Supporting Information

Reversible Heterolytic Si–H Bond Activation by an Intramolecular Frustrated Lewis Pair

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Dedicated to Professor Heribert Offermanns on the occasion of his 75th birthday

All reactions were carried out in flame-dried glassware under an argon atmosphere using a glove box or standard Schlenk techniques. Solvents were dried using a solvent purification system [1]. Deuterated dichloromethane used for NMR spectroscopy was dried over CaH_2, vacuum transferred to a dry Schlenk flask and subsequently degassed by freeze-pump-thaw technique. Dimesitylvinylphosphane (**5**) [2] and Piers' borane $HB(C_6F_5)_2$ (**6**) [3] were prepared according to literature procedures. Commercially available silanes $PhSiH_3$ and Ph_2SiH_2 were dried over CaH_2 and distilled prior to use. NMR spectra were recorded on a Varian Inova 500 MHz and Unity Plus 600 MHz spectrometer. ^{1}H NMR and ^{13}C chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent signal as the internal standard (CD_2Cl_2: δ 5.32 for ^{1}H and δ 53.8 for ^{13}C). A unified scale was used for reporting the NMR chemical shifts of all other nuclei relative to the ^{1}H NMR resonance of tetramethylsilane as recommended by the IUPAC [4]. Elemental analyses were performed using a Foss-Heraeus CHNO-Rapid analyzer. Electrospray ionization (ESI) mass spectra were measured on a Bruker MicroTof instrument. Melting points (decomposition temperatures) were determined using a DSC 2010 apparatus by TA Instruments. IR spectra were recorded on a Varian 3100 FT-IR (Excalibur Series) spectrophotometer using KBr pellets.

X-ray structure determination

The data set for the X-ray crystal structure analysis of compound **8a** was collected with a Nonius KappaCCD diffractometer. Programs used were: COLLECT for data collection [5], DENZO-SMN for data reduction [6], DENZO for absorption correction [7], SHELXS-97 for structure solution [8], SHELXL-97 for structure refinement [9], and SCHAKAL for graphical visualization [10].

CCDC 888686 contains 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.

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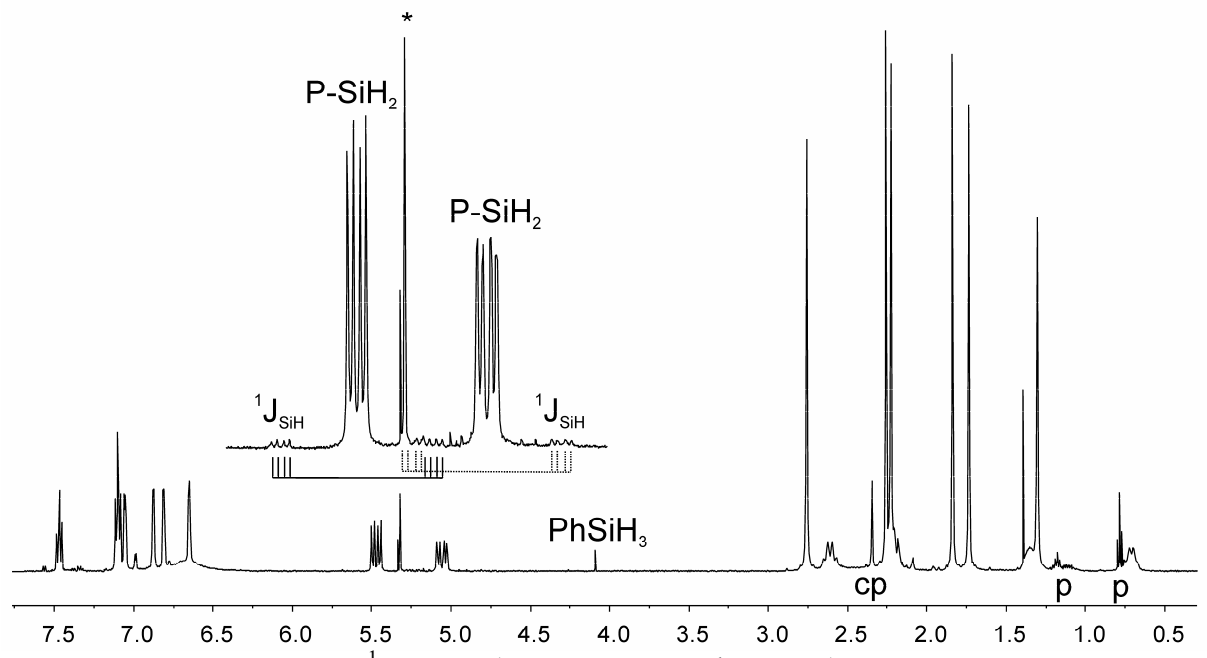
*{2-[Dimesityl(phenylsilyl)phosphonium]ethyl}bis(pentafluorophenyl)hydridoborate (**8a**)*

