Facile 1,1-Carboboration Reaction of a Diarylphosphino-substituted Conjugated Diyne with Tris(pentafluorophenyl)borane

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$^5$ X-Ray crystal structure analyses

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Dedicated to Professor Heinrich Nöth on the occasion of his 85th birthday

Bis(dimesitylphosphanyl)butadiyne (14) reacts with B(C$_6$F$_5$)$_3$ by a 1,1-carboboration sequence. The selective attack at a single phosphanyl-alkyne moiety is observed. First a phosphirenium-borate zwitterion 15 is formed at r. t. Thermolysis (80 °C) results in the E-selective formation of the 1,1-carboboration product, the frustrated Lewis pair (FLP) E-16, which upon heating to 160 °C eventually undergoes isomerization followed by an internal nucleophilic aromatic substitution reaction to give the product 17 featuring a -B(F)(C$_6$F$_5$)$_2$ substituent at the five-membered P-heterocycle. Finally, the FLP E-16 was reacted with n-butylisocyanide to yield the five-membered heterocyclic product 18, formed by P,B addition to the isonitrile carbon atom. Compounds 14, 15, 17, and 18 were characterized by X-ray crystal structure analyses.

Key words: Carboboration, Boron, Phosphorus, Frustrated Lewis Pair

Introduction

The 1,1-carboboration reaction is a method very well suited for synthesizing vinylborane derivatives. It has turned out to be especially useful for preparing alkenylboranes that bear bulky substituents at the carbon-carbon double bond [1, 2]. The first variants involved reactions of alkylnylborate salts that were treated with suitable electrophiles [3 – 5]. However, the most important development in this field is probably due to subsequent work by B. Wrackmeyer et al. [6 – 8]. During the “Wrackmeyer reaction” (see Scheme 1) an acetylenic substrate bearing a suitable substituent X is treated with e. g. triethylborane. Addition of the borane to the ≡C–X terminus of the alkyne induces a 1,2-migration of the X substituent along the acetylenic framework concomitant with a 1,2-alkyl shift from boron to the former C1 terminus of the acetylene [9]. The “Wrackmeyer reaction” usually requires good migrating groups X, preferentially Si-, Ge-, Sn- or Pb-based [7, 8], but also a few transition metal systems can be used [10, 11].

H. Berke [12, 13] and our group [14, 15] have independently found that the application of strongly electrophilic R-B(C$_6$F$_5$)$_2$ reagents greatly facilitates the 1,1-carboboration reaction and extended its scope considerably, making it possible to use simple terminal alkynes as substrates. In these cases hydrogen migration along the acetylenic backbone took place during the 1,1-carboboration sequence. We were even able to react internal alkynes according to this scheme, which provided a novel method for C–C bond activation [16] (Scheme 1).

We have described several extensions of such 1,1-carboboration reactions [17 – 21]. Systems that were proceeding with facile Ar$_2$P migration turned out to be especially interesting. We developed a viable phosphole synthesis based on this chemistry (see Scheme 2) [22] and have shown that unsaturated vicinal P/B frustrated Lewis pairs (FLPs) could easily be prepared along this route [23]. The 1,1-carboboration reactions involving 1,2-phosphanyl migration are likely to proceed via zwitterionic phosphirenium borate intermediates. In one case we were
able to isolate and characterize such a species (11) including its crystal structure determination [24].

We have now extended this chemistry to the reactions of phosphanyl-substituted conjugated diynes. In this account we describe the reaction of bis(dimesitylphosphanyl)butadiyne with B(C₆F₅)₃.

