboboration Reactions Proceeding with Phosphorus−Carbon Bond Cleavage

Olga Ekkert, Gerald Kehr, Roland Fröhlich, and Gerhard Erker*

Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40, 48149 Münster, Germany

Supporting Information

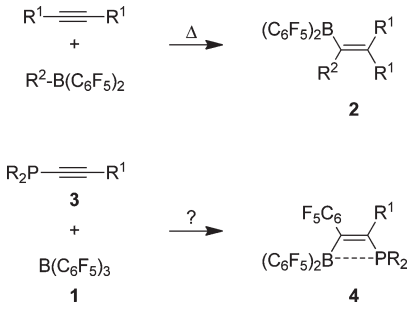
ABSTRACT: A series of diarylphosphinyl-substituted acetylenes of the type $(aryl)_2P-C\equiv C-R$ (aryl = phenyl or mesityl, R = Ph or *n*-propyl) react with the strongly Lewis acid reagent $B(C_6F_5)_3$ in toluene at elevated temperatures (70−105 °C) to give the 1,1-carboboration products **4**. Treatment of bis(diphenylphosphinyl)acetylene with $B(C_6F_5)_3$ under analogous conditions proceeded with phosphinyl migration to yield the 1,1-carboboration product **4d**, bearing a geminal pair of Ph_2P substituents at one former acetylene carbon atom and a C_6F_5 substituent and the remaining $-B(C_6F_5)_2$ group at the other. Prolonged thermolysis of **4d** resulted in an intramolecular aromatic substitution reaction by means of Ph_2P attack on the adjacent C_6F_5 ring to yield the zwitterionic phospha-indene derivative **7**. The compounds **4a**, **4c**, **4d**, and **7** were characterized by X-ray diffraction.

INTRODUCTION

Being able to selectively attack or cleave unactivated strong bonds to the element carbon has been of an increasing interest in methodological developments in chemistry. Much progress has been achieved in recent years in C−H activation,[1] so we by now have quite a spectrum of methods available to selectively attack strong, otherwise unactivated carbon−hydrogen bonds to make their respective positions in carbon-containing frameworks synthetically available.[2] Much less attention has been focused on the chemistry of other nonactivated strong bonds to carbon.[3] Quite recently some interest has arisen in finding new methodologies for selectively cleaving nonactivated carbon−carbon bonds.[4] In this context we have described some remarkable carbon−carbon bond cleavage reactions[5] induced by very reactive, strongly electrophilic borane reagents.[6−8] We had shown that some R-B-$(C_6F_5)_2$ reagents (R = CH_3 or C_6F_5) react with internal alkynes by means of selective 1,1-carboboration reactions[9−11] to yield **2**.[5] In the course of this addition/skeletal rearrangement process, a strong C(sp)−C(sp^3) or C(sp)−C(sp^2) linkage becomes cleaved and an alkyl or aryl group undergoes a formal 1,2-shift to the adjacent acetylene carbon atom (C2) in order to make room at its origin (C1) for the boron attachment with concomitant alkyl or aryl migration from boron to carbon. This remarkable, thermally induced transformation yields novel alkenyl boranes which have been employed as very reactive substrates[5] in metal-catalyzed cross-coupling reactions.

We have now tried to extend this work to the activation of strong carbon−phosphorus σ-bonds (see Scheme 1). There is a very specific methodology available for P−C bond cleavage,[12] but finding novel, rather generally applicable P−C bond activation proceedures is highly desirable, especially if they can be coupled with C−C and B−C bond formation, as implied by the 1,1-carboboration methodology. 1-Bora-2-phospha-alkenes of the type **4** and related systems have been of interest, e.g., to material science.[13,14] We have now reacted a selected series of

Scheme 1



phosphinyl-substituted acetylenes with the strongly electrophilic borane reagent **1** and found that this resulted in clean 1,1-carboboration reactions with formation of the interesting alkenylene-bridged B/P products **4**. We here describe these first representative examples.

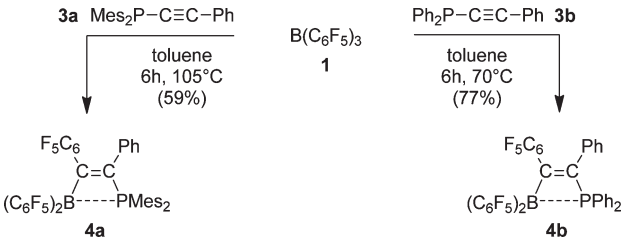
RESULTS AND DISCUSSION

The bulky P-substituted acetylene dimesityl(phenylethynyl)-phosphine (**3a**) was prepared by treatment of lithiated phenylacetylene with Mes_2PCl.[15] Compound **3a** was mixed with the strongly electrophilic borane $B(C_6F_5)_3$ (**1**)[6] in toluene solution and then kept for 6 h at 105 °C. Workup gave the 1,1-carboboration product **4a** in ca. 60% yield (see Scheme 2). The new product was characterized spectroscopically, by C,H elemental analysis, and by an X-ray crystal structure analysis. Suitable single crystals were obtained at −36 °C from toluene/pentane by the diffusion method.

Received: December 8, 2010
Published: March 02, 2011

dx.doi.org/10.1021/ja1110283 | *J. Am. Chem. Soc.* 2011, 133, 4610–4616

Scheme 2



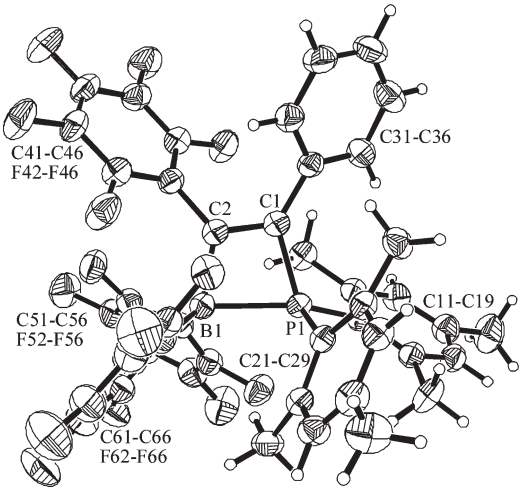
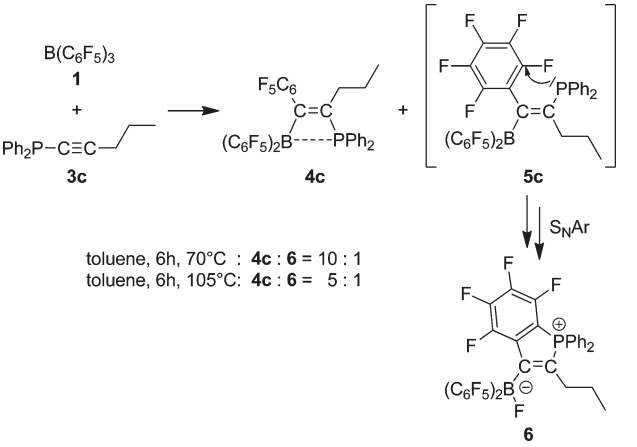


Figure 1. Molecular structure of the 1,1-carboboration product **4a**.

X-ray crystal structure analysis revealed the presence of a rearranged framework typically resulting from a 1,1-carboboration reaction. It shows that both of the substituents that were originally 1,2-positioned in the alkyne C_2 framework are now 1,1-bonded: both the phenyl substituent and the bulky $-PMes_2$ moiety are found bonded to the same carbon atom (C1) of the product **4a** (see Figure 1; bond distances C1−C31 1.479(3) Å, C1−P1 1.833(2) Å, angles C31−C1−P1 134.5(2)°, C2−C1−C31 128.0(2)°). The newly introduced components from the $B(C_6F_5)_3$ reagent are now found bonded to the adjacent former acetylene carbon atom C2, namely the C_6F_5 substituent that was shifted from boron to carbon and the remaining $-B(C_6F_5)_2$ unit (bond distances C2−C41 1.490(3) Å, C2−B1 1.637(3) Å, angles C41−C2−B1 128.2(2)°, C1−C2−C41 123.5(2)°). The bulky $-B(C_6F_5)_2$ and $-PMes_2$ antagonists are found *Z*-attached at the remaining C(2)═C(1) double bond (C1−C2 1.349(3) Å). The boron Lewis acid forms a weak adduct with the adjacent phosphorus Lewis base (B1−P1 2.115(2) Å). The boron atom features a slightly pyramidalized geometry of the C2−$B(C_6F_5)_2$ unit with bond angles C2−B1−C51 114.0(2)°, C2−B1−C61 115.9(2)°, and C51−B1−C61 114.2(2)° (Σ = 344.1°). The coordination sphere at the phosphorus atom P1 is characterized by bond angles C1−P1−C21 113.8(1)°, C1−P1−C11 111.9(1)°, and C11−P1−C21 109.5(1)° (Σ = 335.2°). Overall this has resulted in the formation of a four-membered heterocyclic structure[16] of the 1,1-carboboration product **4a** (angles inside the four-membered ring: C1−C2−B1 108.1(2)°, C2−C1−P1 97.6(1)°, C1−P1−B1 75.3(1)°, C2−B1−P1 70.0(1)°).