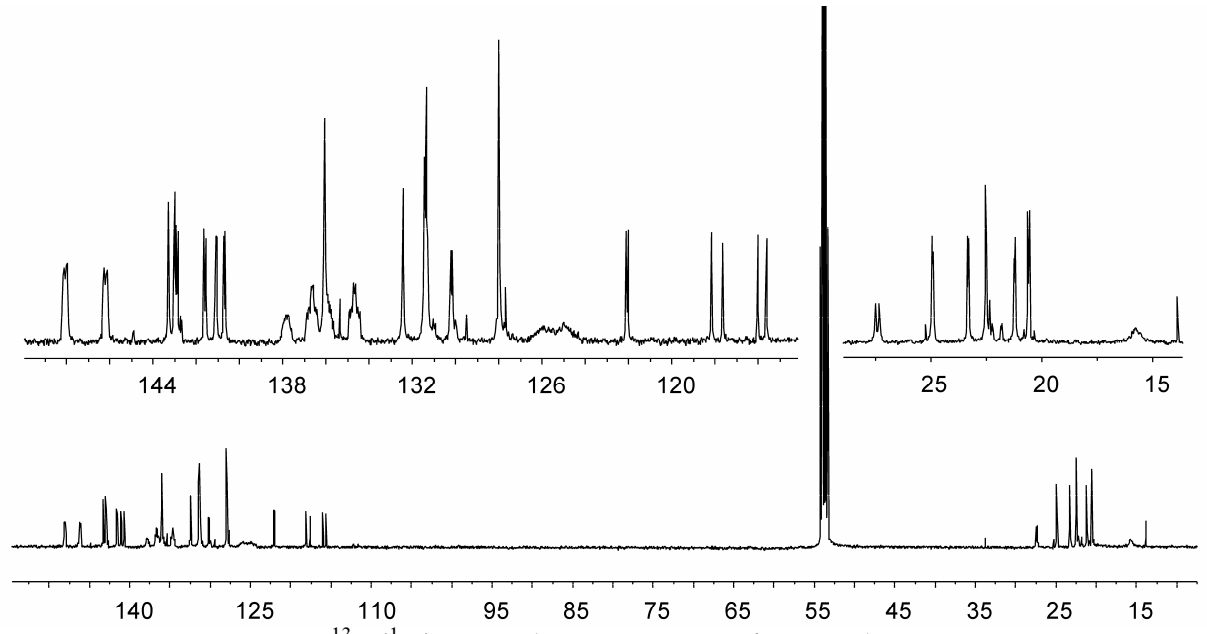
Dimesitylvinylphosphane (**5**) (29.7 mg, 0.10 mmol, 1.00 equiv) and bis(pentafluorophenyl)-borane (**6**) (34.6 mg, 0.10 mmol, 1.00 equiv) were suspended in pentane (4 mL), and the reaction mixture was stirred for 15 min at ambient temperature. To the resulting yellow solution, phenylsilane (123 μL, 108 mg, 1.00 mmol, 10.0 equiv) was added dropwise, whereupon the reaction mixture turned colorless and a white solid precipitated. After an additional 15 min at ambient temperature, the precipitate was isolated by filtration, washed with pentane (3 × 1 mL) and dried briefly in vacuo to yield **8a** as a white powder (61 mg, 81 %) [at 193K in CD_2Cl_2 as a mixture of **7**/$PhSiH_3$: **8a** ~ 2 : 98; at 299K in CD_2Cl_2 as a mixture of **7**/$PhSiH_3$: **8a** ~ 3 : 7]. Single crystals suitable for X-ray diffraction were obtained from a toluene solution of **8a** by slow evaporation of the solvent at ambient temperature. – M. p. 144 °C (decomposition at 150°C). – IR (KBr): ν = 3440 (br), 3070 (w), 2972 (m), 2933 (m), 2848 (w), 2323 (s), 2273 (w), 2154 (s), 1637 (s), 1605 (s), 1559 (m), 1509 (s), 1457 (s), 1391 (m),

1379 (m), 1275 (s), 1259 (s), 1180 (s), 1135 (s), 1124 (s), 1094 (s), 1082 (s), 1029 (m), 973 (s), 946 (s), 925 (s), 873 (s), 857 (s), 808 (w), 768 (m), 749 (m), 739 (s), 723 (w), 699 (s), 643 (s), 609 (m), 604 (m), 569 (w), 557 (m), 467 (w), 452 (m), 411 (m) cm^{-1}. – HRMS ((+)-ESI): *m*/*z* = 789.1943 (calcd. 789.1949 for $C_{38}H_{34}BF_{10}PSiONa$, $[M+ONa]^+$). – $C_{38}H_{34}BF_{10}PSi$ (750.53): calcd. C 60.81, H 4.57; found C 61.06, H 4.61. – ^{1}H NMR (500 MHz, CD_2Cl_2, 193 K): δ = 7.47 (m, 1H, *p*-Ph), 7.10 (m, 2H, *m*-Ph), 7.06 (dm, $^4J_{PH}$= 4.0 Hz, 1H, *m*-Mes^A), 6.88 (dm, $^4J_{PH}$ = 2.5 Hz, 1H, *m*-Mes^B), 6.81 (dm, $^4J_{PH}$ = 2.9 Hz, 1H, *m*'-Mes^A), 6.66 (br, 2H, *o*-Ph), 6.65 (m, 1H, *m*'-Mes^B), 5.47 (dd, $^1J_{SiH}$ = 242.5 Hz, $^2J_{PH}$ = 20.1 Hz, $^2J_{HH}$ = 9.2 Hz, 1H, SiH_2), 5.06 (ddd, $^1J_{SiH}$ = 236.9 Hz, $^2J_{PH}$ = 22.3 Hz, $^2J_{HH}$ = 9.2 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, SiH_2), 2.76 (s, 3H, *o*-CH_3^{MesA}), 2.61, 2.20 (each m, each 1H, $^PCH_2$), 2.26 (s, 3H, *p*-CH_3^{MesA}), 2.23 (s, 3H, *p*-CH_3^{MesB}), 1.84 (s, 3H, *o*-CH_3^{MesB}), 1.74 (s, 3H, *o*'-CH_3^{MesA}), 1.35, 0.71 (each br, each 1H, $^BCH_2$), 1.30 (s, 3H, *o*'-CH_3^{MesB}), n.o. (BH). – $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 193 K): δ = 147.2 (dm, $^1J_{FC} \approx$ 234 Hz, *m*-C_6F_5), 143.3 (d, $^4J_{PC}$ = 2.7 Hz, *p*-Mes^A), 143.0 (d, $^4J_{PC}$ = 2.7 Hz, *p*-Mes^B), 142.9 (d, $^2J_{PC}$ = 7.9 Hz, *o*'-Mes^B), 141.6 (d, $^2J_{PC}$ = 11.1 Hz, *o*-Mes^A), 141.1 (d, $^2J_{PC}$ = 6.4 Hz, *o*'-Mes^A), 140.7 (d, $^2J_{PC}$ = 9.7 Hz, *o*-Mes^B), 136.9 (dm, $^1J_{FC} \approx$ 243 Hz, *p*-C_6F_5), 136.1 (*o*-Ph), 135.7 (dm, $^1J_{FC} \approx$ 247 Hz, *o*-C_6F_5), 132.4 (*p*-Ph), 131.4 (d, $^3J_{PC}$ = 9.8 Hz, *m*-Mes^B), 131.4 (d, $^3J_{PC}$ = 9.8 Hz, *m*'-Mes^B), 131.3 (d, $^3J_{PC}$ = 9.3 Hz, *m*'-Mes^A), 130.1 (d, $^3J_{PC}$ = 11.3 Hz, *m*-Mes^A), 128.0 (*m*-Ph), 125.4 (br m, *i*-C_6F_5), 122.1 (d, $^2J_{PC}$ = 9.5 Hz, *i*-Ph), 117.9 (d, $^1J_{PC}$ = 66.0 Hz, *i*-Mes^A), 115.9 (d, $^1J_{PC}$ = 49.5 Hz, *i*-Mes^B), 27.4 (d, $^1J_{PC}$ = 22.0 Hz, $^PCH_2$), 24.9 (d, $^3J_{PC}$ = 5.0 Hz, *o*-CH_3^{MesA}), 23.3 (d, $^3J_{PC}$ = 6.2 Hz, *o*-CH_3^{MesB}), 22.5 (*o*'-CH_3^{MesB}), 21.2 (d, $^3J_{PC}$ = 5.7 Hz, *o*'-CH_3^{MesA}), 20.62 (*p*-CH_3^{MesA}), 20.56 (*p*-CH_3^{MesB}), 15.8 (br, $^BCH_2$). – $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 193 K): δ = –9.9 ($\nu_{1/2} \approx$ 30 Hz). – ^{19}F NMR (470 MHz, CD_2Cl_2, 193 K): δ = –133.5 (m, 2F, *o*-$C_6F_5^A$), –133.9 (m, 2F, *o*-$C_6F_5^B$), –162.7 (m, 1F, *p*-$C_6F_5^A$), –163.2 (m, 1F, *p*-$C_6F_5^B$), –165.4 (m, 2F, *m*-$C_6F_5^A$), –166.0 (m, 2F, *m*-$C_6F_5^B$),

