Carboboration Reactions of 1,2-Bis[(diarylphosphino)ethynyl]benzenes with Tris(pentafluorophenyl)borane

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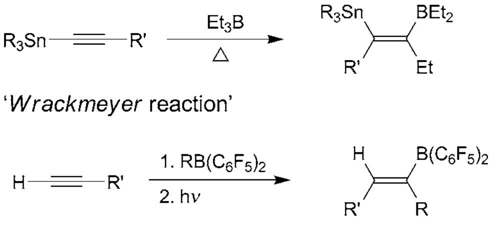
Dedicated to Professor *Dieter Seebach* on the occasion of his 75th birthday

The 1,2-bis[(diarylphosphino)ethynyl]benzene derivatives **1a** (R = Ph) and **1b** (R = *o*-tolyl) undergo 1,1-carboboration at one of their acetylene units upon treatment with $(C_6F_5)_3B$ at elevated temperature to give the products **5a** and **5b**, respectively. At room temperature, we observed the formation of the corresponding phosphireniumborate zwitterions, **7a** and **7b**, respectively, which may be intermediates of the 1,1-carboboration reactions. The reaction of the more bulky 1,2-bis[(dimesitylphosphino)ethynyl]benzene **1c** with $(C_6F_5)_3B$ takes a different course. At 110°, we observed the complete conversion to the benzopentafulvene derivative **8** which is probably formed in a typical carbocation rearrangement sequence after the initial $(C_6F_5)_3B$ *Lewis* acid-addition step. The compounds **5a**, **5b**, **7b**, and **8** were characterized by X-ray crystal-structure analyses.

Introduction. – Various metal-substituted alkynes undergo 1,1-carboboration reactions when treated with trialkylboranes [1]. A typical example of the '*Wrackmeyer* reaction' is shown in *Scheme 1* [2]. We had recently shown that very electrophilic pentafluorophenyl-substituted boranes $RB(C_6F_5)_2$ (R = alkyl or C_6F_5) rapidly undergo 1,1-carboboration reactions with a variety of simple organic alk-1-ynes to yield the respective alkenylboranes [3] (as (*E*)/(*Z*)-mixtures of stereoisomers). Often, subsequent photolysis resulted in efficient (*E*)/(*Z*)-isomerization and render the respective alkenylboranes readily synthetically available [4]. We even extended this reaction

Scheme 1



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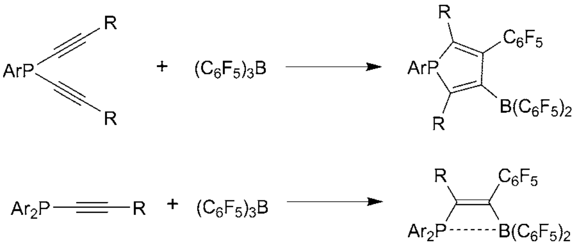
[1]) X-Ray crystal structure analyses.

scheme to the formation of tetrasubstituted alkenylboranes from internal alkynes and the $RB(C_6F_5)_2$ reagents, which represents a novel C–C σ-bond activation process [5]. The resulting alkenylboranes were found themselves to serve as very useful *Lewis* acids, *e.g.*, as catalyst components in the metal-free hydrogenation of several conjugated ynones or enones by frustrated *Lewis* pair (FLP) catalysis [6]. The alkenylboranes were also employed as substrates for *Suzuki–Miyaura* coupling reactions.

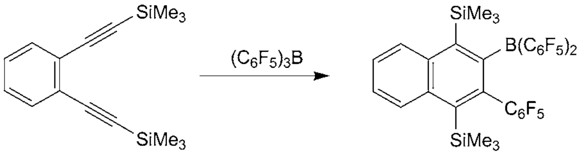
We have extended this advanced 1,1-carbobooration reaction of the $RB(C_6F_5)_2$/alkyne systems to the rapid formation, *e.g.*, of siloles from bis(alkynyl)silanes [7] or of phospholes from bis(alkynyl)phosphanes [8]. (Diarylphosphino)alkynes gave conjugated frustrated P/B *Lewis* pairs upon treatment with, *e.g.*, $(C_6F_5)_3B$ (see *Scheme 2*) [9].

Scheme 2



We have also reacted 1,2-dialkynylbenzene derivatives with the $RB(C_6F_5)_2$ reagents. This resulted in a series of consecutive 1,1-carboboration reactions under mild conditions to eventually give the respective borylated naphthalene derivatives in good yields (see *Scheme 3*) [10].

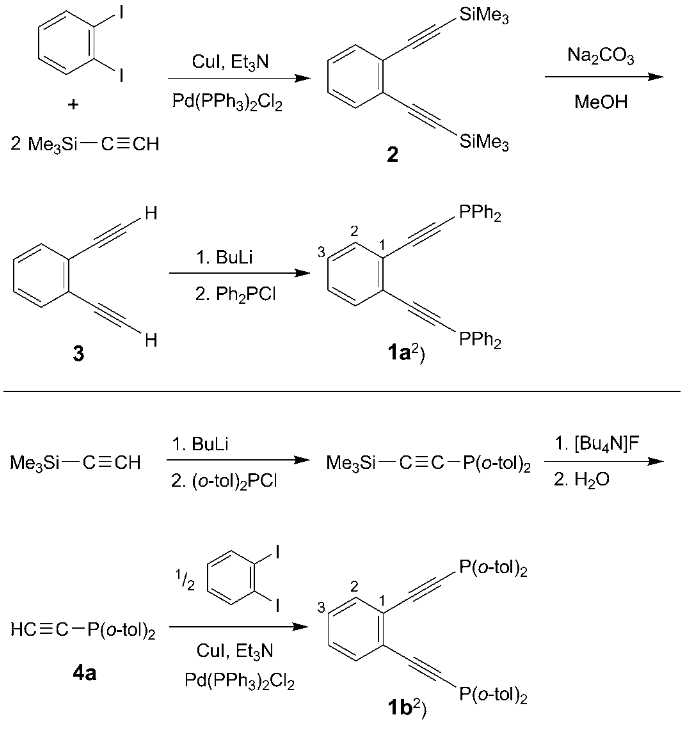
Scheme 3



We have now treated a small series of related 1,2-bis[(diarylphosphino)ethynyl]benzene derivatives with $(C_6F_5)_3B$ and studied their 1,1-carboboration behavior. In one case, we observed a rather unexpected new reaction pathway.

Results and Discussion. – *1,1-Carboboration Reactions.* For this part of our study, we prepared the bis(alkynyl)benzene starting materials **1a** and **1b**. The known compound **1a** [11] was synthesized starting from 1,2-diiodobenzene by *Sonogashira* coupling with (trimethylsilyl)acetylene to give 1,2-bis[(trimethylsilylethynyl]benzene (**2**) in 86% yield (see *Scheme 4*). Compound **2** was desilylated, and then the resulting 1,2-diethynylbenzene (**3**) was deprotonated (BuLi) and reacted with chloro(diphenyl)phosphane to yield 1,2-bis[(diphenylphosphino)ethynyl]benzene (**1a**; yield 78%) over three steps. 1,2-Bis{[di-(*o*-tolyl)phosphino]ethynyl}benzene (**1b**) had not been previously reported to the best of our knowledge. We prepared it directly by a *Sonogashira* coupling variant from 1,2-diiodobenzene and [di(*o*-tolyl)phosphino]acetylene (**4**). The latter was prepared by the 'standard' procedure starting from (trimethylsilyl)acetylene (see *Scheme 4*).

Scheme 4



Compound **1a** was reacted with 1 equiv. of the *Lewis* acid $(C_6F_5)_3B$ in toluene solution overnight at 110°. Workup gave the 1,1-carboboration product **5a** in $>70\%$ yield. The compound was characterized by X-ray diffraction (see *Fig. 1*). In the crystal, compound **5a** shows the presence of one unchanged –C≡C–PPh_2 substituent at the central phenylene unit. The other (diphenylphosphino)ethynyl substituent had undergone the 1,1-carboboration reaction. This has resulted in the addition of the borane to the acetylenic C-atom C(2′)[2] which resulted in a 1,2-migration of the PPh_2 substituent from C(2′) to the adjacent acetylene C-atom C(1′) concomitant with shifting of a C_6F_5 substituent from B- to C-atom. Consequently, we found a geminal pair of $(C_6F_5)_2B$ and C_6F_5 substituents at the sp^2 C-atom C(2′) and the PPh_2 substituent at C(1′) in *cis*-vicinal position to the B-center. There is an internal B–P interaction in the product **5a** (see *Fig. 1*).