Scheme 3



Compound **4a** features a ^{11}B NMR resonance at ca. δ 1 and a broad ^{31}P NMR signal at δ 15.2. It shows a broad ^{13}C NMR signal of the [B]C(2)═ carbon atom at δ 161.2 and the corresponding ═C(1)[P] carbon resonance at δ 146.7 ($^1J_{PC}$ = 46.8 Hz). The ^{19}F NMR resonances of the single carbon bound C_6F_5 group occur at δ −136.0 (*o*), −154.1 (*p*), and −162.4 (*m*), whereas the $B(C_6F_5)_2$ unit shows a set of ^{19}F NMR signals of double intensity at δ −126.9 (*o*), −156.1 (*p*), and −164.0 (*m*), with a chemical shift separation of the *meta*- and *para*-^{19}F resonances [$\Delta\delta(m,p)$] of 7.9.[17]

The analogous reaction of $B(C_6F_5)_3$ (**1**) with the diphenylphosphinyl-substituted acetylene (**3b**, see Scheme 2) proceeded at much lower temperature (6 h, 70 °C) to give the corresponding 1,1-carboboration product **4b** that was isolated in 77% yield after the usual workup procedure. It shows a ^{31}P NMR resonance at δ +13.8 and a ^{11}B NMR signal at δ −6. The ^{19}F NMR signals of the $-B(C_6F_5)_2$ group show a chemical shift difference of $\Delta\delta(m,p)$ = 7.5, with the ^{19}F NMR set of signals of the single carbon bound C_6F_5 group at δ −138.3 (*o*), −154.0 (*p*), and −161.7 (*m*). The ^{13}C NMR resonances of the C═C backbone of the four-membered heterocyclic product **4b** occur at δ 161.3 (br, [B]C═) and δ 143.3 ($^1J_{PC}$ = 53.0 Hz, ═C[P]), respectively.

We next reacted the alkyl P-substituted acetylene 1-diphenylphosphinyl-1-pentyne (**3c**) with $B(C_6F_5)_3$. Like in the **3b**/$B(C_6F_5)_3$ case described above, the **3c**/$B(C_6F_5)_3$ reaction took 6 h at 70 °C in toluene solution to go to completion. We obtained a mixture of two products in a ratio of ca. 10:1 that was isolated in a combined yield of 56%. The major product was identified as the 1,1-carboboration product **4c**. The analogous reaction of **1** and **3c** in toluene-d_8 at 105 °C for 6 h yielded a 5:1 product mixture of **4c** and **6** (see Scheme 3).

We obtained single crystals of **4c** by diffusion of pentane vapor into a dichloromethane solution at −36 °C. In the crystal, compound **4c** shows the typical distorted four-membered heterocyclic structure (B1−P1 bond length: 2.038(3) Å).[17,18] The former acetylene carbon atom C1 now bears both the *n*-propyl substituent and the bulky $-PPh_2$ group, whereas C2 now has a $-C_6F_5$ substituent and the remaining $-B(C_6F_5)_2$ moiety attached to it (Figure 2; bond distances C1−C2 1.345(4) Å, C1−P1 1.802(3) Å, C2−B1 1.651(4) Å, angles C2−C1−P1 96.1(2)°, C1−C2−B1 107.1(2)°, C1−P1−B1 77.8(1)°, C2−B1−P1 78.8(2)°). The sum of C−B−C bonding angles at the boron atom

dx.doi.org/10.1021/ja1110283 |*J. Am. Chem. Soc.* 2011, 133, 4610–4616

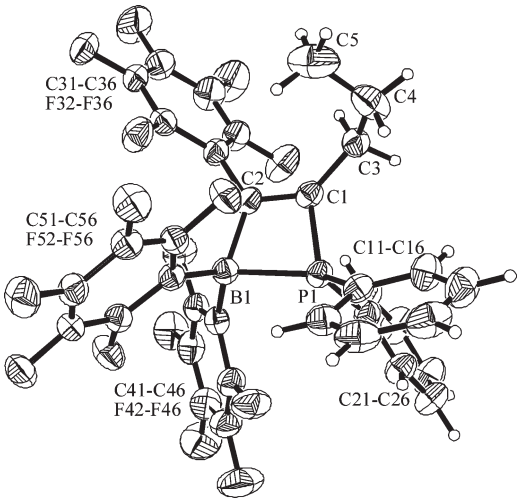
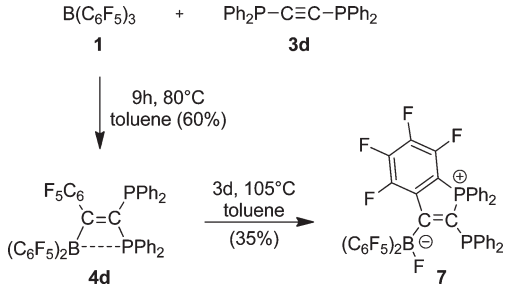


Figure 2. Molecular structure of compound **4c**.

Scheme 4



B1 amounts to 349.2°, and the sum of C−P−C angles at P1 is 332.8°. Compound **4c** shows the typical spectroscopic features of this class of compounds [e.g., ^{11}B NMR δ −6; ^{31}P NMR δ +15.2; ^{13}C NMR δ 161.5 [B]C═, 146.7 ($^{1}J_{PC}$ = 49.1 Hz) ═C[P]; for further details see the Experimental Section and the Supporting Information].

We tentatively assign the minor product from this reaction the structure of compound **6** (see Scheme 3). This is based on its characteristic spectroscopic features, obtained from the **4c**/**6** mixture, and on a comparison with a closely related product (**7**, see below) that was characterized by X-ray diffraction. We assume that compound **6** is the product of an intramolecular nucleophilic substitution reaction,[19] formed subsequent to the 1,1-carboboration reaction by attack of the phosphorus nucleophile on the adjacent C_6F_5 ring. This requires a *Z*-orientation between the two groups, as found in the (not directly observed) 1,1-carboboration isomer **5** (see Scheme 3).

Compound **6** shows the ^{19}F NMR resonance of the B−F unit at δ −184.6 (^{11}B NMR signal at δ 0.6), a set of four ^{19}F NMR signals of the remaining C_6F_4 ring (δ −123.4, −129.7, −139.1, −151.2), and a ^{31}P NMR resonance at δ 33.9 (for further details see the Experimental Section and the Supporting Information).

In the above-described reactions of $B(C_6F_5)_3$ with the phosphinyl-substituted alkynes **3a**−**c**, we assumed that the R_2P group migrated during the course of the 1,1-carboboration sequence. This is likely from the characteristic overall thermal behavior of these reactions, but the R_2P migration had not strictly been

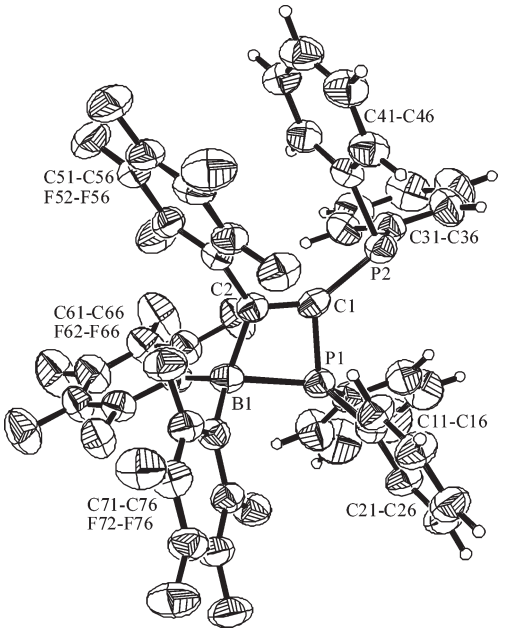


Figure 3. Molecular structure of the 1,1-carboboration product **4d**.

proven. Therefore, we decided to react $B(C_6F_5)_3$ with bis(diphenylphosphinyl)acetylene (**3d**) to create a case where there is no choice for the 1,1-carboboration reaction but to take place with migration of a diphenylphosphinyl group.

