Formation of Allenes by 1,4-Addition of Intermolecular Phosphane/Borane Frustrated Lewis Pairs to a Conjugated Enyne

Philipp Feldhaus, Birgit Wibbeling, Roland Fröhlich, Constantin G. Daniliuc, Gerald Kehr, Gerhard Erker*

Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, Correnstr. 40, 48149 Münster, Germany
Fax +49(251)8336503; E-mail: erker@uni-muenster.de

Received: 04.02.2014; Accepted: 04.03.2014

Abstract: The *t*-$Bu_3P/B(C_6F_5)_3$ frustrated Lewis pair (**6a**) undergoes competing acetylene deprotonation (to give the phosphonium–alkenylborate salt **8**) and 1,4-P/B FLP addition to the conjugated enyne 2-methylbutenyne to yield the zwitterionic allene derivative **9a**. The less basic (*o*-tolyl)$_3P/B(C_6F_5)_3$ system (**6b**) avoids the acetylene deprotonation pathway. The zwitterionic allene derivative **9b** formed by 1,4-P/B FLP addition to the enyne is again a prominent reaction product; here competing 1,2-addition is observed to give the olefinic product **10**. The allene derivatives **9a** and **9b** and their competing products **8** and **10** were characterized by X-ray diffraction.

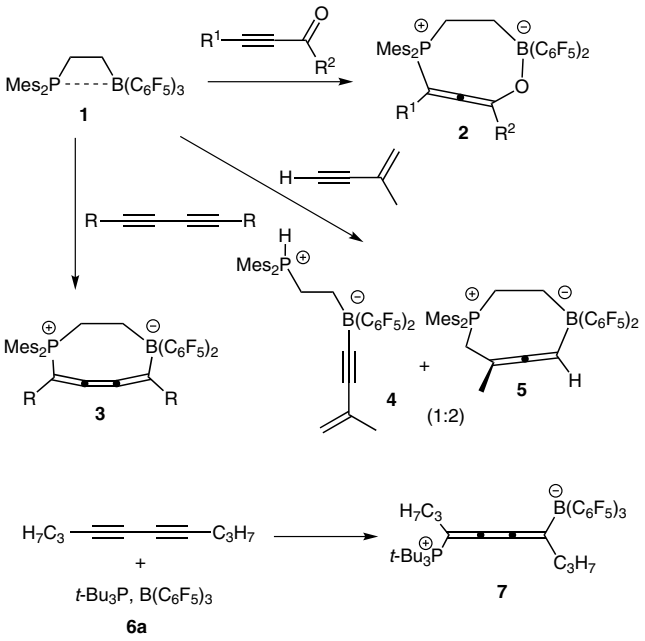
Key words: phosphorus, boron, Lewis pairs, allenes

Frustrated Lewis pairs (FLPs) evade strong mutual adduct formation by steric bulk[1] (sometimes by electronic means).[2] The pair of, for example, coexistent phosphane and borane in solution can then undergo cooperative reactions with a variety of small molecules. Activation of dihydrogen by heterolytic dissociation to give a phosphonium–hydrido borate pair is a most prominent case.[3,4] It has provided the basis for the development of a variety of metal-free catalytic hydrogenation processes.[5] FLPs were shown to react with CO_2,[6] SO_2,[7] nitrogen oxides,[8] CO,[9] isonitriles,[10] etc. Many FLPs add to alkenes or alkynes, with 1-alkynes sometimes competing deprotonation and formation of phosphonium–alkynyl borate salts was observed.[11]

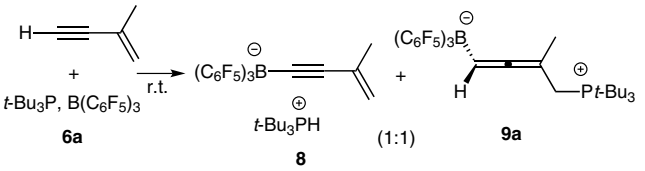
We have previously shown that the reactive intramolecular ethylene-bridged FLP **1** often undergoes 1,4-addition reactions to unsaturated substrates. This was observed when **1** was treated with conjugated ynones,[12] but also upon exposure of **1** to a small series of conjugated diynes and to a conjugated enyne (Scheme 1). In the latter case some competing acetylene deprotonation was also observed.[13] We had begun to investigate some analogous reactions of intermolecular FLPs. We had initially found that the *t*-$Bu_3P/B(C_6F_5)_3$ pair (**6a**) undergoes trans-1,4-addition to 4,6-decadiyne (to yield **7**); with the less bulky 2,4-hexadiyne we observed the formation of a mixture of 1,2- (predominant) and 1,4-addition.[14]

We have now treated the intermolecular FLP *t*-$Bu_3P/B(C_6F_5)_3$ (**6a**) and (*o*-tolyl)$_3P/B(C_6F_5)_3$ (**6b**) with the conjugated enyne 2-methylbutenyne and found some closely related behavior.