In solution, compound **5a** features a ^{31}P-NMR signal of the 'untouched' –C≡C–PPh_2 group at δ –34.2 (with corresponding acetylene ^{13}C-NMR resonances at δ 105.5

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[2] Arbitrary atom numbering; for systematic names, see *Exper. Part.*

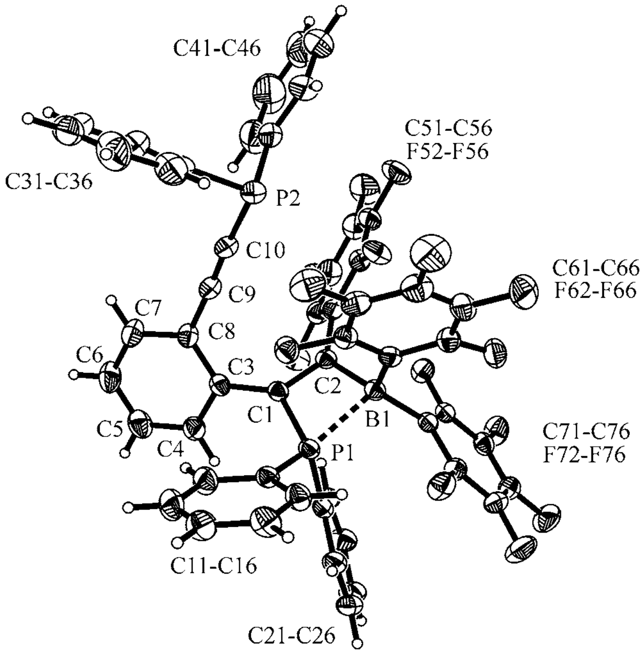

Fig. 1. *Molecular structure of the 1,1-carboboration product* **5a**. Selected bond lengths [Å] and angles [°]: B1–P1: 2.031(3), C1–C2: 1.357(4), C9–C10: 1.198(4); C2–C1–C3: 134.2(3), C2–C1–P1: 96.5(2), C3–C1–P1: 129.4(3), C1–C2–C51: 125.0(2), C1–C2–B1: 105.9(2), C51–C2–B1: 128.9(2), C8–C9–C10: 176.5(3), C9–C10–P2: 171.2(3), $\Sigma\,{}^{C}$B1: 350.3, $\Sigma\,{}^{C}$P1: 335.1, B1–C2–C1–P1: −7.0(2).

(^2J(P,C) = 4.9 Hz) and δ 92.5 (^1J(P,C) = 13.1 Hz)), and a ^{31}P-NMR signal of the unsaturated frustrated *Lewis* pair (FLP) unit at δ +16.6 (with a corresponding ^{11}B-NMR feature at δ −6 and ^{13}C-NMR signals of the P/B-bridging C=C unit at δ 140.3 (^1J(P,C) = 52.3 Hz) and 164.3 (br.), resp.)). The ^{19}F-NMR spectrum shows a set of resonances of the migrated C_6F_5 group and a separate set of ^{19}F *o,p,m*-signals of the remaining $(C_6F_5)_2B$ substituent; the latter features a $\Delta\delta_{p,m}$ of 6.8 ppm.

We have followed the course of the reaction of compound **1a** with $(C_6F_5)_3B$ by NMR spectroscopy at ambient temperature (for details, see the *Supplementary Material*3))). We found initial formation of a phosphane/borane adduct, **6a** (see *Scheme 5*), that is characterized by the appearance of a new ^{31}P-NMR resonance of the $-C{\equiv}C{-}PPh_2 \cdot B(C_6F_5)_3$ group at δ +4 (br.) (^{31}P-NMR feature of the remaining free $-C{\equiv}C{-}PPh_2$ group at δ −31 (br.)) with a corresponding ^{11}B-NMR signal at δ 6 (for further details, see the *Supplementary Material*3))). After 18.5 h, a mixture of three products was observed, namely the adduct **6a**, the final 1,1-carboboration product **5a**, and a new second intermediate **7a**. Prolonged heating to 50° (*ca.* 21 h) resulted in a complete conversion to the FLP product **5a** (see *Scheme 5*). The new intermediate **7a** shows a very characteristic ^{31}P-NMR resonance at δ −110.6, which is typical of a

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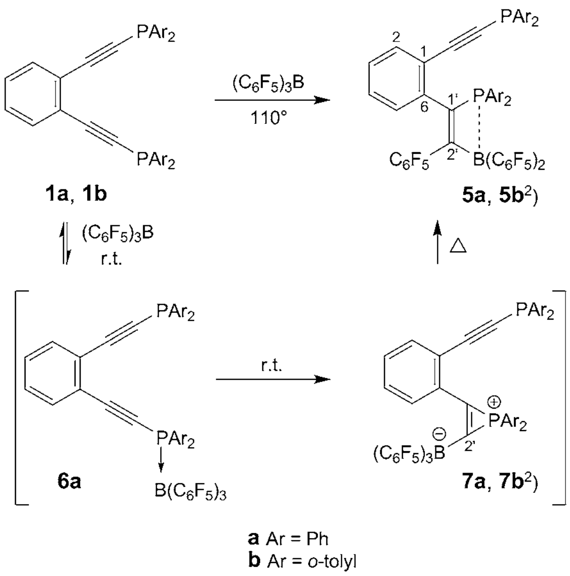
3) *Supplementary Material* may be obtained from the authors upon request.

Scheme 5



phosphirenium cation substructure [8][9][12]. In addition, it features the $-C\equiv C-PPh_2$ resonances (^{31}P: δ −33.0; for further details, see the *Supplementary Material*3)).

The reaction of the *o*-tolyl-substituted compound **1b** with $(C_6F_5)_3B$ is slightly faster. After stirring the mixture overnight at room temperature, we monitored the formation of the products **5b** and **7b** in a 1:3 ratio. Compound **7b** was identified spectroscopically from the mixture (^{31}P-NMR: δ −47.7 ($-C\equiv C-P$(*o*-tolyl)$_2$) and −114.8 (phosphirenium moiety); ^{11}B-NMR: δ −16.0; ^{19}F-NMR: δ −130.9 (*o*), −159.0 (*p*), −164.2 (*m*-C_6F_5))3). Compound **7b** was also characterized by X-ray diffraction (single crystals were obtained from CH_2Cl_2/pentane at −40° by the diffusion method)3).

The X-ray crystal-structure analysis of compound **7b** confirmed the formation of a phosphirenium borate zwitterion (see *Fig. 2*). The compound contains an unsaturated three-membered ring including a phosphonium unit. To it attached is the $(C_6F_5)_3B$ moiety at C(2′)2) (see *Fig. 2*) and the remaining *o*-$C_6H_4-C\equiv C-P$(*o*-tolyl)$_2$ unit.

The reaction of compound **1b** with $(C_6F_5)_3B$ in toluene at 60° overnight eventually gave the FLP product **5b**, which was isolated as a pale yellow solid in 94% yield. The X-ray crystal-structure analysis (*Fig. 3*) shows the presence of a four-membered heterocyclic FLP ring system formed by 1,1-carboboration of one of the $-C\equiv C-P$(*o*-tolyl)$_2$ units; the second phosphinoacetylene moiety remained untouched.

Unusual Carboboration Behavior: Benzopentafulvene Formation. We also investigated the reaction of the considerably more bulky 1,2-bis[(dimesitylphosphino)ethynyl]benzene derivate **1c** with $(C_6F_5)_3B$ under similar reaction conditions. This reaction took quite an unexpected course.

We prepared the starting material by a twofold *Sonogashira*-type coupling reaction of 1,2-diiodobenzene with (dimesitylphosphino)acetylene (**4b**) which was synthesized analogously to the procedure outlined in *Scheme 4* for the preparation of **4a**.

