Phosphirenium-Borate Zwitterion: Formation in the 1,1-Carboboration Reaction of Phosphinylalkynes

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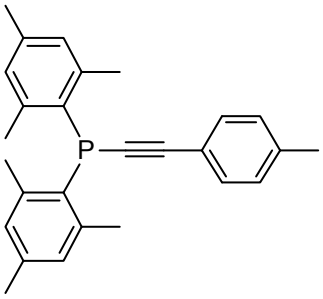
Supporting Information

Experimental Section

All experiments were carried out under a dry Argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents (including deuterated solvents used for NMR) were dried and distilled prior to use. ^{1}H, ^{13}C, ^{11}B, ^{19}F, ^{31}P NMR spectra were recorded on a *Bruker* AV 300 MHz, Varian 500 MHz INOVA or a Varian 600 MHz UNITY plus NMR spectrometer at ambient temperature unless otherwise stated. Chemical shifts are given in ppm relative to solvents (^{1}H and ^{13}C) or an external standard [$\delta(BF_3{\cdot}OEt_2) = 0$ for ^{11}B NMR, $\delta(CFCl_3) = 0$ for ^{19}F NMR and $\delta(85\%\ H_3PO_4) = 0$ for ^{31}P NMR). Coupling constants are in Hz. Elemental analysis data was recorded on a *Elementar Vario El III*. HRMS was recorded on GTC Waters Micromass (Manchester, UK). IR spectra were recorded on a *Varian* 3100 FT-IR (Excalibur Series). Melting points were obtained with a DSC 2010 (*TA Instruments*). X-ray structure analysis: 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 in Enzymology*, 1997, **276**, 307-326), absorption correction Denzo (Z.Otwinowski, D. Borek, W. Majewski & W. Minor, *Acta Cryst.* 2003, **A59**, 228-234), structure solution SHELXS-97 (G.M. Sheldrick, *Acta Cryst.* 1990, **A46**, 467-473), structure refinement SHELXL-97 (G.M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112-122), graphics XP (BrukerAXS, 2000). Graphics show the thermal ellipsoids with 50 % probability, *R* values are given for the observed reflections, wR^2 values for all reflections. CCDC reference numbers 826907 - 826909.

$B(C_6F_5)_3$ was prepared according to procedures reported in the literature (caution: the intermediate involved is explosive) [(a) A. G. Massey, A. J. Park, *J. Organomet. Chem.* 1964, **2**, 245-250. (b) C. Wang, G. Erker, G. Kehr, K. Wedeking and R. Fröhlich, *Organometallics*, 2005, **24**, 4760-4773]. Compound **3c** was prepared according to modified procedures reported in the literature [(a) A. D. Miller, S. A. Johnson, K. A. Tupper, J. L. McBee, T. D. Tilley, *Organometallics*, 2009, **28**, 1252–1262; (b) A. Samb, B. Demerseman, P. H. Dixneuf, C. Mealli, *Organometallics*, 1988, **7**, 26–33].



Synthesis of 3c. *p*-Tolylacetylene (0.49 ml, 3.84 mmol) was dissolved in diethylether (15 ml). Then *n*-butyllithium solution (1.6 M in hexane, 2.4 ml, 3.84 mmol) was added at -78°C. The solution was stirred for 2h at room temperature. Subsequently the reaction mixture was again cooled to -78°C and a solution of chlorodimesitylphosphane (1.17 g, 3.84 mmol) in diethylether (15 ml) was added. The reaction mixture was warmed to room temperature and stirred for 3h. The solvent was removed in vacuum and the residue was extracted with pentane (30 ml) and the product (0.584 g, 1.52 mmol, 40%) could be isolated as a white-yellow solid. Crystals suitable for X-ray crystal structure analysis were grown by slow diffusion of pentane into a solution of **3c** in dichloromethane at –36 °C. **Anal. Calc.** for $C_{27}H_{29}P$: C, 84.34; H, 7.60. Found: C, 84.05; H, 7.43. **IR** (KBr): $\tilde{\nu}$ / cm^{-1} = 2917 (br m), 2148 (w), 1913 (w), 1601 (m), 1463 (s), 1226 (m), 1103 (m), 849 (s), 618 (s), 534 (s). **M.p.** (DSC): 124°C.

^{1}H NMR (500 MHz, 298 K, C_6D_6): δ = 7.23 (d, $^3J_{HH}$ = 8.1 Hz, 2H, *o*-Tol), 6.71 (d, $^3J_{HH}$ = 8.1 Hz, 2H, *m*-Tol), 6.69 (d, $^4J_{PH}$ = 3.3 Hz, 4H, *m*-Mes), 2.58 (s, 12H, *o*-CH_3^{Mes}), 2.05 (s, 6H, *p*-CH_3^{Mes}), 1.91 (s, 3H, Me).

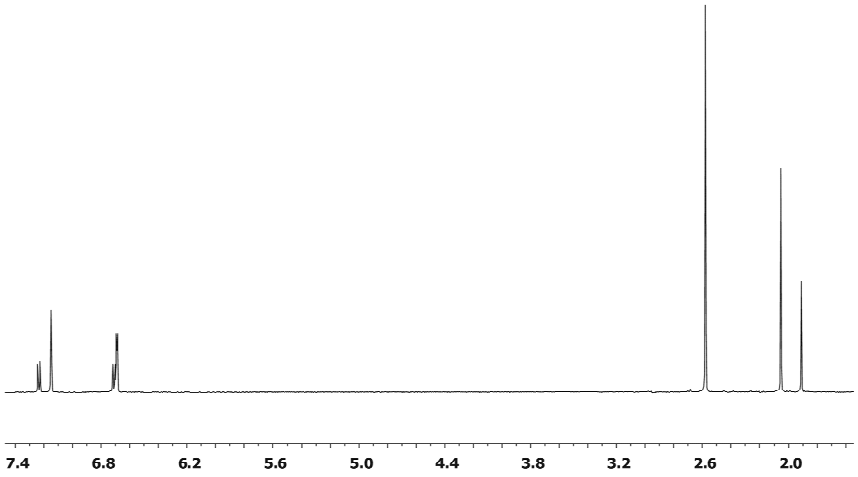
^{13}C{^{1}H} NMR (126 MHz, 298 K, C_6D_6): δ = 142.3 (d, $^2J_{PC}$ = 15.7 Hz, *o*-Mes), 138.4 (*p*-Tol), 138.3 (*p*-Mes), 131.4 (d, $^4J_{PC}$ = 2.1 Hz, *o*-Tol), 130.6 (d, $^1J_{PC}$ = 12.7 Hz, *i*-Mes), 130.4 (d, $^3J_{PC}$ = 3.6 Hz, *m*-Mes), 129.3 (*m*-Tol), 121.3 (d, $^3J_{PC}$ = 1.5 Hz, *i*-Tol), 107.6 (d, $^2J_{PC}$ = 8.4 Hz, ^{Tol}C≡), 87.8 (d, $^1J_{PC}$ = 6.2 Hz, ≡C^P), 23.3 (d, $^3J_{PC}$ = 13.3 Hz, *o*-CH_3^{Mes}), 21.2 (Me), 20.9 (*p*-CH_3^{Mes}).

^{31}P{^{1}H} NMR (202 MHz, 298 K, C_6D_6): δ = -55.7 ($\nu_{1/2}$ ~ 1 Hz).

