1,1-Carboboration Reactions of Strongly Electrophilic 2-Borylethyl Thioethers

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$ X-Ray crystal structure analyses

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Dedicated to Professor Hubert Schmidbaur on the occasion of this 80th birthday

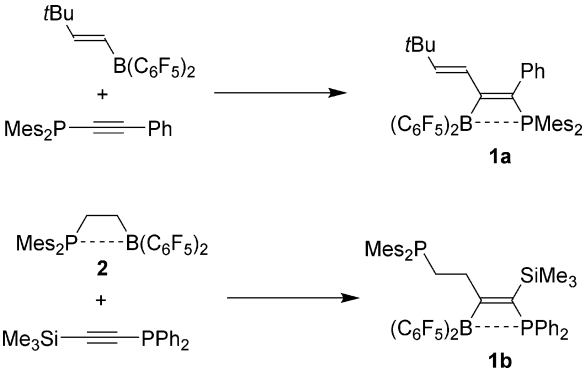
The $RSCH_2CH_2B(C_6F_5)_2$ boranes **3a** (R = Ph) and **3b** (R = Et) were *in situ* generated by $HB(C_6F_5)_2$ hydroboration of the respective vinylthioethers. Their treatment with $R^1–C{\equiv}C–SiMe_3$ acetylenes resulted in clean 1,1-carboboration to give the respective $RSCH_2CH_2$-substituted alkenylboranes **4** (3 examples). Likewise, the reagents **3** underwent 1,1-carboboration with the acetylenes $Ar_2P–C{\equiv}C–SiMe_3$ to give the tetrasubstituted alkenylboranes **6**, featuring a geminal pair of $RSCH_2CH_2/B(C_6F_5)_2$ substituents at one carbon atom and the Me_3Si/PAr_2 pair at the other (3 examples). The compounds **6** feature an internal B···P interaction. The conceptually related $Mes_2PCH_2CH_2B(C_6F_5)_2$ borane (**2**) does not undergo 1,1-carboboration with $ArS–C{\equiv}C–SiMe_3$ but forms the 1,2-P/B-FLP addition product **7** to the acetylene instead. Compounds **4a**, **4c**, **6a**, and **7** were characterized by X-ray diffraction.

Key words: Boron, Sulfur, Alkenylboranes, Frustrated Lewis Pairs (FLPs)

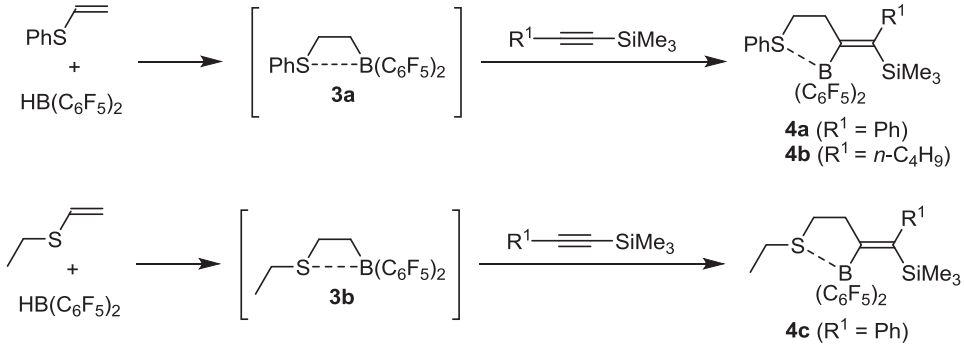
Introduction

The 1,1-carboboration of suitable alkynes is a good method for synthesizing alkenylboranes [1 – 3]. The method is especially well suited for making alkenylboranes with bulky substitution patterns [4]. The early development of this reaction ("Wrackmeyer reaction") relied on metal-containing migrating substituents on the alkyne ($SiMe_3$, SnR_3, PbR_3 and a few others) [5 – 8]; lately the use of very electrophilic boranes containing the $B(C_6F_5)_2$ group greatly widened the scope of the 1,1-carboboration reaction [9, 10], now featuring H [11] and even alkyl or aryl groups as migrating substituents [12]. It had been shown that PAr_2 [13] and even SR groups [14] migrated in these "advanced" 1,1-carboboration reactions, which made it a useful tool for *e. g.* phosphole [15] and even borole synthesis [16].

