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

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[$] X-ray crystal structure analyses

Supporting Information

Table of Contents

General Information. All reactions were carried out under argon atmosphere with Schlenk-type glassware. Solvents were dried using a *Grubbs*-type system [A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* **1996**, *15*, 1518-1520.]. 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). Assignments of the resonances were supported by 2D experiments.

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 (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307-326); absorption correction, DENZO (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr*. **2003**, *A59*, 228-234); structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr*. **1990**, *A46*, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr*. **2008**, *A64*, 112-122) and graphics, XP (BrukerAXS, 2000). Thermal ellipsoids are shown with 30% probability, *R*-values are given for observed reflections, and wR^2 values are given for all reflections. *Exceptions and special features*: For compound **15** a disordered solvent molecule was found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE (A. L. Spek J. Appl. Cryst., 2003, 36, 7-13) was therefore used to remove mathematically the effect of the solvent. The chemical formula and the molecular mass don't include the squeezed part of the solvent molecules. For the compound **18** one disordered molecule of dichloromethane was found in the asymmetric unit. Several restraints (SADI, SIMU, SAME and ISOR) were used in order to improve refinement stability. A second disordered molecule of dichloromethane, which could not be refined satisfactorily, was removed using the program SQUEEZE.

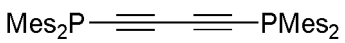
IR spectra were recorded as KBr-pellets or as pure compounds using an ATR-unit on a Varian 3100 FT-IR (Excalibur Series) spectrometer. For the determination of melting points a DSC Q 20 (TA Instruments) was employed

Materials. Tris(pentafluorophenyl)borane was prepared according to literature procedure [a) A. G. Massey, A. J. Park, *J. Organomet. Chem.* **1966**, *5*, 218-225; b) A. G. Massey, A . J. Park, *J. Organomet. Chem.* **1964**, *2*, 245-250, c) A. G. Massey, A. J. Park, F. G. A. Stone, *Proc. Chem. Soc.* **1963**, 212]

Experimental procedures.

Compound 14 (see: J. A. Tsui, T. M. Bolton, B. T. Sterenberg *Can. J. Chem.* **2009**, *87*, 197-204)

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 r. t. Subsequently the solution was cooled to −78 °C to add a solution of $PMes_2Cl$ (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 H_2O (30 mL) at r. t. The organic layer was separated and dried with $MgSO_4$. After filtration the solvent was removed *in vacuo* to yield a dark-yellow solid (6.52 g). It was purified by column chromatography (30x350 mm, SiO_2 / dichloromethane) and crystalization from dichloromethane solution. Yield: 4.78 g (8.15 mmol, 68 %).



Anal. Calc. for $C_{40}H_{44}P_2$: C 81.88, H 7.56; found: C 80.39, H 7.56.

IR (KBr): $\tilde{\nu}$ = 3458 (w), 3384 (w), 3111 (w), 2362 (w), 1457 (w), 662 (w), 516 (m), 493 (s), 474 (s), 462 (s), 441 (m).

M. p.: 175 °C (DSC).

HRMS: *m/z* = 587.2991 (calcd. 587.2996 for $C_{40}H_{45}P_2$).

^{1}H NMR (400 MHz, 295 K, [D$_2$]-dichloromethane): δ = 6.81 (dm, $^4J_{PH}$ = 3.4 Hz, 2H, m-Mes), 2.33 (s, 6H, o-CH_3^{Mes}), 2.23 (s, 3H, p-CH_3^{Mes}).

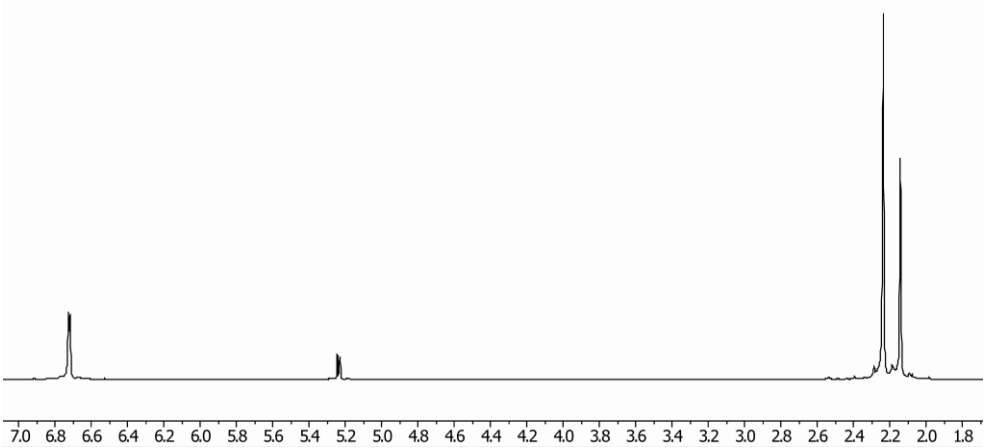
^{13}C{^{1}H} NMR (76 MHz, 295 K, [D$_2$]-dichloromethane): δ = 142.2 (d, $^2J_{PC}$ = 15.9 Hz, o-Mes), 139.3 (p-Mes), 130.2 (d, $^3J_{PC}$ = 4.0 Hz, m-Mes), 128.5 (dd, $^1J_{PC}$ = 10.7 Hz, $^6J_{PC}$ = 1.1 Hz, i-Mes), 92.6 (dd, $^2J_{PC}$ = 11.3 Hz, $^3J_{PC}$ = 3.0 Hz, ≡C)^t, 82.6 (dd, $^1J_{PC}$ = 12.2 Hz, $^4J_{PC}$ = 3.2 Hz, ≡CP)^t, 23.0 (d, $^3J_{PC}$ = 14.2 Hz, o-CH_3^{Mes}), 21.0 (p-CH_3^{Mes}), [^{t} tentatively assigned].

^{31}P{^{1}H} NMR (121 MHz, 295 K, [D$_2$]-dichloromethane): δ = −54.0 ($\nu_{1/2}$ ≈ 1 Hz).

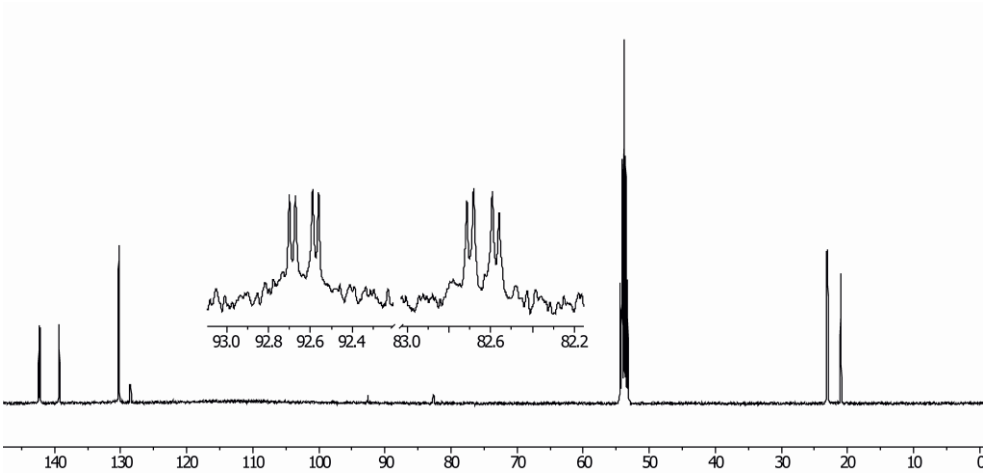
^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, 295 K, [D$_2$]-dichloromethane)[selected trace]: δ^1H / δ^1H = 6.81 / 2.33, 2.23 (m-Mes / o-CH_3^{Mes}, p-CH_3^{Mes}).

^{1}H, ^{13}C GHSQC (400 MHz / 100 MHz, 295 K, [D$_2$]-dichloromethane): δ^1H / δ^{13}C = 6.81 / 130.2 (m-Mes), 2.33 / 23.0 (o-CH_3^{Mes}), 2.23 / 20.9 (p-CH_3^{Mes}).

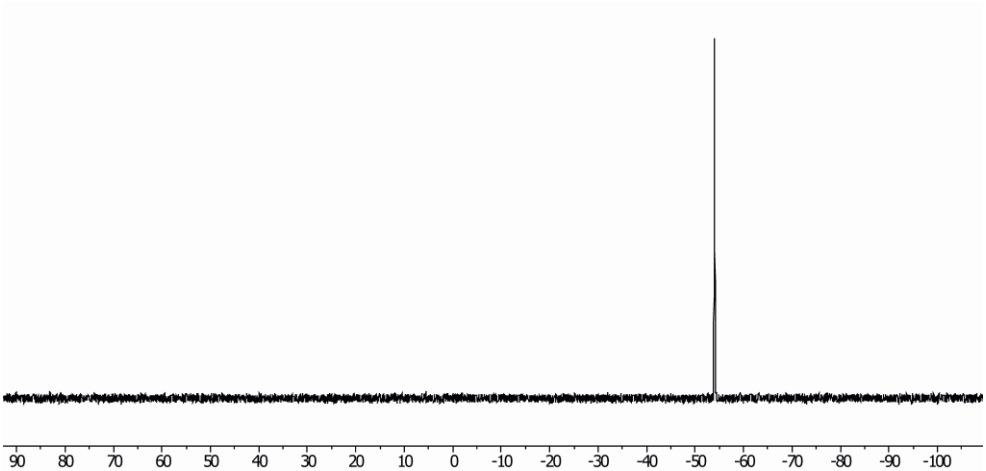
^{1}H, ^{13}C GHMBC (400 MHz / 100 MHz, 295 K, [D$_2$]-dichloromethane): δ^{1}H / δ^{13}C = 6.81 / 142.2, 139.2, 130.2, 23.0, 20.9 (m-Mes / i-Mes, p-Mes, m-Mes, o-CH$_3^{Mes}$, p-CH$_3^{Mes}$), 2.33 / 142.2, 130.2, 128.5, 23.0 (o-CH$_3^{Mes}$ / i-Mes, m-Mes, o-Mes, o-CH$_3^{Mes}$), 2.23 / 139.2, 130.2, 128.5, 20.9 (p-CH$_3^{Mes}$ / p-Mes, m-Mes, o-Mes, p-CH$_3^{Mes}$).



^{1}H NMR (400 MHz, 295 K, [D$_2$]-dichloromethane)

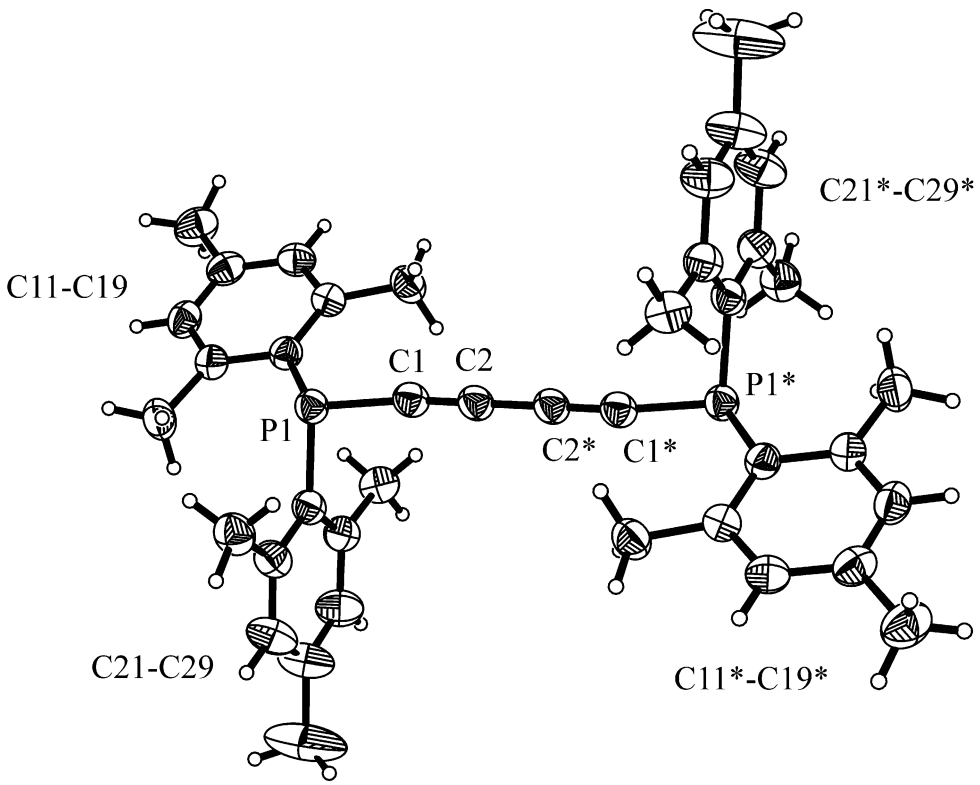


^{13}C{^{1}H} NMR (100 MHz, 295 K, [D$_2$]-dichloromethane)

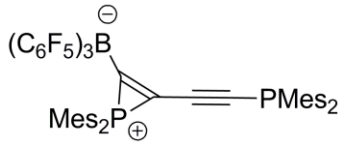


^{31}P{^{1}H} NMR (121 MHz, 299 K, [D$_2$]-dichloromethane)

*X-ray crystal structure analysis of **14**:* formula $C_{40}H_{44}P_2$, M = 586.69, yellow crystal, 0.25 x 0.25 x 0.10 mm^3, a = 8.6357(4), b = 9.6320(4), c = 20.4270(6) Å, β = 93.867(3)°, V = 1695.23(12) $Å^3$, ρ_{calc} = 1.149 gcm^{-3}, μ = 1.343 mm^{-1}, empirical absorption correction ($0.730 \leq T \leq 0.877$), Z = 2, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 22110 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 $Å^{-1}$, 2949 independent (R_{int} = 0.047) and 2703 observed reflections [$I>2\sigma(I)$], 196 refined parameters, R = 0.040, wR^2 = 0.114, max. (min.) residual electron density 0.24 (-0.21) e. $Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.