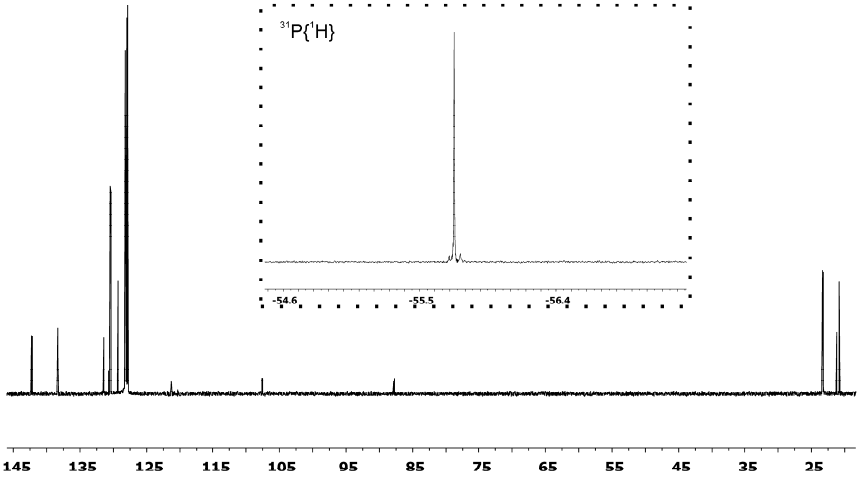
^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, 298 K, C_6D_6): δ^{1}H / δ^{1}H = 7.23 / 6.71 (*o*-Tol / *m*-Tol), 6.42 / 2.58, 2.05 (*m*-Mes / *o*-CH_3^{Mes}, *p*-CH_3^{Mes}).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 298 K, C_6D_6): δ^{1}H / δ^{13}C = 7.23 / 131.4 (*o*- Tol), 6.71 / 129.3 (*m*- Tol), 6.69 / 130.4 (*m*-Mes), 2.58 / 23.3 (*o*-CH_3^{Mes}), 2.05 / 20.9 (*p*-CH_3^{Mes}), 1.91 / 21.2 (Me).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 298 K, C_6D_6): δ^{1}H / δ^{13}C = 7.23 / 138.4, 107.6 (*o*-Tol / *p*-Tol, ^{Tol}C≡), 6.71 / 121.3, 21.2 (*m*-Tol / *i*-, *p*-Tol), 6.69 / 130.6, 23.3, 20.9 (*m*-Mes / *i*-Mes, *o*-, *p*-CH_3^{Mes}), 2.58 / 142.3, 130.4 (*o*-CH_3^{Mes} / *i* -, *m* -Mes), 2.05 / 138.3, 130.4, 121.4 (*p*-CH_3^{Mes} / *p*-, *m*-Mes), 1.91 / 138.4, 129.3, 121.3 (Me / *p*-Tol, *m*-Tol, *i*-Tol).

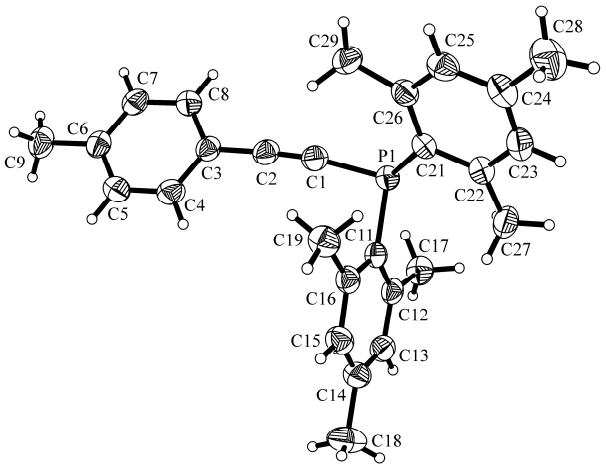


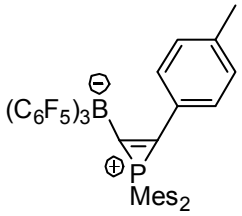
^{1}H NMR (500 MHz, 298 K, C_6D_6) of **3c**.



^{13}C{^{1}H} NMR (126 MHz, 298 K, C_6D_6) and ^{31}P{^{1}H} NMR (202 MHz) of **3c**.

X-Ray crystal structure analysis of 3c. Crystal data for $C_{27}H_{29}P$, M = 384.47, triclinic, $P\bar{1}$ (No. 2), a = 10.1751(5), b = 10.6783 (4), c = 11.6493(7) Å, α = 96.462(2), β = 107.570(4), γ = 109.165(4)°, V = 1107.87(10) Å^3, D_c = 1.153 g cm^{-3}, μ = 1.142 mm^{-1}, *F(000)* = 412, Z = 2, λ = 1.54178 Å, T = 223(2) K, 15949 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 3784 independent (R_{int} = 0.048), and 3388 observed reflections [I ≥ 2σ(I)], 260 refined parameters, R = 0.044, wR^2 = 0.123, GoF = 1.039.





Synthesis of 5. $B(C_6F_5)_3$ (0.400 g, 0.780 mmol) and **3c** (0.300 g, 0.780 mmol) were suspended in pentane (15 ml) and stirred for 30 minutes at room temperature. The suspension was filtered and the residue washed twice with pentane (20 ml). Drying under vacuum gave the product **5** (0.534 g, 0.596 mmol, 76%) as a white solid. Crystals suitable for X-ray crystal structure analysis were grown by slow diffusion of pentane into a solution of **5** in dichloromethane at –36 °C. **Anal. Calc.** for $C_{45}H_{29}BF_{15}P$: C, 60.29; H, 3.26. Found: C, 60.37; H, 3.51. **IR** (KBr): $\tilde{\nu}$ / cm^{-1} = 2926 (br m), 2360 (w), 1643 (m), 1515 (s), 1464 (s), 1092 (s), 980 (s), 823 (m), 648 (m), 564 (m). **Decomp.** (DSC): 189 °C.

^{1}H NMR (500 MHz, 298 K, C_6D_6): δ = 6.96 (d, $^3J_{HH}$ = 8.1 Hz, 2H, *o*-Tol), 6.80 (d, $^3J_{HH}$ = 8.1 Hz, 2H, *m*-Tol), 6.42 (d, $^4J_{PH}$ = 5.2 Hz, 4H, *m*-Mes), 2.08 (s, 12H, *o*-CH_3^{Mes}), 1.92 (s, 3H, Me), 1.87 (s, 6H, *p*-CH_3^{Mes}).

^{13}C{^{1}H} NMR (126 MHz, 298 K, C_6D_6): δ = 151.6 (br, ^{B}C=), 148.7 (dm, $^1J_{FC}$ ~ 240 Hz, *o*-C_6F_5), 144.0 (d, $^4J_{PC}$ = 2.9 Hz, *p*-Mes), 142.9 (d, $^2J_{PC}$ = 11.7 Hz, *o*-Mes), 141.2 (*p*-Tol), 139.7 (dm, $^1J_{FC}$ ~ 250 Hz, *p*-C_6F_5), 137.4 (dm, $^1J_{FC}$ ~ 245 Hz, *m*-C_6F_5), 136.7 (^{Tol}C=), 130.6 (d, $^3J_{PC}$ = 13.4 Hz, *m*-Mes), 129.6 (*m*-Tol), 128.4 (d, $^3J_{PC}$ = 5.3 Hz, *o*-Tol), 125.4 (d, $^2J_{PC}$ = 3.7 Hz, *i*-Tol), 121.5 (br, *i*-C_6F_5), 121.4 (d, $^1J_{PC}$ = 88.0 Hz, *i*-Mes), 22.8 (d, $^3J_{PC}$ = 7.2 Hz, *o*-CH_3^{Mes}), 21.1 (Me), 20.8 (*p*-CH_3^{Mes}).