We had recently shown that the 1,1-carboboration reaction can be used for attaching functional groups at the newly formed alkenylborane. Two typical examples are depicted in Scheme 1, namely the formation of the dienylborane **1a** by the selective transfer of an alkenyl group from boron to the acetylenic carbon [17] and the synthesis of a doubly PAr_2-substituted "frustrated Lewis pair" **1b** by $CH_2–CH_2–PMes_2$ transfer [18]. We have now employed a small series of $RSCH_2CH_2$-substituted boranes as reagents carrying out the 1,1-carboboration reactions of two trimethylsilyl-substituted alkynes.



Scheme 1.



Scheme 2.

This made the respective RS–CH_2CH_2-substituted alkenylboranes readily available. Their preparation and characterization will be described in this article.

Results and Discussion

We had previously described the reaction of phenyl vinylsulfide with Piers' borane [$HB(C_6F_5)_2$]. It gave the *anti*-Markovnikov hydroboration product **3a** of the vinylsulfide functionality. The product **3a** turned out to show an extremely low solubility; it is probably oligomeric, but it was amply identified by the formation of a variety of addition products and derivatives [19]. We have now generated the oligomeric S/B frustrated Lewis pair **3a** *in situ* from PhS-vinyl and $HB(C_6F_5)_2$. After stirring the suspension for 30 min at r. t. in toluene we added phenyl(trimethylsilyl)acetylene and stirred the mixture overnight at 80 °C. Workup gave the product **4a** as a colorless solid in 58 % yield. The product was characterized by C, H elemental analysis, by NMR spectroscopy and X-ray diffraction. This identified it as a 1,1-carboboration product of the borane **3a** with this acetylene. There are two stereoisomers possible, but we have only found one major isomer which was identified as the *E*-**4a** by NMR spectroscopy and X-ray diffraction (see Scheme 2 and Fig. 1).

Compound **4a** shows the typical ^{13}C NMR low-field resonance of an alkenylborane = C2–[B] carbon atom (see Table 1). It features an ^{11}B NMR signal in the range of a tetracoordinated borane. Consistently, we observed a $\Delta\delta^{19}F_{m,p}$ chemical shift difference of the borane-bound C_6F_5 pair of substituents in an intermediate range between typical 3- and 4-coordinate values. Taken together these data point to a weakly coordinated PhS···B structural feature in compound **4a**. This was confirmed by the X-ray crystal structure analysis of compound *E*-**4a** (see Fig. 1 and Table 3). It shows that the borane reagent **3a** has added to the Me_3Si-C≡ carbon atom of the acetylene reagent and induced migration of the $SiMe_3$ group to its adjacent ≡C-Ph acetylenic carbon atom to make room for the PhS–CH_2–CH_2- substituent for its migration from boron to carbon. The formation of the final product **4a** then apparently profits from some internal stabilization by PhS···B coordination.

The *in situ*-formed S/B FLP **3a** was similarly trapped by 1-trimethylsilylhexyne to selectively give the 1,1-carboboration product **4b**. The reaction was carried out directly in [D_8]toluene, and the product was not isolated but characterized from the reaction mixture. The NMR analysis showed that the major isomer was formed that had similar NMR data as compound **4a** (see Table 1).

We have also treated ethyl vinylsulfide with $HB(C_6F_5)_2$. The resulting suspension of the pre-

Table 1. Selected spectroscopic data of compounds **4a–c**.