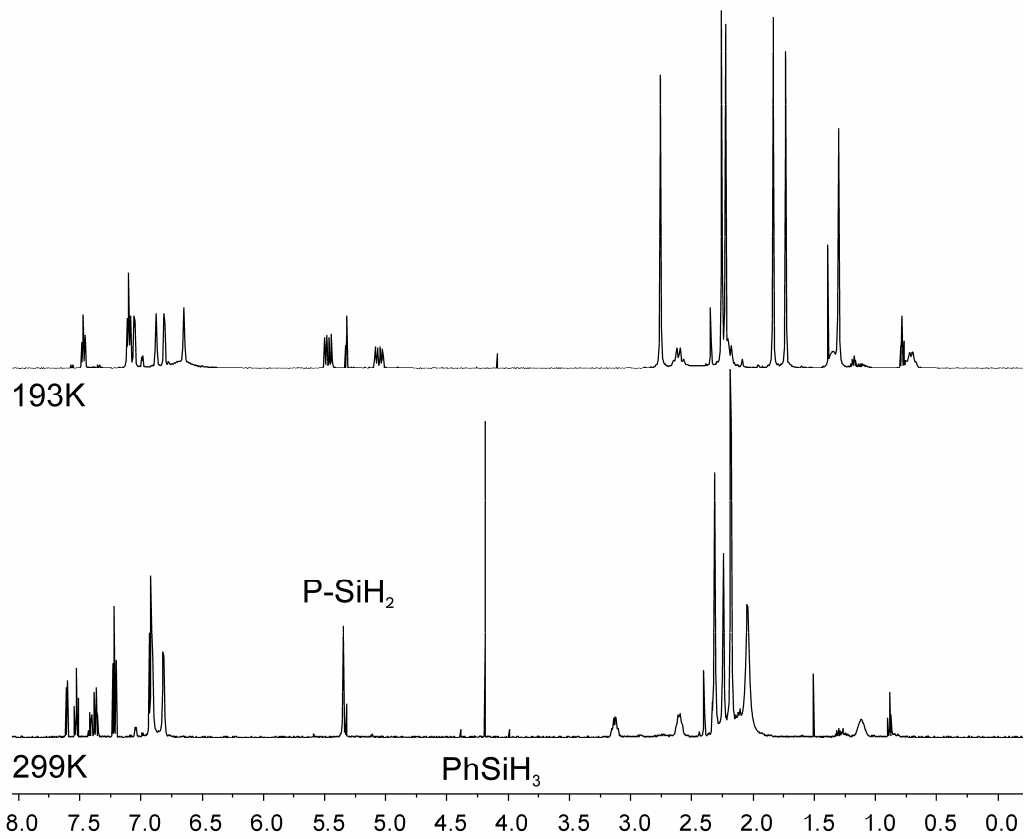
[$\Delta\delta^{19}F_{m,p}$ = 2.7, 2.8]. – $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 193 K): δ = –20 ($\nu_{1/2} \approx$ 360 Hz). – ^{29}Si(dept) NMR (99 MHz, CD_2Cl_2, 193 K): δ = –30.0 (d, $^1J_{PSi}$ = 59.5 Hz).



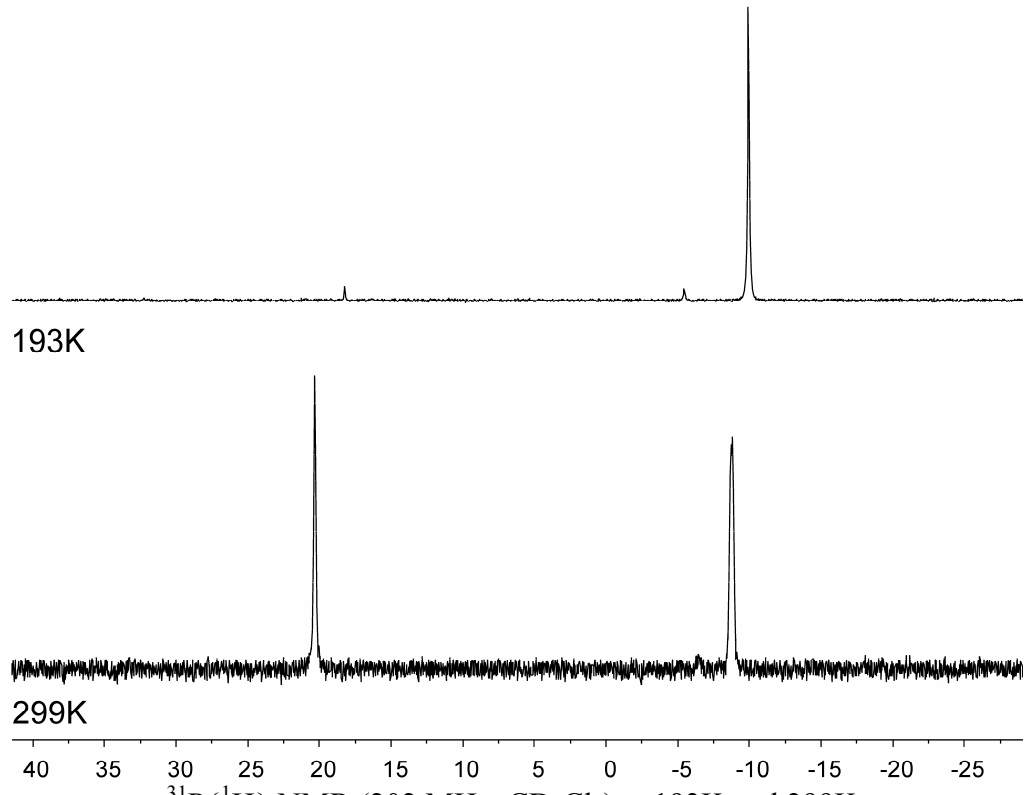
^1H NMR (500 MHz, CD_2Cl_2, 193 K)