^{19}F NMR (470 MHz, 298 K, C_6D_6): δ = -130.3 (m, 6F, *o*-BC_6F_5), -159.5 (t, $^3J_{FF}$ = 20.7 Hz, 3F, *p*-BC_6F_5), -164.5 (m, 6F, *m*-BC_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 5.0].

^{11}B{^{1}H} NMR (160 MHz, 298 K, C_6D_6): δ = -16.5 ($\nu_{1/2}$ ~ 50 Hz).

^{31}P{^{1}H} NMR (121 MHz, 300 K, C_6D_6): δ = -137.8 ($\nu_{1/2}$ ~ 10 Hz).

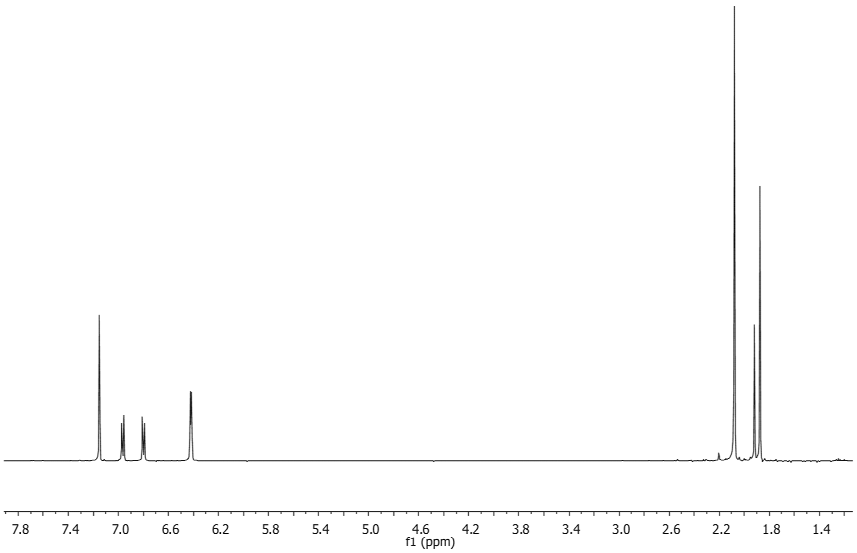
TOCSY (500 MHz, 298 K, C_6D_6): $\delta^1H_{irr.}$ / $\delta^1H_{res.}$ = 6.96 / 6.80 (*o*-Tol / *m*-Tol), 6.80 / 6.96, 1.92 (*m*-Tol / *o*-Tol, Me), 6.42 / 2.08, 1.87 (*m*-Mes / *o*-, *p*-CH_3^{Mes}).

NOE (500 MHz, 298 K, C_6D_6): $\delta^1H_{irr.}$ / $\delta^1H_{res.}$ = 6.96 / 6.80, 2.08 (*o*-Tol / *m*-Tol, *o*-CH_3^{Mes}), 6.80 / 6.96, 1.92 (*m*-Tol / *o*-Tol, Me), 6.42 / 2.08, 1.87 (*m*-Mes / *o*-, *p*-CH_3^{Mes}).

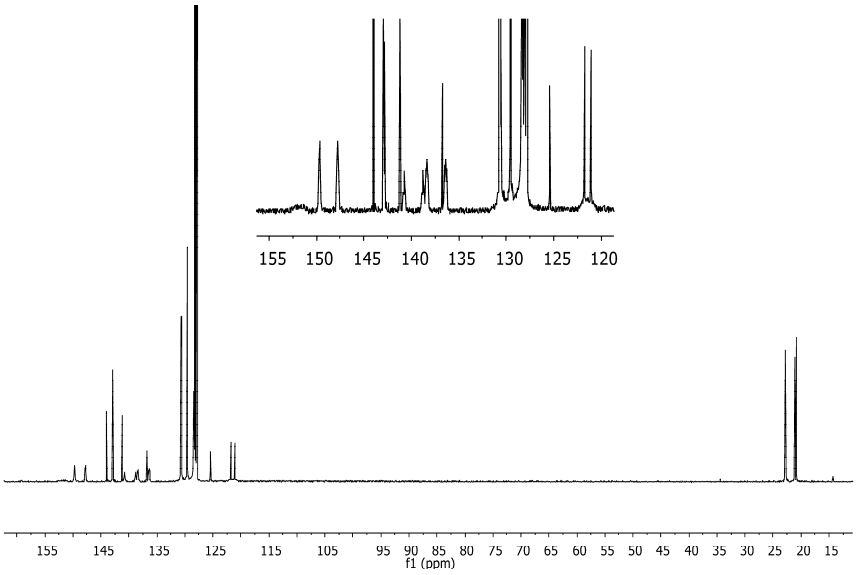
^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, 298 K, C_6D_6): δ^1H / δ^1H = 6.96 / 6.80 (*o*-Tol / *m*-Tol), 6.80 / 6.96, 1.92 (*m*-Tol / *o*-Tol, Me), 6.42 / 2.08, 1.87 (*m*-Mes / *o*-, *p*-CH_3^{Mes}).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 298 K, C_6D_6): δ^1H / $\delta^{13}C$ = 6.96 / 128.4 (*o*-Tol), 6.80 / 129.6 (*m*-Tol), 6.42 / 130.6 (*m*-Mes), 2.08 / 22.8 (*o*-CH_3^{Mes}), 1.92 / 21.1 (Me), 1.87 / 20.8 (*p*-CH_3^{Mes}).

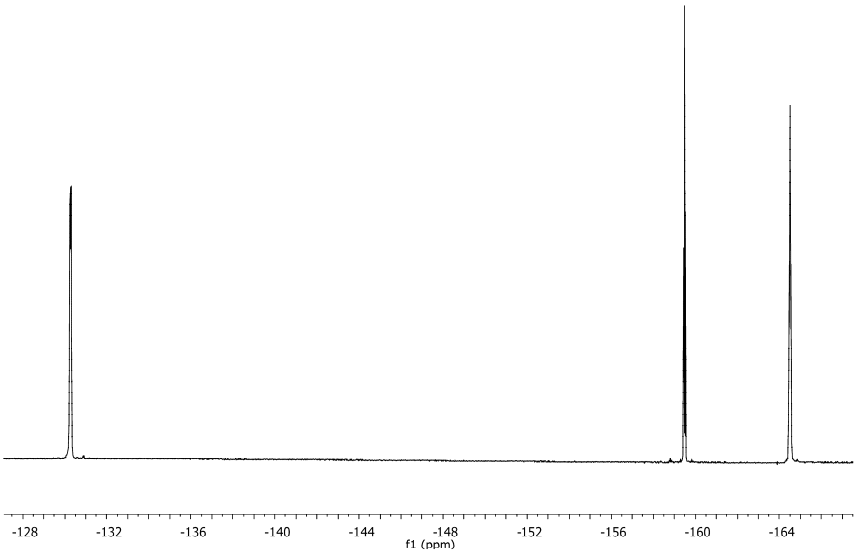
^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 298 K, C_6D_6): δ^1H / $\delta^{13}C$ = 6.96 / 141.2, 136.7, 129.6 (*o*-Tol / *p*-Tol, ^{Tol}C=, *m*-Tol), 6.80 / 128.4, 125.4, 21.1 (*m*-Tol / *o*-Tol, *i*-Tol, Me), 6.42 / 142.9, 121.4, 22.8, 20.8 (*m*-Mes / *o*-, *i*-Mes, *o*-, *p*-CH_3^{Mes}), 2.08 / 142.9, 130.6, 121.4 (*o*-CH_3^{Mes} / *o*-, *m*-, *i*-Mes), 1.92 / 141.2, 129.6, 125.4 (Me / *p*-Tol, *m*-Tol, *i*-Tol), 1.87 / 144.0, 130.6, 121.4 (*p*-CH_3^{Mes} / *p*-, *m*-, *i*-Mes).