**Results and Discussion**

The conjugated diyne starting material 14 was prepared by treatment of *in situ* generated dilithiobutadiyne (13) with mes₂PCl [25] (Scheme 3) in ca. 68% yield after chromatographic purification and crystallization. Compound 14 was characterized by spectroscopy and by X-ray diffraction. In solution it features the typical ¹H and ¹³C NMR signals of the four homotopic mesityl substituents at phosphorus, and it shows a ³¹P NMR resonance at δ = −54.0 ppm. The butadiyne ¹³C NMR pair of resonances occurs at δ = 82.6 (C1, ¹J_PC = 12.2 Hz, ²J_PC = 3.2 Hz) and δ = 92.6 (C2, ²J_PC = 11.3 Hz, ³J_PC = 3.0 Hz) ppm. The X-ray crystal structure analysis of compound 14 (Fig. 1) shows a linear P₂C₄ framework [angles P1–C1–C2 164.4(2)°, C1–C2–C2* 178.0(2)°] with typical bond lengths of P1–C1 1.762(2), C1–C2 1.209(2) and C2–C2* 1.372(3) Å. The (symmetry-equivalent) phosphorus atoms feature typical trigonal pyramidal coordination geometries [sum of PCCC angles 314.3°]. The overall molecule has inversion symmetry.

We then treated the bis(dimesitylphosphanyl)butadiyne starting material 14 with the strong Lewis acid B(C₆F₅)₃. The reaction with one molar equivalent of
the borane gave a selective reaction that involved only a single $\text{mes}_2\text{P}–\text{C}≡\text{C}$ moiety of the substrate. Stirring the mixture for a prolonged time at r.t. resulted in the clean formation of the product 15. This can be regarded as the initial step of a 1,1-carboboration reaction sequence. The borane was added to a terminal butadiyne carbon atom, and the $\text{mes}_2\text{P}$ group started its migration toward the adjacent acetylenic carbon atom (Scheme 3). We have isolated the phosphireniurn-borate product 15 in ca. 70% yield.

In solution it shows a very characteristic $^{31}\text{P}$ NMR resonance [24, 26–28] of the phosphireniurn unit at $\delta = -131.7$ and the $^{31}\text{P}$ NMR signal of the remaining $\text{C}≡\text{C}–\text{Pmes}_2$ group at $\delta = -54.6$ ppm. The $^{11}\text{B}$ NMR signal occurs at $\delta = -16.7$ ppm, typical of a borane anion moiety [corresponding $^{19}\text{F}$ NMR signals at $\delta = -131.2$ ($\sigma$), $-160.5$ ($\rho$), $-165.4$ ($m$) ppm]. The $^{13}\text{C}$ NMR resonances of the phosphireniurn unit were located at $\delta = 152.6$ ($\equiv\text{CB}$) and $\delta = 122.8$ ($\equiv\text{CP}$) ppm, and we found the $^{13}\text{C}$ NMR signals of the remaining alkynyl moiety at $\delta = 113.1$ and $\delta = 93.1$ ppm. Compound 15 was characterized by single crystal X-ray diffraction (Fig. 2). It shows the newly formed three-membered phosphireniurn subunit [C3–P2 1.741(2), C4–P2 1.783(2), C3–C4 1.337(3) Å]. The $\text{B(C}_6\text{F}_5)_3$ moiety is bonded to carbon atom C4 [C4–B1 1.638(3) Å, angle C3–C4–B1 138.2(2)$^\circ$]. Carbon atom C3 bears the $\equiv\text{C}–\text{Pmes}_2$ substituent [C3–C2 1.403(3), C2–C1 1.204(3), C1–P1 1.758(2) Å, angles P1–C1–C2 162.3(2)$^\circ$, C1–C2–C3 177.0(2)$^\circ$, C2–C3–C4 140.9(2)$^\circ$, C2–C3–P2 146.5(1)$^\circ$]. Both, the boron atom B1 and the phosphorus atom P2 show pseudotetrahedral coordination geometries, whereas the remaining phosphorus center

![Scheme 3.](image-url)
Compound 15 was heated for 7 h at 80 °C in an NMR experiment. This resulted in the formation of the 1,1-carboboration product E-16 (Scheme 3). The product shows a 31P NMR signal of the adjacent mes2P substituent at δ = 11.2 ppm. The 19F NMR spectra feature a set of signals (double intensity) of the -B(C6F5)2 group [in the typical borate range: δ = −132.0 (o), −160.9 (p) and −168.2 (m) ppm] and the signals of the -C6F5 group (single intensity) that had been shifted from boron to carbon during the 1,1-carboboration reaction sequence [δ = −138.5 (o), −158.3 (p), −166.6 (m) ppm]. The 31P NMR signal of the remaining -C≡C-Pmes2 group occurs at δ = −59.7 ppm [corresponding acetylenic 13C NMR resonances: δ = 98.7, 102.5 ppm]. Compound 16 was also synthesized on a preparative scale and isolated in 91% yield.