Bis(diphenylphosphinyl)acetylene (**3d**) was synthesized from trichloroethene, *n*-butyllithium (3 equiv), and chlorodiphenylphosphine.[20] The doubly phosphinyl-substituted alkyne **3d** was then reacted with $B(C_6F_5)_3$ (**1**) in toluene at 80 °C. It took ca. 9 h for the reaction to go to completion. The 1,1-carboboration product **4d** was isolated from the reaction mixture in 60% yield (Scheme 4). The product features a pair of ^{31}P NMR signals at δ +24.2 (br, [B]P) and −6.3 (J_{PF} = 28 Hz, $^{2}J_{PP}$ = 10.3 Hz) and a ^{11}B NMR resonance at δ −5. The ^{13}C NMR carbon signals of the C_2 bridge occur at δ 173.7 ([B]C═) and 146.4 (dd, $^{1}J_{PC}$ = 53.0 Hz, 32.7 Hz, ═C[P]$_2$), and the product also shows the typical sets of ^{19}F NMR signals of the geminal pair of C_6F_5 and $-B(C_6F_5)_2$ groups at carbon atom C2.

Compound **4d** was characterized by X-ray diffraction (single crystals were obtained from pentane/dichloromethane at −36 °C by the diffusion method). X-ray crystal structure analysis shows the presence of a geminal pair of diphenylphosphinyl substituents at the former acetylene carbon atom C1 (Figure 3; bond lengths C1−P2 1.826(6) Å, C1−P1 1.807(5) Å, angle P1−C1−P2 125.8(3)°). The phosphorus atom P1 weakly coordinates to the adjacent boron Lewis acid (B1−P1 2.038(7) Å). The sum of C−B1−C bond angles at boron is 348.1°, and the sum of C−P1−C bond angles at its adjacent phosphorus atom P1 is 333.0°, whereas the sum of C−P2−C angles is 307.0°. The $(C_6F_5)_2B$ group is bonded to C2 (B1−C2 1.646(8) Å), which also bears a C_6F_5 substituent (C2−C51 1.489(7) Å). The four-membered heterocyclic framework of the 1,1-carboboration product **4d** shows typical bonding parameters of C2−C1 1.367(7) Å and bond angles C2−C1−P1 95.1(4)°, C1−P1−B1 78.2(2)°, P1−B1−C2 78.9(3)°, and B1−C2−C1 107.3(4)°.

Compound **4d** was shown to undergo a slow isomerization reaction by means of an intramolecular nucleophilic attack of the *Z*-PPh_2 group at the adjacent C_6F_5 substituent. After 3 days at 105 °C in toluene, the product of this intramolecular nucleophilic

dx.doi.org/10.1021/ja1110283 |*J. Am. Chem. Soc.* 2011, 133, 4610–4616

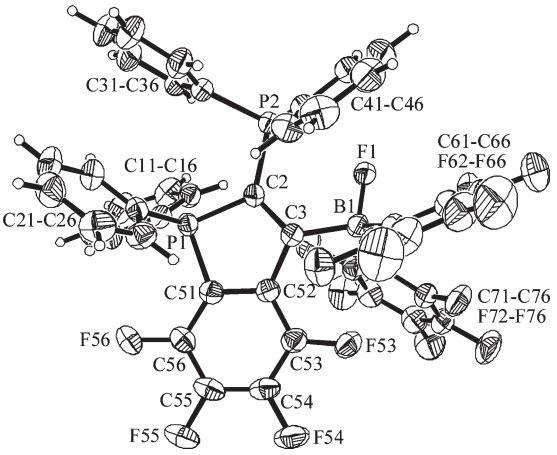


Figure 4. Projection of the product **7** formed by an intramolecular nucleophilic substitution reaction of **4d**.

aromatic substitution reaction, **7**,[19] was isolated as orange crystals in 35% yield. The compound was characterized by X-ray diffraction. It features a phospha-indene-type framework with phosphorus atoms P1 and P2 bonded to the same carbon atom (Figure 4; bond lengths P1−C2 1.794(2) Å, P2−C2 1.845(2) Å, angle P1−C2−P2 124.3(1)°). Phosphorus atom P1 has attacked the C_6F_5 group that is bonded to the ring carbon C3 (C3−C52 1.495(3) Å) and has replaced a fluorine atom (P1−C51 1.790(2) Å). The single fluorine atom is found bonded to boron (B1−F1 1.424(3) Å). The resulting $-B(F)(C_6F_5)_2$ substituent is bonded to the ring carbon atom C3 (C3−B1 1.644(3) Å).

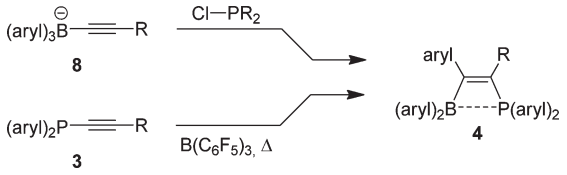
In solution, compound **7** shows a pair of ^{31}P NMR signals at δ 39.1 and −2.5 ($^2J_{PP}$ = 7 Hz), a ^{11}B NMR resonance at δ 0.3, and the signal of the single fluorine atom at boron at δ −171.5 (for further details see the Experimental Section and Supporting Information).

CONCLUSIONS

There is increasing evidence that the 1,1-carboboration reaction is developing from a reaction that is amenable for some special organometallic substrates to a rather general and useful synthetic tool for generating novel carbon frameworks from simple, nonactivated acetylenes that bear ordinary organic substituents.[5,9−11] This development was made possible by using the electrophilic C_6F_5 containing borane **1** and related reagents. We have now shown that this remarkable reaction can even be extended to phosphinyl-substituted alkynes. The reaction requires somewhat forcing conditions, similar to those of the related 1,1-carboboration reactions of simple internal alkynes that we had recently reported, but it proceeds cleanly and gives the respective phosphorus-containing 1,1-carboboration products **4** in good yields (Scheme 5).[21]

Previous examples of the alkenylene-bridged P/B systems **4** had often been synthesized by boron-based nucleophilic substitution routes, employing specifically[22,23] substituted alkynyl borate reagents **8** (Scheme 5). Our new 1,1-carboboration route to these interesting systems now provides a phosphorus based principal synthetic alternative which will probably serve to rapidly expand the scope of utilization these interesting compounds in the material sciences and for synthetic purposes.[5] In view of previous results[9] showing that 1-alkynes and, e.g., trimethylsilylacetylenes very easily undergo 1,1-carboboration

Scheme 5



reactions,[9] substrates such as $R_2P-C\equiv C-H$ and $R_2P-C\equiv C-SiMe_3$ might be good candidates for future extension of this work.

EXPERIMENTAL SECTION

General Procedures. All syntheses involving air- and moisture-sensitive compounds were carried out using standard Schlenk-type glassware (or in a glovebox) under an atmosphere of argon. Solvents were dried with the procedure reported by Grubbs[24] or distilled from appropriate drying agents and stored under an argon atmosphere. NMR spectra were recorded on a Bruker AC 200 P (^1H, 200 MHz; ^{31}P, 81 MHz; ^{11}B, 64 MHz), a Bruker AV 300 (^1H, 300 MHz; ^{13}C, 76 MHz; ^{31}P, 122 MHz; ^{11}B, 96 MHz; ^{19}F, 282 MHz), a Bruker AV 400 (^1H, 400 MHz; ^{13}C, 101 MHz; ^{31}P, 162 MHz), a Varian Inova 500 (^1H, 500 MHz; ^{13}C, 126 MHz; ^{19}F, 470 MHz; ^{11}B, 160 MHz; ^{31}P, 202 MHz), and a Varian UnityPlus 600 (^1H, 600 MHz; ^{13}C, 151 MHz; ^{19}F, 564 MHz; ^{11}B, 192 MHz; ^{31}P, 243 MHz). For ^1H and ^{13}C NMR, chemical shifts δ are given relative to TMS and referenced to the solvent signal. For ^{19}F NMR, chemical shifts δ are given relative to $CFCl_3$ (external reference). For ^{11}B NMR, chemical shifts δ are given relative to $BF_3 \cdot Et_2O$ (external reference). For ^{31}P NMR, chemical shifts δ are given relative to H_3PO_4 (85% in D_2O) (external reference). NMR assignments were supported by additional 2D NMR experiments. Elemental analyses were performed on a Elementar Vario El III. IR spectra were recorded on a Varian 3100 FT-IR (Excalibur Series). Melting points were obtained with a DSC 2010 (TA Instruments). HRMS was recorded on GTC Waters Micromass (Manchester, UK). For X-ray crystal structure analyses, data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (Nonius B.V., 1998); data reduction, Denzo-SMN;[25a] absorption correction, Denzo;[25b] structure solution, SHELXS-97;[25c] structure refinement, SHELXL-97;[25d] and graphics, XP (BrukerAXS, 2000). Thermals ellipsoids are shown with 50% probability, *R* -values are given for the observed reflections, and wR^2 values are given for all reflections.