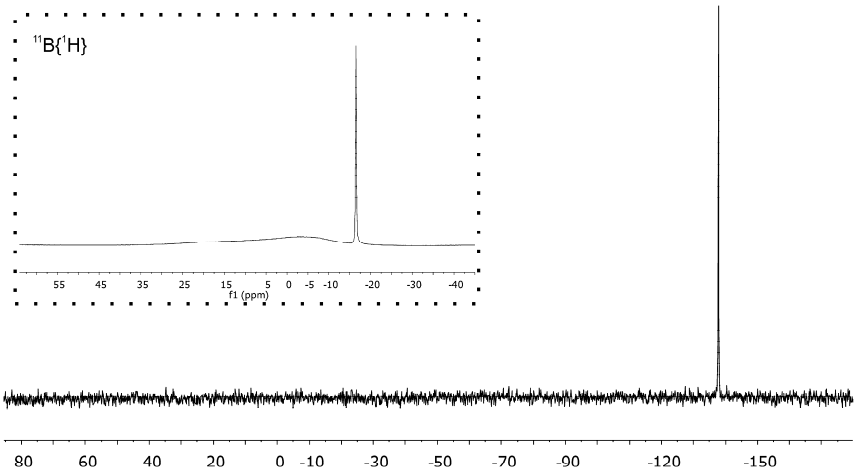
^{1}H NMR (500 MHz, 298 K, C_6D_6) of **5**.



$^{13}C\{^{1}H\}$ NMR (126 MHz, 298 K, C_6D_6) of **5**.

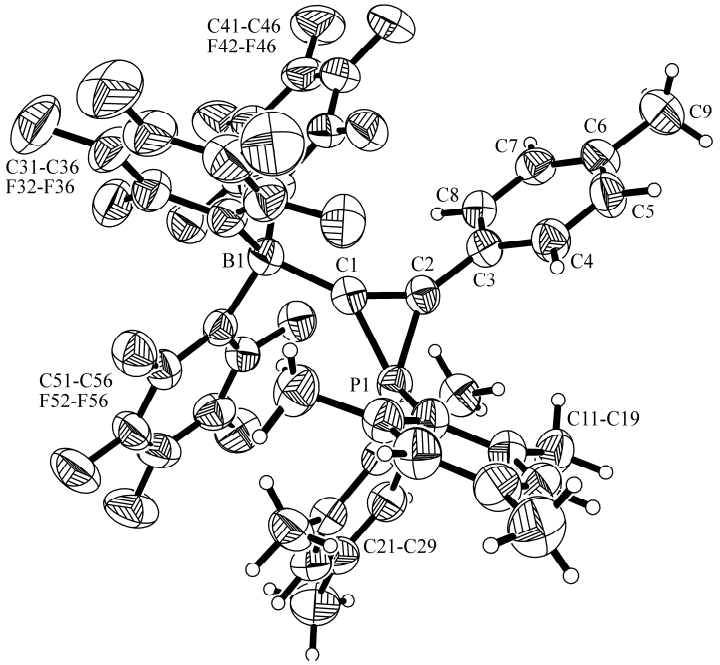


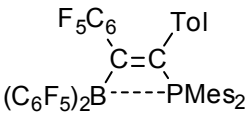
^{19}F NMR (470 MHz, 298 K, C_6D_6) of **5**.



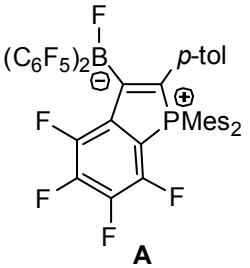
$^{31}P\{^{1}H\}$ NMR (121 MHz, 300 K, C_6D_6) and $^{11}B\{^{1}H\}$ NMR (160 MHz) of **5**.

X-Ray crystal structure analysis of 5. Crystal data for $C_{45}H_{29}BF_{15}P$ * ½ CH_2Cl_2 * ½ C_5H_{12}, M = 975.00, orthorhombic, $Pca2_1$ (No. 29), a = 21.7497(6), b = 22.5390(4), c = 17.9477(6) Å, V = 8798.3(4) Å^3, D_c = 1.472 g cm^{-3}, μ = 1.998 mm^{-1}, $F(000)$ = 3968, Z = 8, λ = 1.54178 Å, T = 223(2) K, 47800 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 14469 independent (R_{int} = 0.074), and 12099 observed reflections [I ≥ 2σ(I)], 1206 refined parameters, R = 0.059, wR^2 = 0.157, GoF = 1.033, Flack parameter 0.50(2).





4c



A

Synthesis of 4c. $B(C_6F_5)_3$ (0.332 g, 0.650 mmol) and **3c** (0.250 g, 0.650 mmol) were dissolved in toluene (20 ml) and stirred for 6h at 105 °C. Subsequently the solvent was removed and the residue was washed twice with pentane (15 ml) and all volatiles were removed in vacuo to yield **4c** (0.379 g, 0.423 mmol, 65%) as a white solid [admixed with 15% of **A**: see O. Ekkert, R. Fröhlich, G. Kehr, G. Erker, *J. Am. Chem. Soc.* **2011**, *133*, 4610-4616]. Crystals suitable for X-ray crystal structure analysis were grown by slow diffusion of pentane into a solution of **4c** in dichloromethane at –36 °C. **HRMS:** Calc. for $C_{45}H_{29}BF_{15}PAg$: 1005.09161. Found: 1005.09180. **IR** (KBr): $\tilde{\nu}$ / cm^{-1} = 2924 (br m), 2624 (w), 2398 (w), 2175 (w), 1643 (s), 1520 (br s), 1277 (s), 1095 (s), 982 (s), 694 (m), 506 (m). **Decomp.** (DSC): 227 °C.

^{1}H NMR (500 MHz, 298 K, CD_2Cl_2): δ = 6.97 (m, 2H, *m*-Tol), 6.86 (m, 2H, *o*-Tol), 6.82 (d, $^4J_{PH}$ = 3.6 Hz, 4H, *m*-Mes), 2.27 (s, 9H, *p*-CH_3^{Mes} / Me), 2.14 (s, 12H, *o*-CH_3^{Mes}).

^{13}C{^{1}H} NMR (126 MHz, 298 K, CD_2Cl_2): δ = 146.9 (d, $^1J_{PC}$ = 48.0 Hz, =C^P), 143.7 (d, $^2J_{PC}$ = 9.1 Hz, *o*-Mes), 142.3 (d, $^4J_{PC}$ = 2.7 Hz, *p*-Mes), 139.3 (*p*-Tol), 134.9 (*i*-Tol), 131.0 (d, $^3J_{PC}$ = 9.3 Hz, *m*-Mes), 129.6 (*m*-Tol), 127.3 (d, $^3J_{PC}$ = 4.0 Hz, *o*-Tol), 123.2 (d, $^1J_{PC}$ = 36.0 Hz, *i*-Mes), 24.0 (d, $^3J_{PC}$ = 5.6 Hz, *o*-CH_3^{Mes}), 21.4 (Me), 20.9 (*p*-CH_3^{Mes}), n.o. (^{B}C=), [C_6F_5 not listed].