The *t*-$Bu_3P/B(C_6F_5)_3$ FLP (**6a**) was treated with a stoichiometric amount of 2-methylbutenyne in dichloromethane solution at ambient temperature (24 h). The NMR spectra of the crude mixture showed the formation of the deprotonation product **8** and the product of 1,4-FLP addition to the conjugated π-system to give the zwitterionic allene derivative **9a** in a ca. 1:1 ratio (Scheme 2). We noted that the mixture contained more than the expected quantity of the *t*-Bu_3PH^+ cation without any additional detectable anion. We assume that some hydrolysis had taken place. The products **8** (33%) and **9a** (21%) could be separated by column chromatography and isolated. Both products were characterized by spectroscopy and by X-ray diffraction.



Scheme 1



Scheme 2

SYNLETT 2014, 25, 1529–1533
Advanced online publication: 11.04.2014
DOI: 10.1055/s-0033-1341071; Art ID: ST-2014-B0098-C

The salt **8** shows a ^{11}B NMR resonance at δ = –21.0. It features ^{19}F NMR signals at δ = –132.6 (*o*), –164.0 (*p*), and –167.4 (*m* of C_6F_5) with a small $\delta^{19}F_{m,p}$ = 3.4 ppm chemical shift difference that is typical for a $RB(C_6F_5)_3^-$ borate situation. The anion of **8** shows ^{1}H NMR signals of the terminal $C(CH_3)=CH_2$ group at δ = 4.97/4.92, and 1.82 (CH_3) ppm. It shows ^{13}C NMR signals of the conjugated enyne moiety at δ = 95.4 [≡C; δ(B^{13}C≡) not observed], 130.8 and 116.8 (=CH_2) ppm.

The X-ray crystal structure analysis of compound **8** (Figure 1) has confirmed that a proton had been abstracted by the phosphane and the enynyl group had become attached to the $(C_6F_5)_3B$ unit. The central B1 to C3 framework is linear [B1–C1: 1.582(5) Å, C1–C2: 1.201(4) Å, C2–C3: 1.442(5) Å, angles B1–C1–C2: 174.9(3)°, C1–C2–C3: 175.7(4)°]. It features the –$C(CH_3)=CH_2$ moiety at its end [C3–C4: 1.351(5) Å, angle C2–C3–C4: 121.2(3)°].

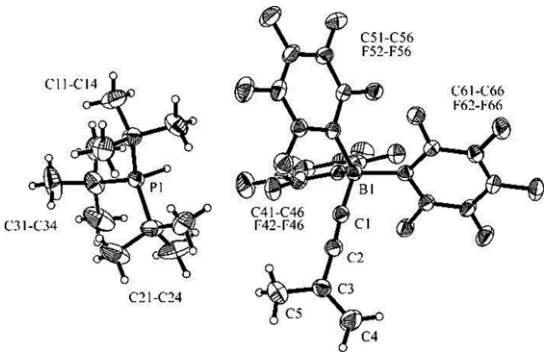


Figure 1 Molecular structure of the salt **8** (thermal ellipsoids are shown with 30% probability)

The allene product **9a** shows a typical =C= ^{13}C NMR resonance[15] at δ = 207.1 ppm with a small $^3J_{PC}$ coupling constant of 6.7 Hz. The adjacent sp^2 carbon atoms of the allene unit give rise to ^{13}C NMR signals at δ = 98.5 (=CHB) and 80.0 ppm, respectively, with corresponding ^{1}H NMR signals at δ = 5.94 (=CHB), 3.13/2.26 {CH_2[P]} and 1.66 (CH_3) ppm. The zwitterionic compound **9a** shows heteronuclear magnetic resonance signals at δ = 49.2 (^{31}P) and –15.6 (^{11}B) ppm, respectively.

The X-ray crystal structure analysis of **9a** features the central allene unit that was formed by 1,4-addition of the P/B FLP to the conjugated enyne [C2–C3: 1.315(7) Å, C3–C4: 1.295(6) Å, angle C2–C3–C4: 174.9(5)°]. It shows the typical perpendicular arrangements of the substituent vectors at the allene termini [B1–C4: 1.628(7) Å, dihedral angle B1–C4···C2–C1: –85.4°] (Figure 2). The P1–C1 bond length in compound **9a** amounts to 1.818(6) Å.[16]