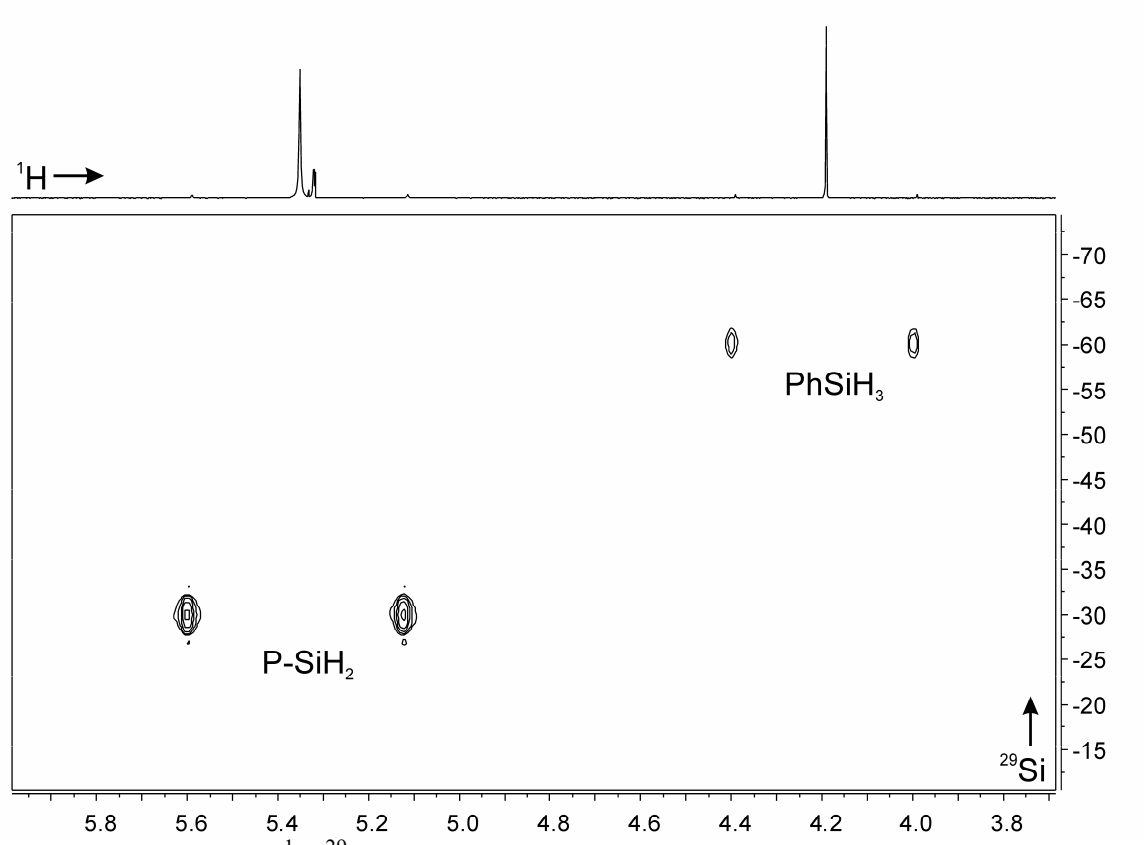
$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 193 K)



^{1}H NMR (500 MHz, CD_2Cl_2) at 193K and 299K [δ = 5.35 (br, $^{1}J_{SiH}$ = 238.0 Hz, 2H, SiH_2), 4.19 (br, $^{1}J_{SiH}$ = 200.1 Hz, 3H, SiH_3)]



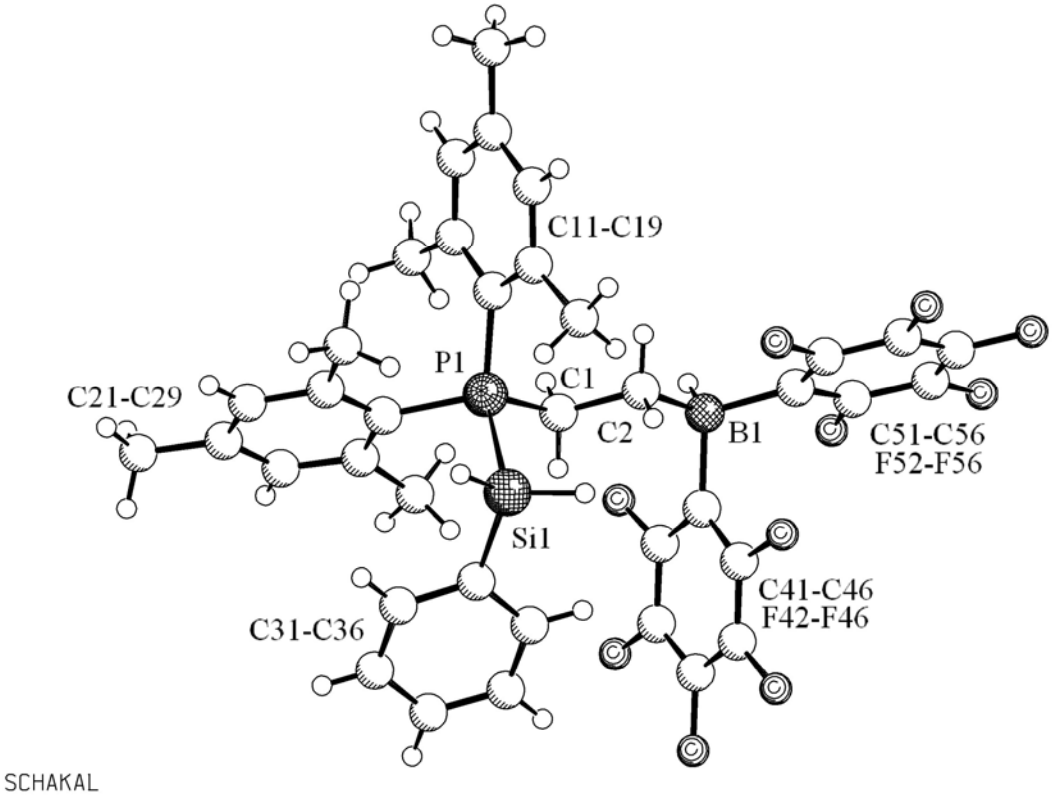
$^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2) at 193K and 299K