Compound 15



A solution of $B(C_6F_5)_3$ (256 mg, 0.5 mmol, 1 eq.) in dichloromethane (8 mL) was added to a solution of **14** (293 mg, 0.5 mmol, 1 eq.) in dichloromethane (5 mL) *via* syringe. The reaction mixture was stirred for three days at r. t. Then the solvent was removed *in vacuo* to yield a brown solid (436 mg, 79 %). The product was purified by crystalization 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.

IR (KBr): $\tilde{\nu}$ = 4155 (w), 3991 (w), 3029 (w), 2980 (w), 2921 (w), 2853 (w), 2733 (w), 2630 (w), 2553 (w), 2475 (w), 2400 (w), 2122 (s), 1986 (w), 1643 (s), 1604 (s), 1559 (w), 1518 (m), 1470 (m), 1380 (m), 1280 (s), 1095 (s), 1032 (m), 977 (s), 885 (s), 849 (s), 811 (m), 784 (s), 746 (m), 681 (s), 652 (s), 619 (m).

M. p.: 134 °C (DSC).

HRMS: *m/z* = 1099.2844 (calcd. 1099.2844 for $C_{58}H_{45}BF_{15}P_2$).

^{1}H NMR (500 MHz, 299 K, [D$_2$]-dichloromethane): δ = 6.87 (d, $^4J_{PH}$ = 5.8 Hz, 2H, m-Mes^{P+}), 6.84 (d, $^4J_{PH}$ = 3.5 Hz, 2H, m-Mes), 2.30 (s, 6H, o-CH$_3^{Mes}$), 2.29 (s, 3H, p-CH$_3^{MesP+}$), 2.26 (s, 3H, p-CH$_3^{Mes}$), 2.11 (s, 6H, o-CH$_3^{MesP+}$).

^{13}C{^{1}H} NMR (125 MHz, 299 K, [D$_2$]-dichloromethane): δ = 152.6 (br. =CB), 148.2 (dm, $^1J_{FC}$ ≈ 240 Hz, C_6F_5), 144.9 (d, $^4J_{PC}$ = 3.3 Hz, p-Mes^{P+}), 143.5 (d, $^2J_{PC}$ = 12.1 Hz, o-Mes^{P+}), 142.1 (d, $^2J_{PC}$ = 16.0 Hz, o-Mes), 139.6 (p-Mes), 139.4 (dm, $^1J_{FC}$ ≈ 250 Hz, C_6F_5), 137.0 (dm, $^1J_{FC}$ ≈ 250 Hz, C_6F_5), 130.7 (d, $^3J_{PC}$ = 13.6 Hz, m-Mes^{P+}), 130.3 (d, $^3J_{PC}$ = 4.1 Hz, m-Mes), 128.1 (d, $^1J_{PC}$ = 9.6 Hz, i-Mes), 122.8 (br, =CP)^t, 120.6 (br, i-C_6F_5), 120.3 (d, $^1J_{PC}$ = 87.0 Hz, i-Mes^{P+}), 113.1 (dd, $^2J_{PC}$ = 20.8 Hz, $^2J_{PC}$ = 8.3 Hz, ≡C)^t, 93.1 (dd, $^1J_{PC}$ = 7.9 Hz, $^3J_{PC}$ = 2.3 Hz, ≡CP)^t, 23.0 (d, $^3J_{PC}$ = 14.0 Hz, o-CH$_3^{Mes}$), 22.5 (d, $^3J_{PC}$ = 7.6 Hz, o-CH$_3^{MesP+}$), 21.3 (d, $^5J_{PC}$ = 1.3 Hz, p-CH$_3^{MesP+}$), 21.0 (p-CH$_3^{Mes}$), [^{t} tentatively assigned].

^{31}P{^{1}H} NMR (202 MHz, 299 K, [D$_2$]-dichloromethane): δ = −54.6 (d, $^3J_{PP}$ = 3.2 Hz, $\nu_{1/2}$ ≈ 2 Hz, P), −131.7 ($\nu_{1/2}$ ≈ 10 Hz, P$^+$).

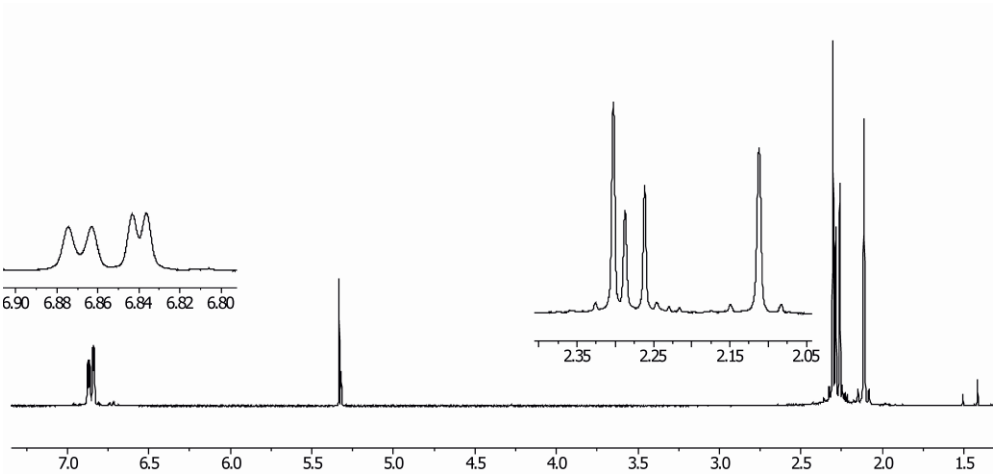
^{11}B NMR (160 MHz, 299 K, [D$_2$]-dichloromethane): δ = −16.7 ($\nu_{1/2}$ ≈ 30 Hz).

^{19}F NMR (470 MHz, 299 K, [D$_2$]-dichloromethane): δ = −131.2 (m, 2F, o-C_6F_5), −160.5 (t, $^3J_{FF}$ = 20.7 Hz, 1F, p-C_6F_5), −165.4 (m, 2F, m-C_6F_5), [$\Delta\delta^{19}F_{m,p}$ = 4.8].

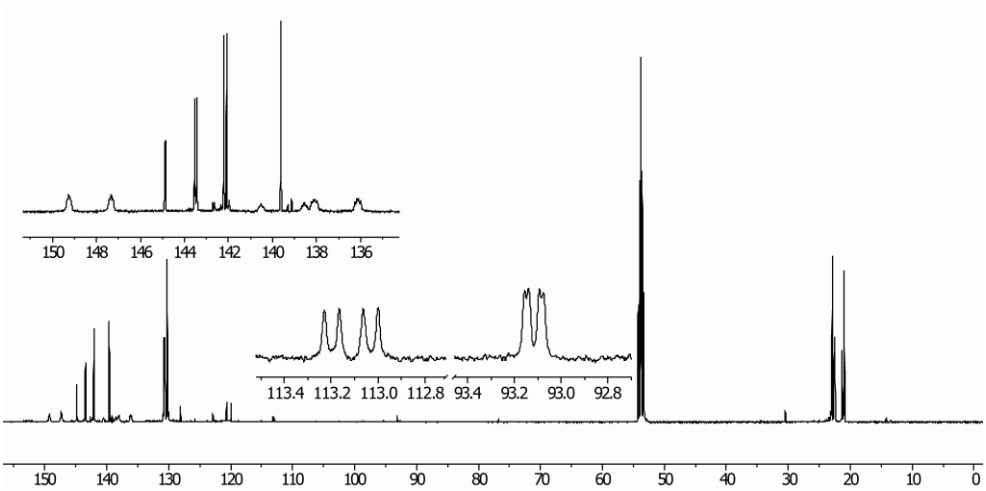
^{1}H, ^{1}H GCOSY (500 MHz / 500 MHz, 299 K, [D$_2$]-dichloromethane)[selected traces]: δ^1H / δ^1H = 6.87 / 2.29, 2.11 (m-Mes^{P+} / p-CH$_3^{MesP+}$, o-CH$_3^{MesP+}$), 6.84 / 2.30, 2.26 (m-Mes / o-CH$_3^{Mes}$, p-CH$_3^{Mes}$).

^{1}H, ^{13}C GHSQC (500 MHz / 125 MHz, 299 K, [D$_2$]-dichloromethane): δ^{1}H / δ^{13}C = 6.87 / 130.7 (m-Mes^{P+}), 6.84 / 130.3 (m-Mes), 2.30 / 23.0 (o-CH$_3^{Mes}$), 2.29 / 21.3 (p-CH$_3^{MesP+}$), 2.26 / 21.0 (p-CH$_3^{Mes}$), 2.11 / 22.5 (o-CH$_3^{MesP+}$).

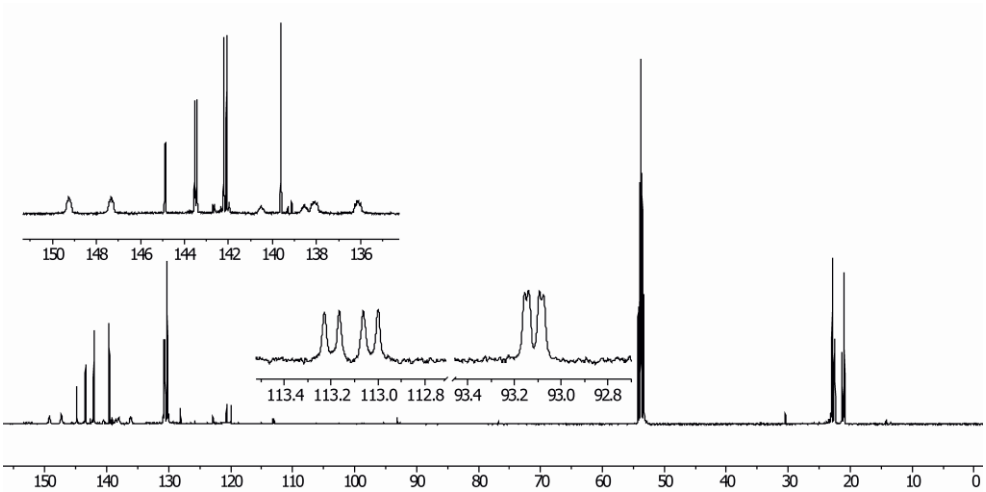
^{1}H, ^{13}C GHMBC (500 MHz / 125 MHz, 299 K, [D$_2$]-dichloromethane): δ^{1}H / δ^{13}C = 6.87 / 143.5, 130.7, 120.3, 22.5, 21.3 (m-Mes^{P+} / o-Mes^{P+}, m-Mes^{P+}, i-Mes^{P+}, o-CH$_3^{MesP+}$, p-CH$_3^{MesP+}$), 6.84 / 142.1, 130.3, 128.1, 23.0, 21.0 (m-Mes / o-Mes, m-Mes, i-Mes, o-CH$_3^{Mes}$, p-CH$_3^{Mes}$), 2.30 / 142.1, 130.3, 128.1 (o-CH$_3^{Mes}$ / o-Mes, m-Mes, i-Mes), 2.29 / 144.9, 130.7 (p-CH$_3^{MesP+}$ / p-Mes^{P+}, m-Mes^{P+}), 2.26 / 139.6, 130.3 (p-CH$_3^{Mes}$ / p-Mes, m-Mes), 2.11 / 143.5, 130.7, 120.3 (o-CH$_3^{MesP+}$ / o-Mes^{P+}, m-Mes^{P+}, i-Mes^{P+}).