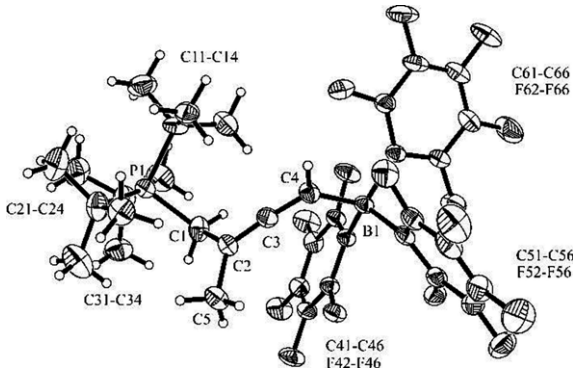
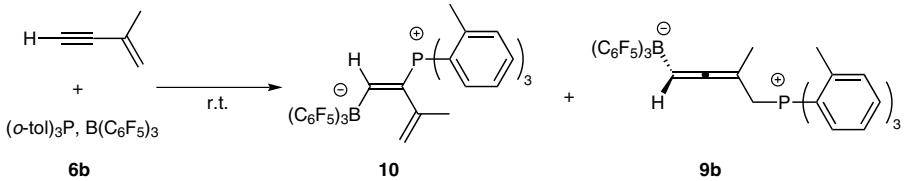


Figure 2 A view of the molecular structure of the allene product **9a** (thermal ellipsoids are shown with 30% probability)

We then treated the 2-methylbutenyne reagent with the $(o\text{-tol})_3P/B(C_6F_5)_3$ FLP. The bulky triarylphosphane is less basic than the previously used *t*-Bu_3P Lewis base. Therefore, we did not observe the formation of the acetylene deprotonation product any more. After 24 hours at room temperature the reaction was complete and we monitored the formation of a ca. 3:4 mixture of the 1,2- and 1,4-P/B FLP addition products **10** and **9b** (Scheme 3). The products were separated by chromatography and crystallization and isolated in 20% (**10**) and 33% (**9b**) yield, respectively. Both compounds were characterized by spectroscopy and by X-ray diffraction.

The 1,2-addition product **10** shows a ^{11}B NMR signal at δ = –16.2 ppm and a ^{31}P NMR signal at δ = 23.4 ppm. The ^{19}F NMR $\Delta\delta^{19}F_{m,p}$ = 4.4 ppm chemical shift difference is in the typical $RB(C_6F_5)_3^-$ borate range. The ^{13}C NMR spectrum (233 K) of compound **10** shows resonances of the central [B]–CH=C[P] unit at δ = 181.2 {[B]–CH= ^{1}H NMR signal at δ = 8.27 ppm} and 124.8 ($^1J_{PC}$ = 64.7 Hz) ppm, respectively. The adjacent –$C(CH_3)=CH_2$ substituent shows ^{1}H NMR signals at δ = 4.97/4.58 (with corresponding ^{13}C NMR signals at δ = 139.3 and 122.6 ppm) and 0.88 (CH_3) ppm, respectively.

The X-ray crystal structure analysis has confirmed the *trans*-1,2-P/B FLP addition to the C≡C triple bond of the enyne to generate compound **10**. It shows typical bonding features of the central *E*-configured trisubstituted C=C double bond [B1–C2: 1.646(3) Å, C2–C1: 1.344(3) Å, C1–P1: 1.828(2) Å, bond angles B1–C2–C1: 132.5(2)°, C2–C1–P1: 118.5(2)°]. Both, the boron atom B1 and the phosphorus atom P1 show pseudotetrahedral coordination geometries (Figure 3). Carbon atom C1 bears the remain-



Scheme 3

ing –C(CH$_3$)=CH$_2$ substituent [C1–C3: 1.499(3) Å, C3–C4: 1.349(3) Å, C3–C5: 1.481(3) Å, angle C1–C3–C4: 118.1(2)°].

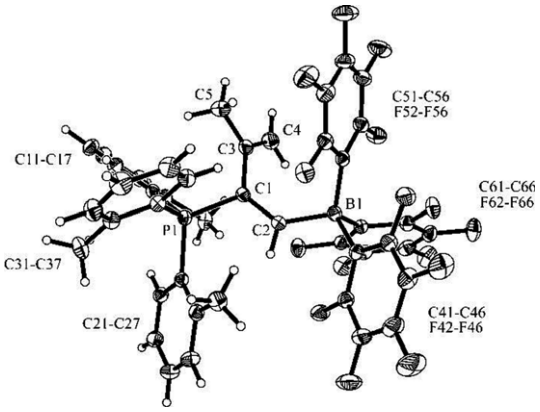


Figure 3 Molecular structure of the 1,2-P/B FLP addition product to 2-methylbutenyne **10** (thermal ellipsoids are shown with 30% probability)

The X-ray crystal structure analysis of the 1,4-P/B FLP addition product **9b** shows the typical allene core [C4–C3: 1.294(5) Å, C3–C2: 1.322(5) Å, angle C2–C3–C4: 175.9(3)°] to which the B(C$_6$F$_5$)$_3$ group [B1–C4: 1.641(6) Å] is bonded at the terminal carbon atom and the methyl substituent and the CH$_2$P(*o*-tolyl)$_3^+$ group is found attached at the other allene terminus [C2–C5: 1.516(5) Å, C2–C1: 1.521(5) Å, C1–P1 1.820(3) Å, angle C1–C2–C5: 113.9(3)°, dihedral angle B1–C4···C2–C1: 98.1°]. Both, the boron atom B1 and the phosphorus atom P1 show pseudotetrahedral coordination geometries in the zwitterionic borate–phosphonium product **9b** (Figure 4).