^{19}F{^{1}H} NMR (470 MHz, 298 K, CD_2Cl_2): δ = -127.3 (br., 4F, *o*), -158.0 (t, $^3J_{FF}$ = 20.5 Hz, 2F, *p*), -165.2 (m, 4F, *m*) ($B(C_6F_5)_2$) [$\Delta\delta^{19}F_{m,p}$ = 7.2], -136.7 (m, 2F, *o*), -156.3 (t, $^3J_{FF}$ = 21.0 Hz, 1F, *p*), -163.7 (m, 2F, *m*) (C_6F_5), [$\Delta\delta^{19}F_{m,p}$ = 7.4]; {**A** [key resonance]: -188.2 (br, B-F)}.

^{11}B{^{1}H} NMR (160 MHz, 298 K, CD_2Cl_2): δ = -0.1 ($\nu_{1/2}$ ~ 350 Hz).

^{31}P{^{1}H} NMR (202 MHz, 298 K, CD_2Cl_2): δ = 14.6 ($\nu_{1/2}$ ~ 50 Hz);
{**A**: δ = 27.3 ($\nu_{1/2}$ ~ 60 Hz)}.

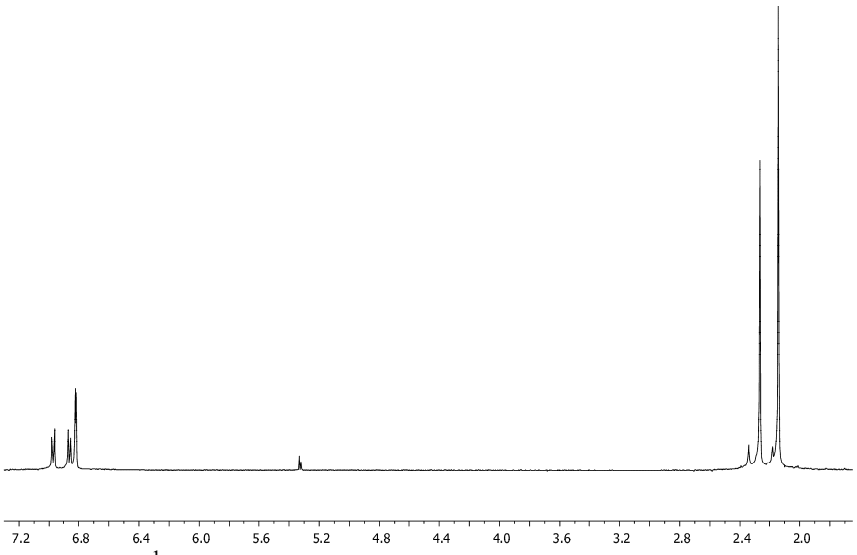
TOCSY (500 MHz, 298 K, CD_2Cl_2): $\delta^1H_{irr.}$ / $\delta^1H_{res.}$ = 6.97 / 6.86 (*m*-Tol / *o*-Tol), 6.86 / 6.97, 2.27 (*o*-Tol / *m*-Tol, Me), 6.82 / 2.27, 2.14 (*m*-Mes / *p*-, *o*-CH_3^{Mes}).

NOE (500 MHz, 298 K, CD_2Cl_2): $\delta^1H_{irr.}$ / $\delta^1H_{res.}$ = 6.97 / 6.86, 2.27 (*m*-Tol / *o*-Tol, Me), 2.27, 2.14 / 6.82 (*p*-CH_3^{Mes}, *o*-CH_3^{Mes} / *m*-Mes).

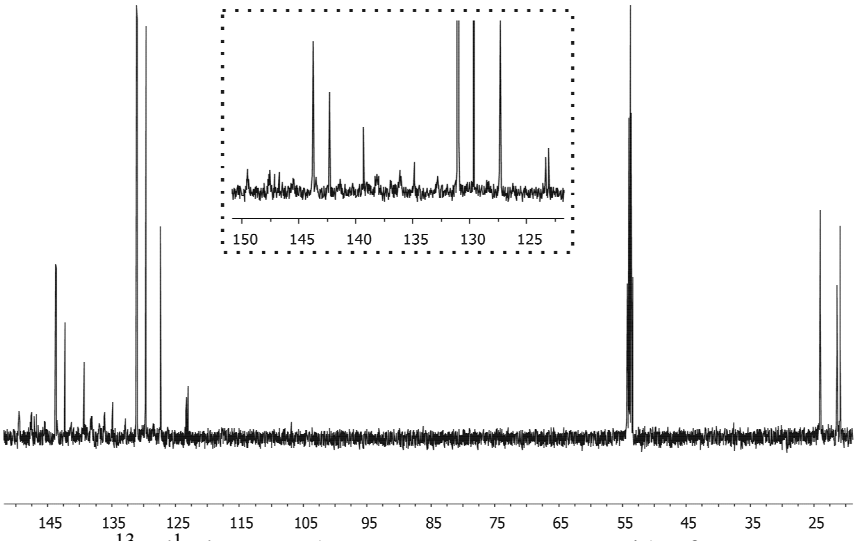
^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, 298 K, CD_2Cl_2): δ^1H / δ^1H = 6.97 / 6.86 (*m*-Tol / *o*-Tol), 6.82 / 2.27, 2.14 (*m*-Mes / *p*-, *o*-CH_3^{Mes}).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 298 K, CD_2Cl_2): δ^{1}H / δ^{13}C = 6.97 / 129.6 (*m*-Tol), 6.86 / 127.3 (*o*-Tol), 6.82 / 131.0 (*m*-Mes), 2.27 / 21.4 (Me), 2.27 / 20.9 (*p*-CH_3^{Mes}), 2.14 / 24.0 (*o*-CH_3^{Mes}).

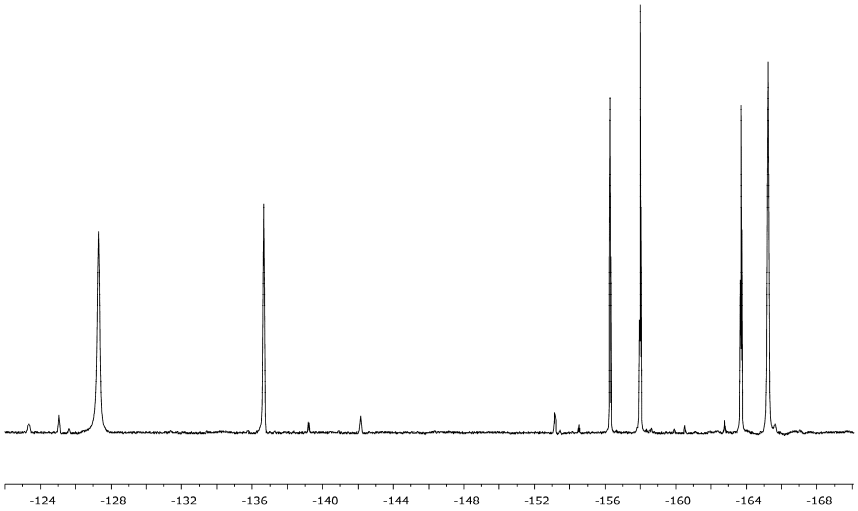
^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 298 K, CD_2Cl_2): δ^{1}H / δ^{13}C = 6.97 / 134.9, 21.4 (*m*-Tol / *i*-Tol, Me), 6.86 / 146.9, 139.3 (*o*-Tol / =C^{P}, *i*-Tol), 6.82 / 143.7, 123.2, 24.0, 20.9 (*m*-Mes / *o*-, *i*-Mes, *o*-, Me), 2.27 / 142.3, 139.3, 131.0, 129.6 (Me, *p*-CH_3^{Mes} / *p*-Mes, *p*-Tol, *m*-Mes, *m*-Tol), 2.14 / 143.7, 131.0, 123.2 (*o*-CH_3^{Mes} / *o*-, *m*-, *i*-Mes).