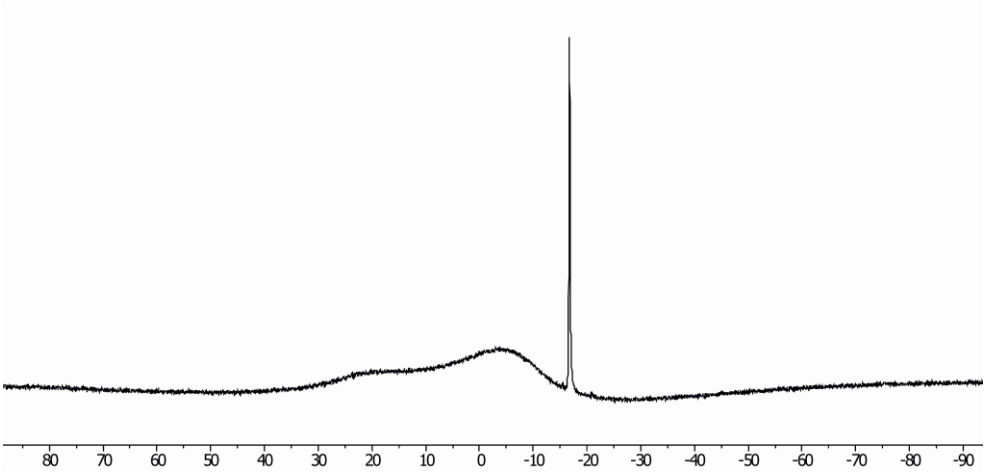
^{1}H NMR (500 MHz, 299 K, [D$_2$]-dichloromethane)



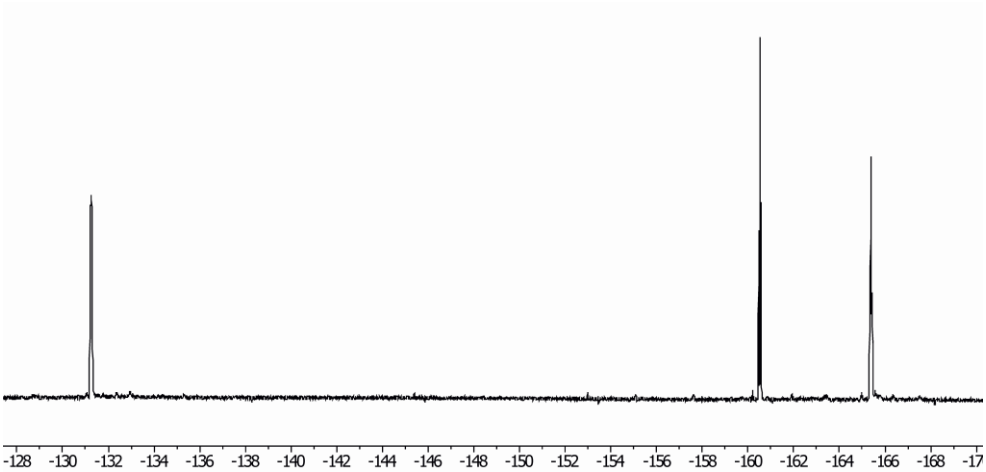
^{13}C{^{1}H} NMR (125 MHz, 299 K, [D$_2$]-dichloromethane)



$^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, $[D_2]$-dichloromethane)

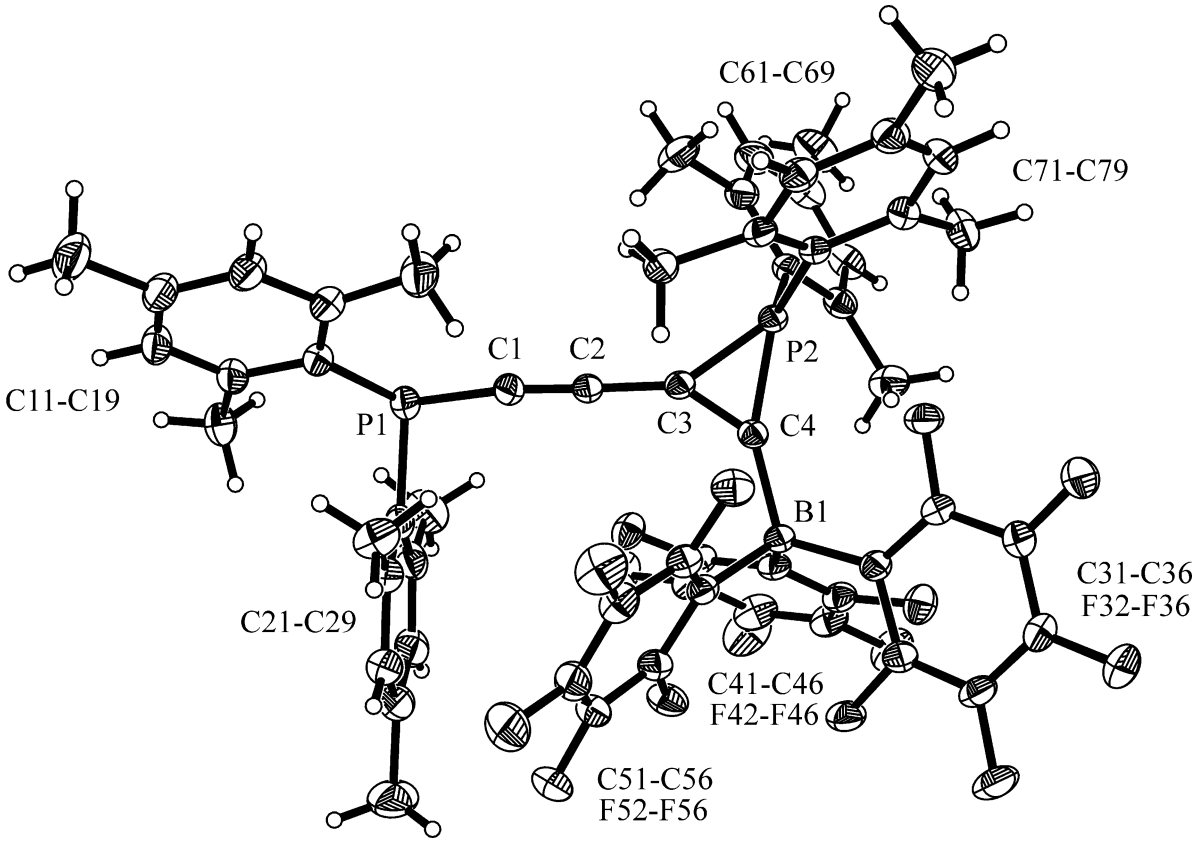


$^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, $[D_2]$-dichloromethane)



^{19}F NMR (470 MHz, 299 K, $[D_2]$-dichloromethane)

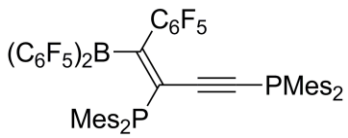
X-ray crystal structure analysis of ***15****:* formula $C_{58}H_{44}BF_{15}P_2$, M = 1098.68 colourless crystal, 0.25 x 0.20 x 0.13 mm^3, a = 11.7211(3), b = 14.6796(8), c = 18.8329(9) Å, α = 95.071(3), β = 94.995(2), γ = 98.570(4)°, V = 3175.1(3) Å^3, ρ_{calc} = 1.149 gcm^{-3}, μ = 1.292 mm^{-1}, empirical absorption correction (0.738 ≤ T ≤ 0.850), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 40550 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 10907 independent (R_{int} = 0.045) and 9120 observed reflections [I>2σ(I)], 698 refined parameters, R = 0.044, wR^2 = 0.128, max. (min.) residual electron density 0.25 (-0.24) e. Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



Compound E-16

NMR tube scale reaction:

Compound **15** (20 mg, 0.018 mmol) in CD_2Cl_2 (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.



^{1}H NMR (500 MHz, 299 K, [D$_2$]-dichloromethane): δ = 6.74 (dm, $^4J_{PH}$ = 3.7 Hz, 2H, m-Mes$^{P=}$), 6.72 (dm, $^4J_{PH}$ = 3.4 Hz, 2H, m-Mes), 2.25 (s, 3H, p-CH$_3^{MesP=}$), 2.22 (s, 3H, p-CH$_3^{Mes}$), 2.15 (s, 6H, o-CH$_3^{MesP=}$), 2.08 (s, 6H, o-CH$_3^{Mes}$).

^{13}C{^{1}H} NMR (125 MHz, 299 K, [D$_2$]-dichloromethane): δ = 163.1 (br. =CB), 142.7 (d, $^2J_{PC}$ = 8.9 Hz, o-Mes$^{P=}$), 142.1 (d, $^2J_{PC}$ = 15.8 Hz, o-Mes), 142.0 (d, $^4J_{PC}$ = 2.9 Hz, p-Mes$^{P=}$), 139.1 (p-Mes), 130.9 (d, $^3J_{PC}$ = 9.0 Hz, m-Mes$^{P=}$), 130.1 (d, $^3J_{PC}$ = 4.0 Hz, m-Mes), 128.9 (dd, $^1J_{PC}$ = 11.0 Hz, $^5J_{PC}$ = 1.4 Hz, i-Mes), 122.7 (d, $^1J_{PC}$ = 35.7 Hz, i-Mes$^{P=}$), n.o. (=CP), 102.5 (dm, $^2J_{PC}$ = 9.3 Hz, ≡C)^t, 98.7 (dd, $^3J_{PC}$ = 14.7 Hz, $^1J_{PC}$ = 5.8 Hz, ≡CP)^t, 23.5 (br d, $^3J_{PC}$ = 6.0 Hz, o-CH$_3^{MesP=}$), 22.6 (d, $^3J_{PC}$ = 14.2 Hz, o-CH$_3^{Mes}$), 21.0 (p-CH$_3^{Mes=}$)^t, 20.9 (d, $^5J_{PC}$ = 1.3 Hz, p-CH$_3^{Mes}$)^t, [C_6F_5 not listed], [^{t} tentatively assigned].

^{31}P{^{1}H} NMR (202 MHz, 299 K, [D$_2$]-dichloromethane): δ = 11.2 ($\nu_{1/2}$ ≈ 40 Hz P$^=$), −59.7 (d, $^4J_{PP}$ = 4.8 Hz, $\nu_{1/2}$ ≈ 1 Hz P).

^{19}F NMR (470 MHz, 299 K, [D$_2$]-dichloromethane): δ = −132.0 (br, 4F, o-C$_6$F$_5^B$), −138.5 (m, 2F, o-C$_6$F$_5$), −158.3 (t, $^3J_{FF}$ = 21.0 Hz, 1F, p-C$_6$F$_5$), −160.9 (t, $^3J_{FF}$ = 20.3 Hz, 2F, p-C$_6$F$_5^B$), −166.6 (m, 2F, m-C$_6$F$_5$), −168.2 (m, 4F, m-C$_6$F$_5^B$), [$\Delta\delta^{19}F_{m,p}(C_6F_5^B)$ = 7.4].

^{19}F, ^{19}F GCOSY (470 MHz / 470 MHz, 299 K, [D$_2$]-dichloromethane): δ^{19}F / δ^{19}F = −138.5 / −166.6 (o-C$_6$F$_5$ / m-C$_6$F$_5$), −158.3 / −166.6 (p-C$_6$F$_5$ / m-C$_6$F$_5$), −160.8 / −168.2 (p-C$_6$F$_5^B$ / m-C$_6$F$_5^B$), −166.6 / −138.5, −158.3 (m-C$_6$F$_5$ / o-C$_6$F$_5$, p-C$_6$F$_5$), −168.2 / −160.8 (m-C$_6$F$_5^B$ / p-C$_6$F$_5^B$).

^{1}H, ^{1}H GCOSY (500 MHz / 500 MHz, 299 K, [D$_2$]-dichloromethane)[selected traces]: δ^1H / δ^1H = 6.74 / 2.25, 2.15 (m-Mes$^{P=}$ / p-CH$_3^{MesP=}$, o-CH$_3^{MesP=}$), 6.72 / 2.22, 2.08 (m-Mes / p-CH$_3^{Mes}$, o-CH$_3^{Mes}$).