We thermolyzed the in situ generated 1,1-carboboration product 16 in an autoclave at 160 °C (24 h, Scheme 3). This resulted in the formation of compound 17, which was isolated in > 90% yield. We assume that under these forcing conditions E-16/Z-16 isomerization might take place followed by internal nucleophilic aromatic substitution at the -C6F5 group by the then adjacent -Pmes2 group [29].

Compound 17 shows the typical 19F NMR signal of the boron-bonded fluoride ([B]-F) at δ = −187.5 ppm and four clearly separated 19F NMR features of the remaining tetrafluorophenylene moiety (δ = −123.9, −124.6, −141.8, −152.3 ppm) in addition to the 19F NMR signals of the residual -B(C6F5)2 group [δ = −134.0 (o), −160.9 (p), −166.5 (m) ppm]. Compound 17 shows a phosphonium 31P NMR signal at δ = 25.9 ppm and the typical 31P NMR signal of the pendent -C≡C-Pmes2 substituent (δ = −55.9 ppm).

The X-ray crystal structure analysis of compound 17 (Fig. 3) shows the newly formed phosphoria-indene moiety [P2–C3 1.819(3), C3–C4 1.363(4) Å] that has the -B(F)(C6F5)2 substituent bonded to it at carbon atom C4 (C4–B1 1.649(4), B1–F1 1.452(4) Å) and the -C≡C-Pmes2 substituent at carbon atom C3 [C3–C2 1.416(4), C2–C1 1.204(4), C1–P1 1.777(3) Å, angles P1–C1–C2 166.7(3)°, C1–C2–C3 171.4(3)°, C2–C3–C4 126.3(3)°, C2–C3–P2 122.4(2)°].

We have started to investigate the reactivity of the 1,1-carboboration product E-16 and describe here its reaction with an alkyl isonitrile. We generated compound E-16 in situ on a preparative scale (see above) and added n-butyllisocyanide. The reaction mixture was then kept at r.t. for ca. 2 d to give the addition product 18 in ca. 69% yield (Scheme 4).

In the crystal (Fig. 4) compound 18 features the newly formed five-membered heterocyclic core structure that was formed by addition of both the borane and the phosphane moiety of the frustrated Lewis pair [30, 31] E-16 to the isonitrile carbon atom [B1–C5 1.652(6), C5–P2 1.886(4), P2–C3 1.818(4), C3–C4 1.361(5), C4–B1 1.652(5) Å]. The C5–N1 bond (1.265(5) Å) is in the C=N double bond range. The newly formed imine type structure is E-configurated.

The sp2-hybridized olefinic ring carbon atom C4 has the C6F5 substituent attached to it (C4–C5 1.485(5) Å) whereas the -C≡C–Pmes2 substituent is

![Scheme 4.](image-url)
bonded to C3 [C3–C2 1.426(5), C2–C1 1.214(5), C1–P1 1.763(4) Å, angles P1–C1–C2 162.0(4)°, C1–C2–C3 174.2(4)°, C2–C3–P2 119.8(3)°, C2–C3–C4 128.5(3)°, sum of P1CCC angles: 314.0°, sum of C5 angles: 359.8°].

In solution we see the NMR signals of a single isomer of compound 18. It shows a $^{11}$B NMR signal at $\delta = -14.7$ and a ring phosphorus resonance at $\delta = 8.5$ ppm. The endocyclic $\text{B(C}_6\text{F}_5)_2$ unit shows a set of $^{19}$F NMR signals with double intensity at $\delta = -129.9$ (o), $\delta = -159.3$ (p) and $\delta = -165.2$ (m) ppm. The $^{19}$F NMR resonances of the single carbon-bound $-\text{C}_6\text{F}_5$ group were located at $\delta = -134.9$ (o), $\delta = -155.2$ (p) and $\delta = -163.6$ (m) ppm. The terminal $-\text{Pmes}_2$ substituent gives rise to a $^{31}$P NMR signal at $\delta = -55.5$ ppm.