Compound	**4a**[a]	**4b**[b]	**4c**[a]
R[S]	Ph	Ph	C_2H_5
R^1	Ph	*n*-C_4H_9	Ph
δ^{13}C1	148.1	144.4	146.7
δ^{13}C2	158.4	156.4	158.4
δ^{13}C3	42.3	38.7	38.9
δ^{13}C4	38.2	37.3	34.1
δ^{1}H(3)	3.05	2.94	2.69
δ^{1}H(4)	3.17	2.55	2.75
δ^{11}B	8.4	10.5	1.6
δ^{29}Si	−8.6	−6.8	−8.9
$\Delta\delta^{19}F_{m,p}$	8.1	8.4	8.2/7.3

[a] In CD_2Cl_2, 299 K; [b] in C_7D_8, 299 K.

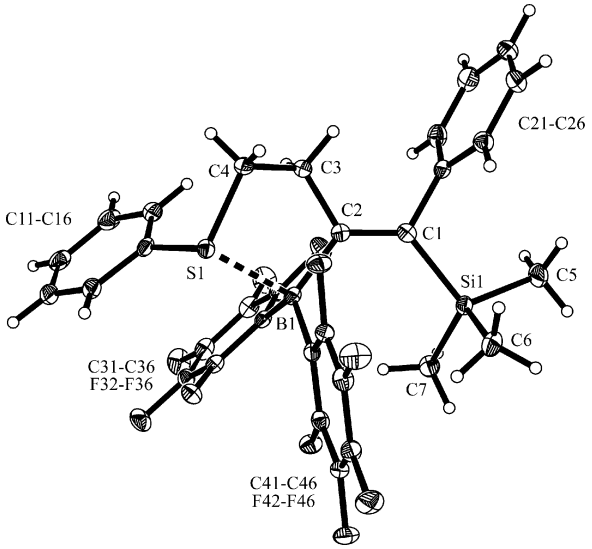


Fig. 1. A view of the molecular structure of the 1,1-carboboration product **4a** (displacement ellipsoids are shown at the 50% probability level; H atoms as spheres with arbitrary radii).

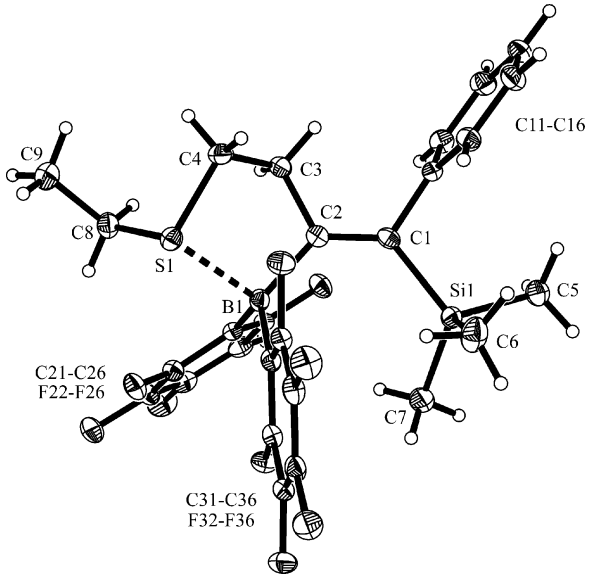
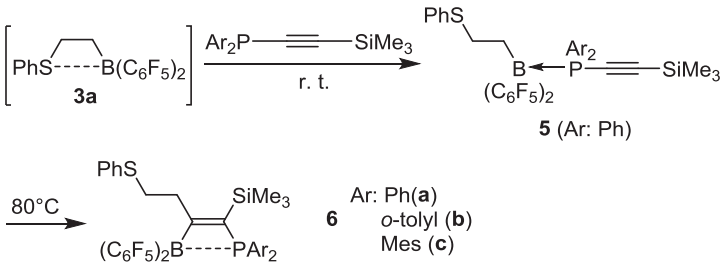