^{1}H, ^{13}C GHSQC (500 MHz / 125 MHz, 299 K, [D$_2$]-dichloromethane): δ^1H / δ^{13}C = 6.74 / 130.9 (m-Mes$^{P=}$), 6.72 / 130.0 (m-Mes), 2.25 / 21.0 (p-CH$_3^{MesP=}$), 2.22 / 20.9 (p-CH$_3^{Mes}$), 2.15 / 23.5 (o-CH$_3^{MesP=}$), 2.08 / 22.6 (o-CH$_3^{Mes}$).

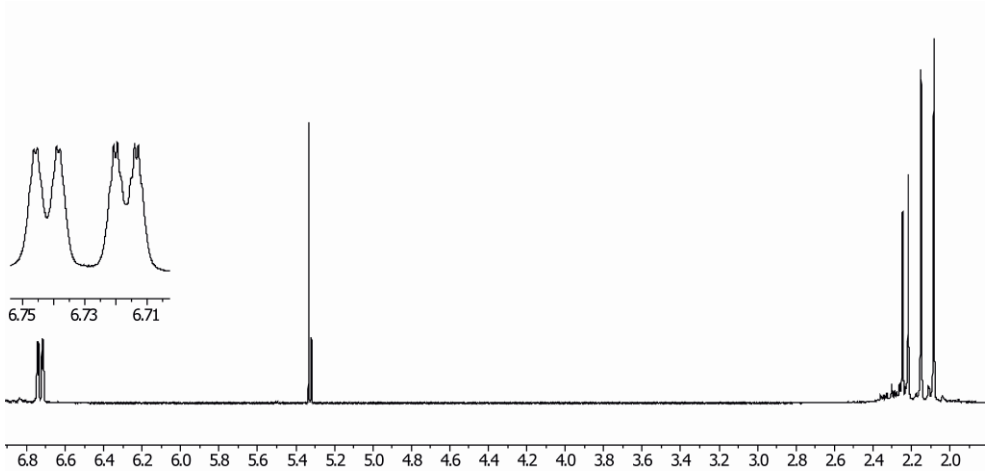
^{1}H, ^{13}C GHMBC (500 MHz / 125 MHz, 299 K, [D$_2$]-dichloromethane): δ^1H / δ^{13}C = 6.74 / 142.7, 130.9, 122.7, 23.5, 21.0 (m-Mes$^{P=}$ / o-Mes$^{P=}$, m-Mes$^{P=}$, i-Mes$^{P=}$, o-CH$_3^{MesP=}$, p-CH$_3^{MesP=}$), 6.72 / 142.1, 130.1, 128.9,

22.6, 20.9 (m-Mes / o-Mes, m-Mes, i-Mes, o-CH_3^{Mes}, p-CH_3^{Mes}), 2.25 / 141.9, 130.9 (p-$CH_3^{MesP=}$ / o-$Mes^{P=}$, m-$Mes^{P=}$), 2.22 / 139.1, 130.1 (p-CH_3^{Mes} / p-Mes, m-Mes), 2.15 / 142.7, 130.9, 122.7 (o-$CH_3^{MesP=}$ / o-$Mes^{P=}$, m-$Mes^{P=}$, i-$Mes^{P=}$), 2.08 / 142.1, 130.1, 128.9 (o-CH_3^{Mes} / o-Mes, m-Mes, i-Mes).

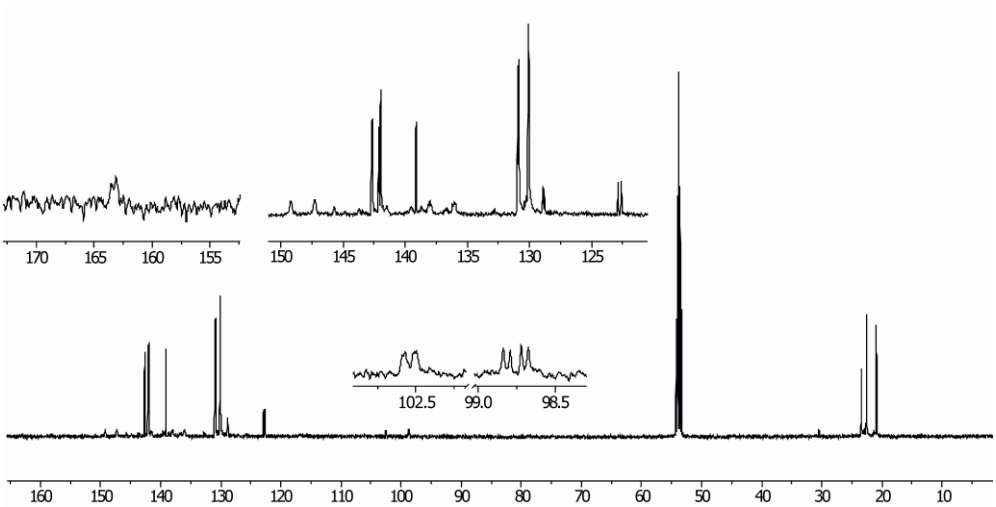
^{1}H{^{1}H} TOCSY (500 MHz, 299 K, [D$_2$]-dichloromethane): δ^1H_{irr} / δ^1H_{res} = 2.15 / 6.74 (o-$CH_3^{MesP=}$ / m-$Mes^{P=}$), 2.08 / 6.72 (o-CH_3^{Mes} / m-Mes).

^{1}H{^{1}H} NOE (500 MHz, 299 K, [D2]-dichloromethane): δ^1Hirr / δ^1Hres = 2.15 / 6.74 (o-CH3$Mes^{P=}$ / m-$Mes^{P=}$), 2.08 / 6.72 (o-CH3Mes / m-Mes).

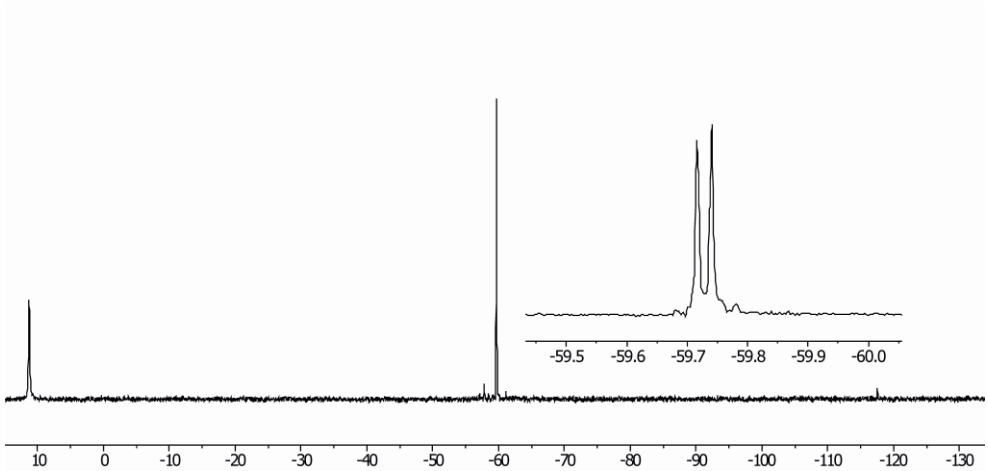
^{1}H, ^{31}P GHMBC (500 MHz / 202 MHz, 299 K, [D2]-dichloromethane): δ^1H / δ^{31}P = 6.74 / 11.2 (m-$Mes^{P=}$ / $P^{=}$), 6.72 / −59.7 (m-Mes / P), 2.25 / 11.2 (p-$CH_3^{MesP=}$ / $P^{=}$), 2.22 / −59.7 (p-CH_3^{Mes} / P), 2.15 / 11.2 (o-$CH_3^{MesP=}$ / $P^{=}$), 2.08 / −59.7 (o-CH_3^{Mes} / P).



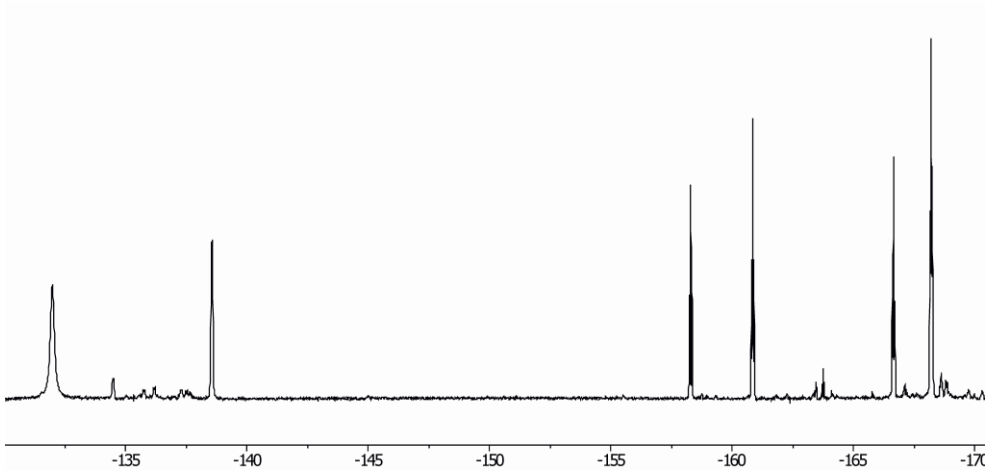
^{1}H NMR (500 MHz, 299 K, [D$_2$]-dichloromethane)



^{13}C{^{1}H} NMR (125 MHz, 299 K, [D$_2$]-dichloromethane)



$^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, [D_2]-dichloromethane)



^{19}F NMR (470 MHz, 299 K, [D_2]-dichloromethane)

Preparative scale: Preparation of E-16:

The phosphane **14** (293 mg, 0.5 mmol, 1 eq.) and $B(C_6F_5)_3$ (256 mg, 0.5 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 reaction process was monitored by ^{1}H and ^{31}P NMR spectroscopy). Subsequently the solvent was removed *in vacuo* to yield a brown solid (502 mg, 91 %).

IR (KBr): $\tilde{\nu}$ = 4012 (w), 3802 (w), 3692 (w), 3155 (w), 3034 (w), 2734 (w), 2578 (w), 2404 (w), 2340 (w), 2222 (w), 2121 (m), 1917 (w), 1885 (w), 1729 (w), 1652 (m), 1608 (w), 1562 (w), 1375 (w), 1294 (w), 1189 (w), 1141 (w), 954 (w), 915 (w), 846 (w), 798 (w), 749 (w), 694 (w).

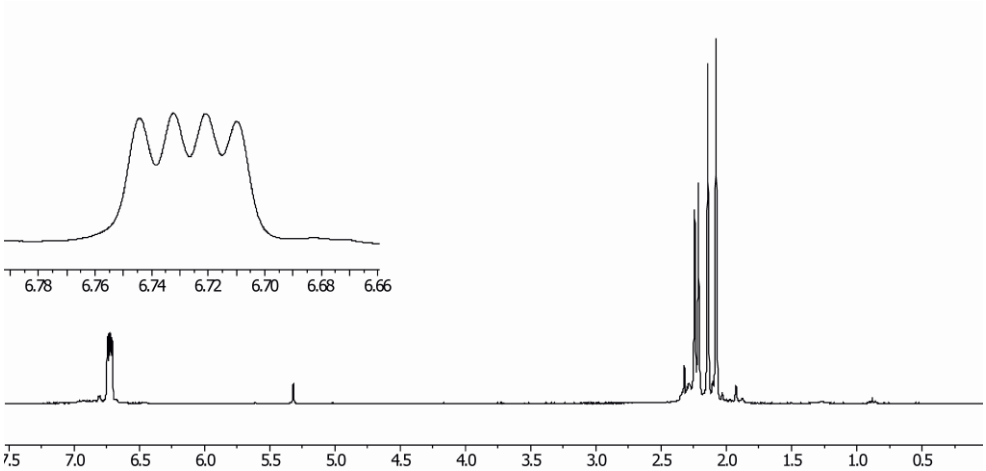
M. p.: 156 °C (DSC).

HRMS: *m/z* = 1099.28225 (calcd. 1099.28505 for $C_{58}H_{45}BF_{15}P_2$).