^{1}H,^{29}Si ghmqc (500/99 MHz, CD_2Cl_2, 298K)

X-ray crystal structure analysis of ***8a***

Formula $C_{38}H_{34}BF_{10}PSi$, M_r = 750.52, colorless crystal, 0.30 × 0.25 × 0.10 mm^3, triclinic, space group $P\bar{1}$ (no. 2), a = 10.4968(3), b = 13.4561(5), c = 13.6874(5) Å, α = 94.254(2)°, β = 109.081(2)°, γ = 99.584(2)°, V = 1784.33(11) Å^3, Z = 2, D_{calcd} = 1.397 g cm^{-3}, μ = 1.716 mm^{-1}, F(000) = 772 e, empirical absorption correction (0.627 ≤ T ≤ 0.847), λ = 1.54178 Å, T = 223 K, ω and φ scans, 25935 reflections collected (±h, ±k, ±l), [(sinθ)/λ]$_{max}$ = 0.60 Å^{-1}, 6133 independent (R_{int} = 0.043) and 5522 observed reflections [$I \geq 2\ \sigma(I)$], 475 refined parameters, R = 0.037, wR^2 = 0.103, max. (min.) residual electron density 0.31 (–0.21) e Å^{-3}.



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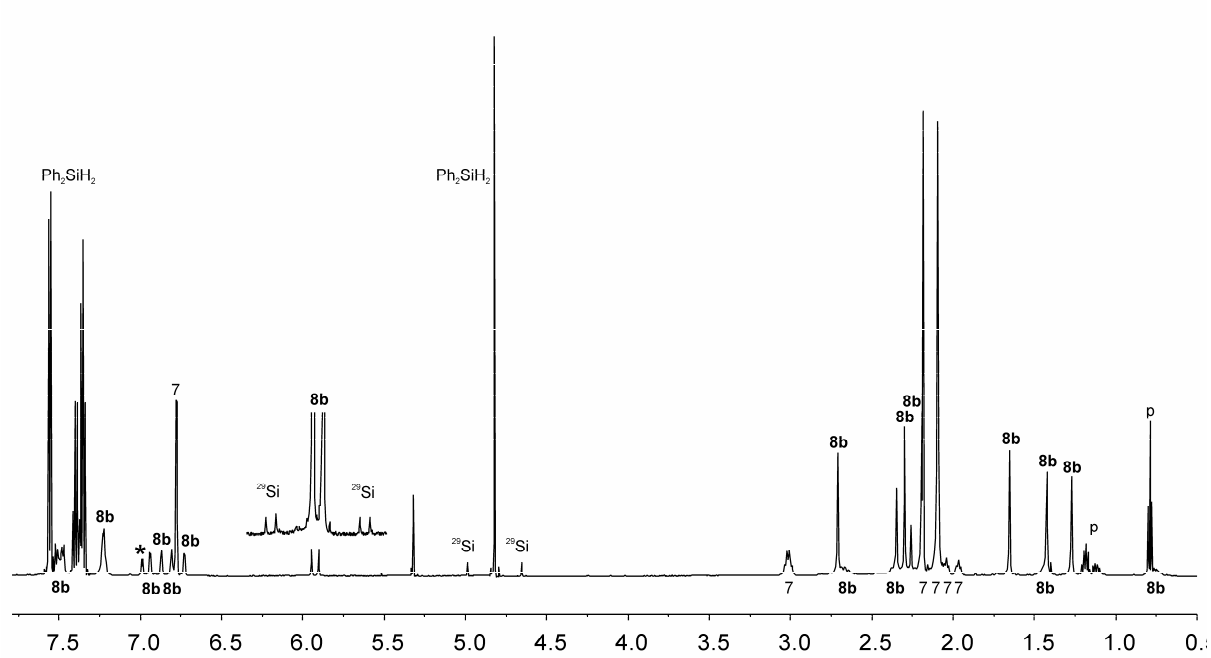
*{2-[Dimesityl(diphenylsilyl)phosphonium]ethyl}bis(pentafluorophenyl)hydridoborate (**8b**)*

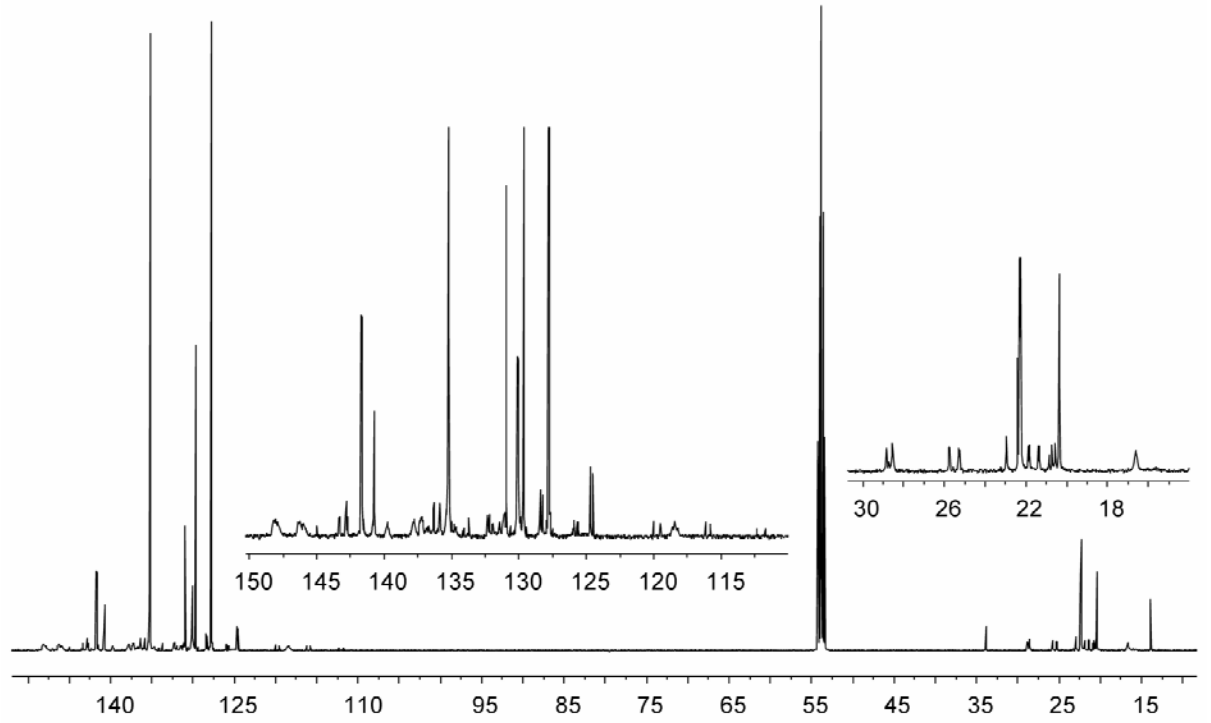
Dimesitylvinylphosphane (**5**) (29.7 mg, 0.10 mmol, 1.00 equiv) and bis(pentafluorophenyl)-borane (**6**) (34.6 mg, 0.10 mmol, 1.00 equiv) were suspended in pentane (4 mL), and the reaction mixture was stirred for 15 min at ambient temperature. To the resulting yellow solution, diphenylsilane (186 µL, 184 mg, 1.00 mmol, 10.0 equiv) was added. Upon cooling to –35 °C, the reaction mixture turned colorless and a white solid precipitated. After an additional 2 h at this temperature, the precipitate was isolated by filtration, washed with cold pentane (3 × 1 mL) and dried briefly in vacuo to yield **8b** as a white powder (69 mg, 83 %). – M. p. 81 °C. – IR (KBr): ν = 3432 (br), 3070 (w), 3049 (w), 3001 (w), 2975 (w), 2925 (m), 2853 (w), 2363 (m), 2345 (m), 2138 (m), 1654 (w), 1637 (m), 1605 (m), 1560 (w), 1541 (w),