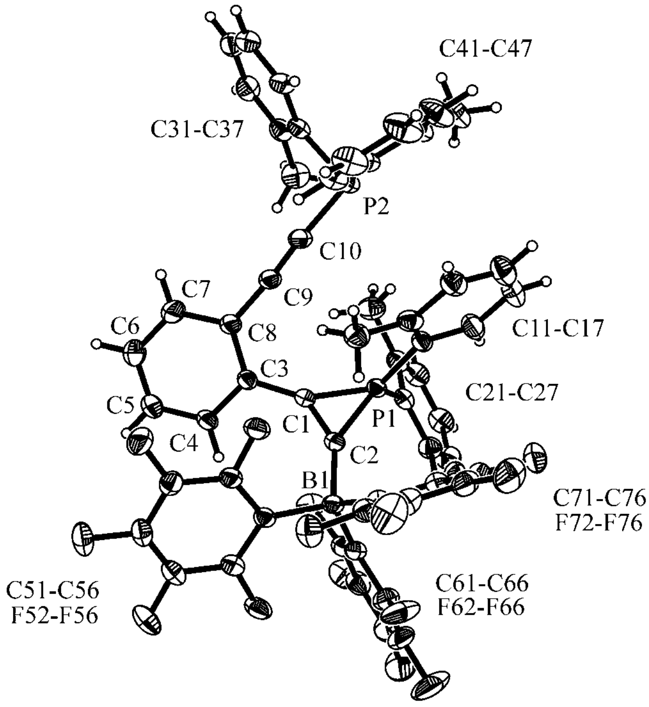


Fig. 2. *Molecular structure of the phosphirenium borate zwitterion* **7b**. Selected bond lengths [Å] and angles [°]: B1–C2: 1.639(3), B1–C61: 1.645(4), C1–C2: 1.337(3), C1–P1: 1.733(2), C2–P1: 1.766(2), C9–C10: 1.207(4), C10–P2: 1.767(3); P1–C1–C2: 68.8(1), C1–C2–P1: 66.3(1), C8–C9–C10: 175.2(3), C9–C10–P2: 169.9(1), C1–P1–C2: 44.9(1), Σ C1: 359.8, Σ C2: 359.9.

Compound **1c** was then mixed with $(C_6F_5)_3B$ (1 equiv.), and the solution was stirred overnight at 110° in toluene solution. Workup gave the benzopentafulvene derivative **8** in close to 90% yield (see *Scheme 6*).The X-ray crystal-structure analysis revealed that compound **8** was formed by means of shifting of a C_6F_5 substituent from B- to P-atom, and a mesityl (=2,4,6-trimethylphenyl, mes) group from P- to C-atom. In addition, a new C–C bond was formed between the pair of acetylene substitutents. The core of compound **8** is made up by a benzopentafulvene framework. A $Pmes_2$ substituent is attached at the exocyclic C=C bond. The same pentafulvene sp^2 C-atom (C(1)^2)) also bears a single mes substituent. The C(2)=C(3) bond (see *Fig. 4*) bears the $(C_6F_5)_2B$ substituent at C(3) and a $P(C_6F_5)$ (mes) group at C(2). There is a P–B interaction between B(1) and P(1).

Scheme 6 depicts a potential rationalization of the formation of the pentafulvene derivative **8** involving a substantial shifting of aryl substituents. The reaction is probably initiated by addition of the strong $(C_6F_5)_3B$ *Lewis* acid to the 'inner' C-atom of an acetylene unit generating a zwitterionic intermediate, **9**, which is prone to C–C coupling with the other acetylene moiety to give **10**. This system would now be set up for a sequence of stabilizing aryl-migration reactions, namely shifting of a mes group from the P-atom to the exocyclic vinyl cation site, and a subsequent C_6F_5 shift from B-

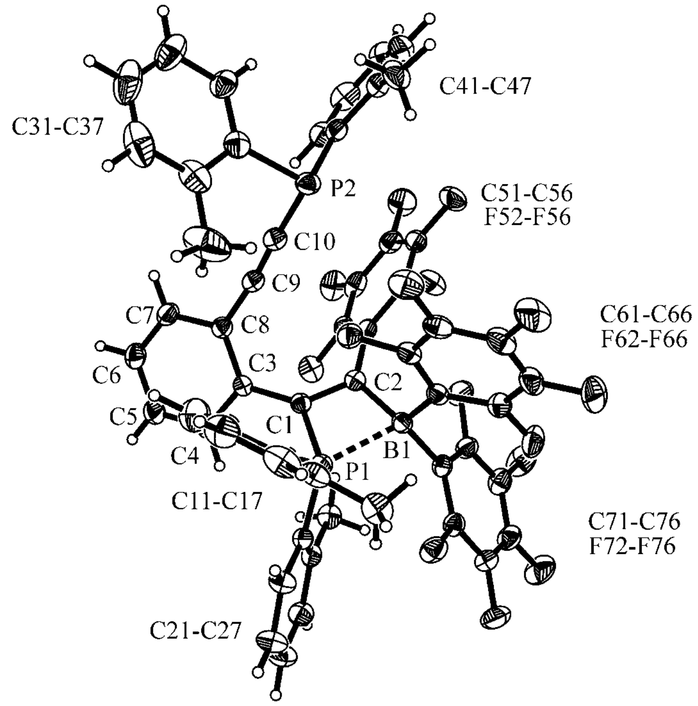
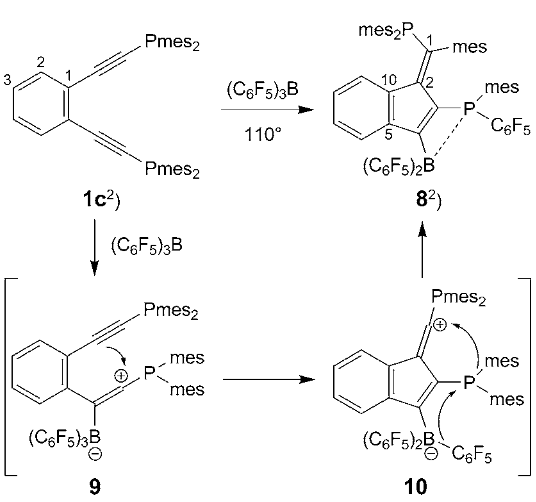


Fig. 3. *Molecular structure of the FLP* **5b**. Selected bond lengths [Å] and angles [°]: B1–P1: 2.061(4), C1–C2: 1.356(5), C9–C10: 1.193(5); C2–C1–C3: 132.4(3), C2–C1–P1: 97.3(2), C3–C1–P1: 130.3(3), C1–C2–C51: 123.8(3), C1–C2–B1: 106.3(3), C51–C2–B1: 129.8(3), C8–C9–C10: 174.1(4), C9–C10–P2: 169.1(4), Σ ^CB1: 348.4, Σ ^CP1: 332.8, B1–C2–C1–P1: 1.2(3).

Scheme 6



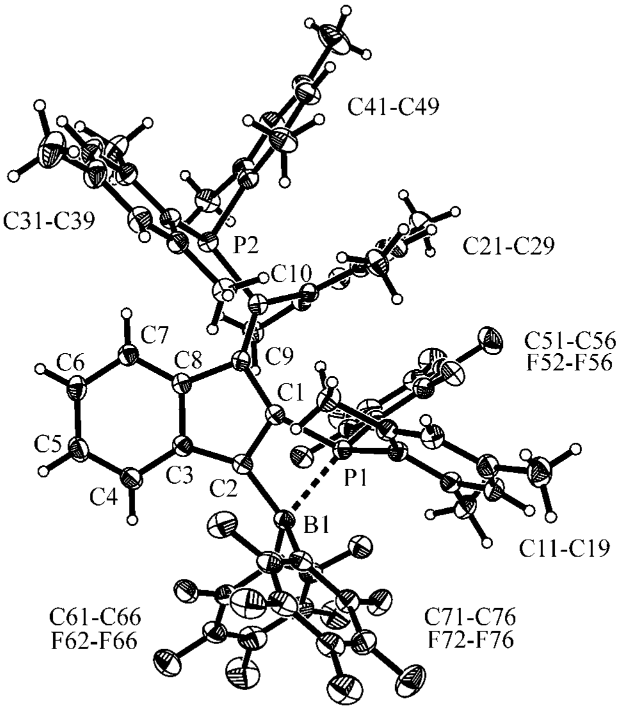


Fig. 4. *Molecular structure of the P/P/B-substituted benzopentafulvene product* **8**. Selected bond lengths [Å] and angles [°]: B1–P1: 2.108(3), C1–C2: 1.371(4), C1–C9: 1.480(4), C2–C3: 1.470(4), C3–C8: 1.417(4), C1–C2: 1.371(4), C9–C10: 1.371(4); C2–C1–C9: 112.6(2), C2–C1–P1: 96.8(2), C9–C1–P1: 150.3(2), C1–C2–C3: 107.2(2), C1–C2–B1: 108.4(2), C3–C2–B1: 144.3(2), ΣC9: 359.7, ΣC10: 355.2, $\Sigma\,^{C}$B1: 346.3, $\Sigma\,^{C}$P1: 337.2, B1–C2–C1–P1: –2.5(2).