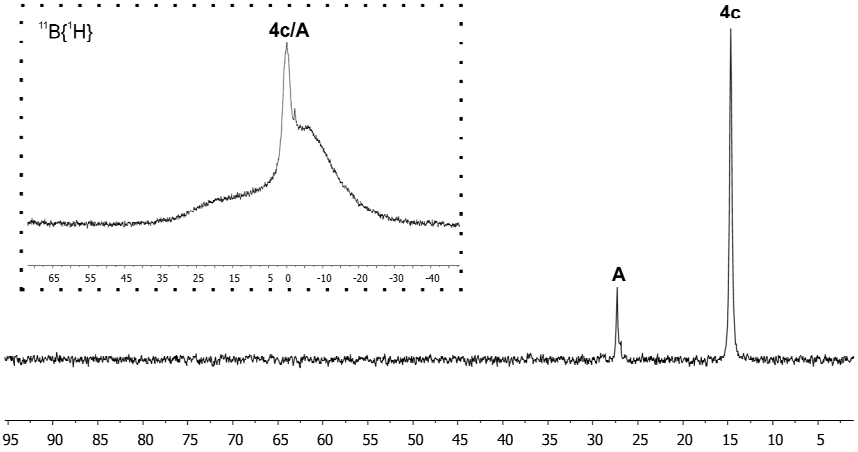
^{1}H NMR (500 MHz, 298 K, CD_2Cl_2) of **4c**.



^{13}C{^{1}H} NMR (126 MHz, 298 K, CD_2Cl_2) of **4c**.

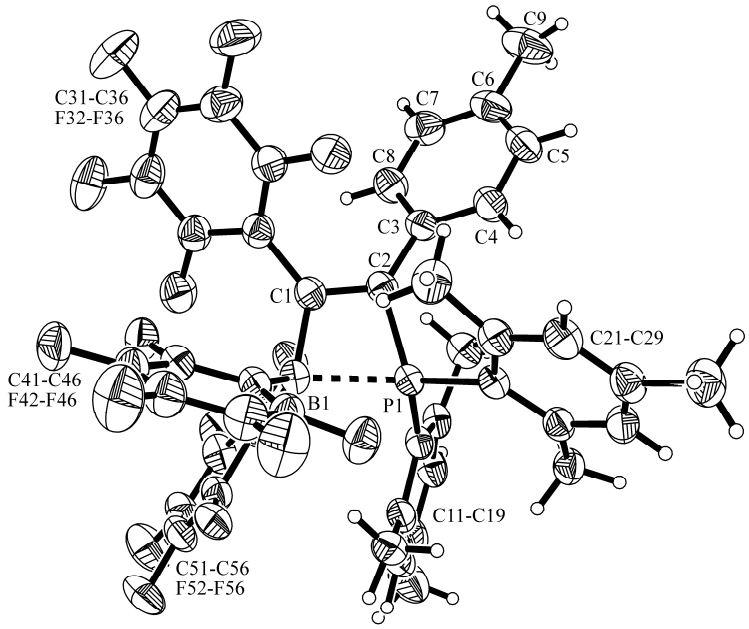


$^{19}F\{^{1}H\}$ NMR (470 MHz, 298 K, CD_2Cl_2) of **4c**.



$^{11}B\{^{1}H\}$ NMR (160 MHz, 298 K, CD_2Cl_2) and $^{31}P\{^{1}H\}$ NMR (202 MHz) of **4c**.

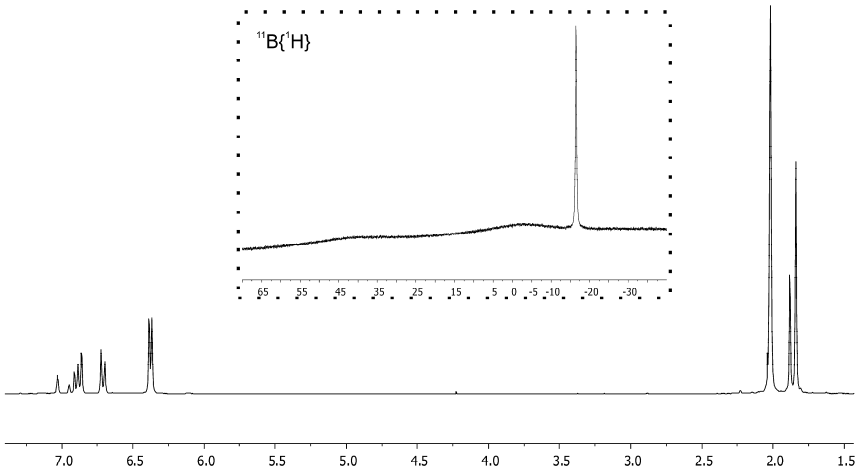
X-Ray crystal structure analysis of 4. Crystal data for $C_{45}H_{29}BF_{15}P$, M = 896.46, triclinic, $P\bar{1}$ (No. 2), a = 12.4342(5), b = 13.4995 (6), c = 14.2303(6) Å, α = 82.805(2), β = 66.678(2), γ = 64.037(2)°, V = 1968.75(14) Å^3, D_c = 1.512 g cm^{-3}, μ = 1.570 mm^{-1}, F(000) = 908, Z = 2, λ = 1.54178 Å, T = 223(2) K, 28030 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 6739 independent (R_{int} = 0.038), and 6261 observed reflections [I ≥ 2σ(I)], 566 refined parameters, R = 0.037, wR^2 = 0.109, GoF = 1.034.



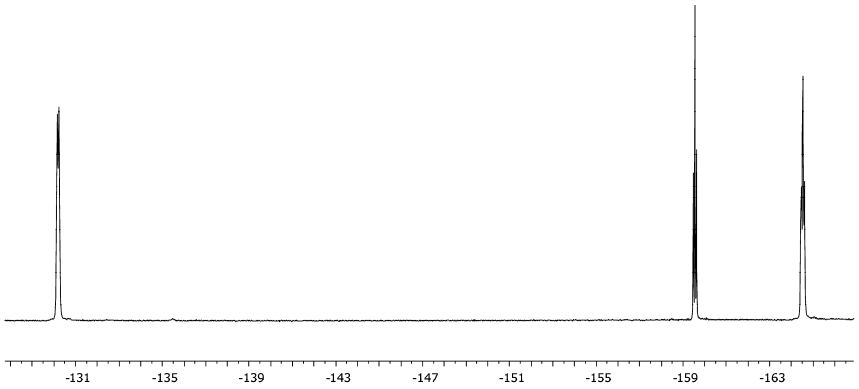
NMR-scale reactions:

a) Heating of **5** (31.0 mg, 0.035 mmol) in d_8-toluene (1 ml) for 6h at 105 °C yielded a mixture of **4c** and **A** in a 1:0.1 ratio (monitored by ^{31}P NMR).