1508 (s), 1458 (s), 1430 (m), 1379 (w), 1272 (m), 1180 (m), 1119 (m), 1082 (s), 1027 (w), 972 (s), 855 (m), 842 (m), 824 (m), 769 (w), 736 (m), 700 (m), 642 (w), 608 (w), 555 (w), 492 (w), 444 (w) cm^{-1}. – HRMS ((+)-ESI): *m*/*z* = 865.2254 (calcd. 865.2263 for $C_{44}H_{38}BF_{10}PSiONa$, $[M+ONa]^+$). – $C_{44}H_{38}BF_{10}PSi$ (826.63): calcd. C 63.93, H 4.63; found C 64.42, H 5.13. – ^1H NMR (600 MHz, CD_2Cl_2, 193 K): δ = 7.52 (br, 1H, *p*-Ph^B), 7.51 (br, 1H, *p*-Ph^A), 7.48 (br m, 2H, *o*-Ph^B), 7.37 (br, 2H, *m*-Ph^B)[1], 7.24 (br, 4H, *o*,*m*-Ph^A), 6.94 (dm, $^4J_{PH}$ = 4.0 Hz, 1H, *m*-Mes^A), 6.87 (dm, $^4J_{PH}$ = 2.4 Hz, 1H, *m*-Mes^B), 6.81 (dm, $^4J_{PH}$ = 2.4 Hz, 1H, *m*'-Mes^B), 6.73 (dm, $^4J_{PH}$ = 2.6 Hz, 1H, *m*'-Mes^A), 5.92 (d, $^1J_{SiH}$ = 235.8 Hz, $^2J_{PH}$ = 25.4 Hz, 1H, SiH), 2.71 (s, 3H, *o*-CH_3^{MesA}), 2.66, 2.36 (each m, each 1H, $^PCH_2$)[1,2], 2.30 (s, 3H, *p*-CH_3^{MesB}), 2.19 (s, 3H, *p*-CH_3^{MesA}), 1.65 (s, 3H, *o*'-CH_3^{MesA}), 1.45, 0.75 (each br, each 1H, $^BCH_2$)[2], 1.42 (s, 3H, *o*'-CH_3^{MesB}), 1.27 (s, 3H, *o*-CH_3^{MesB}), n.o. (BH), [[1] from the ghmbc experiment; [2] from the ghsqc experiment]. – $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 193 K): δ = 143.3 (d, $^4J_{PC}$ = 2.9 Hz, *p*-Mes^B), 142.8 (d, $^2J_{PC}$ = 7.3 Hz, *o*'-Mes^B), 142.8 (d, $^4J_{PC}$ = 2.5 Hz, *p*-Mes^A), 141.7 (*o*-Mes^B)[1], 141.6 (d, $^2J_{PC}$ = 11.0 Hz, *o*-Mes^A), 140.8 (d, $^2J_{PC}$ = 6.2 Hz, *o*'-Mes^A), 136.3 (*o*-Ph^B), 135.8 (*o*-Ph^A), 132.3 (*p*-Ph^A), 132.2 (*p*-Ph^B), 132.0 (d, $^3J_{PC}$ = 9.6 Hz, *m*'-Mes^B), 131.5 (d, $^3J_{PC}$ = 9.4 Hz, *m*-Mes^B), 131.1 (*m*'-Mes^A), 129.9 (d, $^3J_{PC}$ = 11.5 Hz, *m*-Mes^A), 128.4 (*m*-Ph^B), 128.2 (*m*-Ph^A), 125.9 (d, $^2J_{PC}$ = 8.2 Hz, *i*-Ph^B), 125.6 (d, $^2J_{PC}$ = 14.3 Hz, *i*-Ph^A), 119.8 (d, $^1J_{PC}$ = 63.8 Hz, *i*-Mes^A), 116.0 (d, $^1J_{PC}$ = 48.2 Hz, *i*-Mes^B), 28.6 ($^1J_{PC}$ = 22.5 Hz, $^PCH_2$)[1,2], 25.6 (d, $^3J_{PC}$ = 5.2 Hz, *o*-CH_3^{MesA}), 25.3 (d, $^3J_{PC}$ = 6.3 Hz, *o*-CH_3^{MesB}), 23.0 (d, $^3J_{PC}$ = 1.4 Hz, *o*'-CH_3^{MesB}), 21.4 (d, $^3J_{PC}$ = 5.4 Hz, *o*'-CH_3^{MesA}), 20.7 (*p*-CH_3^{MesB}), 20.6 (*p*-CH_3^{MesA}), 15.6 (br, $^BCH_2$)[2], [[1] from the ghmbc experiment; [2] from the ghsqc experiment; C_6F_5 not listed]. – $^{31}P\{^1H\}$ NMR (243 MHz, CD_2Cl_2, 193 K): δ = –8.6 ($\nu_{1/2} \approx$ 30 Hz). – ^{19}F NMR (564 MHz, CD_2Cl_2, 193 K): δ = –133.6 (m, 2F, *o*-$C_6F_5^A$), –134.0 (m, 2F, *o*-$C_6F_5^B$), –162.8 (m, 1F, *p*-$C_6F_5^A$), –163.3 (m, 1F, *p*-$C_6F_5^B$), –165.5 (m, 2F, *m*-$C_6F_5^A$), –166.0 (m, 2F, *m*-$C_6F_5^B$),

