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

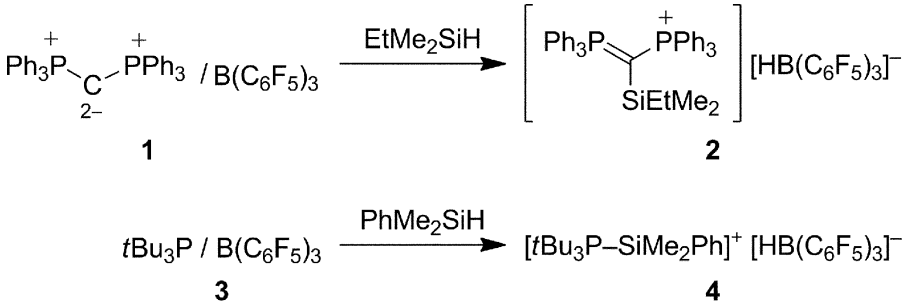
The intramolecular frustrated P/B Lewis pair $Mes_2PCH_2CH_2B(C_6F_5)_2$ (**7**) reacts readily with phenylsilane by heterolytic cleavage of the Si–H bond to give the zwitterion $[Mes_2(PhH_2Si)P^+CH_2CH_2B^-H(C_6F_5)_2]$ (**8a**), which has been fully characterized and its structure confirmed by X-ray crystal structure analysis. Variable-temperature NMR studies revealed that the reaction is reversible. Adduct **8a** is the predominant species (*ca.* 98 %) in CD_2Cl_2 solution at low temperature (193 K), whereas at ambient temperature (299 K) it exists in a *ca.* 7 : 3 equilibrium with unreacted **7** and $PhSiH_3$. Diphenylsilane reacted similarly with the frustrated Lewis pair **7**, however, the equilibrium was found to favor the starting materials in the investigated temperature range.

Key words: Frustrated Lewis Pairs, Silanes, Si–H Bond Activation, Silylphosphonium Ions

Introduction

Hydrosilylation is an important method of reducing organic π-functionalities [1 – 3]. While many transition metal complexes are known to catalyze the Si–H addition to polar as well as nonpolar organic π-substrates, alternative protocols using main-group catalysts are limited [4]. A remarkable exception in this context is the strong Lewis acid tris(pentafluorophenyl)borane, $B(C_6F_5)_3$ [5 – 7] which serves as a potent catalyst [8 – 12], *e. g.*, in the hydrosilylation of ketones and imines [12 – 27]. Piers *et al.* had shown that the role of $B(C_6F_5)_3$ is not to activate the carbonyl function, as one might have thought [28, 29], but that it activates the silane by an abstractive coordination of the hydridic Si–H bond to the Lewis acidic boron atom [30]. Concomitant silyl transfer to the carbonyl group *via* an S_N2-Si mechanism [31] followed by hydride transfer from the borohydride to the activated former carbonyl carbon atom then closes the catalytic cycle to give the respective hydrosilylation product.

Related to the mechanism of the $B(C_6F_5)_3$-mediated Si–H bond activation, frustrated Lewis pairs (FLPs) have been shown to activate dihydrogen heterolytically under mild reaction conditions [32 – 36]. Therefore, it was expected that FLPs would also cleave the Si–H bond of organic hydrosilanes. In a recent example, Alcarazo and co-workers reported the activation of the Si–H bonds in ethyldimethylsilane ($EtMe_2SiH$) and diphenylsilane (Ph_2SiH_2) by the carbon(0)/borane-based FLP hexaphenylcarbodiphosphorane/$B(C_6F_5)_3$ (**1**) (Scheme 1, upper part) [37]. Klankermeyer *et al.* extended the scope by showing that the intermolecular frustrated P/B Lewis pair $tBu_3P/B(C_6F_5)_3$ (**3**) is also capable of cleaving the Si–H bond in dimethylphenylsilane (Me_2PhSiH) under mild conditions [38] (Scheme 1, lower part). The resulting zwit-