Fig. 2. A view of the molecular structure of the 1,1-carboboration product **4c** (displacement ellipsoids are shown at the 50% probability level; H atoms as spheres with arbitrary radii).

sumably oligomeric hydroboration product (**3b**, see Scheme 2) was subsequently treated with phenyl(trimethylsilyl)acetylene (80 °C, overnight, toluene) to give the 1,1-carboboration product **4c** as a colorless solid, isolated in 66% yield (characterized by C, H elemental analysis, by NMR spectroscopy, and by X-ray diffraction). It shows the typical spectroscopic and structural features of the C_3-bridged internally S···B-coordinated S/B FLP product (see Tables 1 and 3 and Fig. 2).

We then treated the *in situ*-generated system **3a** with a small series of diarylphosphino-(trimethylsilyl)acetylenes [aryl = phenyl (**a**), *o*-tolyl (**b**), mesityl (**c**)]. The reaction of **3a** with Ph_2P–C≡C–$SiMe_3$ at r. t. (10 min) in CD_2Cl_2 gave the P/B adduct **5** (Scheme 3). It was characterized *in situ* by NMR (^{11}B: $\delta = -8.7$; ^{31}P: $\delta = -1.1$; ^{29}Si: δ −14.0; $\Delta\delta^{19}F_{m,p} = 6.0$ ppm; for further details including the depicted NMR spectra see the Supporting Information available online; see note at the end of the paper for availability). We then generated compound **3a** *in situ* in toluene (r. t., 60 min) and treated the resulting suspension with Ph_2P–C≡C–$SiMe_3$ (80 °C overnight). Workup eventually gave the product **6a** as a colorless powder in 36% yield (Scheme 3). Single crystals of compound **6a** suitable for its characterization by X-ray diffraction were obtained by slow crystallization from pentane at −32 °C. The X-ray crystal structure analysis has confirmed that the product **6a** had been formed by a selective 1,1-carboboration reaction (see Fig. 3).



Scheme 3.

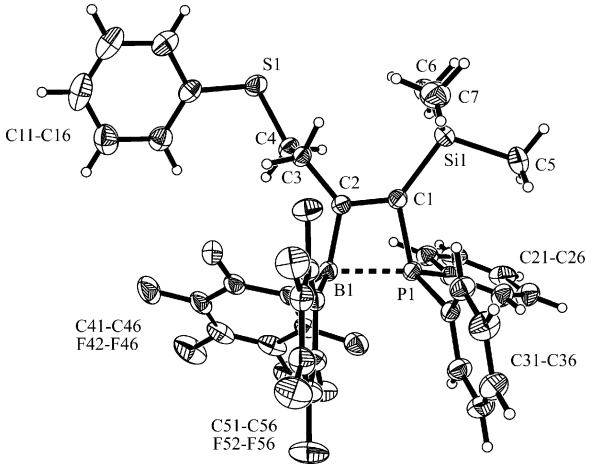


Fig. 3. A view of the molecular structure of the 1,1-carboboration product **6a** (displacement ellipsoids are shown at the 30 % probability level; H atoms as spheres with arbitrary radii).

It shows that both the $B(C_6F_5)_2$ group and its former $PhSCH_2$–CH_2 substituent are now formally attached at the former acetylenic carbon atom C2. We assume that it was the $SiMe_3$ group that had consequently migrated along the acetylenic core C_2 framework to become attached at C1, geminally oriented to the PPh_2 substituent. The tetracoordinated C=C double bond of the product **6a** is found *E*-configurated. It features a marked B···P interaction (see Fig. 3).

The NMR features indicate an analogous structure of compound **6a** in solution (CD_2Cl_2, 299 K, see Table 2). It features typical heteroatom NMR data of an internal B–P-coordinated system. The ^{11}B NMR chemical shift and the $\Delta\delta^{19}F_{m,p}$ NMR chemical shift difference at the C_6F_5 substituents indicate a stronger internal Lewis acid and Lewis base interaction in the P/B compound **6a** than it was observed for the related S/B systems **4** (see above).