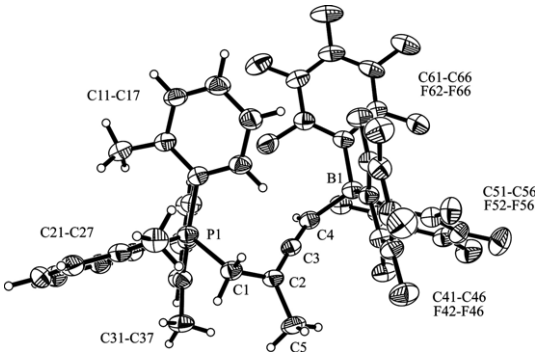


Figure 4 Molecular structure of compound **9b** (thermal ellipsoids are shown with 30% probability)

In solution compound **9b** shows ^{11}B and ^{31}P NMR resonances at δ = –15.7 and 25.4 ppm, respectively. The compound shows a typical central =C= allene C(sp) ^{13}C NMR signal at δ = 206.7 ppm (with $^3J_{PC}$ = 9.2 Hz coupling constant). The ^{13}C NMR signal of the adjacent allene [B]–C(sp^2)(H)= unit appears at δ = 99.2 ppm as a typical 1:1:1:1 intensity quartet ($^1J_{BC}$ = ca. 50 Hz). The corresponding allenic ^{1}H NMR resonance occurs at δ = 5.55 ppm. The ^{13}C NMR signal of the remaining allene terminus was located at δ = 80.7 ppm.[17]

The intramolecular P/B FLP **1** has a pronounced tendency of undergoing 1,4-addition reactions to conjugated π systems. The cyclic allene **5** is actually the major product of the reaction of **1** with 2-methylbutenyne, although a minor product **4** was obtained originating from acetylene deprotonation. The intermolecular P/B FLPs **6a** and **6b** react similarly albeit with a slightly lower selectivity. In both cases there is a pronounced tendency of 1,4-P/B addition to the conjugated enyne 2-methylbutenyne. In both cases the corresponding allene (**9a**,**b**) is a prominent product. Not unexpectedly, the rather basic *t*-Bu$_3$P Lewis base gives rise to a competing formation of the phosphonium–alkynylborate salt by the deprotonation route. This type of product seems to be absent in the reaction involving the less basic (*o*-tolyl)$_3$P Lewis base. It seems that the bulkiness of the Lewis base is a determining feature of the 1,2- vs. 1,4-addition reaction. The less basic but also sterically less bulky (*o*-tolyl)$_3$P/(B(C$_6$F$_5$)$_3$ system avoids the deprotonation reaction but allows for the formation of some 1,2-P/B FLP addition product.[14]

Acknowledgment

Financial support from the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Supporting Information for this article is available online at http://www.thieme-connect.com/products/ejournals/journal/10.1055/s-00000083.

References and Notes

(1) Stephan, D. W.; Erker, G. *Angew. Chem. Int. Ed.* **2010**, *49*, 46.
(2) (a) Stute, A.; Kehr, G.; Daniliuc, C. G.; Fröhlich, R.; Erker, G. *Dalton Trans.* **2013**, *42*, 4487. (b) Rosorius, C.; Kehr, G.; Fröhlich, R.; Grimme, S.; Erker, G. *Organometallics* **2011**, *30*, 4211.
(3) (a) Welch, G. C.; San Juan, R. R.; Masuda, J. D.; Stephan, D. W. *Science* **2006**, *314*, 1124. (b) Geier, S. J.; Gilbert, T. M.; Stephan, D. W. *J. Am. Chem. Soc.* **2008**, *130*, 12632.
(4) (a) Spies, P.; Erker, G.; Kehr, G.; Bergander, K.; Fröhlich, R.; Grimme, S.; Stephan, D. W. *Chem. Commun.* **2007**, 5072. (b) Spies, P.; Schwendemann, S.; Lange, S.; Kehr, G.; Fröhlich, R.; Erker, G. *Angew. Chem. Int. Ed.* **2008**, *47*, 7543.
(5) Stephan, D. W.; Erker, G. *Topics Curr. Chem.* **2013**, *332*, 85.
(6) (a) Mömming, C. M.; Otten, E.; Kehr, G.; Fröhlich, R.; Grimme, S.; Stephan, D. W.; Erker, G. *Angew. Chem. Int. Ed.* **2009**, *48*, 6643. (b) Peuser, I.; Neu, R. C.; Zhao, X.; Ulrich, M.; Schirmer, B.; Tannert, J. A.; Kehr, G.; Fröhlich, R.; Grimme, S.; Erker, G.; Stephan, D. W. *Chem. Eur. J.* **2011**, *17*, 9640. (c) Zhao, X.; Stephan, D. W. *Chem. Commun.* **2011**, *47*, 1833. (d) Takeuchi, K.; Stephan, D. W. *Chem. Commun.* **2012**, *48*, 11304.
(7) (a) Sajid, M.; Klose, A.; Birkmann, B.; Liang, L.; Schirmer, B.; Wiegand, T.; Eckert, H.; Lough, A. J.; Fröhlich, R.; Daniliuc, C. G.; Grimme, S.; Stephan, D. W.; Kehr, G.; Erker, G. *Chem. Sci.* **2013**, *4*, 213. (b) Sajid, M.; Kehr, G.; Wiegand, T.; Eckert, H.; Schwickert, C.; Pöttgen, R.;