Materials. Dimesitylchlorophosphine,[15] diphenyl(phenylethynyl)-phosphine (**3b**)[26] and $B(C_6F_5)_3$ (**1**)[6] were prepared according to literature procedures. The compounds **3a**,[22a] **3c**[27] and **3d**[20] were prepared in a similar fashion to **3b**.

Synthesis of Compound 4a. $B(C_6F_5)_3$ (**1**) (0.400 g, 0.780 mmol) and **3a** (0.290 g, 0.780 mmol) were dissolved in toluene (20 mL) and stirred for 6 h at 105 °C. While the reaction mixture was stirred overnight at room temperature, a white solid precipitated. After isolation via cannula filtration, the residue was washed twice with pentane (15 mL). Drying under vacuum gave the product (0.406 g, 0.460 mmol, 59%) as a white solid. Crystals suitable for X-ray crystal structure analysis were grown by slow diffusion of pentane into a solution of **4a** in toluene at −36 °C. Anal. Calcd for $C_{44}H_{27}BF_{15}P$: C, 59.89; H, 3.08. Found: C, 59.84; H, 3.14. IR (KBr): $\tilde{\nu}/cm^{-1}$ = 3406 (br m), 3026 (w), 2934 (w), 2359 (m), 1639 (s), 1518 (s), 1456 (s), 1287 (m), 1094 (s), 980 (s), 761 (m), 506 (m). Decomp (DSC): 231 °C. ^1H NMR (500 MHz, 298 K, C_6D_6): δ = 7.04 (m, 2H, *o*-Ph), 6.82 (m, 3H, *m*-, *p*-Ph), 6.43 (d, $^4J_{PH}$ = 3.3 Hz, 4H, *m*-Mes), 2.13 (s, 12H, *o*-CH_3^{Mes}), 1.89 (s, 6H, *p*-CH_3^{Mes}). $^{13}C\{^1H\}$ NMR (126 MHz, 298 K, C_6D_6): δ = 161.2 (br, ^BC=), 146.7 (d, $^1J_{PC}$ = 46.8 Hz, =C^P), 143.4 (d, $^2J_{PC}$ = 8.8 Hz, *o*-Mes), 142.1 (d, $^4J_{PC}$ = 2.7 Hz, *p*-Mes), 137.9 (d, $^2J_{PC}$ = 1.9 Hz,

dx.doi.org/10.1021/ja1110283 |*J. Am. Chem. Soc.* 2011, 133, 4610–4616

i-Ph), 131.0 (d, $^3J_{PC}$ = 9.1 Hz, *m*-Mes), 129.0 (*p*-Ph), 128.8 (*m*-Ph), 127.3 (d, $^3J_{PC}$ = 3.6 Hz, *o*-Ph), 123.3 (d, $^1J_{PC}$ = 34.6 Hz, *i*-Mes), 24.0 (d, $^3J_{PC}$ = 5.9 Hz, *o*-CH_3^{Mes}), 20.5 (*p*-CH_3^{Mes}) [C_6F_5 not listed]. $^{19}F\{^1H\}$ NMR (470 MHz, 298 K, C_6D_6): δ = −126.9 (br, 4F, *o*-BC_6F_5), −136.0 (m, 2F, *o*-C_6F_5), −154.1 (t, $^3J_{FF}$ = 21.7 Hz, 1F, *p*-C_6F_5), −156.1 (t, $^3J_{FF}$ = 21.1 Hz, 2F, *p*-BC_6F_5), −162.4 (m, 2F, *m*-C_6F_5), −164.0 (m, 4F, *m*-BC_6F_5) [$\Delta\delta^B(m,p)$ = 7.9]. $^{11}B\{^1H\}$ NMR (160 MHz, 298 K, C_6D_6): $\delta \approx$ 1 ($\nu_{1/2} \approx$ 700 Hz). $^{31}P\{^1H\}$ NMR (202 MHz, 298 K, C_6D_6): δ = 15.2 ($\nu_{1/2} \approx$ 40 Hz).

X-ray crystal structure analysis of **4a**: formula $C_{44}H_{27}BF_{15}P$, M = 882.44, colorless crystal 0.40 × 0.30 × 0.25 mm, a = 12.2935(3), b = 21.9361(7), and c = 14.0308(5) Å, β = 102.427(1)°, V = 3695.1(2) Å^3, ρ_{calc} = 1.586 g cm^{-3}, μ= 1.663 mm^{-1}, empirical absorption correction ($0.556 \le T \le 0.681$), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ= 1.54178 Å, T = 223(2) K, ω and φ scans, 28 710 reflections collected ($\pm h, \pm k, \pm l$), [(sin θ)/λ] = 0.60 Å^{-1}, 6493 independent (R_{int} = 0.044) and 5823 observed reflections [$I \ge 2\,\sigma(I)$], 556 refined parameters, R = 0.044, wR^2 = 0.124, max (min) residual electron density 0.32 (−0.28) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Synthesis of Compound 4b. $B(C_6F_5)_3$ (**1**) (0.536 g, 1.05 mmol) and **3b** (0.300 g, 1.05 mmol) were dissolved in toluene (20 mL) and stirred for 6 h at 70 °C. Subsequently the solvent was removed, the residue was washed twice with pentane (15 mL), and all volatiles were removed in vacuo to yield **4b** (0.634 g, 0.803 mmol, 77%) as a yellow solid. Anal. Calcd for $C_{38}H_{15}BF_{15}P$: C, 57.17; H, 1.89. Found: C, 57.10; H, 2.40. IR (KBr) $\tilde{\nu}$/cm^{-1} = 3406 (br m), 3064 (w), 2360 (m), 1646 (s), 1519 (s), 1463 (s), 1285 (m), 1096 (s), 966 (s), 693 (s), 518 (m). Mp (DSC): 251 °C. Decomp (DSC): 272 °C. ^1H NMR (500 MHz, 298 K, C_6D_6): δ = 7.36 (m, 4H, *o*-Ph^P), 7.12 (m, 2H, *o*-Ph), 6.88 (m, 3H, *p*-Ph/*p*-Ph^P), 6.84 (m, 2H, *m*-Ph), 6.76 (m, 4H, *m*-Ph^P). $^{13}C\{^1H\}$ NMR (126 MHz, 298 K, C_6D_6): δ = 161.3 (br, ^{B}C═), 148.7 (dm, $^1J_{FC} \approx$ 240 Hz), 144.0 (dm, $^1J_{FC} \approx$ 250 Hz), 141.0 (dm, $^1J_{FC} \approx$ 250 Hz), 140.5 (dm, $^1J_{FC} \approx$ 250 Hz), 138.1 (dm, $^1J_{FC} \approx$ 250 Hz), 137.6 (dm, $^1J_{FC}$ = 250 Hz, C_6F_5), 143.3 (d, $^1J_{PC}$ = 53.0 Hz, ═C^P), 135.2 (d, $^2J_{PC}$ = 1.9 Hz, *i*-Ph), 132.5 (*p*-Ph^P), 132.1 (d, $^2J_{PC}$ = 9.3 Hz, *o*-Ph^P), 129.7 (*p*-Ph), 129.4 (*m*-Ph), 129.3 (d, $^3J_{PC}$ = 10.4 Hz, *m*-Ph^P), 127.0 (d, $^3J_{PC}$ = 3.2 Hz, *o*-Ph), 124.6 (d, $^1J_{PC}$ = 43.8 Hz, *i*-Ph^P), 115.8 (br, *i*-C_6F_5). $^{19}F\{^1H\}$ NMR (470 MHz, 298 K, C_6D_6): δ = −129.9 (m, 4F, *o*-BC_6F_5), −138.3 (m, 2F, *o*-C_6F_5), −154.0 (t, $^3J_{FF}$ = 21.5 Hz, 1F, *p*-C_6F_5), −156.1 (m, 2F, *p*-BC_6F_5), −161.7 (m, 2F, *m*-C_6F_5), −163.6 (m, 4F, *m*-BC_6F_5) [$\Delta\delta^B(m,p)$ = 7.5]. $^{11}B\{^1H\}$ NMR (160 MHz, 298 K, C_6D_6): δ = −6 ($\nu_{1/2} \approx$ 320 Hz). $^{31}P\{^1H\}$ NMR (202 MHz, 298 K, C_6D_6): δ = 13.8 ($\nu_{1/2} \approx$ 60 Hz).