We also prepared the closely related P/B products **6b** [P(*o*-tolyl)$_2$] and **6c** ($PMes_2$) by the 1,1-carboboration reactions of the *in situ*-generated S/B system **3a** with (*o*-tolyl)$_2$P–C≡C–$SiMe_3$ or Mes_2P–C≡C–$SiMe_3$ and isolated the products in 48 % (**6b**) and 34 % (**6c**) yield. Both compounds showed similar NMR spectra to those of **6a** (see Table 2) indicating similar structures with internal P···B coordination (for details see Table 2 and the Supporting Information).

Eventually we treated the P/B FLP **2** (see Scheme 1) with the acetylene (*p*-tolyl)S–C≡C–$SiMe_3$ to learn whether the carboboration of the acetylene by the P/B system **2** can be achieved. The reaction was performed in pentane (r. t., 18 h) to eventually give the product **7** which we isolated in 47 % yield as a colorless powder. Compound **7** was characterized by C, H elemental analysis, by X-ray diffraction and by NMR spectroscopy. The X-ray crystal structure analysis (single crystals were obtained by slow evaporation of a pentane solution at −32 °C) revealed that the product in this case was not formed by 1,1-carboboration, but the alkyne had added to the pair of heteroatoms of the P/B FLP **2** to form the respective six-membered heterocycle (see Scheme 4 and Fig. 4). This is a typical FLP addition product [20].

The X-ray crystal structure analysis characterized compound **7** as a zwitterionic phosphonium cation type with an internal borate anion formed by regioselective

Table 2. Selected spectroscopic data of compounds **6a**–**c**[a].

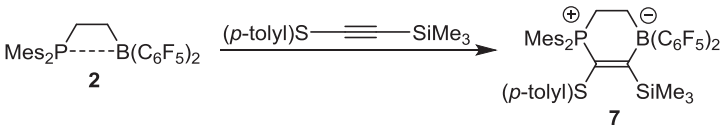
Compound	**6a**[b]	**6b**[b]	**6c**[b]
PAr_2	PPh_2	P(*o*-tol)$_2$	$PMes_2$
δ^{13}C1	139.1	140.0	144.8
$^1J_{PC}$	27.2	27.1	24.2
δ^{13}C2	205.6	202.1	196.5
C3	40.2	40.9	40.4
$^3J_{PC}$	50.0	52.3	51.8
δ^{13}C4	32.8	33.0	32.6
δ^1H(3)	3.12	3.04	2.99
δ^1H(4)	2.88	2.91	2.83
δ^{11}B	−6.7	−2.7	0.5
δ^{29}Si	−10.8	−10.9	−10.0
$^2J_{PSi}$	6.9	6.0	7.4
$\Delta\delta^{19}F_{m,p}$	6.5	6.4	5.8

[a] Chemical shifts as δ values in ppm, J in Hz; [b] in CD_2Cl_2, 299 K.

Table 3. Selected structural data of compounds **4a**, **4c**, and **6a**[a].

Compound	**4a**	**4c**	**6a**
R[S]	Ph	C_2H_5	Ph
R^1	Ph	Ph	PPh_2
C1–C2	1.353(2)	1.346(3)	1.359(3)
C2–C3	1.523(2)	1.522(3)	1.510(3)
C3–C4	1.526(2)	1.522(3)	1.533(3)
B1–S1	2.169(2)	2.112(2)	–
B1–P1	–	–	2.030(3)
$\Sigma\angle C1^{R1SiC}$	359.7	360.0	359.5
$\Sigma\angle C2^{CCB}$	360.0	359.9	360.0
$\Sigma\angle B1^{CCC}$	351.4	348.3	346.7
R1–C1–C2–B1	178.6(1)	−175.7(2)	10.0(2)
C2–C3–C4–S1	−37.4(1)	−46.5(2)	−167.1(2)

[a] Bond lengths in Å and angles in deg.