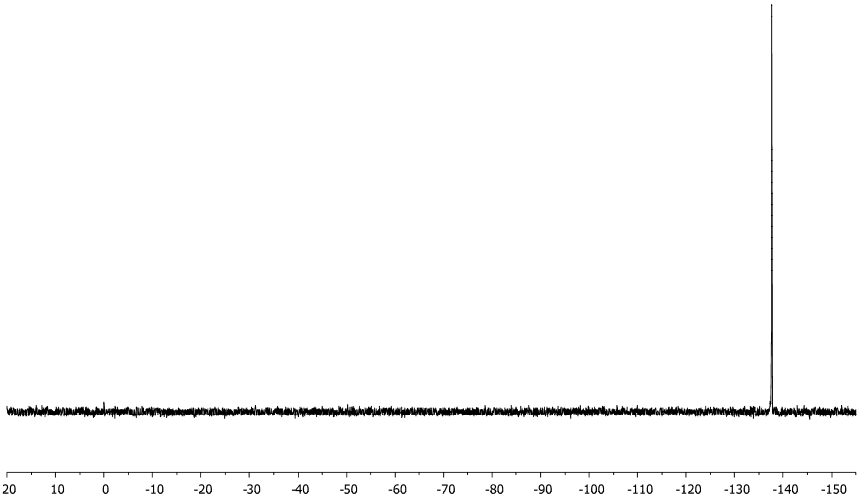
NMR spectra before heating



^{1}H NMR (300 MHz, 298 K, D_8-toluene) and ^{11}B{^{1}H} NMR (96 MHz): before heating of **5**

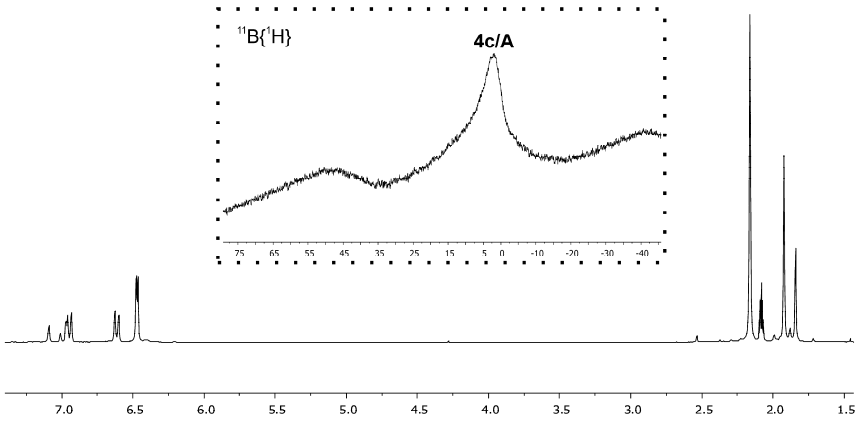


^{19}F NMR (282 MHz, 298 K, D_8-toluene): before heating of **5**

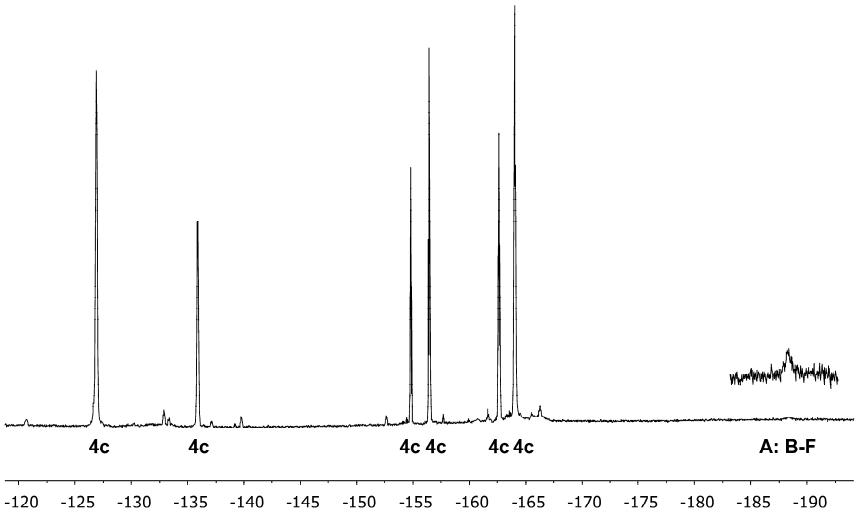


^{31}P NMR (122 MHz, 298 K, D_8-toluene): before heating of **5**

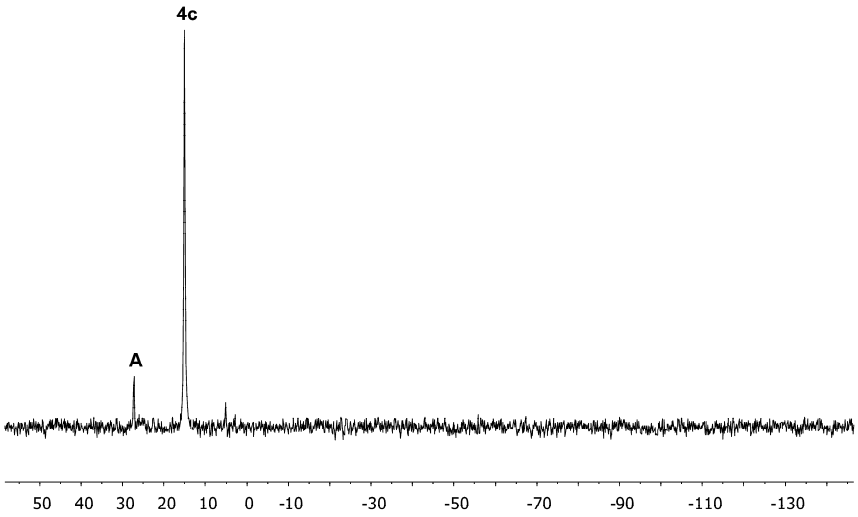
NMR spectra after heating at 105°C for 6h



^{1}H NMR (300 MHz, 298 K, D_8-toluene) and ^{11}B{^{1}H} NMR (96 MHz): after heating of **5** for 6h



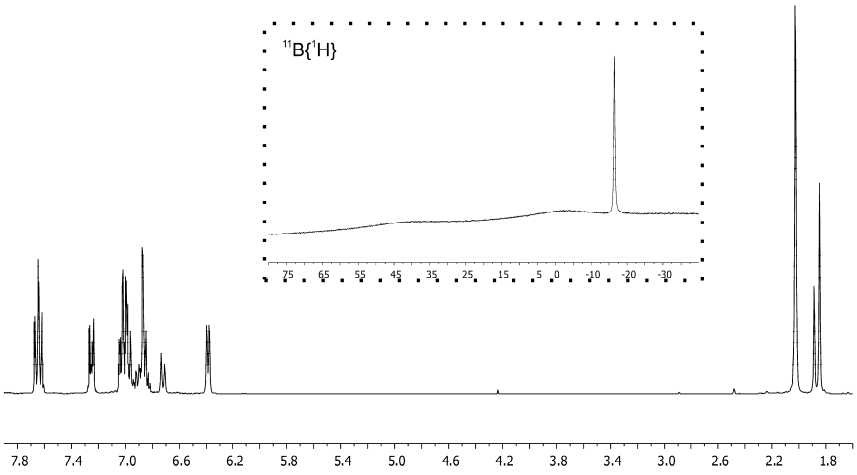
^{19}F NMR (282 MHz, 298 K, D_8-toluene): after heating of **5** for 6h