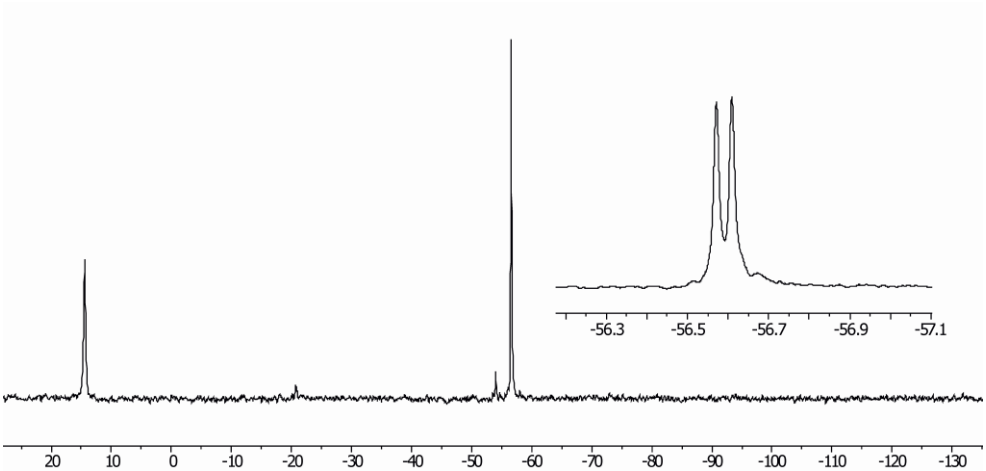
^{1}H NMR (300 MHz, 299 K, [D$_2$]-dichloromethane): δ = 6.74 (d, $^{4}J_{PH}$ = 3.7 Hz, 2H, m-Mes$^{P=}$), 6.71 (d, $^{4}J_{PH}$ = 3.4 Hz, 2H, m-Mes), 2.24 (s, 3H, p-CH$_3^{MesP=}$), 2.21 (s, 3H, p-CH$_3^{Mes}$), 2.14 (s, 6H, o-CH$_3^{MesP=}$), 2.08 (s, 6H, o-CH$_3^{Mes}$).

^{31}P{^{1}H} NMR (121 MHz, 299 K, [D$_2$]-dichloromethane): δ = 14.4 ($\nu_{1/2} \approx$ 35 Hz, 1P, P$^{=}$), −56.6 (d, $^{4}J_{PP}$ = 4.8 Hz, 1P, P).

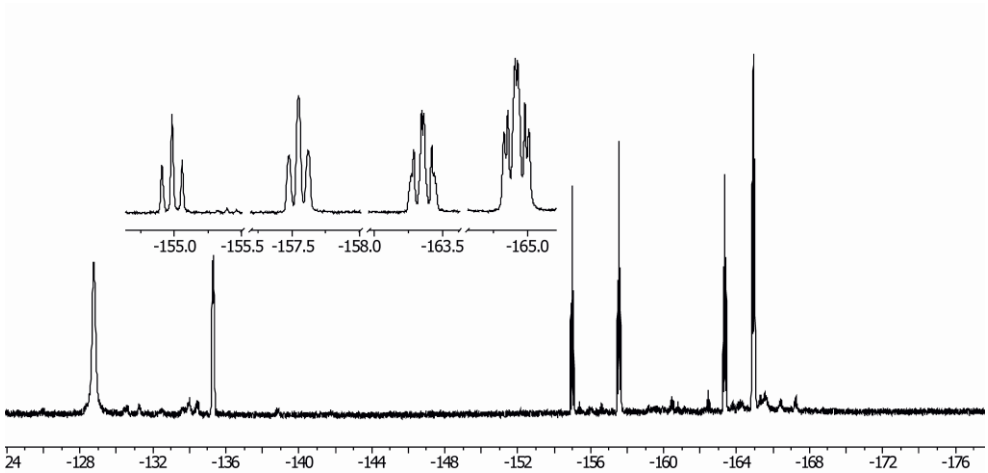
^{19}F NMR (282 MHz, 299 K, [D$_2$]-dichloromethane): δ = −131.9 (s, 4F, o-C$_6$F$_5^{B}$), −138.5 (m, 2F, o-C$_6$F$_5$), −158.1 (m, 1F, p-C$_6$F$_5$), −160.7 (m, 2F, p-C$_6$F$_5^{B}$), −166.5 (m, 2F, m-C$_6$F$_5$), −168.1 (m, 4F, m-C$_6$F$_5^{B}$), [$\Delta\delta^{19}$F$_{m,p}$(C$_6$F$_5^{B}$) = 7.4].



^{1}H NMR (300 MHz, 299 K, [D$_2$]-dichloromethane)



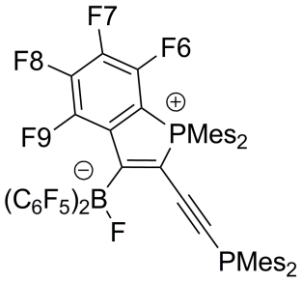
^{31}P{^{1}H} NMR (121 MHz, 299 K, [D$_2$]-dichloromethane)



^{19}F NMR (282 MHz, 299 K, [D_2]-dichloromethane)

Compound 17

Compound **14** (293 mg, 0.5 mmol, 1 eq.) and tris(pentafluorophenyl)borane (256 mg, 0.5 mmol, 1 eq.) were dissolved in CH_2Cl_2 (12 mL). The reaction mixture was transferred into a sealed vial which was kept in a dichloromethane equipped autoclave reaction vessel. 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.



IR (KBr): $\tilde{\nu}$ = 2970 (w), 2928 (w), 2218 (w), 2120 (w), 2037 (w), 1643 (w), 1603 (w), 1557 (w), 1513 (w), 1490 (w), 1460(m), 1381 (w), 1330 (w), 1291 (w), 1279 (w), 1179 (w), 1157 (w), 1093 (m), 1066 (w), 1020 (w), 974 (m), 960 (w), 901 (w), 859 (w), 806 (w), 784 (w), 775 (w), 765 (w), 738 (w), 701(w), 677 (w) 663 (w).

M. p.: 160 °C (DSC).

HRMS: *m/z* = 1121.2647 (calcd. 1121.2674 for $C_{58}H_{44}BF_{15}P_2Na$).

^{1}H NMR (500 MHz, 299 K, [D_2]-dichloromethane): δ = 6.90 (dm, $^4J_{PH}$ = 5.1 Hz, 2H, m-Mes^{P+}), 6.75 (dm, $^4J_{PH}$ = 3.5 Hz, 2H, m-Mes), 2.34 (s, 3H, p-CH_3^{MesP+}), 2.23 (s, 3H, p-CH_3^{Mes}), 2.11 (s, 6H, o-CH_3^{Mes}), 2.04 (s, 6H, o-CH_3^{MesP+}).

^{13}C{^{1}H} NMR (126 MHz, 299 K, [D_2]-dichloromethane): δ = 179.8 (m, =CB)^t, 145.7 (d, $^4J_{PC}$ = 3.1 Hz, p-Mes^{P+}), 143.3 (d, $^2J_{PC}$ = 10.9 Hz, o-Mes^{P+}), 142.5 (d, $^2J_{PC}$ = 16.8 Hz, o-Mes), 139.3 (p-Mes), 132.8 (d,

$^3J_{PC}$ = 12.2 Hz, m-Mes^{P+}), 130.1 (d, $^3J_{PC}$ = 4.1 Hz, m-Mes), 127.8 (dd, $^1J_{PC}$ = 11.5 Hz, $^5J_{PC}$ = 2.1 Hz, i-Mes), 120.7 (d, $^1J_{PC}$ = 81.0 Hz, =CP)^t, 112.5 (d, $^1J_{PC}$ = 78.9 Hz, i-Mes^{P+}), 103.5 (dd, $^2J_{PC}$ = 13.9 Hz, $^2J_{PC}$ = 10.1 Hz, ≡C)^t, 102.1 (dd, $^3J_{PC}$ = 18.1 Hz, $^1J_{PC}$ = 12.9 Hz, ≡CP)^t, 23.3 (br d, $^3J_{PC}$ = 5.8 Hz, o-CH$_3^{MesP+}$), 22.4 (d, $^3J_{PC}$ = 15.1 Hz, o-CH$_3^{Mes}$), 21.4 (p-CH$_3^{MesP+}$), 21.0 (p-CH$_3^{Mes}$), [C_6F_5, C_6F_4 not listed], [^{t} tentatively assigned].

^{31}P{^{1}H} NMR (202 MHz, 299 K, [D$_2$]-dichloromethane): δ = 25.9 ($\nu_{1/2}$ ≈ 35 Hz, P$^+$), −55.9 ($\nu_{1/2}$ ≈ 25 Hz, P).

^{11}B{^{1}H} NMR (160 MHz, 299 K, [D$_2$]-dichloromethane): δ = -0.3 ($\nu_{1/2}$ ≈ 200 Hz).

^{19}F NMR (470 MHz, 299 K, [D$_2$]-dichloromethane): δ = −123.9 (m, 1F, F9)^t, −124.6 (m, 1F, F6), −134.0 (m, 4F, o-C_6F_5), −141.8 (m, 1F, F8)^t, −152.3 (m, 1F, F7)^t, −160.9 (t, $^3J_{FF}$ = 19.9 Hz, 2F, p-C_6F_5), −166.5 (m, 4F, m-C_6F_5), -187.5 (br, 1F, BF), [$\Delta\delta^{19}F_{m,p}(C_6F_5)$ = 5.6], [^{t} tentatively assigned].

^{19}F, ^{19}F GCOSY (470 MHz / 470 MHz, 299 K, [D$_2$]-dichloromethane): δ^{19}F / δ^{19}F = −123.8 / −141.7 (F4^{C6F4} / F3^{C6F4}), −124.6 / −141.7, −152.2 (F1^{C6F4} / F3^{C6F4}, F2^{C6F4}), −134.0 / −166.5 (o-C_6F_5 / m-C_6F_5), −141.7 / −123.8, −152.2 (F3^{C6F4} / F4^{C6F4}, F2^{C6F4}), −152.2 / −124.6 (F2^{C6F4} / F1^{C6F4}), −160.8 / −166.5 (p-C_6F_5 / m-C_6F_5), −166.5 / −134.0, −160.8 (m-C_6F_5 / o-C_6F_5, p-C_6F_5).

^{19}F, ^{1}H HOESY (564 MHz / 600 MHz, 299 K, [D$_2$]-dichloromethane): δ^{19}F / δ^1H = −124.6 / 2.04 (F1^{C6F4} / o-CH$_3^{MesP+}$), −134.0 / 2.11, 2.04 (o-C_6F_5 / o-CH$_3^{Mes}$, o-CH$_3^{MesP+}$), −160.8 / 2.11 (p-C_6F_5 / o-CH$_3^{Mes}$), −166.5 / 2.11, 2.04 (m-C_6F_5 / o-CH$_3^{Mes}$, o-CH$_3^{MesP+}$).

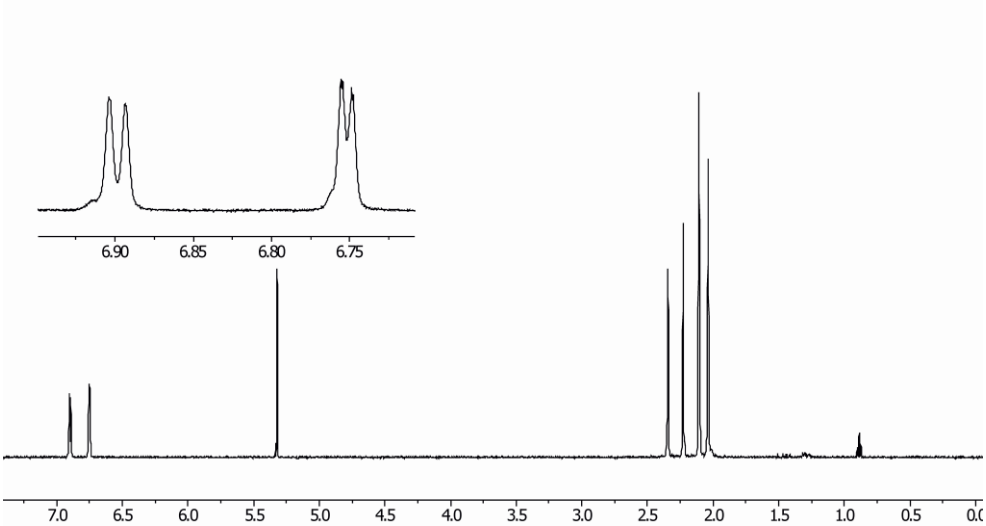
^{1}H, ^{1}H GCOSY (500 MHz / 500 MHz, 299 K, [D$_2$]-dichloromethane)[selected traces]: δ^1H / δ^1H = 6.90 / 2.34, 2.04 (m-Mes^{P+} / p-CH$_3^{MesP+}$, o-CH$_3^{MesP+}$), 6.75 / 2.23, 2.11 (m-Mes / p-CH$_3^{Mes}$, o-CH$_3^{Mes}$).