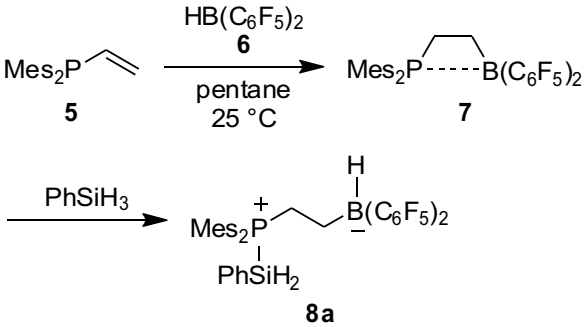
Scheme 1. Heterolytic Si–H bond activation by intermolecular frustrated Lewis pairs.

terion **4** was characterized by X-ray diffraction. These results prompted us to describe the results of our study of the reaction of the intramolecular frustrated P/B Lewis pair **7** with silanes. Herein, we describe the reversible heterolytic Si–H bond cleavage of phenylsilane ($PhSiH_3$) and of diphenylsilane (Ph_2SiH_2) by FLP **7** and report the solid-state structure of the resulting silylphosphonium hydridoborate **8a**.

Results and Discussion

*Synthesis and molecular structure of the silylphosphonium hydridoborate **8a***

To test the potential of the ethylene-bridged frustrated P/B pair **7** [39–41] in the Si–H bond activation of phenylsilane, FLP **7** was generated *in situ* by treatment of dimesitylvinylphosphane (**5**) with Piers' borane $HB(C_6F_5)_2$(**6**) [42, 43] at ambient temperature in pentane (**5** → **7**, Scheme 2). During stirring for 15 min, the hydroboration reaction went to completion, and a yellow solution of FLP **7** was obtained. To this solution a 10 fold excess of phenylsilane was



Scheme 2. Synthesis of intramolecular FLP **7** and heterolytic Si–H bond cleavage of Ph_3SiH (Mes = 2,4,6-trimethylphenyl).

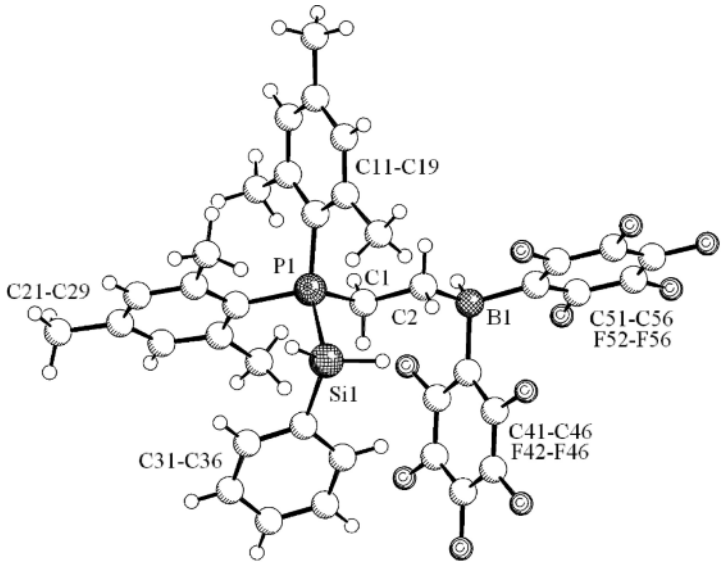


Fig. 1. Molecular structure of the zwitterion **8a**. Selected bond lengths (Å), angles (deg), and dihedral angles (deg): P1–Si1 2.309(1), P1–C1 1.829(2), C1–C2 1.538(2), C2–B1 1.635(2); C1–P1–Si1 103.94(6), C11–P1–Si1 122.76(6), C21–P1–Si1 99.41(5), C41–B1–C51 108.6(1), P1–Si1–C31 102.61(6), C31–Si1–H1 112.2(9), C31–Si1–H2 113.8(8), H1–Si1–H2 113.9(12); P1–C1–C2–B1 176.1(1).

added dropwise, whereupon the reaction mixture immediately turned colorless and a colorless precipitate formed, which was identified as the product of the heterolytic cleavage of $PhSiH_3$ by FLP **7** (**7** → **8a**, Scheme 2). The highly hygroscopic silylphosphonium hydridoborate **8a** [44–63] was isolated as a colorless solid in 81 % yield and characterized by elemental analysis, spectroscopic methods, and X-ray diffraction. Single crystals were obtained from a toluene solution by slow evaporation of the solvent at ambient temperature.