Scheme 4.

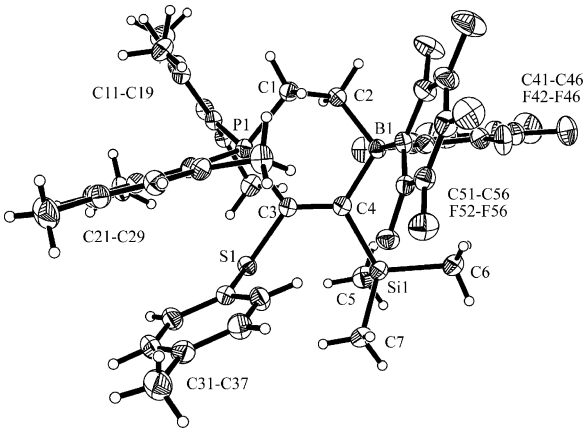


Fig. 4. Molecular structure of compound **7** (displacement ellipsoids are shown at the 30 % probability level; H atoms as spheres with arbitrary radii). Selected bond lengths (Å) and angles (deg): P1–C1 1.815(2), C1–C2 1.532(4), C2–B1 1.646(4), B1–C4 1.667(4), C4–C3 1.351(3), C3–P1 1.822(2); C2–B1–C4 109.3(2), C41–B1–C51 111.0(2), C1–P1–C3 106.3(1), C11–P1–C21 109.2(1), C3–S1–C31 106.0(1), P1–C1–C2–B1 −71.1(2), P1–C3–C4–B1 1.7(3), C3–P1–C1–C2 42.5(2).

alkyne addition to the P/B FLP **2**. The phosphonium moiety shows a distorted tetrahedral coordination geometry at phosphorus. Hindered rotation of the mesityl and C_6F_5 substituents gave rise to the ^{1}H NMR observation of two pairs of diastereotopic methylene hydrogen atoms of the bridging [P]–CH_2–CH_2–[B] ethylene moiety (for details see the Supporting Information). Compound **7** shows a typical borate ^{11}B NMR signal at $\delta = -12.4$ ppm and a typical phosphonium ^{31}P NMR signal at $\delta = 5.1$ ppm.

Conclusion

The scope of the 1,1-carboboration reaction seems to be steadily increasing. With this study we have shown that we can use *in situ*-generated R^2-$B(C_6F_5)_2$ FLPs with thioether-containing substituents [$R^2 = PhSCH_2CH_2$ or $EtSCH_2CH_2$] as reagents undergoing the 1,1-carboboration reaction with a small series of trimethylsilyl-substituted alkynes to give the respective tetrasubstituted alkenylboranes **4** and **6**. In these cases it is the RS–CH_2CH_2- substituent at the boron atom that selectively migrates from boron to carbon during the multi-rearrangement process. Quite surprisingly, only single geometric isomers of the compounds **4** were obtained, a reaction behavior that was markedly different from many of our earlier reported examples that were stereo-unselective [11]. At this time we do not have an ample explanation for this behavior. In the phosphorus-containing examples **6** it is probably the formation of the marked B–P interaction in the product that determines the selective formation of the *E*-alkenyl boranes. It seems that the formation of the addition product **7** marks a limiting situation where FLP addition to the alkyne has become favored over 1,1-carboboration.

Our examples of the selective formation of the RS–CH_2CH_2-substituted alkenylboranes by 1,1-carboboration extends the scope of this method. It had been shown that related alkenylboranes obtained by the "advanced" $B(C_6F_5)_2$-containing variation can undergo cross-coupling reactions to form the respective boron-free organic follow-up products easily. Other highly substituted alkenylboranes obtained by this method had been used as selective Lewis acid compounds in catalytic metal-free FLP hydrogenation reactions of electron-poor alkenes and alkynes.

Experimental Section

All syntheses involving air- and moisture-sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of argon.