to P-atom to eventually give the product **8**. This tentative descriptive pathway needs to be supported or confirmed by additional experimental and theoretical evidence. At this time, *Scheme 6* only offers a description of a possible pathway of the unexpected formation of compound **8**.

Conclusions. – The 1,2-bis[(diarylphosphino)ethynyl]benzene derivatives **1** do not undergo the sequence of 1,1-carboboration reactions upon treatment with $(C_6F_5)_3B$ to eventually yield the respective naphthalene derivatives as their Me_3Si-substituted analogs do (see *Scheme 2*). The Ar_2P groups are good migrating groups in the 1,1-carboboration sequence, but, at the same time, they can coordinate to the adjacent boryl functionality at the stage of the first 1,1-carboboration step. This is probably the reason why the systems **1a** or **1b** undergo only a simple 1,1-carboboration reaction with $(C_6F_5)_3B$ under our typical reaction conditions and stop at the stage of the internally interacting vicinal frustrated P/B *Lewis* pairs **5a** and **5b**, respectively. The more bulky $Pmes_2$ derivative **1c** apparently is not able to make sufficient use of this way of product stabilization. In this case, the usual 1,1-carboboration pathway is not followed at all, but, instead, we have observed a typical *Lewis* acid-initiated carbocation-dominated reaction pathway [13] leading to the formation of a benzopentafulvene framework by C–C coupling *via* typical carbocation reaction paths, including stabilizing aryl-migration reactions to eventually give a stable product. Our study indicates that acetylene/$(C_6F_5)_3B$ chemistry has closely competing reaction pathways available which can be switched by subtle choice of parameters, here apparently the actual steric bulk of the aryl substituents at the P-atom.

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Experimental Part

General. All reactions were carried out under Ar with *Schlenk*-type glassware or in a glovebox. Solvents (including deuterated solvents used for NMR spectroscopy) were dried and distilled under Ar prior to use. The following instruments were used for physical characterization of the compounds. M.p./dec. temp.: *DSC 2010* (*TA-Instruments*) apparatus; determined by the baseline method. IR: *Varian 3100 FT-IR* (*Excalibur Series*) spectrometer; $\tilde{\nu}$ in cm^{-1}. NMR: *Bruker AC 200 P* (^{1}H, 200 MHz), *Varian 500 MHz INOVA* (^{1}H, 500 MHz; ^{13}C, 126 MHz), *Varian UNITY plus* NMR spectrometer (^{1}H, 600 MHz; ^{13}C, 151 MHz); assignments of the NMR resonances are supported by 2D experiments; chemical shifts δ in ppm rel. to $SiMe_4$ (^{1}H (residual ^{1}H resonance of the respective deuterated solvent) and ^{13}C (^{13}C resonance of the respective deuterated solvent)), $BF_3 \cdot OEt_2$ (^{11}B), $CFCl_3$ (^{19}F), and 80% H_3PO_4 (^{31}P); J in Hz. Elemental analyses: *Foss-Heraeus CHNO-Rapid*. X-Ray diffraction: Data sets were collected with a *Nonius KappaCCD* diffractometer. Programs used: data collection, COLLECT (*Nonius B.V.*, 1998); data reduction, Denzo-SMN [14]; absorption correction, Denzo [15]; structure solution SHELXS-97 [16]; structure refinement SHELXL-97 [17], and graphics, XP (*Bruker AXS*, 2000). Thermals ellipsoids are shown with 30% probability, R values are given for observed reflections, and wR^2 values are given for all reflections.

1,1′-(1,2-Phenylenediethyne-2,1-diyl)bis[1,1-diphenylphosphane] (**1a**). *1,2-Diethynylbenzene* (**3**; 200 mg, 1.59 mmol, 1 equiv.) was dissolved in THF (20 ml) and cooled to 0°. A 1.6M soln. of BuLi (2 ml, 3.17 mmol, 2 equiv.) in hexane was added slowly, and the resulting mixture was allowed to warm to r.t. and stirred for 2 h. After addition of chloro(diphenyl)phosphane (700 mg, 3.17 mmol, 2 equiv.), the soln. was stirred at r.t. overnight. Then, the solvent was removed *in vacuo*, the residue was suspended in CH_2Cl_2 (50 ml) and filtered over *Celite*. The soln. was concentrated to a volume of *ca.* 20 ml and filtered over a short column filled with silica gel. After drying *in vacuo*, **1a** was collected as a yellow-brown oil (614 mg, 1.25 mmol, 78%), which crystallized after several weeks to a slightly yellow solid. M.p. 76°. IR (ATR): 3068*w*, 3052*w*, 2163*w*, 1586*w*, 1476*s*, 1433*s*, 1328*w*, 1307*w*, 1273*w*, 1230*w*, 1204*w*, 1183*w*, 1159*w*, 1096*m*, 1068*m*, 1026*m*, 999*m*, 950*w*, 912*w*, 873*m*, 808*m*, 757*s*, 736*s*, 692*s*. ^{1}H-NMR (600 MHz, (D_8)toluene, 298 K)^2): 7.66 (*m*, 4 *o*-H, Ph); 7.14 (*m*, H–C(2)); 6.99 (*m*, 4 *m*-H, Ph); 6.94 (*m*, 2 *p*-H, Ph); 6.68 (*m*, H–C(3)). ^{13}C{^{1}H}-NMR (151 MHz, (D_8)toluene, 298 K)^2): 136.8 (*d*, ^1J(P,C) = 7.1, C_{ipso}, Ph); 133.1 (*d*, ^2J(P,C) = 21.2, *o*-C); 132.7 (*d*, ^4J(P,C) = 1.7, C(2)); 129.0 (*p*-C); 128.9 (*d*, ^3J(P,C) = 7.6, *m*-C); 128.5 (C(3)); 125.8 (*m*, C(1)); 106.6 (*d*, ^2J(P,C) = 3.7, C≡); 91.5 (*d*, ^1J(P,C) = 10.4, ≡CP). ^{31}P{^{1}H}-NMR (243 MHz, (D_8)toluene, 298 K): −32.7 ($\nu_{1/2} \approx 3$). Anal. calc. for $C_{34}H_{24}P_2$ (494.50): C 82.58, H 4.89; found: C 82.23, H 4.89.