Cardenas, A. J. P.; Warren, T. H.; Fröhlich, R.; Daniliuc, C. G.; Erker, G. *J. Am. Chem. Soc.* **2013**, *135*, 8882.
(8) (a) Otten, E.; Neu, R. C.; Stephan, D. W. *J. Am. Chem. Soc.* **2009**, *131*, 9918. (b) Cardenas, A. J. P.; Culotta, B. J.; Warren, T. H.; Grimme, S.; Stute, A.; Fröhlich, R.; Kehr, G.; Erker, G. *Angew. Chem. Int. Ed.* **2011**, *50*, 7567. (c) Sajid, M.; Stute, A.; Cardenas, A. J. P.; Culotta, B. J.; Hepperle, J. A. M.; Warren, T. H.; Schirmer, B.; Grimme, S.; Studer, A.; Daniliuc, C. G.; Fröhlich, R.; Petersen, J. L.; Kehr, G.; Erker, G. *J. Am. Chem. Soc.* **2012**, *134*, 10156. (d) Menard, G.; Hatnean, J. A.; Cowley, H. J.; Lough, A. J.; Rawson, J. M.; Stephan, D. W. *J. Am. Chem. Soc.* **2013**, *135*, 6446. (e) Pereira, J. C. M.; Sajid, M.; Kehr, G.; Wright, A. M.; Schirmer, B.; Qu, Z.-W.; Grimme, S.; Erker, G.; Ford, P. C. *J. Am. Chem. Soc.* **2014**, *136*, 513.
(9) (a) Dobrovetsky, R.; Stephan, D. W. *J. Am. Chem. Soc.* **2013**, *135*, 4974. (b) Sajid, M.; Elmer, L.-M.; Rosorius, C.; Daniliuc, C. G.; Grimme, S.; Kehr, G.; Erker, G. *Angew. Chem. Int. Ed.* **2013**, *52*, 2243. (c) Sajid, M.; Lawzer, A.; Dong, W.; Rosorius, C.; Sander, W.; Schirmer, B.; Grimme, S.; Daniliuc, C. G.; Kehr, G.; Erker, G. *J. Am. Chem. Soc.* **2013**, *135*, 18567. (d) Sajid, M.; Kehr, G.; Daniliuc, C. G.; Erker, G. *Angew. Chem. Int. Ed.* **2014**, *53*, 1118.
(10) Ekkert, O.; Miera, G. G.; Wiegand, T.; Eckert, H.; Schirmer, B.; Petersen, J. L.; Daniliuc, C. G.; Fröhlich, R.; Grimme, S.; Kehr, G.; Erker, G. *Chem. Sci.* **2013**, *4*, 2657.
(11) (a) Ullrich, M.; Seto, K. S.-H.; Lough, A. J.; Stephan, D. W. *Chem. Commun.* **2009**, 2335. (b) Dureen, M. A.; Stephan, D. W. *J. Am. Chem. Soc.* **2009**, *131*, 8396. (c) Mömming, C. M.; Frömel, S.; Kehr, G.; Fröhlich, R.; Grimme, S.; Erker, G. *J. Am. Chem. Soc.* **2009**, *131*, 12280. (d) 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. (e) Dureen, M. A.; Brown, C. C.; Stephan, D. W. *Organometallics* **2010**, *29*, 6594. (f) Voss, T.; Chen, C.; Kehr, G.; Nauha, E.; Erker, G.; Stephan, D. W. *Chem. Eur. J.* **2010**, *16*, 3005. (g) Voss, T.; Sortais, J.-B.; Fröhlich, R.; Kehr, G.; Erker, G. *Organometallics* **2011**, *30*, 584. (h) Zhao, X.; Stephan, D. W. *Chem. Sci.* **2012**, *3*, 2123.
(12) Xu, B.; Kehr, G.; Fröhlich, R.; Wibbeling, B.; Schirmer, B.; Grimme, S.; Erker, G. *Angew. Chem. Int. Ed.* **2011**, *50*, 7183.
(13) Mömming, C. M.; Kehr, G.; Wibbeling, B.; Fröhlich, R.; Schirmer, B.; Grimme, S.; Erker, G. *Angew. Chem. Int. Ed.* **2010**, *49*, 2414.
(14) Feldhaus, P.; Schirmer, B.; Wibbeling, B.; Daniliuc, C. G.; Fröhlich, R.; Grimme, S.; Kehr, G.; Erker, G. *Dalton Trans.* **2012**, *41*, 9135.
(15) Kalinowski, H.-O.; Berger, S.; Braun, S. In *^{13}C NMR-Spektroskopie*; Thieme: Stuttgart, **1984**.
(16) **Compounds 8 and 9a**
Tri-*tert*-butylphosphane (102 mg, 0.50 mmol) in CH_2Cl_2 (3 mL) was added to a solution of tris(pentafluorophenyl)-borane (256 mg, 0.50 mmol) in CH_2Cl_2 (10 mL). After addition of 2-methyl-1,3-butenyne (33 mg, 47.5 µL, 0.50 mmol) the reaction mixture was stirred for 24 h at r.t. Subsequently, all volatiles were removed under reduced pressure and the obtained residue was dried in vacuo to give a ca. 1:1 mixture of compounds **8** and **9a** (302 mg). The both products were separated by column chromatography (silica gel; eluent: *n*-pentane–CH_2Cl_2, 3:5). Drying of the respective fraction in vacuo gave compound **8** (131.9 mg, 33%) and compound **9a** (81.6 mg, 21%). Crystals suitable for the X-ray crystal structure analysis for both compound **8** and compound **9a** were obtained from a solution of the respective compound in CH_2Cl_2 layered by *n*-pentane at –40 °C.
Analytical Data of Compound 8