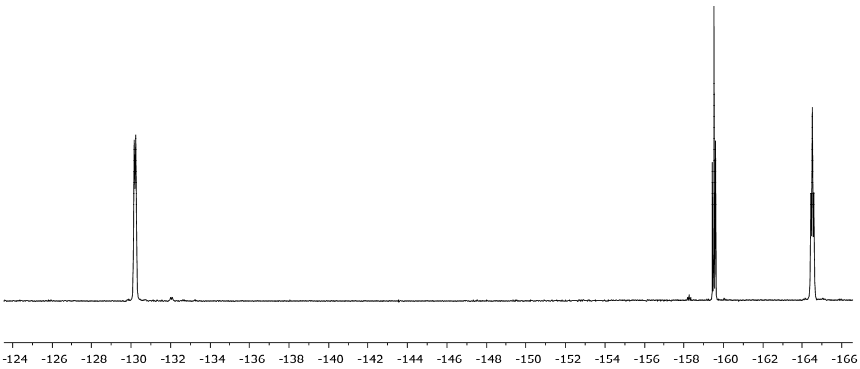
^{31}P{^{1}H} NMR (122 MHz, 298 K, D_8-toluene): after heating of **5** for 6h

b) Heating of **5** (43.0 mg, 0.048 mmol) and **3a** (17.9 mg, 0.062 mmol) in d_8-toluene (1 ml) for 48h at 70 °C resulted in a reaction mixture of **4c**, **4a**, **3c** and **3a** in a ca. 5.8 : 1 : 1 : 3.4 ratio [traces of **5** and **A**] (monitored by ^{31}P NMR).

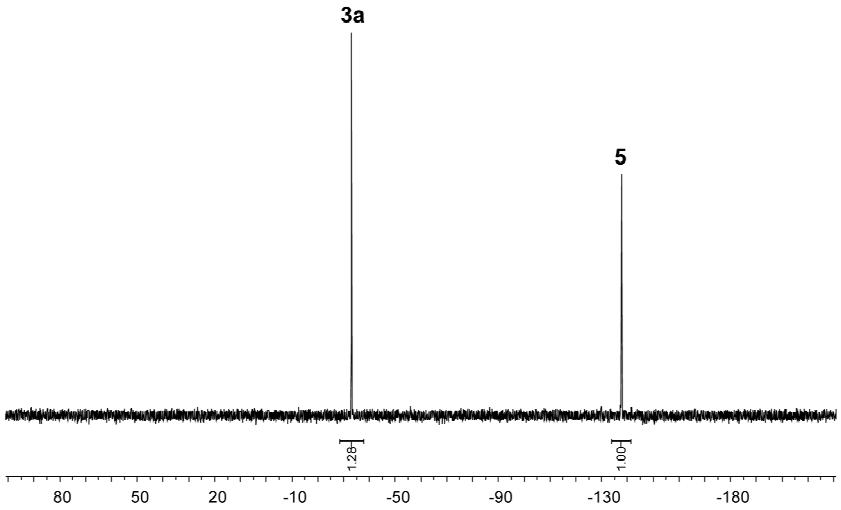
NMR spectra before heating



^{1}H NMR (300 MHz, 298 K, D_8-toluene) and ^{11}B NMR (96 MHz): before heating the reaction mixure of **5** and **3a**

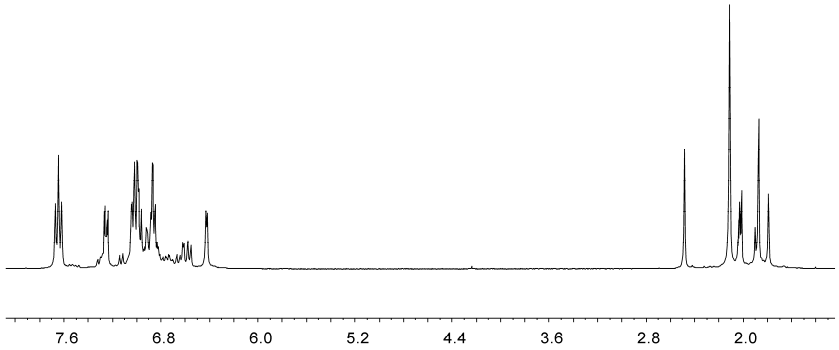


^{19}F NMR (282 MHz, 298 K, D_8-toluene): before heating the reaction mixure of **5** and **3a**

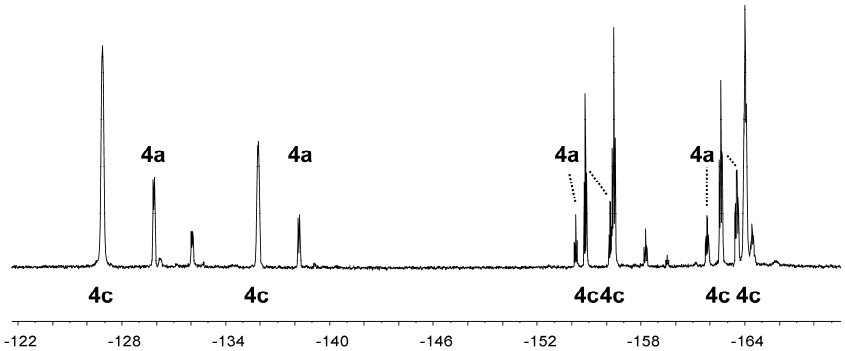


^{31}P NMR (122 MHz, 298 K, D_8-toluene): before heating the reaction mixure of **5** and **3a**

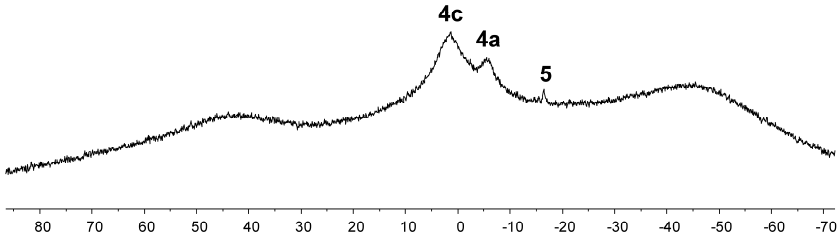
NMR spectra after heating at 70°C for 48h



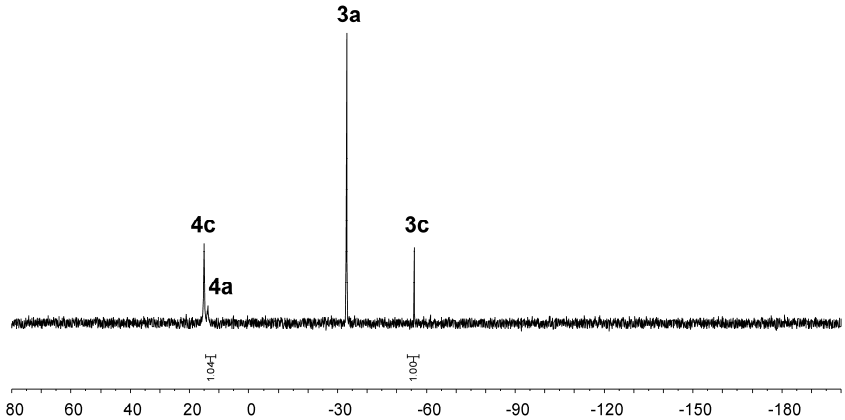
^{1}H NMR (300 MHz, 298 K, D_8-toluene): heating the reaction mixure of **5** and **3a** (70°C, 48h)



^{19}F NMR (282 MHz, 298 K, D_8-toluene): heating the reaction mixure of **5** and **3a** (70°C, 48h)



^{11}B NMR (96 MHz, 298 K, D_8-toluene): heating the reaction mixure of **5** and **3a** (70°C, 48h)



^{31}P NMR (122 MHz, 298 K, D_8-toluene): heating the reaction mixure of **5** and **3a** (70°C, 48h)