Synthesis of Compounds 4c and 6. $B(C_6F_5)_3$ (**1**) (0.400 g, 0.780 mmol) and **3c** (0.197 g, 0.780 mmol) were dissolved in toluene (20 mL) and stirred for 6 h at 70 °C. Subsequently the solvent was removed, and the residue was washed twice with pentane. The solid was suspended in toluene and filtered via cannula. After removal of toluene in vacuo, a mixture of **4c** and **6** (ratio 10:1) (0.333 g, 0.440 mmol, 56%) was obtained as a white solid. Crystals of **4c** suitable for X-ray crystal structure analysis were grown by slow diffusion of pentane into a solution of **4c**/**6** in dichloromethane at −36 °C. For the mixture **4c**:**6** = 10:1: Anal. Calcd for $C_{35}H_{17}BF_{15}P$: C, 55.00; H, 2.24. Found: C, 54.51; H, 1.95. IR (KBr): $\tilde{\nu}$/cm^{-1} = 3406 (br m), 3060 (w), 2973 (m), 2880 (w), 2357 (w), 1645 (s), 1518 (s), 1468 (s), 1383 (m), 1288 (m), 1110 (s), 971 (s), 922 (m), 744 (m), 506 (m). Mp (DSC) (**4c**): 214 °C. mp (DSC) (**6**): 186 °C. Decomp (DSC): 270 °C [for further details see the Supporting Information]. For **4c**: ^1H NMR (400 MHz, 300 K, C_6D_6): δ = 7.27 (m, 4H, *o*-Ph), 6.93 (m, 2H, *p*-Ph), 6.86 (m, 4H, *m*-Ph), 2.19 (m, 2H, ═CH_2), 1.20 (m, 2H, CH_2), 0.55 (m, 3H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, 300 K, C_6D_6): δ = 161.5 (br, ^{B}C═), 146.7 (d, $^1J_{PC}$ = 49.1 Hz, ═C^P), 132.38 (d, $^2J_{PC}$ = 8.4 Hz, *o*-Ph), 132.36 (d, $^4J_{PC}$ = 3.3 Hz, *p*-Ph), 129.2 (d, $^3J_{PC}$ = 10.6 Hz, *m*-Ph), 125.4 (d, $^1J_{PC}$ = 42.1 Hz, *i*-Ph), 115.8 (br s, *i*-BC_6F_5), 33.2 (═CH_2), 21.3 (d, $^3J_{PC}$ = 1.6 Hz, CH_2), 14.0 (CH_3) [C_6F_5 not listed]. $^{19}F\{^1H\}$ NMR (470 MHz, 298 K, C_6D_6): δ = −129.7 (m, 4F, *o*-BC_6F_5), −139.6 (m, 2F, *o*-C_6F_5), −154.5 (t, $^3J_{FF}$ = 21.6 Hz, 1F, *p*-C_6F_5), −156.4 (m, 2F, *p*-BC_6F_5), −161.9 (m, 2F, *m*-C_6F_5), −163.7 (m, 4F, *m*-BC_6F_5) [$\Delta\delta^B(m,p)$ = 7.3]. $^{11}B\{^1H\}$ NMR (96 MHz, 300 K, C_6D_6): δ = −6 ($\nu_{1/2} \approx$ 260 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, 300 K, C_6D_6): δ = 15.2 ($\nu_{1/2} \approx$ 80 Hz). For **6** [selected resonances are listed]: ^1H NMR (400 MHz, 300 K, C_6D_6): δ = 7.26 (m, 4H, *o*-Ph), 7.01 (m, 2H, *p*-Ph), 6.88 (m, 4H, *m*-Ph), 2.95 (m, 2H, ═CH_2), 1.34 (m, 2H, CH_2), 0.56 (m, 3H, CH_3) [assignment by 2 D NMR experiments]. $^{13}C\{^1H\}$ NMR (101 MHz, 300 K, C_6D_6): δ = 135.7 (*p*-Ph), 133.1 (d, $^2J_{PC}$ = 11.4 Hz, *o*-Ph), 130.6 (d, $^3J_{PC}$ =13.1 Hz, *m*-Ph), 127.8 (d, $^1J_{PC} \approx$ 55 Hz, ═C^P), 30.6 (═CH_2), 24.6 (CH_2), 21.2 (CH_3) [assignment by 2 D NMR experiments]. $^{19}F\{^1H\}$ NMR (470 MHz, 298 K, C_6D_6): δ = −123.4 (br s, 1F, C_6F_4), −129.7 (br s, 1F, C_6F_4), −132.9 (m, 4F, *o*-BC_6F_5), −139.1 (m, 1F, C_6F_4), −151.2 (m, 1F, C_6F_4), −159.6 (t, $^3J_{FF}$ = 20.6 Hz, 2F, *p*-BC_6F_5), −165.1 (m, 4F, *m*-BC_6F_5), −184.6 (br m, 1F, B−F) [$\Delta\delta^B(m,p)$ = 5.5]. $^{11}B\{^1H\}$ NMR (96 MHz, 300 K, C_6D_6): δ = 0.6 ($\nu_{1/2} \approx$ 140 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, 300 K, C_6D_6): δ = 33.9 ($\nu_{1/2} \approx$ 20 Hz).

X-ray crystal structure analysis of **4c**: formula $C_{35}H_{17}BF_{15}P$, M = 764.27, colorless crystal 0.30 × 0.07 × 0.01 mm, a = 9.5993(5), b = 11.3438(8), and c = 15.4280(15) Å, α = 87.124(5), β = 89.616(4), and γ = 70.239(3)°, V = 1579.0(2) Å^3, ρ_{calc} = 1.607 g cm^{-3}, μ = 1.843 mm^{-1}, empirical absorption correction ($0.608 \le T \le 0.982$), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ= 1.54178 Å, T = 223(2) K, ω and φ scans, 23 382 reflections collected ($\pm h, \pm k, \pm l$), [(sin θ)/λ] = 0.60 Å^{-1}, 5445 independent (R_{int} = 0.070) and 4230 observed reflections [$I \ge 2\,\sigma(I)$], 470 refined parameters, R = 0.049, wR^2 = 0.123, max (min) residual electron density 0.25 (−0.33) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