The X-ray crystal structure analysis of zwitterion **8a** (Fig. 1) confirmed that the reaction of FLP **7** with $PhSiH_3$ had resulted in heterolytic splitting of one Si–H bond of the silane with formation of a silylphosphonium cation intramolecularly connected to a hydridoborate anion. The bulky $[Mes_2(PhH_2Si)P]^+$ and $[HB(C_6F_5)_2]^-$ groups are oriented in an antiperiplanar conformation at the bridging $–CH_2–CH_2–$ unit ($\theta_{P1-C1-C2-B1} = 176.1(1)°$).

NMR solution studies

The NMR spectra of compound **8a** in CD_2Cl_2 solution are strongly temperature dependent. At sufficiently low temperature (193 K) we found the rotation around the P–C(mesityl) bonds frozen on the NMR time scale. Consequently, a total of six mesityl CH_3 singlets and four aromatic *m*-mesityl proton resonances are detected in the ^{1}H NMR spectrum of **8a** at 193 K (Fig. 2). The hydrogen atoms of the P-bound SiH_2 unit are diastereotopic under these conditions, resulting in the observed doublet of doublets pattern with ^{29}Si satellites ($^1J_{SiH} \approx 240$ Hz) and $^2J_{PH}$ coupling constants of 20.1 and 22.3 Hz, respectively (Fig. 2). Similarly, the hydrogen atoms at the $–CH_2–CH_2–$ linkage are pairwise diastereotopic as are the C_6F_5 substituents at the boron atom. The ^{11}B NMR spectrum of **8a** shows a signal at $\delta = -20$ ppm, which is in the typical $[HBR(C_6F_5)_2]^-$ borate range, and the ^{31}P NMR spectrum shows a resonance at $\delta = -9.9$ ppm. The ^{29}Si NMR signal occurs at $\delta = -30.0$ ppm, significantly downfield shifted compared to $PhSiH_3$ ($\delta = -60.2$ ppm, C_6D_6, 299 K), with a coupling constant of $^1J_{PSi} = 59.5$ Hz.

Warming the solution of **8a** to ambient temperature allows for free rotation around the P–C(mesityl) bonds. Most significantly, this results in the observation of a singlet with ^{29}Si satellites of the P–SiH_2 unit and a single set of signals of the pair of mesityl groups at the phosphorus atom in the ^{1}H NMR spectrum. Concurrently, only three ^{19}F NMR resonances of the now symmetry-equivalent C_6F_5 groups at the boron atom are observed.

The heterolytic Si–H bond cleavage is reversible, and the equilibrium **7** + $PhSiH_3 \rightleftarrows$ **8a** shifts toward the side of the starting materials with increasing temperature. While we have monitored a *ca.* 98 % composition of addition product **8a** in CD_2Cl_2 solution at 193 K, the ratio of **8a** to unreacted FLP **7** and $PhSiH_3$ changed to approximately 7 : 3 at 299 K (Scheme 3).

We next treated the *in situ* generated FLP **7** with a 10 fold excess of diphenylsilane. In this case, the reaction

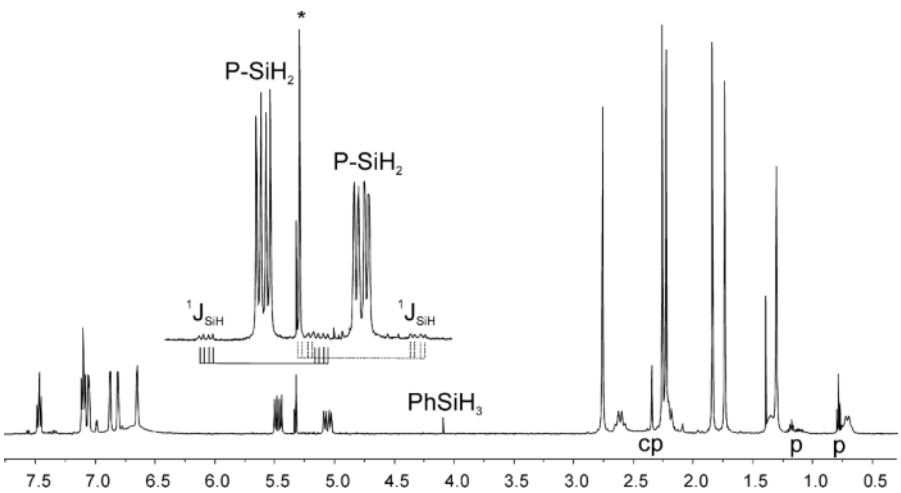
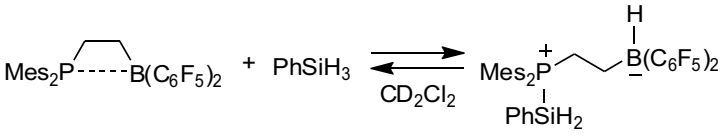
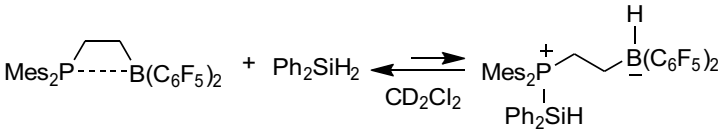