The phosphanes were synthesized according to a modified literature procedure [21]. Bis(pentafluorophenyl)borane was synthesized according to a modified literature procedure [22, 23]. Phenylvinylsulfide and ethylvinylsulfide were purchased from Sigma Aldrich and TCI.

*Preparation of compound **4a***

Bis(pentafluorophenyl)borane (56.1 mg, 0.162 mmol, 1.0 eq.) in toluene (5 mL) was added to a solution of

phenylvinylsulfide (22.1 mg, 0.162 mmol, 1.0 eq.) in toluene (5 mL) to give a colorless suspension, which was stirred for 30 min at room temperature. Thereafter trimethylsilylphenylacetylene (28.3 mg, 31.8 μL, 0.162 mmol, 1.0 eq.) was added, and the light-yellow reaction mixture was stirred at 80 °C for overnight. Subsequently all volatiles were removed *in vacuo,* and pentane (5 mL) was added to the yellow residue. Then, immediately after the addition of pentane (5 mL), all volatiles were removed *in vacuo,* and pentane (5 mL) was added again to finally give a colorless precipitate. The supernatant solution of the suspension was removed, and the colorless solid was dried *in vacuo* to give compound **4a** (61.4 mg, 0.094 mmol, 58 %) as a colorless powder. Crystals suitable for the X-ray crystal structure analysis were obtained by slow evaporation of a dichloromethane solution of compound **4a** at −32 °C. – $C_{31}H_{23}BF_{10}SSi$: calcd. C 56.72 H 3.53; found C 56.33 H 3.33. – ^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): $\delta = 7.35$ (m, 1H, *p*-Ph^S), 7.31 (m, 2H, *m*-Ph), 7.23 (m, 2H, *m*-Ph^S), 7.17 (m, 1H, *p*-Ph), 7.11 (m, 2H, *o*-Ph^S), 6.96 (m, 2H, *o*-Ph), 3.17 (m, 2H, SCH_2), 3.05 (m, 2H, CH_2), −0.42 ppm (s, $^2J_{SiH} = 6.6$ Hz, 9H, $SiCH_3$). – ^{13}C{^{1}H} NMR (125 MHz, 299 K, CD_2Cl_2): $\delta = 158.4$ (br, BC=), 149.4 (*i*-Ph), 148.9 (dm, $^1J_{FC} \sim 240$ Hz, C_6F_5), 148.1 (br, =CSi), 141.0 (dm, $^1J_{FC} \sim 250$ Hz, C_6F_5), 137.5 (dm, $^1J_{FC} \sim 250$ Hz, C_6F_5), 130.7 (*p*-Ph^S), 130.5 (*i*-Ph^S), 130.0 (*o*-Ph^S), 129.5 (*m*-Ph^S), 128.4 (*m*-Ph), 127.3 (*o*-Ph), 125.2 (*p*-Ph), 116.9 (br, *i*-C_6F_5), 42.3 (CH_2), 38.2 (SCH_2), 0.2 ppm ($^1J_{SiC} = 52.3$ Hz, $SiCH_3$). – ^{11}B{^{1}H} NMR (160 MHz, 299 K, CD_2Cl_2): $\delta = 8.4$ ppm ($\nu_{1/2} \sim 400$ Hz). – ^{19}F NMR (470 MHz, 299 K, CD_2Cl_2): $\delta = -127.2$ (br, 2F, *o*-C_6F_5), −156.4 (tm, $^3J_{FF} = 20.5$ Hz, 1F, *p*-C_6F_5), −164.5 ppm (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p} = 8.1$]. – ^{29}Si{^{1}H} DEPT (99 MHz, 299 K, CD_2Cl_2): $\delta = -8.6$ ppm ($\nu_{1/2} \sim 2$ Hz).