1,1′-(1,2-Phenylenediethyne-2,1-diyl)bis[1,1-bis(2-methylphenyl)phosphane] (**1b**). 1,2-Diiodobenzene (250 mg, 0.76 mmol, 1 equiv.) and CuI (10 mg, 7 mol%) were mixed in Et_3N (20 ml) and degassed for 30 min at 60° (Ar flow on the soln.). *Ethynylbis(2-methylphenyl)phosphane* (**4a**; 362 mg, 1.52 mmol, 2 equiv.) was dissolved in THF (20 ml), and $PdCl_2(PPh_3)_2$ (27 mg, 5 mol%) was added. Both suspensions were combined at r.t. and stirred for 2 d at 60°. After cooling to r.t., the solvent was removed *in vacuo*, the residue taken up in Et_2O, and the obtained suspension was filtered over *Celite*. The solvent of the filtrate was removed *in vacuo*, and the crude product purified by flash chromatography (FC; SiO_2, pentane/CH_2Cl_2 4:1) to yield **1b** (277 mg, 0.50 mmol, 66%) as a highly viscous, slightly yellow oil, which crystallized after several weeks to a slightly yellow solid. M.p. 136°. IR (ATR): 3057*w*, 3006*w*, 2970*w*, 2918*w*, 1588*w*, 1468*m*, 1451*m*, 1379*w*, 1273*m*, 1231*w*, 1202*m*, 1161*w*, 1131*w*, 1099*w*, 1064*w*, 1033*m*, 873*m*, 807*m*, 745*s*, 715*s*, 670*w*, 640*w*. ^{1}H-NMR (500 MHz, CD_2Cl_2, 299 K)^2): 7.58 (*m*, 2 *o*-H, tol); 7.51 (*m*, H–C(2)); 7.31 (*m*, H–C(3)); 7.25 (*m*, 2 *p*-H, tol); 7.17 (*m*, 2 *m*′-H, tol); 7.12 (*m*, 2 *m*-H, tol); 2.44 (*s*, 2 Me). ^{13}C{^{1}H}-NMR (126 MHz, CD_2Cl_2, 299 K)^2): 142.2 (*d*, ^2J(P,C) = 27.4, *o*′-C); 133.4 (*d*, ^2J(P,C) = 3.1, *o*-C); 133.3 (*d*, ^1J(P,C) = 6.2, C_{ipso}, tol); 132.9 (*d*, *J*(P,C) = 1.9, C(2)); 130.5 (*d*, ^3J(P,C) = 5.2, *m*′-C); 129.6 (*p*-C); 128.9 (C(3)); 126.7 (*m*, *m*-C); 125.6 (*m*, C(1)); 106.6 (*d*, ^2J(P,C) = 4.2, C≡); 90.4 (*d*, ^1J(P,C) = 10.1, ≡CP); 21.3 (*d*, ^3J(P,C) = 21.0, Me). ^{31}P{^{1}H}-NMR (202 MHz, CD_2Cl_2, 299 K): –47.7 ($\nu_{1/2} \approx 1$). Anal. calc. for $C_{38}H_{32}P_2$ (550.61): C 82.89, H 5.89; found: C 82.48, H 5.92.

1,1′-(1,2-Phenylenediethyne-2,1-diyl)bis[1,1-bis(2,4,6-trimethylphenyl)phosphane] (**1c**). 1,2-Diiodobenzene (605 mg, 1.84 mmol, 1 equiv.) and CuI (20 mg, 5 mol%) were mixed in Et_3N (20 ml) and degassed for 30 min at 60° (Ar flow). *Ethynylbis(2,4,6-trimethylphenyl)phosphane* (**4b**; 1.08 g, 3.67 mmol, 2 equiv.) was dissolved in THF (15 ml), and $PdCl_2(PPh_3)_2$ (60 mg, 5 mol%) was added. Then, both suspensions were combined at r.t. and stirred for 3 d at 60°. After cooling to r.t., the solvent was removed *in vacuo*, the residue was taken up in Et_2O and filtered over *Celite*. The solvent was removed *in vacuo* again, and the crude product purified by FC (pentane/CH_2Cl_2 10:1 → 5:1) to give **1c** (590 mg, 0.90 mmol, 49%). Slightly yellow solid. M.p. 183°. IR (KBr): 3054*w*, 3019*m*, 2957*s*, 2916*s*, 2853*m*, 2369*m*, 2341*m*, 1734*w*, 1717*w*, 1699*w*, 1684*w*, 1674*w*, 1653*w*, 1636*w* 1602*m*, 1558*m*, 1540*m*, 1521*w*, 1507*w*, 1473*s*, 1457*s*, 1438*s*, 1405*m*, 1373*m*, 1290*m*, 1270*m*, 1244*m*, 1229*m*, 1203*m*, 1157*w*, 1097*m*, 1209*s*, 985*w*, 939*w*, 873*m*, 850*s*, 806*m*, 749*s*, 723*w*, 668*w*, 652*w*, 634*w*, 619*m*, 599*w*. ^{1}H-NMR (400 MHz, CD_2Cl_2, 298 K)^2): 7.33 (*m*, H–C(2)); 7.21 (*m*, H–C(3)); 6.78 (*d*, ^3J(H,H) = 3.2, 4 *m*-H, mes); 2.37 (*s*, 4 *o*-Me); 2.21 (*s*, 2 *p*-Me). ^{13}C{^{1}H}-NMR (101 MHz, CD_2Cl_2, 298 K)^2): 142.4 (*d*, ^2J(P,C) = 12.4, *o*-C); 138.7 (*p*-C); 132.5 (*d*, ^4J(P,C) = 2.6, C(2)); 130.2 (*d*, ^3J(P,C) = 3.8, *m*-C); 129.8 (*d*, ^1J(P,C) = 15.7, C_{ipso}, mes); 128.3 (C(3)); 125.9 (br., C(1)); 105.5 (*d*, ^2J(P,C) = 8.2, C≡); 92.3 (*d*, ^1J(P,C) = 9.2, ≡CP); 23.1 (*d*, ^3J(P,C) = 14.1, *o*-Me); 21.0 (*p*-Me). ^{31}P-NMR (162 MHz, CD_2Cl_2, 298 K): –56.6. Anal. calc. for $C_{46}H_{48}P_2$ (662.82): C 83.35, H 7.30; found: C 81.88, H 7.18.

*((*E*)-2-[Bis(2,3,4,5,6-pentafluorophenyl)boryl]-1-{2-[2-(diphenylphosphino)ethynyl]phenyl}-2-(2,3,4,5,6-pentafluorophenyl)ethenyl)diphenylphosphane* (**5a**). Compound **1a** (49.5 mg, 0.10 mmol, 1 equiv.) and $(C_6F_5)_3B$ (51.2 mg, 0.10 mmol, 1 equiv.) were dissolved separately in toluene (each 5 ml), and then the solns. were combined at r.t. The resulting mixture was stirred at 110° overnight. After cooling to r.t., the solvent of the black soln. was removed *in vacuo*, and pentane (5 ml) was added and directly removed *in vacuo* to remove remaining toluene (3 ×). The crude product was taken up in CH_2Cl_2 (20 ml) and filtered over silica. The solvent was removed *in vacuo* and pentane (5 ml) was added and directly removed *in vacuo* again to obtain **5a** (71.0 mg, 0.07 mmol, 71%). Slightly yellow solid. M.p. 224°. IR (KBr): 3063*w*, 2958*w*, 2928*w*, 2872*w*, 1646*m*, 1517*s*, 1466*s*, 1436*s*, 1383*m*, 1315*w*, 1288*m*, 1093*s*, 1052*m*, 985*s*, 974*s*, 924*m*, 847*w*, 822*w*, 786*w*, 767*m*, 747*m*, 693*s*. Anal. calc. for $C_{52}H_{24}BF_{15}P_2$ (1006.48): C 62.05, H 2.40; found: C 62.30, H 2.77. Single crystals suitable for X-ray crystal structure analysis were obtained by diffusion of pentane into a sat. soln. of **5a** in CH_2Cl_2 at –40°.

X-Ray Crystal Data for **5a**^{4}). Formula $C_{52}H_{24}BF_{15}P_2$, M_r 1006.46, colorless crystal, 0.25 × 0.13 × 0.10 mm, $a = 15.2751(5)$, $b = 16.2970(8)$, $c = 21.0193(9)$ Å, $\alpha = 97.514(4)$, $\beta = 110.270(2)$, $\gamma = 91.854(2)°$, $V = 4849.3(4)$ Å^3, $\varrho_{calc} = 1.379$ g cm^{-3}, $\mu = 1.647$ mm^{-1}, empirical absorption correction ($0.683 \leq T \leq 0.852$), $Z = 4$, , triclinic, space group $P\bar{1}$ (No. 2), λ 1.54178 Å, T 223(2) K, ω and φ scans, 58065 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin \theta)/\lambda] = 0.60$ Å^{-1}, 16659 independent ($R_{int} = 0.070$) and 11884 observed reflections $[I > 2\sigma(I)]$, 1262 refined parameters, $R = 0.054$, $wR^2 = 0.138$, max. (min.) residual electron density, 0.25 (–0.35) e Å^{-3}, H-atoms calculated and refined as riding atoms.