NMR-Scale Reactions. (a) Heating of $B(C_6F_5)_3$ (**1**) (81.0 mg, 0.159 mmol) and **3c** (40.2 mg, 0.159 mmol) in toluene-d_8 (1 mL) for 2 h at 105 °C resulted in a reaction mixture of **4c** and **6** in a 5:1 ratio (monitored by ^{31}P NMR). Continuing heating (105 °C) for an additional 48 h did not change the **4c**/**6** ratio (5:1). (b) Heating of a light-protected sample of $B(C_6F_5)_3$ (**1**) (83.2 mg, 0.163 mmol) and **3c** (41.0 mg, 0.163 mmol) in toluene-d_8 (1 mL) for 6 h at 105 °C resulted in a reaction mixture of **4c** and **6** in a 5:1 ratio (monitored by ^{31}P NMR). The control experiment without light protection, reacting $B(C_6F_5)_3$ (**1**) (82.2 mg, 0.161 mmol) and **3c** (40.5 mg, 0.161 mmol) in toluene-d_8 (1 mL) for 6 h at 105 °C also resulted in a reaction mixture of **4c** and **6** in a 5:1 ratio. For **6**: ^1H NMR (500 MHz, 298 K, C_7D_8): δ = 7.29 (m, 4H, *o*-Ph), 7.07 (m, 2H, *p*-Ph), 6.94 (m, 4H, *m*-Ph), 2.87 (m, 2H, ═CH_2), 1.25 (m, 2H, CH_2), 0.49 (t, $^3J_{HH}$ = 7.3 Hz 3H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, 298 K, C_7D_8): δ = 179.4 (br, ═C^B), 135.9 (d, $^4J_{PC}$ = 3.3 Hz *p*-Ph), 133.3 (d, $^2J_{PC}$ = 11.5 Hz, *o*-Ph), 130.7 (d, $^3J_{PC}$ =13.1 Hz, *m*-Ph), 127.9 (d, $^1J_{PC} \approx$ 65 Hz, ═C^P; from the ghmbc experiment), 115.4 (d, $^1J_{PC}$ = 83.0 Hz, *i*-Ph), 30.7 (t, J = 13.9 Hz, ═CH_2), 24.7 (t, J = 2.8 Hz, CH_2), 13.95 (CH_3) [C_6F_5 not listed]. $^{19}F\{^1H\}$ NMR (470 MHz, 298 K, C_7D_8): δ = −123.8 (br s, 1F, C_6F_4), −129.3 (m, 1F, C_6F_4), −132.8 (m, 4F, *o*-BC_6F_5), −139.9 (m, 1F, C_6F_4), −151.5 (m, 1F, C_6F_4), −160.1 (t, $^3J_{FF}$ = 20.5 Hz, 2F, *p*-BC_6F_5), −165.4 (m, 4F, *m*-BC_6F_5), −184.4 (br m, 1F, B−F) [$\Delta\delta^B(m,p)$ = 5.3]. $^{11}B\{^1H\}$ NMR (160 MHz, 298 K, C_7D_8): δ = 0.6 ($\nu_{1/2} \approx$ 140 Hz). $^{31}P\{^1H\}$ NMR (202 MHz, 298 K, C_7D_8): δ = 33.9 ($\nu_{1/2} \approx$ 20 Hz). (c) Heating of $B(C_6F_5)_3$ (**1**) (82.2 mg, 0.161 mmol) and **3c** (40.5 mg, 0.161 mmol) in toluene-d_8 (1 mL) for 3 h at 105 °C by simultaneous irradiation (Heraeus Nolelight HPK 125 W, Pyrex filter) resulted in a reaction mixture of **4c** and **6** in a 5:1 ratio (monitored by ^{31}P NMR).

Synthesis of Compound 4d. $B(C_6F_5)_3$ (**1**) and **3d** (35.5 mg, 0.09 mmol) were dissolved in toluene (20 mL) and stirred for 9 h at 80 °C. Subsequently toluene was removed, and the residue was washed twice with pentane. The solid was dissolved in less toluene to let the impurities precipitate overnight at room temperature. Afterward the toluene solution

was separated. Removal of all volatiles in vacuo yielded **4d** (0.174 g, 0.19 mmol, 60%) as a white-yellow solid. Crystals suitable for X-ray crystal structure analysis were grown by slow diffusion of pentane into a solution of **4d** in dichloromethane at −36 °C. HRMS: calcd for $BP_2H_{20}C_{44}F_{15}H$, 907.09740; found, 907.10066. IR (ATR): $\tilde{\nu}/cm^{-1}$ = 2383 (br w), 2313 (w), 1646 (w), 1515 (m), 1464 (s), 1384 (w), 1092 (s), 970 (s), 901 (m), 740 (s), 690 (s). Mp (DSC): 258 °C. ^{1}H NMR (500 MHz, 298 K, C_7D_8): δ = 7.26 (m, 2H, *o*-Ph^P), 7.10 (m, 2H, *o*-Ph^{P+}), 6.83 (m, 1H, *p*-Ph^{P+}), 6.71 (m, 3H, *p*-Ph^P, *m*-Ph^{P+}), 6.66 (m, 2H, *m*-Ph^P). ^{13}C{^{1}H} NMR (126 MHz, 298 K, C_7D_8): δ = 173.7 (br, ^{B}C=), 146.4 (dd, $^1J_{PC}$ = 53.0 Hz, $^1J_{PC}$ = 32.7 Hz, =C^P), 135.0 (d, $^2J_{PC}$ = 22.8 Hz, *o*-Ph^{P+}), 133.1 (d, $^2J_{PC}$ = 10 Hz, *o*-Ph^P), 132.5 (dd, $^1J_{PC}$ = 9.5 Hz, $^3J_{PC}$ = 3.3 Hz, *i*-Ph^{P+}), 132.1 (d, $^4J_{PC}$ = 3.0 Hz, *p*-Ph), 129.9 (d, $^4J_{PC}$ = 1.0 Hz, *p*-Ph^{P+}), 128.8 (d, $^3J_{PC}$ = 11.3 Hz, *m*-Ph^P), 128.7 (d, $^3J_{PC}$ = 9.1 Hz, *m*-Ph^{P+}), 124.8 (d, $^1J_{PC}$ = 44.3 Hz, *i*-Ph^P) [C_6F_5 not listed]. ^{19}F{^{1}H} NMR (470 MHz, 298 K, C_7D_8): δ = −128.8 (m, 4F, *o*-BC_6F_5), −138.0 (m, 2F, *o*-C_6F_5), −156.2 (t, $^3J_{FF}$ = 21.3 Hz, 1F, *p*-C_6F_5), −156.4 (t, $^3J_{FF}$ = 21.3 Hz, 2F, *p*-BC_6F_5), −163.1 (m, 2F, *m*-C_6F_5), −163.7 (m, 4F, *m*-BC_6F_5) [$\Delta\delta^B(m,p)$ = 7.3]. ^{11}B{^{1}H} NMR (160 MHz, 298 K, C_7D_8): δ = −5 ($\nu_{1/2} \approx$ 230 Hz). ^{31}P{^{1}H} NMR (202 MHz, 298 K, C_7D_8): δ = −6.3 (td, J_{PF} = 28.4 Hz, $^2J_{PP+}$ = 10.3 Hz, P), 24.2 (br, $\nu_{1/2} \approx$ 70 Hz, P$^+$).

X-ray crystal structure analysis of **4d**: formula $C_{44}H_{20}BF_{15}P_2 \cdot CH_2Cl_2$, M = 991.28, colorless crystal 0.10 × 0.10 × 0.04 mm, a = 9.7976(2), b = 10.8460(4), and c = 21.1870(7) Å, α = 95.231(2), β = 102.492(2), and γ = 104.305(2)°, V = 2104.94(11) Å^3, ρ_{calc} = 1.564 g cm^{-3}, μ = 3.023 mm^{-1}, empirical absorption correction (0.752 ≤ T ≤ 0.889), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ= 1.54178 Å, T = 223(2) K, ω and φ scans, 25 965 reflections collected (±h,±k,±l), [(sinθ)/λ] = 0.60 Å^{-1}, 6932 independent (R_{int} = 0.110) and 4337 observed reflections [$I \geq 2\,\sigma(I)$], 596 refined parameters, R = 0.077, wR^2 = 0.224, max (min) residual electron density 0.70 (−0.82) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Synthesis of Compound 7. Heating of a solution of **4d** (0.08 mmol, 72.4 mg) in toluene for 3d at 105 °C followed by cooling at room temperature gave the precipitated product **7** (0.028 mmol, 25.1 mg, 35%) as orange crystals. These crystals were suitable for X-ray analysis, after filtration via cannula and washing with very small amount of toluene. HRMS: calcd for $C_{44}H_{20}BF_{15}P_2H$, 907.09665; found, 907.09354. IR (ATR): $\tilde{\nu}/cm^{-1}$ = 1666 (w), 1588 (w), 1514 (m), 1493 (m), 1453 (s), 1379 (w), 1274 (m), 1091 (br s), 955 (m), 743 (s), 691 (s). Decomp (DSC): 276 °C. ^{1}H NMR (500 MHz, 298 K, CD_2Cl_2): δ = 7.82 (m, 2H, *p*-Ph^{P+}), 7.64 (m, 4H, *m*-Ph^{P+}), 7.62 (m, 4H, *o*-Ph^{P+}), 7.19 (m, 4H, *o*-Ph^P), 7.11 (m, 2H, *p*-Ph^P), 6.92 (m, 4H, *m*-Ph^P). ^{13}C{^{1}H} NMR (126 MHz, 298 K, CD_2Cl_2): δ = 189.7 (br, =C^B), 135.8 (d, $^4J_{PC}$ = 2.5 Hz, *p*-Ph^{P+}), 135.7 (d, $^2J_{PC}$ = 23.2 Hz, *o*-Ph^P), 133.6 (d, $^2J_{PC}$ = 12.3 Hz, *o*-Ph^{P+}), 130.8 (d, $^3J_{PC}$ = 13.3 Hz, *m*-Ph^{P+}), 129.5 (d, $^4J_{PC}$ = 0.8 Hz, *p*-Ph^P), 128.2 (d, $^3J_{PC}$ = 8.4 Hz, *m*-Ph^P), 115.5 (d, $^1J_{PC}$ = 84.6 Hz, *i*-Ph^{P+}) [=C^P, *i*-Ph^P not observed; C_6F_4, C_6F_5 not listed]. ^{19}F{^{1}H} NMR (470 MHz, 298 K, CD_2Cl_2): δ = −123.5 (br, 1F, C_6F_4), −129.5 (m, 1F, C_6F_4), −133.3 (m, 4F, *o*-BC_6F_5), −141.8 (m, 1F, C_6F_4), −152.4 (m, 1F, C_6F_4), −161.1 (t, $^3J_{FF}$ = 20.5 Hz, 2F, *p*-BC_6F_5), −166.2 (m, 4F, *m*-BC_6F_5), −171.5 (br, 1F, B−F) [$\Delta\delta^B(m,p)$ = 5.1]. ^{11}B{^{1}H} NMR (160 MHz, 298 K, CD_2Cl_2): δ = 0.3 ($\nu_{1/2} \approx$ 150 Hz). ^{31}P{^{1}H} NMR (202 MHz, 298 K, CD_2Cl_2): δ = 39.1 ($\nu_{1/2} \approx$ 30 Hz, P$^+$), −2.5 (dd, J_{PF} = 177.8 Hz, $^2J_{PP+}$ = 7.1 Hz, P).