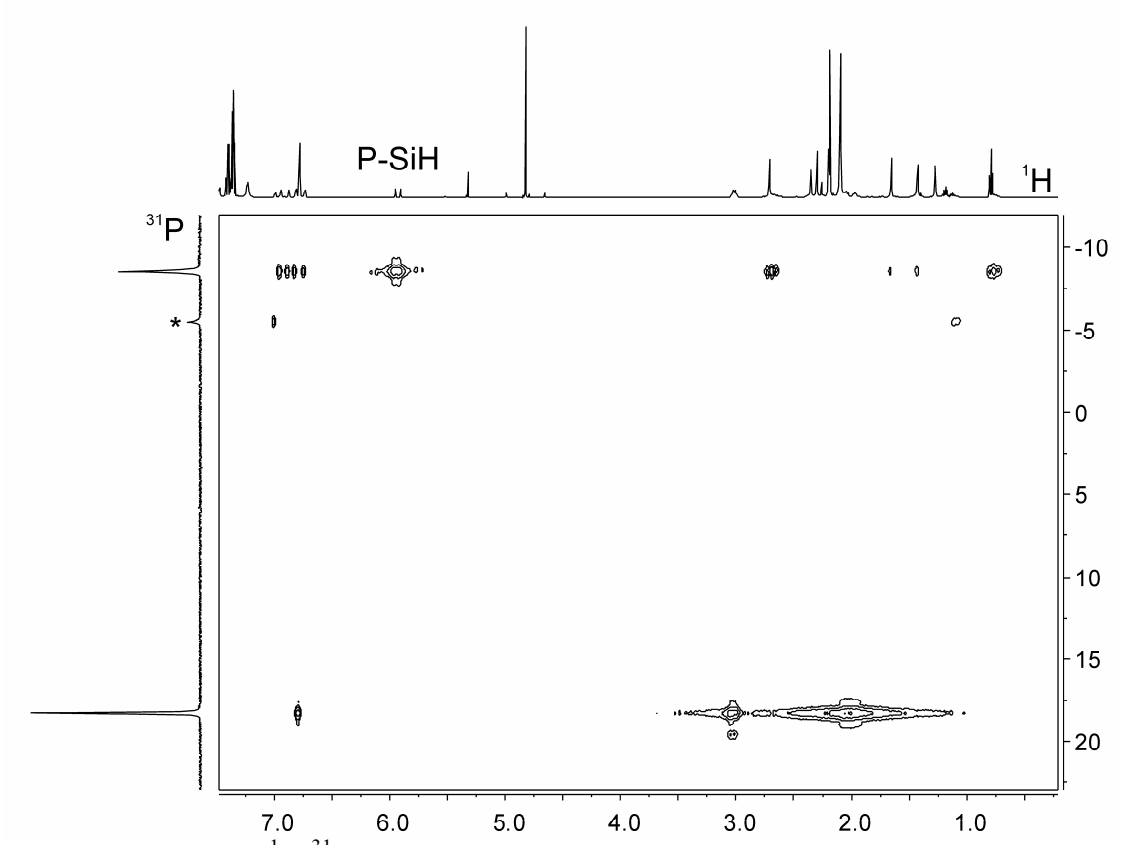
[$\Delta\delta^{19}F_{m,p}$ = 2.7, 2.7]. – $^{11}B\{^1H\}$ NMR (192 MHz, CD_2Cl_2, 193 K): δ = –20 ($\nu_{1/2} \approx$ 350 Hz). – ^{29}Si(dept) NMR (119 MHz, CD_2Cl_2, 193 K): δ = –15.2 (d, $^1J_{PSi}$ = 48.5 Hz).



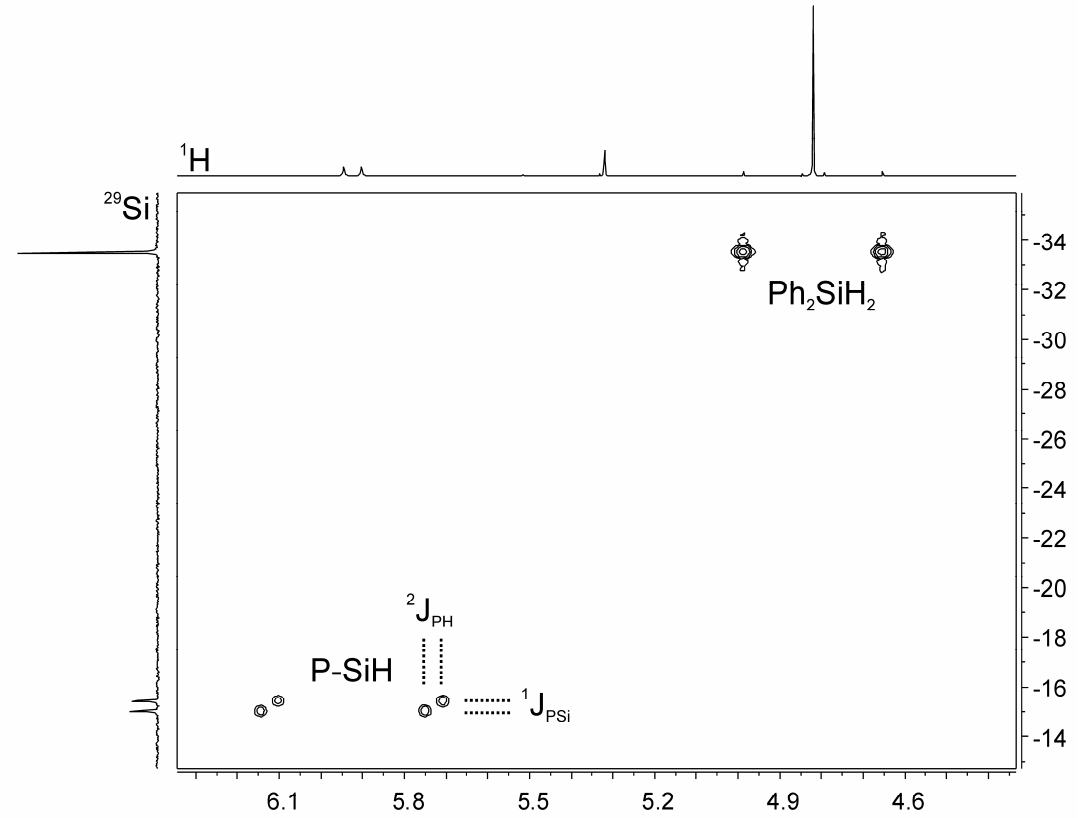
^1H NMR (600 MHz, CD_2Cl_2, 193 K) [* unidentified PH compound, p: pentane]