Conclusion

Bis(dimesitylphosphanyl)butadiyne (14) reacts cleanly with the strong Lewis acid $\text{B(C}_6\text{F}_5)_3$. It undergoes a typical 1,1-carboboration reaction that proceeds via a phosphirenium-borate intermediate (here: 15). Further heating leads to completion of the 1,1-carboboration reaction with formation of the internal frustrated Lewis pair $E$-16. It has previously been shown that related syn-1-boryl-2-phosphanyl alkenes [32] or arenes [33] may serve as bifunctional donor/acceptor ligands in transition metal coordination chemistry and form the respective five-membered chelate metal complexes or related coordination systems (Fig. 5). In our case the FLP $E$-16 serves in a “metal-like” role, namely as a combined donor/acceptor system for a typical organic ligand, namely $n$-butylisocyanide.

It is also remarkable that $\text{B(C}_6\text{F}_5)_3$ undergoes a very selective 1,1-carboboration reaction at only one acetylene unit of the bifunctional substrate 14 without touching the other $-\text{C}\equiv\text{C–Pmes}_2$ function. We shall see whether we can eventually utilize this remaining functionality to prepare new multi-functionalized FLP derivatives.

Experimental Section

All reactions were carried out under argon atmosphere with Schlenk-type glassware. Solvents were dried using a Grubbs-type system [34]. The following instruments were
used for physical characterization of the compounds. Elemental analyses: Foss-Heraeus CHN-O-Rapid NMR: Varian Inova 500 (1H, 500 MHz; 13C, 126 MHz), Varian UnityPlus 600 (1H, 600 MHz; 13C, 151 MHz). Chemical shifts (δ) are given in ppm. Assignments of the resonances were supported by 2D experiments. For the determination of melting points a DSC Q 20 (TA Instruments) was employed.

**Compound 14**

Compound 14 was prepared analogously to a published synthetic procedure for bis(diphenylphosphino)butadiyne [25]: First a solution of n-butyllithium (30 mL, 48 mmol, 4 eq.) in THF (75 mL) was protected from light and cooled down to −78 °C. Then a solution of hexachlorobutadiene (1.9 mL, 12 mmol, 1 eq.) in THF (10 mL) was added via syringe within a period of 15 min. The reaction mixture was stirred for 15 min at −78 °C and additional 2.5 h at rt. Subsequently the solution was cooled to −78 °C and added to a solution of PMes2Cl (7.31 g, 24 mmol, 2 eq.) in THF (30 mL) during 15 min. After one hour stirring at −78 °C the dark reaction mixture was hydrolyzed with H2O (30 mL) at rt. The organic layer was separated and dried with MgSO4. After filtration the solvent was removed in vacuo to yield a dark-yellow solid (6.52 g). It was purified by column chromatography (30 × 350 mm, SiO2/dichloromethane) and crystallization from dichloromethane solution. Yield: 4.78 g (8.15 mmol, 68%); m.p. 175 °C. −1H NMR (400 MHz, 295 K, CD2Cl2): δ = 6.81 (br, J1H = 3.4 Hz, 2H, m-Mes), 2.33 (s, 6H, o-CH3Mes), 2.23 (s, 3H, p-CH3Mes), −13C1H NMR (76 MHz, 295 K, CD2Cl2): δ = 142.2 (dd, JPC = 15.9 Hz, o-Mes), 139.3 (p-Mes), 130.2 (dd, JPC = 4.0 Hz, m-Mes), 128.5 (dd, JPC = 10.7 Hz, 6JPC = 1.1 Hz, i-Mes), 92.6 (dd, JPC = 11.3 Hz, 3JPC = 3.0 Hz, ≡PC), 82.6 (dd, JPC = 12.2 Hz, 4JPC = 3.2 Hz, ≡PC ≡PC), 23.0 (dd, JPC = 14.2 Hz, o-CH3Mes), 21.0 (p-CH3Mes), [l tentatively assigned]. −31P1H NMR (121 MHz, 295 K, CD2Cl2): δ = −54.0 (m1/2 ≈ 1 Hz) − HRMS: m/z = 587.2991 (calcd. 587.2996 for C38H42P2) − C38H42P2: calc. C 81.88, H 7.56; found C 80.39, H 7.56.