X-ray crystal structure analysis of **7**: formula $C_{44}H_{20}BF_{15}P_2 \cdot C_7H_8$, M = 998.48, orange crystal 0.30 × 0.23 × 0.15 mm, a = 10.4606(4), b = 13.1363(5), and c = 16.4911(7) Å, α = 91.614(2), β = 103.553(2), and γ = 95.609(3)°, V = 2189.39(15) Å^3, ρ_{calc} = 1.515 g cm^{-3}, μ = 1.816 mm^{-1}, empirical absorption correction (0.612 ≤ T ≤ 0.772), Z = 2, triclinic, space group $P\bar{1}$ bar (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 29 350 reflections collected (±h,±k,±l), [(sin θ)/λ] = 0.60 Å^{-1}, 7643 independent (R_{int} = 0.043) and 7024 observed reflections [$I \geq 2\,\sigma(I)$], 610 refined parameters, R = 0.050, wR^2 = 0.142, max (min) residual electron density 0.79 (−0.55) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

■ ASSOCIATED CONTENT

Supporting Information. Additional experimental and spectroscopic details and X-ray crystallographic data (CIF) for **4a**, **4c**, **4d**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
erker@uni-muenster.de

■ ACKNOWLEDGMENT

Financial support from the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

■ REFERENCES

(1) (a) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890–931.(b) Shi, F.; Larock, R. C. In *Topics in Current Chemistry*; Springer-Verlag: Berlin Heidelberg, 2010; Vol. 292, pp 123−164.

(2) (a) Balcells, D.; Clot, E.; Eisenstein, O. *Chem. Rev.* **2010**, *110*, 749–823. (b) Giri, R.; Shi, B.-F.; Engle, K. M.; Maugel, N.; Yu, J.-Q. *Chem. Soc. Rev.* **2009**, *38*, 3242–3272.

(3) (a) Amii, H.; Uneyama, K. *Chem. Rev.* **2009**, *109*, 2119–2183. (b) Burdeniuc, J.; Jedlicka, B.; Crabtree, R. H. *Chem. Ber./Recl.* **1997**, *130*, 145–154. (c) Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev.* **1994**, *94*, 373–431.

(4) (a) Chaplin, A. B.; Weller, A. S. *Organometallics* **2010**, *29*, 2332–2342. (b) Li, T.; García, J. J.; Brennessel, W. W.; Jones, W. D. *Organometallics* **2010**, *29*, 2430–2445. (c) Gunay, A.; Jones, W. D. *J. Am. Chem. Soc.* **2007**, *129*, 8729–8735. (d) Jones, W. D. *Nature* **1993**, *364*, 676–677.

(5) Chen, C.; Kehr, G.; Fröhlich, R.; Erker, G. *J. Am. Chem. Soc.* **2010**, *132*, 13594–13595.

(6) (a) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245–250. (b) Massey, A. G.; Park, A. J.; Stone, F. G. A. *Proc. Chem. Soc., London* **1963**, 212–213.

(7) Spence, R. E. v. H.; Piers, W. E.; Sun, Y.; Parvez, M.; MacGillivray, L. R.; Zaworotko, M. J. *Organometallics* **1998**, *17*, 2459–2469.

(8) (a) Parks, D. J.; Piers, W. E. *Tetrahedron* **1998**, *54*, 15469–15488; (b) Parks, D. J.; Spence, R. E. v. H.; Piers, W. E. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 809–811; *Angew. Chem.* **1995**, *107*, 895–897. (c) Spence, R. E. v. H.; Piers, W. E. *Organometallics* **1995**, *14*, 4617–4624.

(9) (a) Chen, C.; Voss, T.; Fröhlich, R.; Kehr, G.; Erker, G. *Org. Lett.* **2010**, *13*, 62–65. (b) Chen, C.; Fröhlich, R.; Kehr, G.; Erker, G. *Chem. Commun.* **2010**, *46*, 3580–3582. (c) Wrackmeyer, B.; Tok, O. L.; Klimkina, E. V.; Milius, W. *Eur. J. Inorg. Chem.* **2010**, 2276–2282. (d) Dierker, G.; Ugolotti, J.; Kehr, G.; Fröhlich, R.; Erker, G. *Adv. Synth. Catal.* **2009**, *351*, 1080–1088. (e) Khan, E.; Bayer, S.; Kempe, R.; Wrackmeyer, B. *Eur. J. Inorg. Chem.* **2009**, 4416–4424. (f) Wrackmeyer, B. *Heteroat. Chem.* **2006**, *17*, 188–208 and references cited therein. (g) Wrackmeyer, B. *Coord. Chem. Rev.* **1995**, *145*, 125–156.

(10) (a) Chen, C.; Eweiner, F.; Wibbeling, B.; Fröhlich, R.; Senda, S.; Ohki, Y.; Tatsumi, K.; Grimme, S.; Kehr, G.; Erker, G. *Chem. Asian J.* **2010**, *5*, 2199–2208. (b) Jiang, C.; Blacque, O.; Berke, H. *Organometallics* **2010**, *29*, 125–133.

(11) (a) Fan, C.; Mercier, L. G.; Piers, W. E.; Tuononen, H. M.; Parvez, M. *J. Am. Chem. Soc.* **2010**, *132*, 9604–9606. (b) Fan, C.; Piers, W. E.; Parvez, M.; McDonald, R. *Organometallics* **2010**, *29*, 5132–5139. (c) Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* **2000**, *65*, 3090–3098.

(12) (a) Boduszek, B.; Halama, A.; Zon, J. *Tetrahedron* **1997**, *53*, 11399–11410. (b) Hammond, P. S.; Kirchner, M. B.; Lieske, C. N. *J. Org. Chem.* **1990**, *55*, 6051–6054. (c) Dubois, R. A.; Garrou, P. E.; Lavin, K. D.; Allcock, H. R. *Organometallics* **1986**, *5*, 460–466. (d) Sakakura, T.; Kobayashi, T. A.; Hayashi, T.; Kawabata, Y.; Tanaka, M.; Ogata, I. *J. Organomet. Chem.* **1984**, *267*, 171–177. (e) Sekine, M.; Satoh, M.; Yamagata, H.; Hata, T. *J. Org. Chem.* **1980**, *45*, 4162–4167. (f) Frank, A. W. *Can. J. Chem.* **1968**, *46*, 3573–3577.

(13) Fukazawa, A.; Yamada, H.; Yamaguchi, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 5582–5585; *Angew. Chem.* **2008**, *120*, 5664–5667.

(14) (a) Spies, P.; Schwendemann, S.; Lange, S.; Kehr, G.; Fröhlich, R.; Erker, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 7543–7546; *Angew. Chem.* **2008**, *120*, 7654–7657. (b) Yuan, Z.; Collings, J. J.; Taylor, N. J.; Marder, T. B.; Jardin, C.; Halet, J.-F. *J. Solid State Chem.* **2000**, *154*, 5–12. (c) Yuan, Z.; Taylor, N. J.; Ramachandran, R.; Marder, T. B. *Appl. Organomet. Chem.* **1996**, *10*, 305–316. (d) Yuan, Z.; Taylor, N. J.; Sun, Y.; Marder, T. B.; Williams, I. D.; Cheng, L.-T. *J. Organomet. Chem.* **1993**, *449*, 27–37. (e) Yuan, Z.; Taylor, N. J.; Marder, T. B.; Williams, I. D.; Kurtz, S. K.; Cheng, L.-T. *J. Chem. Soc., Chem. Commun.* **1990**, 1489–1492.