Anal. Calcd for $C_{35}H_{33}BF_{15}P$: C, 53.87; H, 4.26. Found: C, 53.04; H, 4.22. Mp 141 °C (DSC). ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 5.05 (d, $^1J_{PH}$ = 428.6 Hz, 1 H, PH), 4.97 (dq, $^2J_{PH}$ = 2.7 Hz, $^4J_{HH}$ = 1.0 Hz, 1 H, =CH_2^Z), 4.92 (dq, $^2J_{PH}$ = 2.7 Hz, $^4J_{HH}$ = 1.5 Hz, 1 H, =CH_2^E), 1.82 (dd, $^4J_{HH}$ = 1.5 Hz, $^4J_{HH}$ = 1.0 Hz, 3 H, CH_3), 1.63 (d, $^3J_{PH}$ = 15.9 Hz, 27 H, *t*-Bu). ^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ = 148.6 (dm, $^1J_{FC}$ = ca. 240 Hz, C_6F_5), 138.5 (dm, $^1J_{FC}$ = ca. 250 Hz, C_6F_5), 136.9 (dm, $^1J_{FC}$ = ca. 240 Hz, C_6F_5), 130.8 (=C), 124.8 (br, *ipso*-C_6F_5), 116.8 (=CH_2), 95.4 (br, ≡C), 38.1 (d, $^1J_{PC}$ = 26.8 Hz, *t*-Bu), 30.4 (*t*-Bu), 24.4 (CH_3); resonance for ≡CB was not observed. ^{31}P NMR (243 MHz, 299 K, CD_2Cl_2): δ = 60.4 (dm, $^1J_{PH}$ = 428.6 Hz). ^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = –21.0 ($\nu_{1/2}$ = ca. 25 Hz). ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = –132.6 (m, 2 F, *o*-C_6F_5), –164.0 (t, $^3J_{FF}$ = 20.3 Hz, 1 F, *p*-C_6F_5), –167.4 (m, 2 F, *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p}$ = 3.4].
Analytical Data of Compound 9a
HRMS: *m/z* calcd for $C_{35}H_{33}BF_{15}PNa^+$: 803.2072; found: 803.2031. Decomposition: 247 °C (DSC). ^{1}H NMR (600 MHz, 298 K, CD_2Cl_2): δ = 5.94 (br m, 1 H, =CH), 3.13 (ddd, $^2J_{PH}$ = 16.2 Hz, $^2J_{HH}$ = 14.8 Hz, $^5J_{HH}$ = 3.1 Hz, 1 H, CH_2), 2.26 (ddd, $^2J_{PH}$ = 15.5 Hz, $^2J_{HH}$ = 14.8 Hz, $^5J_{HH}$ = 1.3 Hz, 1 H, CH_2), 1.66 (br d, $^4J_{PH}$ = 3.1 Hz, 3 H, CH_3), 1.57 (d, $^3J_{PH}$ = 13.9 Hz, 27 H, *t*-Bu). ^{13}C{^{1}H} NMR (151 MHz, 298 K, CD_2Cl_2): δ = 207.1 (d, $^3J_{PC}$ = 6.7 Hz, =C=), 148.4 (dm, $^1J_{FC}$ = ca. 238 Hz, C_6F_5), 138.4 (dm, $^1J_{FC}$ = ca. 231 Hz, C_6F_5), 136.8 (dm, $^1J_{FC}$ = ca. 233 Hz, C_6F_5), 125.1 (br, *i*-C_6F_5), 98.5 [br q (1:1:1:1), $^1J_{BC}$ = ca. 50 Hz, =CH], 80.0 (br m, =C), 39.7 (d, $^1J_{PC}$ = 27.4 Hz, *t*-Bu), 30.4 (*t*-Bu), 23.5 (d, $^1J_{PC}$ = 31.4 Hz, CH_2), 23.1 (d, $^3J_{PC}$ = 3.2 Hz, CH_3). ^{31}P{^{1}H} NMR (243 MHz, 298 K, CD_2Cl_2): δ = 49.2 ($\nu_{1/2}$ = ca. 10 Hz). ^{11}B{^{1}H} NMR (192 MHz, 298 K, CD_2Cl_2): δ = –15.6 ($\nu_{1/2}$ = ca. 15 Hz). ^{19}F NMR (564 MHz, 298 K, CD_2Cl_2): δ = –132.2 (m, 2 F *o*-C_6F_5), –163.6 (t, $^3J_{FF}$ = 20.4 Hz, 1 F, *p*-C_6F_5), –167.4 (m, 2 F, *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p}$ = 3.8].
(17) **Compounds 10 and 9b**
A solution of tri-*ortho*-tolylphosphane (152 mg, 0.50 mmol) in CD_2Cl_2 (4 mL) was added to a solution of tris(pentafluorophenyl)borane (256 mg, 0.50 mmol) in CD_2Cl_2 (4 mL) at r.t. Then the reaction mixture was added to 2-methyl-1,3-butenyne (33 mg, 47.5 µL, 0.50 mmol), and the resulting mixture was stirred for 10 min. After one day, an aliquot of the reaction mixture was investigated by NMR experiments at low temperature. A mixture of compound **10** (1,2-addition), compound **9b** (1,4-addition) and tri-*ortho*-tolylphosphane. [**10**/**9b**/phosphane = ca. 28:37:35 (^{1}H NMR at 248 K)] was characterized. Then the volume of the reaction mixture was reduced to one half followed by separation of the compounds by column chromatography (silica gel; eluent CH_2Cl_2–*n*-pentane = 2:3). The first fraction contained compound **10** admixed with tri-*ortho*-tolylphosphane, which subsequently was purified by crystallization from a solution of compound **10** in CH_2Cl_2 layered by *n*-pentane to give compound **10** (89 mg, 20%). The second fraction contained compound **9b** (148.9 mg, 33%). Crystals suitable for the X-ray crystal structure analysis for both compounds **10** and **9b**, respectively, were obtained from a solution of the respective compound in CH_2Cl_2 layered with *n*-pentane at –40 °C.
Analytical Data of Compound 10
Anal. Calcd for $C_{44}H_{27}BF_{15}P{\cdot}CH_2Cl_2$: C, 55.87; H, 3.02. Found: C, 55.50; H, 2.55. Mp 98 °C (DSC). ^{1}H NMR (500 MHz, 233 K, CD_2Cl_2): δ = 8.27 (br d, $^3J_{PH}$ = 37.0 Hz, 1 H, =CH), 7.86 (*o*), 7.63 (*p*), 7.51 (*m*), 7.33 (*m′*) (4 × m, 4 × 1 H, *o*-tol[a]), 7.65 (*p*), 7.60 (*o*), 7.43 (*m*), 7.36 (*m′*) (4 × m, 4 × 1 H,