NMR-Scale Reaction of **1a** *with* $(C_6F_5)_3B$. Compound **1a** (49.5 mg, 0.10 mmol, 1 equiv.) was dissolved in (D_8)toluene (*ca.* 1 ml), and $(C_6F_5)_3B$ (51.2 mg, 0.10 mmol, 1 equiv.) was added. The resulting soln. was heated overnight to 110°, then cooled to r.t. NMR Experiments showed full conversion to **5a**. ^{1}H-NMR (600 MHz, (D_8)toluene, 298 K)^2): 7.41 (*m*, 4 *o*-H, $Ph^{\equiv}$); 7.30 (*m*, 4 *o*-H, $Ph^{=}$); 7.23 (*dm*, ^3J(H,H) = 7.6,

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4) CCDC-900201 to 900204 contain the supplementary crystallographic data for compounds **5a**, **5b**, **7b**, and **8**, resp. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif.

H–C(2)); 7.17 (dm, ^3J(H,H) = 7.7, H–C(5)); 6.95 (*m*, 4 *m*-H, Ph$^{\equiv}$); 6.93 (*m*, 2 *p*-H, Ph$^{\equiv}$); 6.83 (*m*, 2 *p*-H, Ph$^{=}$); 6.72 (*m*, 4 *m*-H, Ph$^{=}$); 6.68 (*m*, H–C(3)); 6.63 (*m*, H–C(4)). ^{13}C{^{1}H}-NMR (151 MHz, (D$_8$)toluene, 298 K)^2): 164.3 (br., =CB); 140.3 (*d*, ^1J(P,C) = 52.3, =CP); 137.9 (br., C(6)); 136.3 (*d*, ^1J(P,C) = 7.1, C$_{ipso}$, Ph$^{\equiv}$); 135.8 (*d*, ^4J(P,C) = 2.0, C(2)); 132.8 (*d*, ^2J(P,C) = 21.8, *o*-C, Ph$^{\equiv}$); 132.3 (*d*, ^4J(P,C) = 2.2, *p*-C, Ph$^{=}$); 132.1 (*d*, ^2J(P,C) = 9.4, *o*-C, Ph$^{=}$); 129.34 (C(4)); 129.25 (*d*, ^3J(P,C) = 10.3, *m*-C, Ph$^{=}$); 129.2 (*p*-C, Ph$^{\equiv}$); 129.0 (C(3)); 128.8 (*d*, ^3J(P,C) = 7.7, *m*-C, Ph$^{\equiv}$); 127.3 (*d*, ^3J(P,C) = 2.8, C(5)); 125.4 (*d*, ^1J(P,C) = 43.2, C$_{ipso}$, Ph$^{=}$); 121.8 (*d*, ^3J(P,C) = 5.5, C(1)); 105.5 (*d*, ^2J(P,C) = 4.9, C≡); 92.5 (*d*, ^1J(P,C) = 13.1, ≡CP); C$_6$F$_5$ not listed. ^{11}B{^{1}H}-NMR (192 MHz, (D$_8$)toluene, 298 K): -5.8 ($\nu_{1/2} \approx 400$ Hz). ^{31}P{^{1}H}-NMR (243 MHz, (D$_8$)toluene, 298 K): 16.6 ($\nu_{1/2} \approx 60$, P$^{=}$); -34.2 (*m*, P$^{\equiv}$). ^{19}F-NMR (564 MHz, (D$_8$)toluene, 298 K): -129.2 (br., 4 *o*-F, C$_6$F$_5$B); -136.0 (*m*, 2 *o*-F, C$_6$F$_5$); -154.0 (*t*, ^3J(F,F) = 21.2, *p*-F, C$_6$F$_5$); -156.8 (*t*, ^3J(F,F) = 19.5, 2 *p*-F, C$_6$F$_5$B); -161.7 (*m*, 2 *m*-F, C$_6$F$_5$); -163.6 (*m*, 4 *m*-F, C$_6$F$_5$B); $\Delta\delta(^{19}\mathrm{F}_{\mathrm{m,p}}(\mathrm{B})) = 6.8$; $\Delta\delta(^{19}\mathrm{F}_{\mathrm{m,p}}(\mathrm{C})) = 7.7$.

*[2-(2-{(*E*)-1-[Bis(4-methylphenyl)phosphino]-2-[bis(2,3,4,5,6-pentafluorophenyl)boryl]-2-(2,3,4,5,6-pentafluorophenyl)ethenyl}phenyl)ethynyl]bis(4-methylphenyl)phosphane* (**5b**). Compound **1b** (27.6 mg, 0.05 mmol, 1 equiv.) and (C$_6$F$_5$)$_3$B (25.6 mg, 0.05 mmol, 1 equiv.) were dissolved separately in toluene (each 5 ml), and then both solns. were combined at r.t. The resulting mixture was stirred at 60° overnight. After cooling to r.t., the solvent of the slightly yellow soln. was removed *in vacuo*, and pentane (5 ml) was added and directly removed *in vacuo* to remove remaining toluene (3 ×) to afford **5b** (50.0 mg, 0.05 mmol, 94%). Slightly yellow solid. M.p. 227°. IR (KBr): 3067*w*, 2961*w*, 2938*w*, 2863*w*, 1645*s*, 1591*m*, 1559*w*, 1518*s*, 1465*s*, 1383*s*, 1314*w*, 1286*s*, 1200*m*, 1095*s*, 1052*m*, 919*s*, 893*s*, 847*m*, 822*m*, 783*m*, 753*s*, 716*m*, 677*m*. Anal. calc. for C$_{56}$H$_{32}$BF$_{15}$P$_2$ (1062.59): C 63.30, H 3.04; found: C 63.45, H 3.16. Single crystals suitable for X-ray crystal structure analysis were obtained by diffusion of pentane into a sat. soln. of **5b** in CH$_2$Cl$_2$ at $-40°$.

X-Ray Crystal Data for **5b**^{4}). Formula C$_{56}$H$_{32}$BF$_{15}$P$_2$ · 0.5 CH$_2$Cl$_2$, M_r 1105.03, colorless crystal, 0.21 × 0.18 × 0.08 mm, $a = 16.9931(4)$, $b = 12.1550(6)$, $c = 25.1051(9)$ Å, $\beta = 105.728(3)°$, $V = 4991.3(3)$ Å^3, $\varrho_{\mathrm{calc}} = 1.471$ g cm^{-3}, $\mu = 2.133$ mm^{-1}, empirical absorption correction ($0.663 \leq T \leq 0.847$), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), λ 1.54178 Å, T 223(2) K, ω and φ scans, 31284 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.60$ Å^{-1}, 8631 independent ($R_{\mathrm{int}} = 0.057$) and 6290 observed reflections [$I > 2\sigma(I)$], 692 refined parameters, $R = 0.062$, $wR^2 = 0.164$, max. (min.) residual electron density 0.54 (-0.50) e Å^{-3}, the H-atoms calculated and refined as riding atoms.