(15) (a) Lambert, J. B.; So, J.-H. *J. Org. Chem.* **1991**, *56*, 5960–5964. (b) Bartlett, R. A.; Olmstead, M. M.; Power, P. P.; Siegel, G. A. *Inorg. Chem.* **1987**, *26*, 1941–1946. (c) Goldwhite, H.; Kaminski, J.; Millhauser, G.; Ortiz, J.; Vargas, M.; Vertal, L. *J. Organomet. Chem.* **1986**, *310*, 21–25.

(16) See for comparison: (a) Axenov, K. V.; Mömming, C. M.; Kehr, G.; Fröhlich, R.; Erker, G. *Chem.—Eur. J.* **2010**, *16*, 14069–14073. (b) Spies, P.; Erker, G.; Kehr, G.; Bergander, K.; Fröhlich, R.; Grimme, S.; Stephan, D. W. *Chem. Commun.* **2007**, 5072–5074.

(17) (a) Beringhelli, T.; Donghi, D.; Maggioni, D.; D'Alfonso, G. *Coord. Chem. Rev.* **2008**, *252*, 2292–2313. (b) Piers, W. E. *Adv. Organomet. Chem.* **2005**, *52*, 1–76. (c) Jacobson, H.; Berke, H.; Döring, S.; Kehr, G.; Erker, G.; Fröhlich, R.; Meyer, O. *Organometallics* **1999**, *18*, 1724–1735. (d) See for comparison: Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1966**, *5*, 218–223.

(18) See for comparison: (a) Ullrich, M.; Lough, A. J.; Stephan, D. W. *Organometallics* **2010**, *29*, 3647–3654. (b) Spies, P.; Fröhlich, R.; Kehr, G.; Erker, G.; Grimme, S. *Chem.—Eur. J.* **2008**, *14*, 333–343. (c) Bradley, D. C.; Hursthouse, M. B.; Motevalli, M.; Dao-Hong, Z. *J. Chem. Soc., Chem. Commun.* **1991**, 7–8.

(19) (a) Vagedes, D.; Erker, G.; Kehr, G.; Bergander, K.; Kataeva, O.; Fröhlich, R.; Grimme, S.; Mück-Lichtenfeld, C. *Dalton Trans.* **2003**, 1337–1344. (b) Vagedes, D.; Erker, G.; Kehr, G.; Fröhlich, R.; Grimme, S.; Mück-Lichtenfeld, C. *Z. Naturforsch.* **2003**, *58b*, 305–310. (c) Vagedes, D.; Kehr, G.; König, D.; Wedeking, K.; Fröhlich, R.; Erker, G.; Mück-Lichtenfeld, C.; Grimme, S. *Eur. J. Inorg. Chem.* **2002**, 2015–2021. (d) Vagedes, D.; Erker, G.; Fröhlich, R. *J. Organomet. Chem.* **2002**, *641*, 148–155.

(20) Synthesis of the lithium salt: Kang, Y. K.; Deria, P.; Caroll, P. J.; Therien, M. J. *Org. Lett.* **2008**, *10*, 1341–1344. Modified procedure: Miller, A. D.; Johnson, S. A.; Tupper, K. A.; Mc Bee, J. L.; Tilley, T. D. *Organometallics* **2009**, *28*, 1252–1262. See also:Anderson, D. M.; Hitchcock, P. B.; Lappert, M. F. *J. Organomet. Chem.* **1989**, *363*, C7–C11.

(21) Di-*tert*-butylphosphinylacetylene reacts in a different way with $ClB(C_6F_5)_2$: (a) Zhao, X.; Otten, E.; Song, D.; Stephan, D. W. *Chem.—Eur. J.* **2010**, *16*, 2040–2044. (b) Zhao, X.; Gilbert, T. M.; Stephan, D. W. *Chem.—Eur. J.* **2010**, *16*, 10304–10308.

(22) (a) Balueva, A. S.; Mustakimov, E. R.; Nikonov, G. N.; Struchkov, Y. T.; Pisarevsky, A. P.; Musin, R. R. *Russ. Chem. Bull.* **1996**, *45*, 174–179; *Izv. Akad. Nauk, Ser. Khim.* **1996**, 183–187; (b) Balueva, A. S.; Nikonov, G. N. *Russ. Chem. Bull.* **1993**, *42*, 341–343; *Izv. Akad. Nauk, Ser. Khim.* **1993**, 378–380; (c) Arbuzov, B. A.; Nikonov, G. N.; Balueva, A. S.; Kamalov, R. M.; Stepanov, G. S.; Pudovik, M. A.; Litvinov, I. A.; Lenstra, A. T. H.; Geise, H. J. *Russ. Chem. Bull.* **1992**, *41*, 1266–1271; *Izv. Akad. Nauk, Ser. Khim.* **1992**, 1638–1644; (d) Nikonov, G. N.; Balueva, A. S. *Russ. Chem. Rev.* **1992**, *61*, 335; *Usp. Khim.* **1992**, *61*, 616–646; (e) Valueva, A. S.; Nikonov, G. N.; Kamalov, R. M.; Khailova, N. A.; Pudovik, M. A. *Russ. Chem. Bull.* **1991**, *40*, 1088–1090; *Izv. Akad. Nauk SSSR, Ser. Khim.* **1991**, 1209–1211; (f) Balueva, A. S.; Nikonov, G. N.; Vul'fson, S. G.; Sarvarova, N. N.; Arbuzov, B. A. *Russ. Chem. Bull.* **1990**, *39*, 2367–2370; *Izv. Akad. Nauk SSSR, Ser. Khim.* **1990**, 2613–2616; (g) Troepol'skaya, T. V.; Ermolaeva, L. V.; Vagina, G. A.; Balueva, A. S.; Erastov, O. A. *Russ. Chem. Bull.* **1990**, *39*, 17–20; *Izv. Akad. Nauk SSSR, Ser. Khim.* **1990**, 24–27; (h) Balueva, A. S.; Efremov, Y. Y.; Nekhoroshkov, V. M.; Erastov, O. A. *Russ. Chem. Bull.* **1989**, *38*, 2557–2560; *Izv. Akad. Nauk SSSR, Ser. Khim.* **1989**, 2793–2796; (i) Balueva, A. S.; Erastov, O. A.; Zyablikova, T. A. *Russ. Chem. Bull.* **1989**, *38*, 882; *Izv. Akad. Nauk SSSR, Ser. Khim.* **1989**, 975–976; (j) Balueva, A. S.; Erastov, O. A. *Russ. Chem. Bull.* **1988**, *37*, 151–153; *Izv. Akad. Nauk SSSR, Ser. Khim.* **1988**, 163–165; (k) Balueva, A. S.; Erastov, O. A. *Russ. Chem. Bull.* **1987**, *36*, 1113; *Izv. Akad. Nauk SSSR, Ser. Khim.* **1987**, 1199–1200. (l) Binger, P.; Köster, R. *J. Org. Chem.* **1974**, *73*, 205–210.

(23) See also: Grobe, J.; Lütke-Brochtrup, K.; Krebs, B.; Läge, M.; Niemeyer, H.-H.; Würthwein, E.-U. *Z. Naturforsch.* **2006**, *61b*, 882–895.

(24) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

(25) (a) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307–326. (b) Otwinowski, Z.; Borek, D.; Majewski, W.; Minor, W. *Acta Crystallogr.* **2003**, *A59*, 228–234. (c) Sheldrick, G.M. *Acta Crystallogr.* **1990**, *A46*, 467–473. (d) Sheldrick, G.M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

(26) Miller, A. D.; Johnson, S. A.; Tupper, K. A.; McBee, J. L.; Tilley, T. D. *Organometallics* **2009**, *28*, 1252–1262. See also:Samb, A.; Demerseman, B.; Dixneuf, P. H.; Mealli, C. *Organometallics* **1988**, *7*, 26–33.

(27) See also: Beletskaya, I. P.; Afanasiev, V. V.; Kazankova, M. A.; Efimova, I. V. *Org. Lett.* **2003**, *5*, 4309–4311.