o-tol[b]), 7.65 (*p*), 7.52 (*m*′), 7.27 (*m*), 7.27 (*o*) (4 × m, 4 × 1 H, *o*-tol[c]), 4.97 (s, 1 H, $=CH_2^Z$), 4.58 (s, 1 H, $=CH_2^E$), 2.63 (s, 3 H, CH_3 of *o*-tol[c]), 1.63 (s, 6 H, CH_3 of *o*-tol[a,b]), 0.88 (s, 3 H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, 233 K, CD_2Cl_2): δ = 181.2 (br, =CH), 147.7 (dm, $^1J_{FC}$ = ca. 242 Hz, C_6F_5), 145.1 (d, $^2J_{PC}$ = 8.0 Hz, *ortho*′), 134.8 (d, $^2J_{PC}$ = 11.4 Hz, *ortho*), 134.7 (d, $^4J_{PC}$ = 2.1 Hz, *para*), 133.3 (d, $^3J_{PC}$ = 10.2 Hz, *meta*′), 126.8 (d, $^3J_{PC}$ = 12.2 Hz, *meta*), 116.0 (d, $^1J_{PC}$ = 80.7 Hz, *ipso*) (of *o*-tol[c]), 144.1 (d, $^2J_{PC}$ = 7.7 Hz, *ortho*′), 134.5 (d, $^2J_{PC}$ = 12.0 Hz, *ortho*), 134.2 (d, $^4J_{PC}$ = 2.6 Hz, *para*), 133.4 (d, $^3J_{PC}$ = 11.4 Hz, *meta*′), 126.9 (d, $^3J_{PC}$ = 12.8 Hz, *meta*), 118.1 (d, $^1J_{PC}$ = 83.2 Hz, *ipso*) (of *o*-tol[o]), 143.3 (d, $^2J_{PC}$ = 6.8 Hz, *ortho*′), 136.2 (d, $^2J_{PC}$ = 13.5 Hz, *ortho*), 134.1 (d, $^4J_{PC}$ = 2.4 Hz, *para*), 132.9 (d, $^3J_{PC}$ = 10.3 Hz, *meta*′), 126.9 (d, $^3J_{PC}$ = 12.8 Hz, *meta*), 120.7 (d, $^1J_{PC}$ = 80.6 Hz, *ipso*) (of *o*-tol[a]), 139.3 (d, $^2J_{PC}$ = 14.6 Hz, =C), 138.1 (dm, $^1J_{FC}$ = ca. 240 Hz, C_6F_5), 136.3 (dm, $^1J_{FC}$ = ca. 240 Hz, C_6F_5), 124.0 (br, *i*-C_6F_5), 124.8 (d, $^1J_{PC}$ = 64.7 Hz, =CP), 122.6 (d, $^3J_{PC}$ = 10.9 Hz, $=CH_2$), 23.1 (br, CH_3 of *o*-tol[c]), 22.9 (CH_3), 22.7 (d, $^3J_{PC}$ = 1.8 Hz, CH_3 of *o*-tol[b]), 22.5 (d, $^3J_{PC}$ = 3.7 Hz, CH_3 of *o*-tol[a]). $^{31}P\{^1H\}$ NMR (202 MHz, 233 K, CD_2Cl_2): δ = 23.4 ($\nu_{1/2}$ = ca. 60 Hz). $^{11}B\{^1H\}$ NMR (160 MHz, 233 K, CD_2Cl_2): δ = –16.2 ($\nu_{1/2}$ = ca. 60 Hz). ^{19}F NMR (282 MHz, 295 K, CD_2Cl_2): δ = –131.6 (m, 2 F, *o*-C_6F_5), –162.2 (m, 1 F, *p*-C_6F_5), –166.6 (m, 2 F, *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p}$ = 4.4].