**Compound 15**

A solution of B(C6F5)2 (256 mg, 0.55 mmol, 1 eq.) in dichloromethane (8 mL) was added to a solution of 14 (293 mg, 0.55 mmol, 1 eq.) in dichloromethane (5 mL) via syringe. The reaction mixture was stirred for 3 h at rt. Then the solvent was removed in vacuo to yield a brown solid (436 mg, 79%). The product was purified by crystallization from dichloromethane-pentane solution to get colorless crystals (384 mg, 70%). Crystals suitable for X-ray crystals structure analysis were obtained by diffusion of pentane into a dichloromethane solution of 15 at −40 °C. M. p. 134 °C. −1H NMR (500 MHz, 299 K, CD2Cl2): δ = 6.87 (dd, JPH = 5.8 Hz, 2H, m-MesP), 6.84 (dd, JPH = 3.5 Hz, 2H, m-MesP), 2.30 (s, 6H, o-CH3MesP), 2.29 (s, 3H, p-CH3MesP), 2.26 (s, 3H, p-CH3MesP), 2.11 (s, 6H, o-CH3MesP), −13C1H NMR (125 MHz, 299 K, CD2Cl2): δ = 152.6 (br. −CB), 148.2 (dd, JPC ≈ 240 Hz, Cδ,F3), 144.9 (dd, JPC ≈ 3.3 Hz, p-MeP), 143.5 (dd, JPC ≈ 12.1 Hz, o-MeP), 142.1 (dd, JPC = 16.0 Hz, o-Mes), 139.6 (p-Mes), 139.4 (dm, JPC ≈ 250 Hz, Cα,F3), 137.0 (dm, JPC ≈ 250 Hz, Cβ,F3), 130.7 (dd, JPC = 13.6 Hz, m-MesP), 130.3 (dd, JPC = 4.1 Hz, m-Mes), 128.1 (dd, JPC = 9.6 Hz, i-Mes), 122.8 (br, JPC = 175 °C). −19F NMR (470 MHz, 299 K, CD2Cl2): δ = −131.2 (m, 2F, o-C6F5), −160.5 (t, JFF = 20.7 Hz, 1F, p-C6F5), −165.4 (m, 2F, m-C6F5), [δF: Fm = 4.8]. − HRMS: m/z = 1099.2844 (calcd. 1099.2844 for C38H42BF6P2).

**Compound E-16**

NMR tube scale: Compound 15 (20 mg, 0.018 mmol) in CD2Cl2 (1.5 mL) was heated in a flame-sealed NMR tube for 7 h at 80 °C. Then the sample was investigated by NMR spectroscopy. −1H NMR (500 MHz, 299 K, CD2Cl2): δ = 6.74 (dm, JPH = 3.7 Hz, 2H, m-MesP), 6.72 (dm, JPH = 3.4 Hz, 2H, m-MesP), 2.25 (s, 3H, p-CH3MesP), 2.22 (s, 3H, p-CH3MesP), 2.15 (s, 6H, o-CH3MesP), 2.08 (s, 6H, o-CH3MesP), −13C1H NMR (125 MHz, 299 K, CD2Cl2): δ = 163.1 (br. =CB), 142.7 (dd, JPC = 8.9 Hz, o-MesP), 142.1 (dd, JPC = 15.8 Hz, o-MesP), 142.0 (dd, JPC = 2.9 Hz, p-MesP), 139.1 (p-Mes), 130.9 (dd, JPC = 9.0 Hz, m-MesP), 130.1 (dd, JPC = 4.0 Hz, m-MesP), 128.9 (dd, JPC = 14.0 Hz, i-Mes), 128.7 (dd, JPC = 35.7 Hz, i-Mes), 21.0 (p-CH3MesP), 20.9 (dd, JPC = 1.3 Hz, p-CH3MesP) [C6F5 not listed], [l tentatively assigned]. −31P1H NMR (202 MHz, 299 K, CD2Cl2): δ = −11.2 (v1/2 ≈ 1 Hz P = 40° P), −59.7 (dd, JPC = 4.8 Hz, v1/2 ≈ 1 Hz P), −19F NMR (470 MHz, 299 K, CD2Cl2): δ = −130.2 (br, 4F, o-C6F5), −138.5 (m, 2F, p-C6F5), −158.3 (t, JFF = 21.0 Hz, 1F, p-C6F5), −160.9 (t, JFF = 20.3 Hz, 2F, m-C6F5), −166.6 (m, 2F, m-C6F5), −168.2 (m, 4F, m-C6F5), [δF: Fm = 7.4].