NMR-Scale Reaction of **1b** *with (C$_6$F$_5$)$_3$B.* Compound **1b** (27.6 mg, 0.05 mmol, 1 equiv.) was dissolved in (D$_8$)toluene (*ca.* 1 ml), and (C$_6$F$_5$)$_3$B (25.6 mg, 0.05 mmol, 1 equiv.) was added. The resulting soln. was heated overnight to 110°, then cooled to r.t. NMR Experiments showed full conversion to **5b**. ^{1}H-NMR (600 MHz, (D$_8$)toluene, 299 K)^2): 7.43 (*m*, 2 *o*-H, tol$^{\equiv}$); 7.36 (br., 2 *o*-H, tol$^{=}$); 7.09 (*m*, H–C(2)); 7.00 (*m*, H–C(5)); 7.00 (*m*, 2 *p*-H, tol$^{\equiv}$); 6.93 (*m*, 2 *m*-H, tol$^{\equiv}$); 6.91 (*m*, 2 *m*′-H, tol$^{\equiv}$); 6.86 (*m*, 2 *p*-H, tol$^{=}$); 6.66 (*m*, 2 *m*-H, tol$^{=}$); 6.61 (*m*, 2 *m*′-H, tol$^{=}$); 6.59 (*m*, H–C(4)); 6.57 (*m*, H–C(3)); 2.36 (*s*, 2 Me$^{\equiv}$); 1.89 (*s*, 2 Me$^{=}$). ^{13}C{^{1}H}-NMR (151 MHz, (D$_8$)toluene, 299 K)^2): 165.1 (br., =CB); 142.6 (*d*, ^2J(P,C) = 9.6, *o*′-C, tol$^{=}$); 142.4 (*d*, ^2J(P,C) = 27.4, *o*′-C, tol$^{\equiv}$); 140.9 (*d*, ^1J(P,C) = 52.0, =CP); 138.6 (C(6)); 136.3 (*d*, *J*(P,C) = 2.9, C(2)); 134.3 (*d*, ^2J(P,C) = 8.2, *o*-C, tol$^{=}$); 133.4 (*d*, ^1J(P,C) = 7.0, C$_{ipso}$, tol$^{\equiv}$); 132.9 (*d*, ^2J(P,C) = 2.7, *o*-C, tol$^{\equiv}$); 132.4 (*d*, ^4J(P,C) = 2.7, *p*-C, tol$^{=}$); 132.0 (*d*, ^3J(P,C) = 9.3, *m*′-C, tol$^{=}$); 130.7 (*d*, ^3J(P,C) = 5.6, *m*′-C, tol$^{\equiv}$); 129.6 (*p*-C, tol$^{\equiv}$); 129.3 (C(4)); 128.8 (C(3))^5), 127.4 (C(5)); 126.7 (*d*, ^3J(P,C) = 10.0, *m*-C, tol$^{=}$); 126.5 (*d*, ^3J(P,C) = 1.9, *m*-C, tol$^{\equiv}$); 125.5 (*d*, ^1J(P,C) = 23.6, C$_{ipso}$, tol$^{=}$); 121.9 (*d*, ^3J(P,C) = 5.0, C(1)); 105.6 (*d*, ^2J(P,C) = 5.8, C≡); 92.1 (*d*, ^1J(P,C) = 12.4, ≡CP); 21.5 (br. *d*, ^3J(P,C) = 4.4, Me$^{=}$); 21.0 (*d*, ^3J(P,C) = 21.4, Me$^{\equiv}$); C$_6$F$_5$ not listed. ^{11}B{^{1}H}-NMR (192 MHz, (D$_8$)toluene, 299 K): -3.2 ($\nu_{1/2}$ *ca.* 600 Hz). ^{31}P{^{1}H}-NMR (243 MHz, (D$_8$)toluene, 299 K): 20.0 ($\nu_{1/2} \approx 60$, P$^{=}$); -48.1 ($\nu_{1/2} \approx 40$, P$^{\equiv}$). ^{19}F-NMR (564 MHz, (D$_8$)toluene, 299 K): -126.9 (br., 4 *o*-F, C$_6$F$_5$B); -135.5 (br., 2 *o*-F, C$_6$F$_5$); -153.9 (*t*, ^3J(F,F) = 21.0, *p*-F, C$_6$F$_5$); -156.3 (*t*, ^3J(F,F) = 20.1, 2 *p*-F, C$_6$F$_5$B); -162.4 (br., 2 *m*-F, C$_6$F$_5$); -163.6 (br., 4 *m*-F, C$_6$F$_5$B); $\Delta\delta(^{19}\mathrm{F}_{\mathrm{m,p}}(\mathrm{B})) = 7.3$; $\Delta\delta(^{19}\mathrm{F}_{\mathrm{m,p}}(\mathrm{C})) = 8.5$.

Reaction of **1b** *with B(C$_6$F$_5$)$_3$ at Room Temperature. Generation of [3-(2-{[Bis(2-methylphenyl)phosphanyl]ethynyl}phenyl)-1,1-bis(2-methylphenyl)-1*H*-phosphirenium-2-yl][tris(pentafluorophenyl)]borate(1–)* (**7b**). Compound **1b** (27.5 mg, 0.05 mmol, 1 equiv.) and B(C$_6$F$_5$)$_3$ (25.6 mg, 0.05 mmol,

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5) Assignment based on GHSQC experiment.

1 equiv.) were dissolved separately in toluene (2 ml each). The solns. were combined and stirred at r.t. overnight. Then, the solvent was removed *in vacuo* and pentane (5 ml) was added and directly removed *in vacuo* again (3 ×), to yield a mixture of **5b** and **7b** (ratio of *ca.* 1:3, ^{31}P-NMR) as a slightly yellow solid (47.0 mg, 0.04 mmol, 88%). **7b** was characterized by NMR spectroscopy from the reaction mixture. Single crystals of **7b** were obtained by diffusion of pentane into a sat. soln. of the reaction mixture in CH_2Cl_2 at – 40°. ^{11}B{^{1}H}-NMR (160 MHz, (D_8)toluene, 299 K): – 16.0 ($\nu_{1/2} \approx 40$ Hz). ^{31}P{1H}-NMR (202 MHz, (D_8)toluene, 299 K): – 47.7 ($\nu_{1/2} \approx 1.5$ Hz, $P^{\equiv}$); – 114.8 ($\nu_{1/2} \approx 15$ Hz, phosphireniumborate fragment). ^{19}F-NMR (470 MHz, (D_8)toluene, 299 K): – 130.9 (*m*, 2 *o*-F, C_6F_5B); – 159.0 (*t*, ^3J(F,F) = 20.5 Hz, 1 *p*-F, C_6F_5B); – 164.2 (*m*, 2 *m*-F, C_6F_5B); $\Delta\delta(^{19}F_{m,p}(B)) = 5.2$.

X-Ray Crystal Data for **7b**[4]. Formula $C_{56}H_{32}BF_{15}P_2 \cdot 0.5\ CH_2Cl_2 \cdot 0.5\ C_5H_{12}$, M_r 1141.10 colorless crystal, 0.35 × 0.30 × 0.10 mm, $a = 14.0325(5)$, $b = 14.5631(2)$, $c = 15.0569(6)$ Å, $\alpha = 66.601(2)$, $\beta = 65.245(3)$, $\gamma = 81.536(2)°$, $V = 2563.76(14)$ Å^3, $\varrho_{calc} = 1.478$ g cm^{-3}, $\mu = 2.094$ mm^{-1}, empirical absorption correction ($0.527 \leq T \leq 0.819$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 1.54178$ Å, $T = 223(2)$ K, ω and φ scans, 36235 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.60$ Å^{-1}, 8769 independent ($R_{int} = 0.037$) and 8171 observed reflections $[I > 2\sigma(I)]$, 745 refined parameters, $R = 0.055$, $wR^2 = 0.153$, max. (min.) residual electron density 0.74 (– 0.62) e Å^{-3}, H-atoms calculated and refined as riding atoms.