^{1}H, ^{13}C GHSQC (500 MHz / 125 MHz, 299 K, [D$_2$]-dichloromethane): δ^1H / δ^{13}C = 6.90 / 132.8 (m-Mes^{P+}), 6.75 / 130.1 (m-Mes), 2.34 / 21.4 (p-CH$_3^{MesP+}$), 2.23 / 21.0 (p-CH$_3^{Mes}$), 2.11 / 22.4 (o-CH$_3^{Mes}$), 2.04 / 23.2 (o-CH$_3^{MesP+}$).

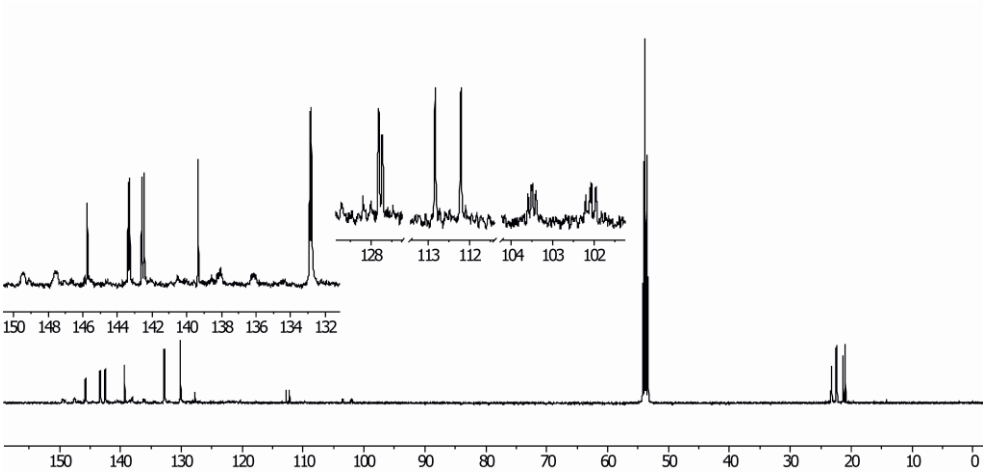
^{1}H, ^{13}C GHMBC (500 MHz / 125 MHz, 299 K, [D$_2$]-dichloromethane): δ^1H / δ^{13}C = 6.90 / 132.8, 112.5, 23.3, 21.4 (m-Mes^{P+} / m-Mes^{P+}, i-Mes^{P+}, o-CH$_3^{MesP+}$, p-CH$_3^{MesP+}$), 6.75 / 130.1, 127.8, 22.4, 21.0 (m-Mes / m-Mes, i-Mes, o-CH$_3^{Mes}$, p-CH$_3^{Mes}$), 2.34 / 145.7, 132.8 (p-CH$_3^{MesP+}$ / p-Mes^{P+}, m-Mes^{P+}), 2.23 / 139.3, 130.1 (p-CH$_3^{Mes}$ / p-Mes, m-Mes), 2.11 / 142.5, 130.1, 127.8 (o-CH$_3^{Mes}$ / o-Mes, m-Mes, i-Mes), 2.04 / 143.3, 132.8, 112.5 (o-CH$_3^{MesP+}$ / o-Mes^{P+}, m-Mes^{P+}, i-Mes^{P+}).

^{1}H{^{1}H} TOCSY (500 MHz, 299 K, [D$_2$]-dichloromethane): δ^1H_{irr} / δ^1H_{res} = 6.90 / 2.34, 2.04 (m-Mes^{P+} / p-CH$_3^{MesP+}$, o-CH$_3^{MesP+}$), 6.75 / 2.23, 2.11 (m-Mes / p-CH$_3^{Mes}$, o-CH$_3^{Mes}$), 2.34 / 6.90, 2.04 (p-CH$_3^{MesP+}$ / m-Mes^{P+}, o-CH$_3^{MesP+}$), 2.23 / 6.75, 2.11 (p-CH$_3^{Mes}$ / m-Mes, o-CH$_3^{Mes}$), 2.11 / 6.75, 2.23 (o-CH$_3^{Mes}$ / m-Mes, p-CH$_3^{Mes}$), 2.04 / 6.90, 2.34 (o-CH$_3^{MesP+}$ / m-Mes^{P+}, p-CH$_3^{MesP+}$).

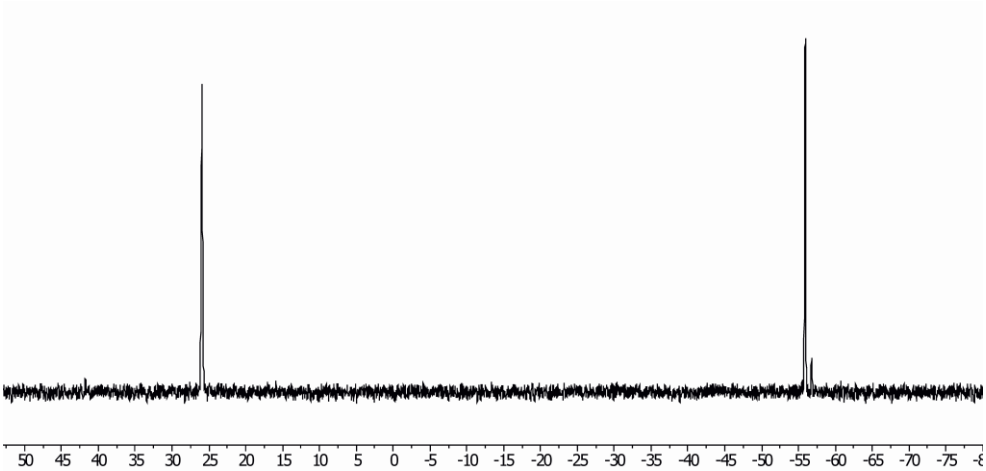
^{1}H, ^{31}P GHMBC (600 MHz / 242 MHz, 299 K, [D$_2$]-dichloromethane): δ^{1}H / δ^{31}P = 6.90 / 25.9 (m-Mes^{P+} / P^{+}), 6.75 / −55.9 (m-Mes / P), 2.34 / 25.9 (p-CH$_3^{MesP+}$ / P^{+}), 2.23 / −55.9 (p-CH$_3^{Mes}$ / P), 2.11 / −55.9 (o-CH$_3^{Mes}$ / P), 2.04 / 25.9 (o-CH$_3^{MesP+}$ / P^{+}).



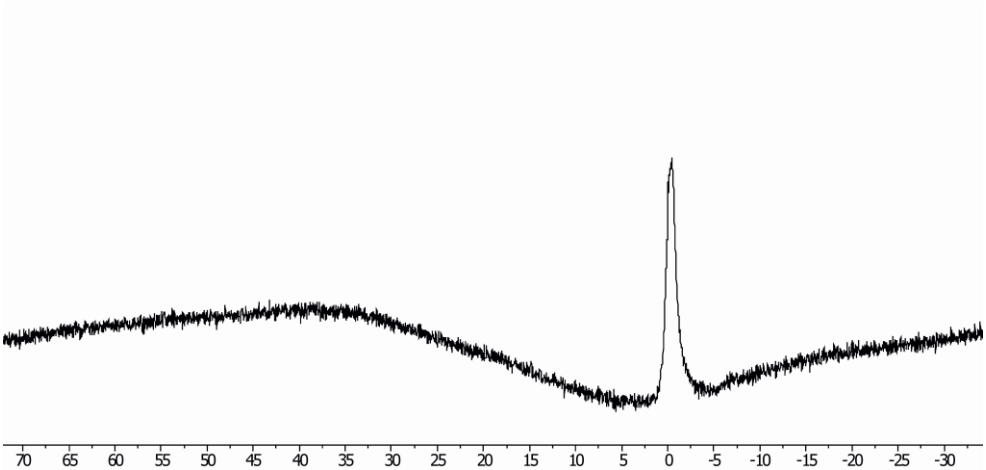
^{1}H NMR (500 MHz, 299 K, [D$_2$]-dichloromethane)



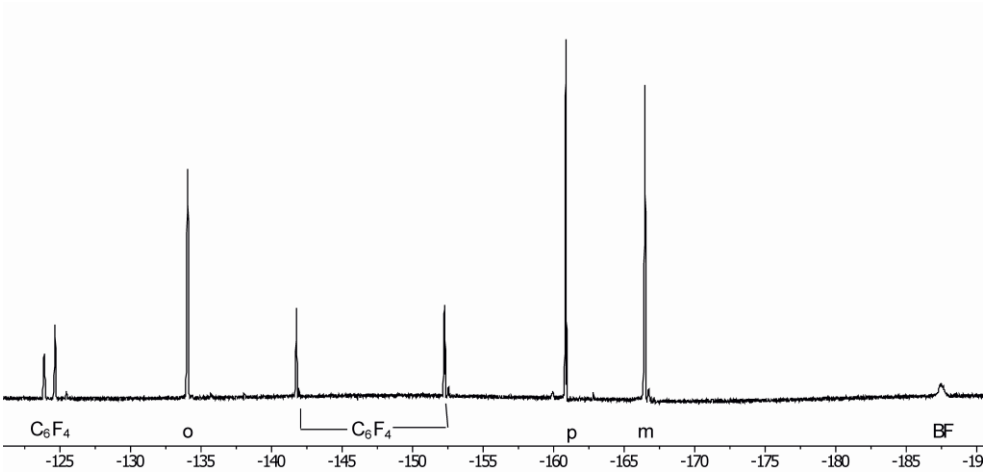
^{13}C{^{1}H} NMR (125 MHz, 299 K, [D$_2$]-dichloromethane)



^{31}P NMR (202 MHz, 299 K, [D_2]-dichloromethane)

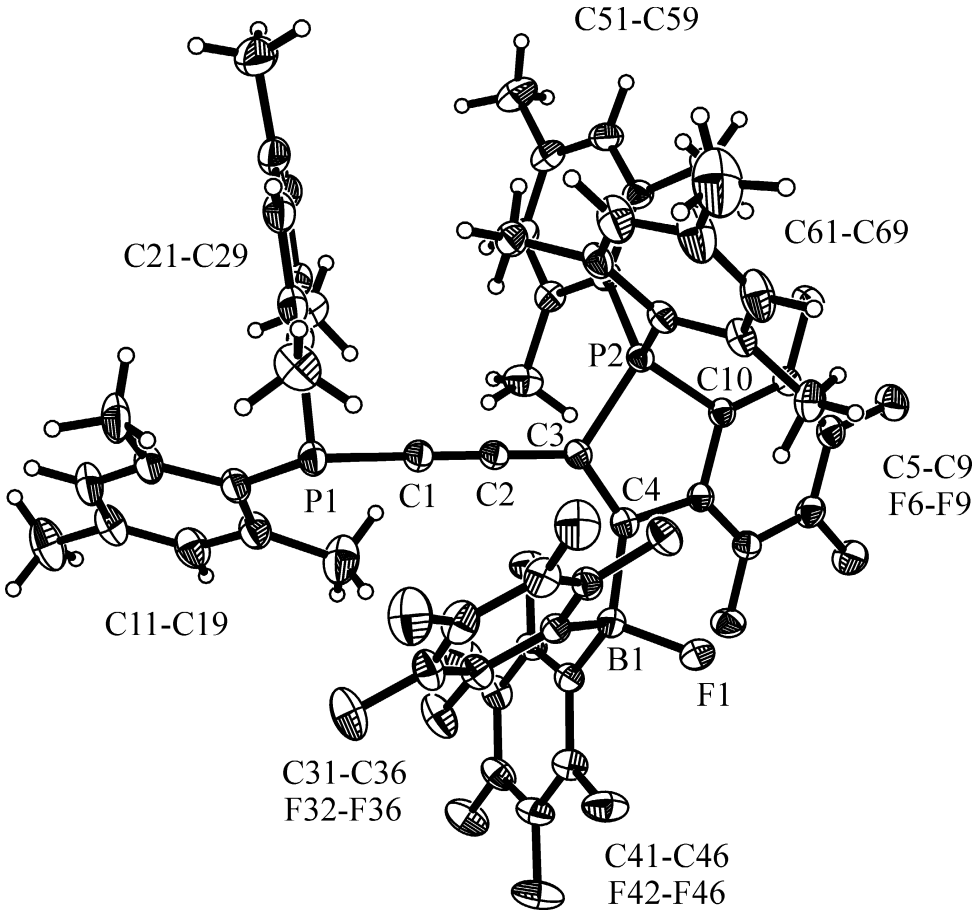


^{11}B{^{1}H} NMR (160 MHz, 299 K, [D_2]-dichloromethane)

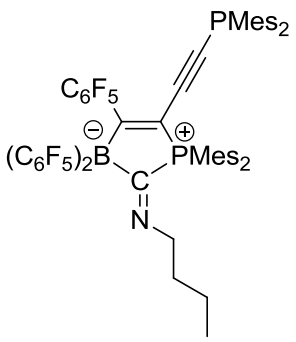


^{19}F NMR (470 MHz, 299 K, [D_2]-dichloromethane)

X-ray crystal structure analysis of ***17****:* formula $C_{58}H_{44}BF_{15}P_2$, M = 1098.68 yellow crystal, 0.30 x 0.15 x 0.03 mm^3, a = 10.6613(2), b = 12.6853(3), c = 19.9278(4) Å, α = 75.576(1), β = 78.833(1), γ = 84.997(1)°, V = 2558.55(9) $Å^3$, ρ_{calc} = 1.426 gcm^{-3}, μ = 0.179 mm^{-1}, empirical absorption correction (0.948 ≤ T ≤ 0.994), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 23662 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 $Å^{-1}$, 8809 independent (R_{int} = 0.050) and 7314 observed reflections [I>2σ(I)], 697 refined parameters, R = 0.056, wR^2 = 0.129, max. (min.) residual electron density 0.29 (-0.27) e. $Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.