Preparative scale: The phosphane 14 (293 mg, 0.55 mmol, 1 eq.) and B(C6F5)2 (256 mg, 0.55 mmol, 1 eq.) were dissolved in deuterated dichloromethane (6 mL) and stirred for
one day at r.t. Then the reaction mixture was heated at 80 °C for additional 3 d (the process was monitored by 1H and 31P NMR spectroscopy). Subsequently the solvent was removed 

\[\text{CH}_2Cl_2/\text{pentane} \text{ yielded light orange crystals}\]

were dissolved in dichloromethane (12 mL). The reaction mixture was transferred into a sealed vial which was kept in a autoclave reaction vessel containing dichloromethane. The autoclave was heated up to 160 °C for 24 h. After cooling to r.t. the volume of the reaction mixture was reduced to get a brown oil. Crystallization from dichloromethane-pentane yielded light orange crystals (509 mg; 92%) suitable for X-ray crystal structure analysis.

**Compound 17**

(293 mg, 0.5 mmol, 1 eq.) and tris(pentafluorophenyl)borane (256 mg, 0.5 mmol, 1 eq.) were dissolved in dichloromethane (12 mL). Repeating the above procedure three times gave a crude reaction mixture which was then collected and purified by column chromatography on silica using a mixture of CHCl₃/CH₂Cl₂ (1:1) as eluent.

**Data sets**

Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (Nonius B.V., 1998); data reduction DENZO-SMN, 

**Table 1**

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**Figure 1**

A single crystal of the title compound was selected and mounted on a glass fiber and data were collected on a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (Nonius B.V., 1998); data reduction DENZO-SMN, 

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X-Ray crystal structure analysis of **14** formula C_{30}H_{44}F_{2}P, \(M_r = 586.69\), yellow crystal, 0.25 \times 0.25 \times 0.10 \text{mm}^3, monoclinic, space group \(P2_1/n\) (no. 14), \(a = 8.6357(4)\), \(b = 9.6320(4)\), \(c = 20.4270(6)\), \(\alpha = 93.867(3)\), \(\beta = 2\), \(V = 1695.23(12)\), \(\rho_{\text{calc}} = 1.15 \text{g cm}^{-3}\), \(\mu = 1.3 \text{mm}^{-1}\), empirical absorption correction (0.730 \(\leq T \leq 0.877\), \(\lambda = 1.54178 \text{Å}, T = 223(2)\), \(\phi\) scans, 22110 reflections collected \((\pm h, \pm k, \pm l)\), \(\left|\langle\sin \theta/\lambda\rangle\right| = 0.60 \text{Å}^{-1}\), 2949 independent \((R_{\text{int}} = 0.047)\) and 2703 observed reflections \([I > 2\sigma(I)]\), 196 refined parameters, \(R = 0.040\), \(wR^2 = 0.114\), (max.) residual electron density 0.24 (−0.21) e Å\(^{-3}\), hydrogen atoms calculated and refined as riding atoms.