Analytical Data of Compound 9b

HRMS: *m/z* calcd for $C_{44}H_{27}BF_{15}PNa^+$: 905.1604; found: 905.1602. Mp 110 °C (DSC). ^1H NMR (500 MHz, 298 K, CD_2Cl_2): δ = 7.67 (*p*), 7.65 (*o*), 7.45 (*m*′), 7.37 (*m*) (4 × m, 4 × 3 H, *o*-tol), 5.55 (br m, 1 H, =CH), 4.12, 3.24 (2 × m, 2 × 1 H, CH_2), 2.15 (s, 9 H, CH_3 of *o*-tol), 1.27 (m, 3 H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, 298 K, CD_2Cl_2): δ = 206.7 (d, $^3J_{PC}$ = 9.2 Hz, =C=), 148.4 (dm, $^1J_{FC}$ = ca. 240 Hz, C_6F_5), 143.7 (d, $^2J_{PC}$ = 8.6 Hz, *o*′ of *o*-tol), 138.4 (dm, $^1J_{FC}$ = ca. 245 Hz, C_6F_5), 136.8 (dm, $^1J_{FC}$ = ca. 250 Hz, C_6F_5), 135.9 (d, $^2J_{PC}$ = 11.7 Hz, *o* of *o*-tol), 135.3 (d, $^4J_{PC}$ = 2.9 Hz, *p* of *o*-tol), 133.9 (d, $^3J_{PC}$ = 11.0 Hz, *m*′ of *o*-tol), 127.6 (d, $^3J_{PC}$ = 12.7 Hz, *m* of *o*-tol), 125.1 (br, *i*-C_6F_5), 117.5 (d, $^1J_{PC}$ = 80.6 Hz, *i* of *o*-tol), 99.2 [br q (1:1:1:1), $^1J_{BC}$ = ca. 51 Hz, =CH], 80.7 (br m, =C), 31.3 (d, $^1J_{PC}$ = 47.8 Hz, CH_2), 23.1 (d, $^3J_{PC}$ = 3.8 Hz, CH_3 of *o*-tol), 20.4 (d, $^3J_{PC}$ = 4.6 Hz, CH_3). $^{31}P\{^1H\}$ NMR (202 MHz, 298 K, CD_2Cl_2): δ = 25.4 ($\nu_{1/2}$ = ca. 10 Hz). $^{11}B\{^1H\}$ NMR (160 MHz, 298 K, CD_2Cl_2): δ = –15.7 ($\nu_{1/2}$ = ca. 20 Hz). ^{19}F NMR (470 MHz, 298 K, CD_2Cl_2): δ = –132.2 (m, 2 F *o*-C_6F_5), –163.6 (t, $^3J_{FF}$ = 20.3 Hz, 1 F, *p*-C_6F_5), –167.4 (m, 2 F, *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p}$ = 3.7].