*((1*E*)-3-[Bis(2,3,4,5,6-pentafluorophenyl)boryl]-1-{[bis(2,4,6-trimethylphenyl)phosphino](2,4,6-trimethylphenyl)methylene}-1*H*-inden-2-yl)(2,3,4,5,6-pentafluorophenyl)(2,4,6-trimethylphenyl)phosphane* (**8**). Compound **1c** (66.2 mg, 0.10 mmol, 1 equiv.) and $(C_6F_5)_3B$ (51.2 mg, 0.10 mmol, 1 equiv.) were dissolved separately in toluene (5 ml). The colorless solns. were combined at r.t., and a direct change of the color to red was observed. The mixture was stirred overnight at 110° and then cooled to r.t. The solvent was removed *in vacuo*, pentane (5 ml) was added and directly removed *in vacuo* to remove remaining toluene (three times) to afford **8** (101 mg, 0.08 mmol, 89%). Orange solid. M.p. 275° (dec.). IR (KBr): 3024*m*, 2064*m*, 2923*m*, 2857*w*, 2735*w*, 1643*m*, 1605*m*, 1558*w*, 1518*s*, 1466*s*, 1417*m*, 1384*m*, 1328*w*, 1287*m*, 1249*w*, 1094*s*, 1031*w*, 974*s*, 920*w*, 886*w*, 850*m*, 763*m*, 705*w*, 677*w*, 647*w* 610*w*. ^{1}H-NMR (500 MHz, CD_2Cl_2, 253 K)[2]: 7.67 (*d*, ^3J(H,H) = 7.9, H–C(9))[6]; 7.28 (*m*, H–C(8))[6]; 7.27 (*m*, H–C(6))[6]; 7.06 (*m*, H–C(7))[6]; 6.87 (*d*, *J* = 6.0, *m*′-H, mes_aPC(1)); 6.82 (*s*, *m*-H, mes_aPC(1)); 6.71 (*s*, *m*′-H, mesPC(3)); 6.53 (*d*, *J* = 5.3, *m*-H, mesPC(3)); 6.51 (*s*, *m*′-H, mes_bPC(1)); 6.38 (*d*, *J* = 6.4, *m*-H, mes_bPC(1)); 6.30 (*s*, *m*′-H, mesC(1)); 5.89 (*s*, *m*-H, mesC(1)); 2.45 (*s*, *o*-Me, mes_aPC(1)); 2.34 (*s*, *o*′-Me, mesPC(3)); 2.27 (*s*, *p*-Me, mes_aPC(1)); 2.20 (*s*, *o*-Me, mes_bPC(1)); 2.17 (*s*, *o*′-Me, mes_aPC(1)); 2.13 (*s*, *p*-Me, mesPC(3)); 2.05 (*s*, *o*-Me, mesC(1)); 2.03 (*s*, *p*-Me, mes_bPC(1)); 1.87 (*s*, *o*-Me, mesPC(3), *p*-Me, mesC(1)); 1.79 (*s*, *o*′-Me, mesC(1)); 1.78 (*s*, *o*′-Me, mes_bPC(1)). ^{13}C{^{1}H}-NMR (126 MHz, CD_2Cl_2, 253 K)[2]: 176.8 (br., =C(4)B); 152.6 (*d*, *J*(P,C) = 41.4); not observed (C(1), C(2)); 145.7 (*d*, ^2J(P,C) = 35.1, *o*-C, mes_bPC(1)); 143.8 (*d*, ^2J(P,C) = 4.1, *o*′-C, mes_bPC(1)); 142.7 (*d*, ^2J(P,C) = 3.8, *o*-C, mes_aPC(1)); 141.3 (*m*, *o*′-C, mesPC(3)); 141.1 (*d*, ^4J(P,C) = 2.3, *p*-C, mesPC(3)); 140.9 (C(10))[6]; 140.6 (*d*, ^2J(P,C) = 35.5, *o*′-C, mes_aPC(1)); 140.6 (br. *d*, ^2J(P,C) = 17.8, *o*-C, mesPC(3)); 140.0 (*m*, C(5))[6]; 139.1 (*p*-C, mes_bPC(1)); 138.42 (*p*-C, mes_aPC(1)); 138.42 (*d*, ^3J(P,C) = 3.2, *o*′-C, mesC(1)); 137.9 (*d*, *J* = 2.0, *p*-C, mesC(1)); 136.1 (*o*-C, mesC(1)); 136.0 (*d*, ^2J(P,C) = 3.7, C_{ipso}, mesC(1)); 133.8 (*dd*, *J*(P,C) = 52.9, *J*(P,C) = 3.5, C(3))[6]; 132.4 (*d*, ^1J(P,C) = 12.9, C_{ipso}, mes_aPC(1)); 129.82 (*d*, *J*(P,C) = 7.2, *m*′-C, mes_aPC(1)); 129.76 (*d*, *J*(P,C) = 8.1, *m*′-C, mesPC(3)); 129.7 (*m*′-C, mes_bPC(1)); 129.4 (*d*, ^3J(P,C) = 10.6, *m*-C, mesPC(3)); 129.0 (*m*-C, mes_aPC(1)); 128.4 (*d*, ^3J(P,C) = 8.9, *m*-C, mes_bPC(1)); 128.2 (*m*′-C, mesC(1)); 127.7 (C(7)); 126.7 (*m*-C, mesC(1)); 126.5 (C(8)); 125.5 (*d*, ^1J(P,C) = 9.9, C_{ipso}, mes_bPC(1)); 125.1 (br., C(9)); 124.4 (*d*, *J*(P,C) = 15.3, C(6)); 122.0 (*dm*, ^1J(P,C) = 48.0, C_{ipso}, mesPC(3)); 26.0 (*o*-Me, mes_aPC(1)); 25.0 (br., *o*′-Me, mesPC(3)); 24.4 (*o*′-Me, mes_bPC(1)); 23.1 (*d*, ^3J(P,C) = 26.3, *o*-Me, mes_bPC(1)); 23.0 (*d*, ^3J(P,C) = 25.0, *o*′-Me, mes_aPC(1)); 22.5 (*o*-Me, mesC(1)); 21.5 (br., *o*-Me, mesPC(3)); 21.4 (*m*, *o*′-Me, mesC(1)); 20.8 (*p*-Me, mes_aPC(1)); 20.6 (*p*-Me, mes_bPC(1)); 20.5 (*p*-Me, mesPC(3)); 20.1 (*p*-Me, mesC(1)); C_6F_5 not listed. ^{11}B{^{1}H}-NMR (160 MHz, CD_2Cl_2, 253 K): 1.7 (very broad). ^{31}P{^{1}H}-NMR (202 MHz, CD_2Cl_2, 253 K)[2]: – 15.0 ($\nu_{1/2} \approx 8$, P–C(1)); – 15.7 ($\nu_{1/2} \approx 40$, P–C(3)). ^{31}P-NMR (202 MHz, CD_2Cl_2, 253 K)[2]: – 15.0 ($\nu_{1/2} \approx 20$, P–C(1)); – 15.7 ($\nu_{1/2} \approx 45$, P–C(3)). ^{19}F-NMR (470 MHz, CD_2Cl_2, 253 K): – 122.3 (*o*), – 127.6 (*o*′), – 148.2 (*p*), – 160.6 (*m*′), – 160.8 (*m*) (each *m*, each 1 F, C_6F_5P); $\Delta\delta(^{19}F(m,p)) = 12.6$;

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[6] Tentative assignment.

$\Delta\delta(^{19}F(m',p)) = 12.4$); -126.8 (2 F, o), -158.7 (1 F, p), -165.4 (2 F, m) (each m, $BC_6F_5{}^a$); $\Delta\delta(^{19}F_{m,p}) = 6.7$); -129.4 (2 F, o), -156.5 (1 F, p), -165.2 (2 F, m) (each m, $C_6F_5B^b$); $\Delta\delta(^{19}F_{m,p}) = 8.7$). Anal. calc. for $C_{64}H_{48}BF_{15}P_2$ (1174.80): C 65.43, H 4.12; found: C 65.04, H 4.06. Single crystals suitable for X-ray crystal structure analysis were obtained by slow evaporation of the solvent of a sat. soln. of **8** in CH_2Cl_2 at $-40°$.

X-Ray Crystal Data for **8**[4]. Formula $C_{64}H_{48}BF_{15}P_2 \cdot CH_2Cl_2$, M_r 1259.70 colorless crystal, $0.17 \times 0.10 \times 0.07$ mm, $a = 15.1216(6)$, $b = 15.6072(4)$, $c = 15.9848(5)$ Å, $\alpha = 98.755(2)$, $\beta = 115.201(3)$, $\gamma = 112.655(3)°$, $V = 2915.43(17)$ Å^3, $\varrho_{calc} = 1.435$ g cm^{-3}, $\mu = 2.307$ mm^{-1}, empirical absorption correction ($0.695 \leq T \leq 0.855$), $Z = 2$, triclinic, space group, $P\bar{1}$ (No. 2), λ 1.54178 Å, T 223(2) K, ω and φ scans, 41291 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.60$ Å^{-1}, 10056 independent ($R_{int} = 0.040$) and 8612 observed reflections $[I > 2\sigma(I)]$, 778 refined parameters, $R = 0.054$, $wR^2 = 0.142$, max. (min.) residual electron density 0.67 (-0.95) e Å^{-3}, H-atoms calculated and refined as riding atoms.

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