X-Ray crystal structure analysis of **15** formula C_{58}H_{44}F_{15}P_{2}, \(M_r = 1098.68\), colorless crystal, 0.25 \times 0.20 \times 0.13 mm\(^3\), triclinic, space group \(P\overline{1}\) (no. 2), \(a = 11.7211(3)\), \(b = 14.6796(8)\), \(c = 18.8329(9)\), \(\alpha = 95.071(3)\), \(\beta = 94.995(2)\), \(\gamma = 98.570(4)\), \(Z = 2\), \(V = 3175.1(3)\), \(\rho_{\text{calc}} = 1.15 \text{g cm}^{-3}\), \(\mu = 1.3 \text{mm}^{-1}\), empirical absorption correction (0.738 \(\leq T \leq 0.850\), \(\lambda = 1.54178 \text{Å}, T = 223(2)\), \(\phi\) scans, 40550 reflections collected \((\pm h, \pm k, \pm l)\), \(\left|\langle\sin \theta/\lambda\rangle\right| = 0.60 \text{Å}^{-1}\), 10907 independent \((R_{\text{int}} = 0.049)\) and 9120 observed reflections \([I > 2\sigma(I)]\), 698 refined parameters, \(R = 0.044\), \(wR^2 = 0.128\), (max.) residual electron density 0.25 (−0.24) e Å\(^{-3}\), hydrogen atoms calculated and refined as riding atoms.

X-Ray crystal structure analysis of **17** formula C_{33}H_{44}F_{15}P_{2}, \(M_r = 1098.68\), yellow crystal, 0.30 \times 0.15 \times 0.03 mm\(^3\), triclinic, space group \(P\overline{1}\) (no. 2), \(a = 10.6613(2)\), \(b = 12.6853(3)\), \(c = 19.9278(4)\), \(\alpha = 75.576(1)\), \(\beta = 78.835(1)\), \(\gamma = 84.997(1)\), \(Z = 2\), \(V = 2558.55(9)\), \(\rho_{\text{calc}} = 1.43 \text{g cm}^{-3}\), \(\mu = 0.2 \text{mm}^{-1}\), empirical absorption correction (0.948 \(\leq T \leq 0.994\), \(\lambda = 0.71073 \text{Å}, T = 223(2)\), \(\phi\) scans, 23662 reflections collected \((\pm h, \pm k, \pm l)\), \(\left|\langle\sin \theta/\lambda\rangle\right| = 0.60 \text{Å}^{-1}\), 8809 independent \((R_{\text{int}} = 0.050)\) and 7314 observed reflections \([I > 2\sigma(I)]\), 697 refined parameters, \(R = 0.056\), \(wR^2 = 0.129\), (max.) residual electron density 0.29 (−0.27) e Å\(^{-3}\), hydrogen atoms calculated and refined as riding atoms.

X-Ray crystal structure analysis of **18** formula C_{58}H_{33}F_{15}NP_{2} \times CH_{2}Cl_{2}, \(M_r = 1266.74\), colorless crystal, 0.25 \times 0.20 \times 0.03 mm\(^3\), monoclinic, space group \(P2_1/c\) (no. 14), \(a = 13.4724(6)\), \(b = 21.7726(13)\), \(c = 21.4217(6)\), \(\beta = 94.999(3)\), \(Z = 4\), \(V = 6259.7(5)\), \(\rho_{\text{calc}} = 1.34 \text{g cm}^{-3}\), \(\mu = 2.2 \text{mm}^{-1}\), empirical absorption correction (0.614 \(\leq T \leq 0.938\), \(\lambda = 1.54178 \text{Å}, T = 223(2)\), \(\phi\) scans, 50772 reflections collected \((\pm h, \pm k, \pm l)\), \(\left|\langle\sin \theta/\lambda\rangle\right| = 0.60 \text{Å}^{-1}\), 10639 independent \((R_{\text{int}} = 0.081)\) and 6522 observed reflections \([I > 2\sigma(I)]\), 843 refined parameters, \(R = 0.064\), \(wR^2 = 0.187\), (max.) residual electron density 0.31 (−0.44) e Å\(^{-3}\), hydrogen atoms calculated and refined as riding atoms.

CCDC 930182 (14), 930183 (15), 930184 (17), and 930185 (18) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Supporting information**

Further information on the materials and apparatus used, the experimental procedures including syntheses and structure determinations and pictures of spectra are given as Supporting Information available online (DOI: 10.5560/ZNB.2013-3088).

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Facile 1,1-Carboboration of a Diarylphosphino-substituted Conjugated Diyne