Fig. 2. ^{1}H NMR spectrum (500 MHz) of compound **8a** in CD_2Cl_2 (*) at 193 K (p = pentane, cp = cyclopentane).



193 K	ca. 2	:	98
299 K	ca. 30	:	70

Scheme 3. Temperature-dependent equilibrium between FLP **7**, $PhSiH_3$ and the zwitterionic adduct **8a** in CD_2Cl_2 solution.



193 K	ca. 60	:	40
299 K	ca. 89	:	11

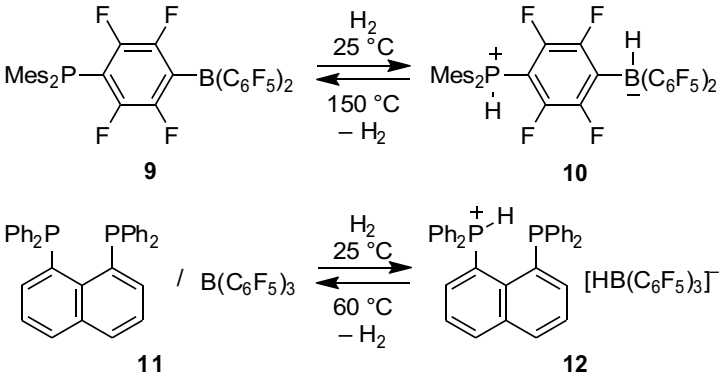
Scheme 4. Temperature-dependent equilibrium between FLP **7**, Ph_2SiH_2 and the zwitterionic adduct **8b** in CD_2Cl_2 solution.

mixture in pentane remained yellow at room temperature, but turned colorless with formation of a colorless precipitate upon cooling to −35 °C. After additional 2 h at this temperature, we isolated silylphosphonium hydridoborate **8b** as an amorphous colorless solid in 83 % yield. The product was characterized by spectroscopy and elemental analysis.

A solution of the salt **8b** in CD_2Cl_2 showed a low-temperature ^{1}H NMR spectrum at 193 K that already contained a 3 : 2 mixture of the starting materials and the zwitterionic product **8b** (Scheme 4). The latter features the typical ^{1}H NMR resonances of the separated mesityl methyl groups and four aromatic *m*-mesityl singlets. Compound **8b** is characterized at 193 K by a ^{31}P NMR signal at $\delta = -8.6$ ppm, a ^{11}B NMR signal at $\delta = -20$ ppm, and a ^{29}Si NMR resonance at $\delta = -15.2$ ppm ($^1J_{PSi} = 48.5$ Hz). Warming the sample to 299 K results in a further shift of the **7** + $Ph_2SiH_2 \rightleftarrows$ **8b** equilibrium toward the starting materials.

Conclusion

Many FLPs activate dihydrogen under mild conditions [64, 65]. However, the heterolytic FLP splitting of dihydrogen is rarely reversible. The systems **9** [66]



Scheme 5. Reversible H_2 activation by FLPs **9** and **11**/$B(C_6F_5)_3$.

and **11** [67] are notable exceptions (Scheme 5), and there are a few other reversible H_2-activating FLP systems known [68–72]. Often silanes are more reactive in hydrosilylation chemistry than dihydrogen is in the related catalytic hydrogenation of polar substrates. Therefore, our disclosure of a particularly mild and reversible Si–H bond cleavage of the silanes $PhSiH_3$ and Ph_2SiH_2 by our reactive intramolecular frustrated P/B Lewis pair $Mes_2PCH_2CH_2B(C_6F_5)_2$ (**7**) is quite remarkable. The reversibility of Si–H bond breaking needs to be taken into account when planning FLP-catalyzed hydrosilylation reactions and can become a favorable feature when FLP-induced transformations of silanes themselves are considered [15, 31, 38]. In this context, fundamental understanding of the Si–H bond activation mode by FLPs will provide an experimental basis for useful developments.