Compound 18



Compound **14** (293 mg, 0.5 mmol, 1 eq.) and tris(pentaflourophenyl)borane (256 mg, 0.5 mmol, 1 eq.) were dissolved in dichloromethane (24 mL). The reaction mixture was stirred for 2 d and heated at 75 °C for 10 h. 12 mL of that mixture were separated to another Schlenk tube and treated with *n*-butyl isonitrile (21 mg, 0.25 mmol, 1 eq.). The reaction mixture was stirred for 2 d (r.t.) and the solvent removed *in vacuo* to get a brown solid (203 mg, 69 %). Suitable crystals for X-ray crystal structure analysis were obtained by diffusion of pentane into a dichloromethane solution at −40 °C.

Anal. Calc. for $C_{63}H_{53}BF_{15}NP_2$: C 64.03, H 4.52, N 1.19; found: C 63.62, H 4.47, N 1.01.

IR (KBr): $\tilde{\nu}$ = 4074 (w), 3949 (w), 3802 (w), 3412 (w), 3025 (w), 2983 (w), 2962 (w), 2923 (w), 2857 (w), 2733 (w), 2550 (w), 2401 (w), 2345 (w), 2307 (w), 2225 (w), 2100 (w), 1763 (w), 1733 (w), 1645 (s), 1602 (m), 1557 (w), 1437 (w), 1376 (w), 1314 (w), 1282 (m), 1249 (w), 1210 (w), 1183 (w), 1143 (w), 1100 (s), 1030 (w), 970 (m), 922 (m), 876 (w), 850 (s), 818 (w), 797 (w), 777 (s), 753 (m), 736 (s), 698 (s).

M. p.: 141 °C (DSC).

^{1}H NMR (500 MHz, 299 K, [D$_2$]-dichloromethane): δ = 6.82 (dm, $^4J_{PH}$ = 4.1 Hz, 4H, m-Mes^{P+}), 6.69 (dm, $^4J_{PH}$ = 3.4 Hz, 4H, m-Mes), 3.38 (m, 2H, CH_2^N), 2.28 (s, 6H, p-CH_3^{MesP+}), 2.20 (s, 6H, p-CH_3^{Mes}), 2.19 (s, 12H, o-CH_3^{MesP+}), 2.05 (s, 12H, o-CH_3^{Mes}), 1.50 (m, 2H, CH_2^{CH2}), 1.25 (m, 2H, CH_2^{CH3}), 0.81 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (125 MHz, 299 K, [D$_2$]-dichloromethane): δ = n.o. (=CB), 145.1 (d, $^2J_{PC}$ = 11.0 Hz, o-Mes^{P+}) 143.6 (br, p-Mes^{P+}), 141.9 (d, $^2J_{PC}$ = 16.0 Hz, o-Mes), 139.0 (p-Mes), 131.6 (d, $^3J_{PC}$ = 10.3 Hz, m-Mes^{P+}), 130.0 (d, $^3J_{PC}$ = 3.7 Hz, m-Mes), 128.9 (dd, $^1J_{PC}$ = 11.3 Hz, $^5J_{PC}$ = 1.2 Hz, i-Mes), n.o. (=CP), n.o. (C=N), 120.2 (br dm, $^1J_{PC}$ = 53.5 Hz, i-Mes^{P+}), 104.2 (m, ≡C)^t, 99.6 (m, ≡CP)^t, 55.4 (br, CH_2^N), 31.8 (d, *J* = 1.4 Hz, CH_2^{CH2}), 23.9 (d, $^3J_{PC}$ = 5.9 Hz, o-CH_3^{MesP+}), 22.5 (d, $^3J_{PC}$ = 14.3 Hz, o-CH_3^{Mes}), 21.0 (d, $^5J_{PC}$ = 1.4 Hz, p-CH_3^{MesP+}), 20.9 (p-CH_3^{Mes}), 20.8 (d, *J* = 0.6 Hz, CH_2^{CH3}), 13.8 (CH_3), [C_6F_5 not listed], [^{t} tentatively assigned].

^{31}P{^{1}H} NMR (202 MHz, 299 K, [D$_2$]-dichloromethane): δ = 8.5 ($\nu_{1/2}$ ≈ 550 Hz, P^+), −55.5 ($\nu_{1/2}$ ≈ 15 Hz, P).

^{11}B{^{1}H} NMR (160 MHz, 299 K, [D$_2$]-dichloromethane): δ = −14.7 (d, $^3J_{PB}$ ≈ 40 Hz).

^{19}F NMR (470 MHz, 299 K, [D$_2$]-dichloromethane): δ = −129.9 (m, 4F, o-$C_6F_5^B$), −134.9 (br, 2F, o-C_6F_5), −155.2 (t $^3J_{FF}$ = 21.1 Hz, 1F, p-C_6F_5), −159.3 (t, $^3J_{FF}$ = 20.1 Hz, 2F, p-$C_6F_5^B$), −163.6 (m, 2F, m-C_6F_5), −165.2 (m, 4F, m-$C_6F_5^B$).

^{19}F, ^{19}F GCOSY (470 MHz / 470 MHz, 299 K, [D$_2$]-dichloromethane): δ^{19}F / δ^{19}F = −129.9 / −165.2 (o-$C_6F_5^B$ / m-$C_6F_5^B$), −134.9 / −129.9 (o-C_6F_5 / o-$C_6F_5^B$), −155.2 / −163.6 (p-C_6F_5 / m-C_6F_5), −159.3 / −165.2 (p-$C_6F_5^B$ / m-$C_6F_5^B$), −163.6 / −155.2 (m-C_6F_5 / p-C_6F_5), −163.6 / −155.2 (m-C_6F_5 / p-C_6F_5), −165.2 / −129.9, −159.3 (m-$C_6F_5^B$ / o-$C_6F_5^B$, p-$C_6F_5^B$).

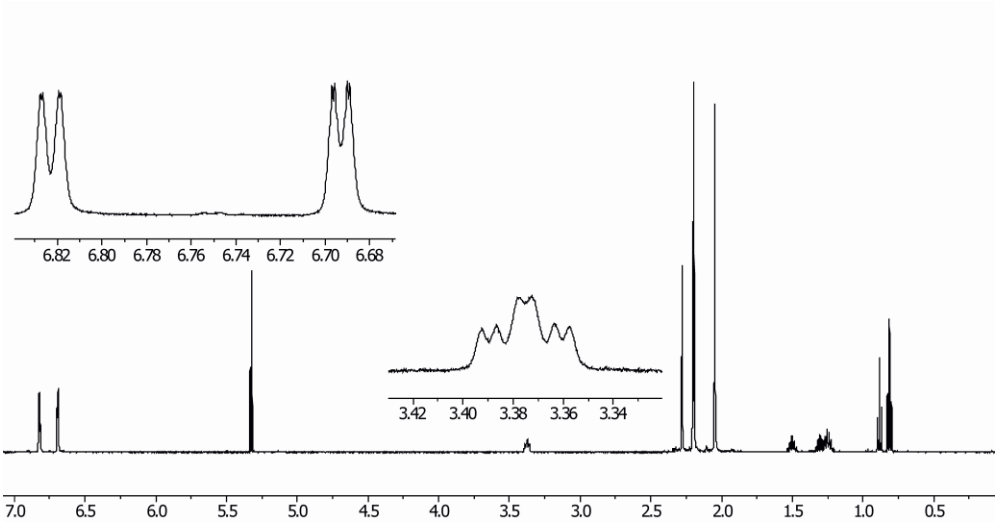
^{1}H, ^{1}H GCOSY (500 MHz / 500 MHz, 299 K, [D$_2$]-dichloromethane)[selected traces]: δ^1H / δ^1H = 6.82 / 2.28, 2.19 (m-Mes^{P+} / p-CH_3^{MesP+}, o-CH_3^{MesP+}), 6.69 / 2.20, 2.05 (m-Mes / p-CH_3^{Mes}, o-CH_3^{Mes}), 3.38 / 1.50 (CH_2^N / CH_2^{CH2}), 1.50 / 3.38, 1.25 (CH_2^{CH2} / CH_2^N, CH_2^{CH3}), 1.25 / 3.38, 1.50, 0.81 (CH_2^{CH3} / CH_2^N, CH_2^{CH2}, CH_3).

^{1}H, ^{13}C GHSQC (500 MHz / 125 MHz, 299 K, [D$_2$]-dichloromethane): δ^1H / δ^{13}C = 6.82 / 131.6 (m-Mes^{P+}), 6.69 / 129.9 (m-Mes), 3.38 / 55.4 (CH_2^N), 2.28 / 21.0 (p-CH_3^{MesP+}), 2.20 / 20.9 (p-CH_3^{Mes}), 2.19 / 23.9 (o-CH_3^{MesP+}), 2.05 / 22.5 (o-CH_3^{Mes}), 1.50 / 31.8 (CH_2^{CH2}), 1.25 / 20.8 (CH_2^{CH3}), 0.81 / 13.8 (CH_3).

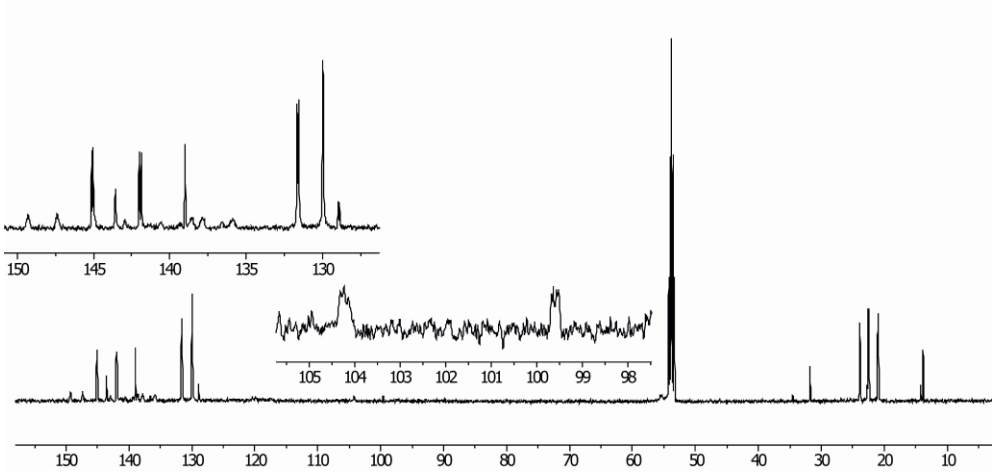
^{1}H, ^{13}C GHMBC (500 MHz / 125 MHz, 299 K, [D$_2$]-dichloromethane): δ^1H / δ^{13}C = 6.82 / 145.1, 131.6, 119.5, 23.9, 21.0 (m-Mes^{P+} / o-Mes^{P+}, m-Mes^{P+}, n.a., o-CH_3^{MesP+}, p-CH_3^{MesP+}), 6.69 / 141.9, 130.0, 128.9, 22.5, 20.9 (m-Mes / o-Mes, m-Mes, n.a., o-CH_3^{Mes}, p-CH_3^{Mes}), 3.37 / 31.8, 20.8 (CH_2^N / CH_2^{CH2}, CH_2^{CH3}), 2.28 / 143.6, 131.6 (p-CH_3^{MesP+} / p-Mes^{P+}, m-Mes^{P+}), 2.20 / 139.0, 129.9 (p-CH_3^{Mes} / p-Mes, m-Mes), 2.19 / 145.1, 131.6, 119.5 (o-CH_3^{MesP+} / o-Mes^{P+}, m-Mes^{P+}, n.a.), 2.05 / 141.9, 130.0, 128.9 (o-CH_3^{Mes} / o-Mes, m-Mes, i-Mes), 1.50 / 55.4, 20.8, 13.8 (CH_2^{CH2} / CH_2^N, CH_2^{CH3}, CH_3), 1.25 / 55.4, 31.8, 13.8 (CH_2^{CH3} / CH_2^N, CH_2^{CH2}, CH_3), 0.81 / 31.8, 20.8 (CH_3 / CH_2^{CH2}, CH_2^{CH3}).