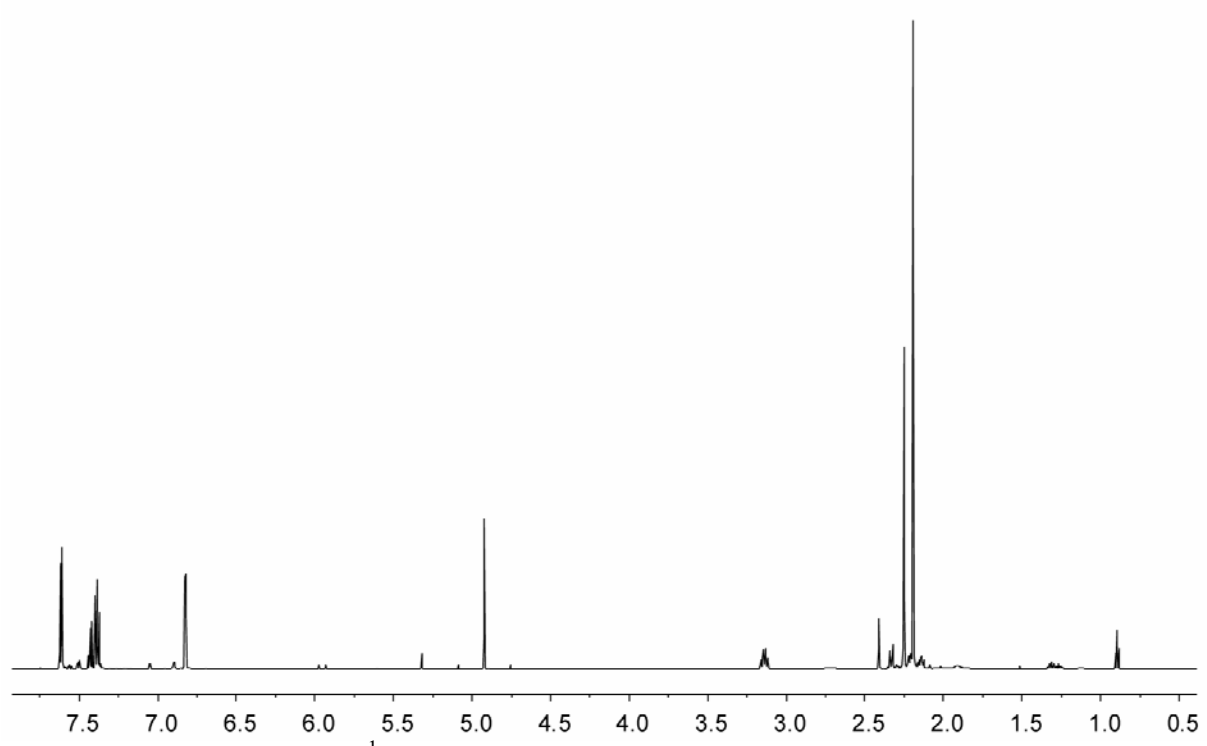
$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 193 K)



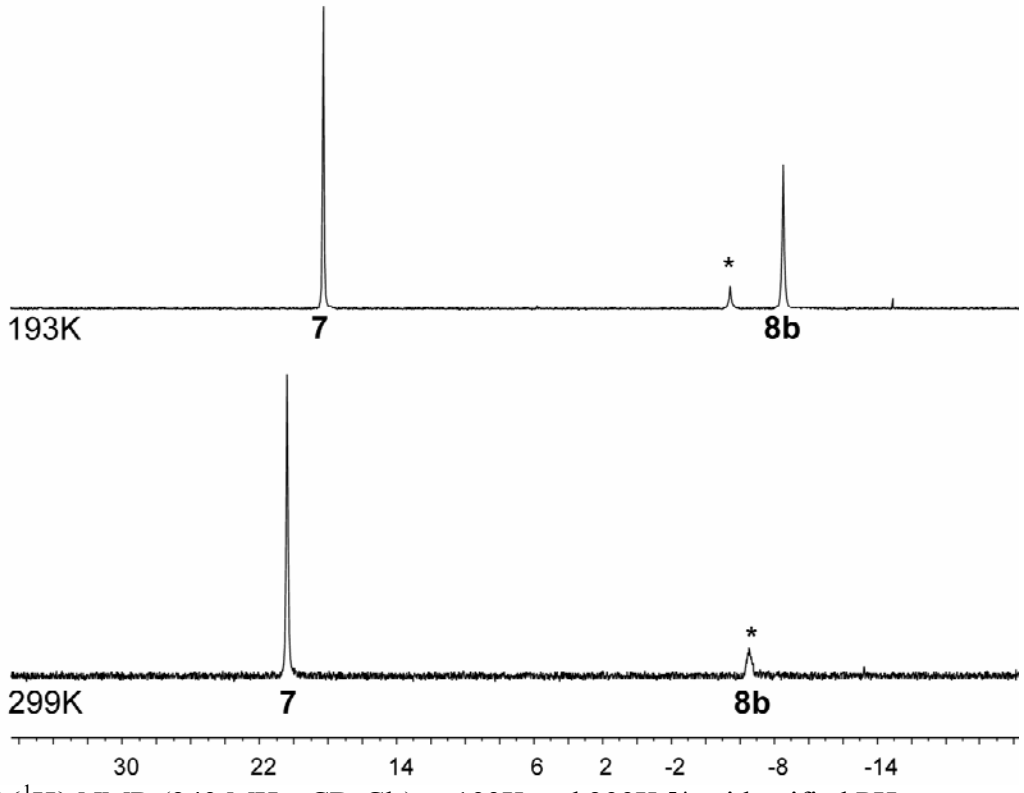
^{1}H,^{31}P ghmqc (600/243 MHz, CD_2Cl_2, 193K)
[projections: ^{31}P{^{1}H} and ^{1}H spectra; * unidentified PH compound]



^{1}H,^{29}Si ghmqc (600/119 MHz, CD_2Cl_2, 193K) [projections: ^{29}Si(dept) and ^{1}H spectra]



^{1}H NMR (600 MHz, CD_2Cl_2, 299 K)



^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2) at 193K and 299K [*unidentified PH compound]