Experimental Section

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 [73]. 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**) [39–41] and Piers' borane $HB(C_6F_5)_2$ (**6**) [42, 43] 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 a Unity Plus 600 MHz spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent signal as the internal standard (CD_2Cl_2: $\delta = 5.32$ ppm for ^{1}H and $\delta = 53.8$ ppm 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 [74]. 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.

*Preparation of **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 colorless 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 colorless powder (61 mg, 81 %). 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). – ^{1}H NMR (500 MHz, CD_2Cl_2, 193 K): $\delta = 7.47$ (m, 1 H, *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{^{1}H} NMR (126 MHz, CD_2Cl_2, 193 K): $\delta = 147.2$ (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{^{1}H} NMR (202 MHz, CD_2Cl_2, 193 K): $\delta = -9.9$ ($\nu_{1/2} \approx 30$ Hz). – ^{19}F NMR (470 MHz, CD_2Cl_2, 193 K): $\delta = -133.5$ (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{^{1}H} NMR (160 MHz, CD_2Cl_2, 193 K): $\delta = -20$ ($\nu_{1/2} \approx 360$ Hz). – ^{29}Si(dept) NMR (99 MHz, CD_2Cl_2, 193 K): $\delta = -30.0$ (d, $^1J_{PSi} = 59.5$ Hz). – IR (KBr): $\nu = 3440$ (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.

*Preparation of **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 colorless 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 colorless powder (69 mg, 83 %); m. p. 81 °C. – ^{1}H NMR (600 MHz, CD_2Cl_2, 193 K): $\delta = 7.52$ (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): $\delta = 143.3$ (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): $\delta = -8.6$ ($\nu_{1/2} \approx 30$ Hz). – ^{19}F NMR (564 MHz, CD_2Cl_2, 193 K): $\delta = -133.6$ (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): $\delta = -20$ ($\nu_{1/2} \approx 350$ Hz). – ^{29}Si(dept) NMR (119 MHz, CD_2Cl_2, 193 K): $\delta = -15.2$ (d, $^1J_{PSi} = 48.5$ Hz). – IR (KBr): $\nu = 3432$ (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.

X-Ray crystal 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 [75], DENZO-SMN for data reduction [76], DENZO for absorption correction [77], SHELXS-97 for structure solution [78, 79], SHELXL-97 for structure refinement [80, 81], and SCHAKAL for graphical visualization [82].

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

Formula $C_{38}H_{34}BF_{10}PSi$, $M_r = 750.52$, colorless crystal, $0.30 \times 0.25 \times 0.10$ mm^3, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.4968(3)$, $b = 13.4561(5)$, $c = 13.6874(5)$ Å, $\alpha = 94.254(2)°$, $\beta = 109.081(2)°$, $\gamma = 99.584(2)°$, $V = 1784.33(11)$ $Å^3$, $Z = 2$, $D_{calcd} = 1.40$ $g\,cm^{-3}$, $\mu = 1.7$ mm^{-1}, $F(000) = 772$ e, empirical absorption correction ($0.627 \leq T \leq 0.847$), $\lambda = 1.54178$ Å, $T = 223$ K, ω and φ scans, 25935 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin\theta)/\lambda]_{max} = 0.60$ $Å^{-1}$, 6133 independent ($R_{int} = 0.043$) and 5522 observed reflections [$I > 2\sigma(I)$], 475 refined parameters, $R = 0.037$, $wR^2 = 0.103$, max. (min.) residual electron density 0.31 (−0.21) e $Å^{-3}$.

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.

Supporting information

Additional experimental and spectroscopic details, in particular pictures of the most prominent NMR spectra, are given as Supporting Information available online (DOI: 10.5560/ZNB.2012-0181).

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