^{1}H TOCSY (500 MHz, 299 K, [D$_2$]-dichloromethane): δ^1H_{irr} / δ^1H_{res} = 6.82 / 2.28, 2.19 (m-Mes^{P+} / p-CH_3^{MesP+}, o-CH_3^{MesP+}), 6.69 / 2.20, 2.05 (m-Mes / p-CH_3^{Mes}, o-CH_3^{Mes}), 3.38 / 1.50, 1.25, 0.81 (CH_2^N / CH_2^{CH2}, CH_2^{CH3}, CH_3), 2.28 / 6.82, 2.19 (p-CH_3^{MesP+} / m-Mes^{P+}, o-CH_3^{MesP+}), 2.05 / 6.69, 2.20 (o-CH_3^{Mes} / m-Mes, p-CH_3^{Mes}), 1.50 / 3.38, 1.25, 0.81 (CH_2^{CH2} / CH_2^N, CH_2^{CH3}, CH_3), 1.25 / 3.38, 1.50, 0.81 (CH_2^{CH3} / CH_2^N, CH_2^{CH2}, CH_3), 0.81 / 3.38, 1.50, 1.25 (CH_3 / CH_2^N, CH_2^{CH2}, CH_2^{CH3}).

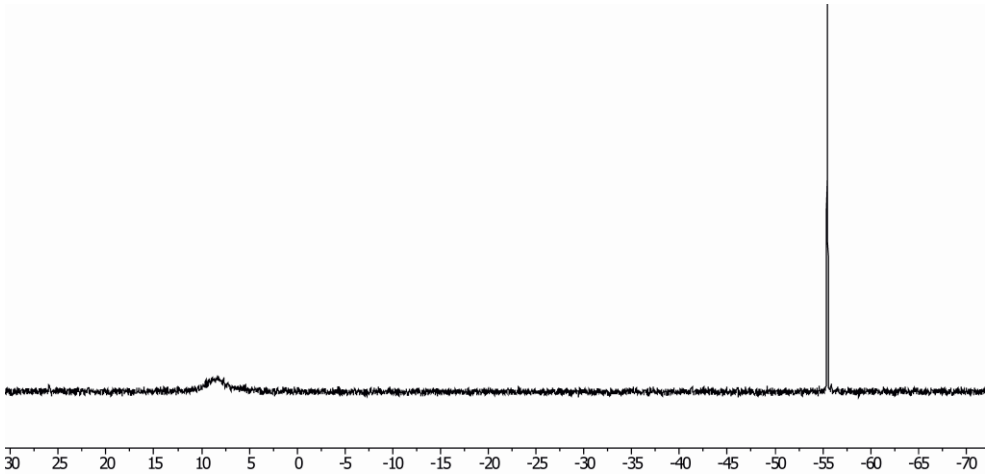
^{1}H, ^{31}P GHMBC (500 MHz / 202 MHz, 299 K, [D2]-dichloromethane): δ^1H / δ^{31}P = 6.69 / −55.4 (m-Mes / P), 2.20 / −55.4 (p-CH_3^{Mes} / P), 2.05 / −55.4 (o-CH_3^{Mes} / P).



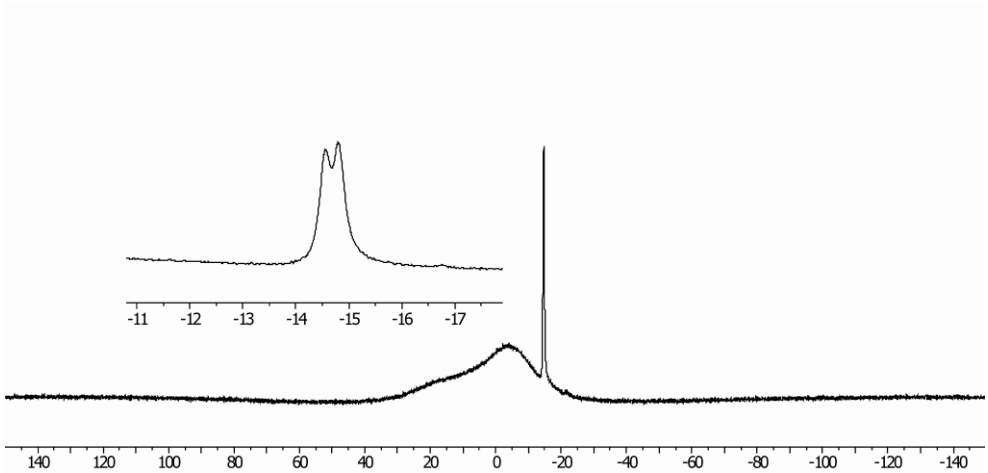
^{1}H NMR (500 MHz, 299 K, [D_2]-dichloromethane)



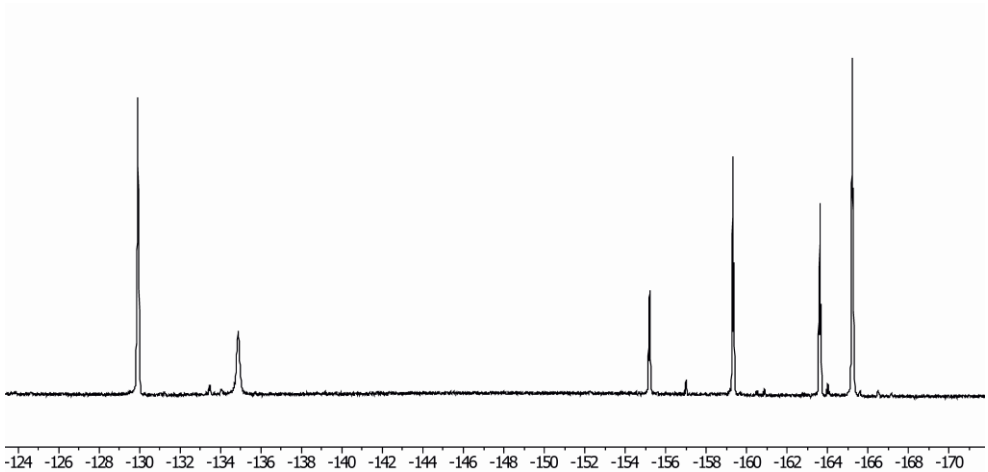
^{13}C{^{1}H} NMR (125 MHz, 299 K, [D_2]-dichloromethane)



^{31}P NMR (202 MHz, 299 K, [D_2]-dichloromethane)

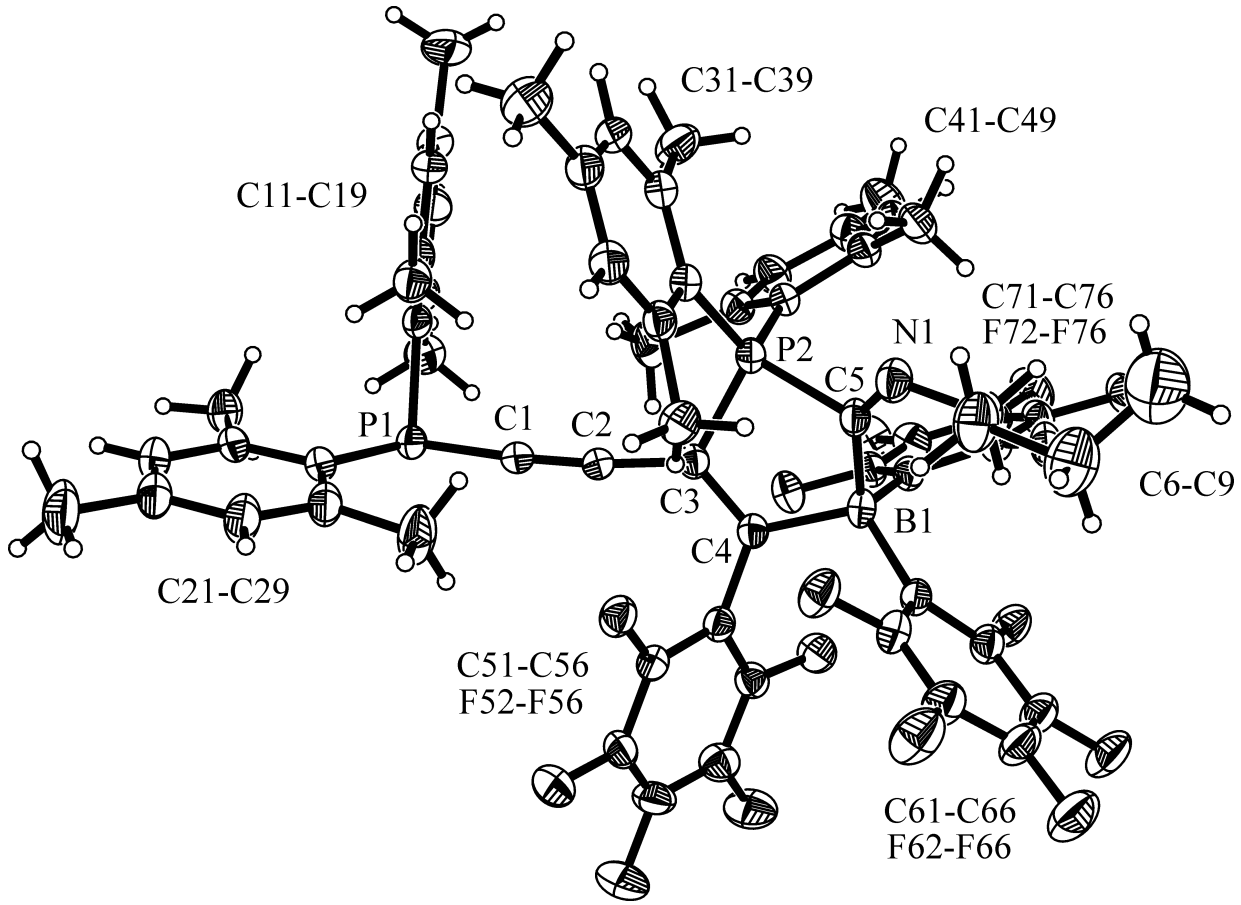


$^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, [D_2]-dichloromethane)



^{19}F NMR (470 MHz, 299 K, [D_2]-dichloromethane)

*X-ray crystal structure analysis of **18**:* formula $C_{63}H_{53}BF_{15}NP_2$ x CH_2Cl_2, M = 1266.74, colourless crystal, 0.25 x 0.20 x 0.03 mm^3, a = 13.4724(6), b = 21.7726(13), c = 21.4217(6) Å, β = 94.999(3)°, V = 6259.7(5) $Å^3$, ρ_{calc} = 1.344 gcm^{-3}, μ = 2.154 mm^{-1}, empirical absorption correction ($0.614 \leq T \leq 0.938$), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 50772 reflections collected ($\pm h$, $\pm k$, $\pm l$), [$(\sin\theta)/\lambda$] = 0.60 $Å^{-1}$, 10639 independent (R_{int} = 0.081) and 6522 observed reflections [$I>2\sigma(I)$], 843 refined parameters, R = 0.064, wR^2 = 0.187, max. (min.) residual electron density 0.31 (-0.44) e. $Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.


C31-C39
C41-C49
C11-C19
C71-C76
F72-F76
N1
P2
C5
P1
C1
C2
C3
C6-C9
B1
C4
C21-C29
C51-C56
F52-F56
C61-C66
F62-F66