*Preparation of compound **4c***

Bis(pentafluorophenyl)borane (80.0 mg, 0.231 mmol, 1.0 eq.) was dissolved in toluene (2 mL) and added to a solution of ethylvinylsulfide (20.4 mg, 0.231 mmol, 1.0 eq.) in toluene (10 mL). After the resulting suspension was stirred for 30 min trimethylsilylphenylacetylene (40.3 mg, 0.231 mmol, 1.0 eq.) was added. The brownish reaction mixture was stirred at 80 °C for overnight. Then all volatiles were removed *in vacuo,* and the obtained residue was extracted with pentane (5 mL) to give a colorless precipitate. The supernatant solution of the suspension was removed, and the residue was dried *in vacuo* to give the compound **4c** as a colorless powder (66.2 mg). The supernatant solution was stored at −32 °C for 3 d to give a colorless solid (27.0 mg). The two solid fractions were combined to give compound **4c** (93.2 mg, 0.153 mmol, 66 %) as a colorless powder. Crystals suitable for the X-ray crystal structure analysis were obtained by slow evaporation of a dichloromethane solution of compound **4c** at −32 °C. – $C_{27}H_{23}BF_{10}SSi$: calcd. C 53.30 H 3.81; found C 53.10 H 3.51. – ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): $\delta = 7.29$ (m, 2H, *m*-Ph), 7.15 (m, 1H, *p*-Ph), 6.92 (m, 2H, *o*-Ph), 2.75 (br, 2H, SCH_2), 2.69 (m, 2H, CH_2), 2.18 (q, $^3J_{HH} = 7.4$ Hz, 2H, CH_2^{Et}), 1.25 (t, $^3J_{HH} = 7.4$ Hz, 3H, CH_3^{Et}), −0.44 ppm (s, $^2J_{SiH} = 6.6$ Hz, 9H, $SiCH_3$). – ^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): $\delta = 158.4$ (br, BC=), 149.3 (*i*-Ph), 149.1 (dm, $^1J_{FC} \sim 240$ Hz, C_6F_5), 146.7 (=CSi), 140.9 (dm, $^1J_{FC} \sim 250$ Hz, C_6F_5), 137.7 (dm, $^1J_{FC} \sim 250$ Hz, C_6F_5), 128.3 (*m*-Ph), 127.4 (br, *o*-Ph), 125.1 (*p*-Ph), 116.7 (br, *i*-C_6F_5), 38.9 (CH_2), 34.1 (SCH_2), 30.2 (CH_2^{Et}), 12.8 (CH_3^{Et}), 0.2 ppm ($^1J_{SiC} = 52.3$ Hz, $SiCH_3$). – ^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): $\delta = 1.6$ ppm ($\nu_{1/2} \sim 350$ Hz). – ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): $\delta = -126.3$, −127.9, −129.5 (each br, Σ4F, *o*-C_6F_5), −156.0, −156.9 (each br, each 1F, *p*-C_6F_5), −164.2 ppm (br, 4F, *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p} = 8.2/7.3$]. – ^{29}Si{^{1}H} DEPT (119 MHz, 299 K, CD_2Cl_2): $\delta = -8.9$ ppm ($\nu_{1/2} \sim 1$ Hz)

*Preparation of compound **6a***

Bis(pentafluorophenyl)borane (56.1 mg, 0.162 mmol, 1.0 eq.) in toluene (2 mL) was added to a solution of phenylvinylsulfide (22.1 mg, 0.162 mmol, 1.0 eq.) in toluene (10 mL) to give a suspension which was stirred for 1 h at room temperature. Thereafter diphenylphosphino(trimethylsilyl)acetylene (45.7 mg, 0.162 mmol, 1.0 eq.) was added. The brownish/yellow reaction mixture was stirred at 80 °C for overnight. After cooling to room temperature all volatiles were removed *in vacuo,* and the obtained residue was dissolved in pentane (3 mL). Then all volatiles were removed *in vacuo*, and the resulting residue was dissolved in hexane (3 mL). The hexane solution was stored at −32 °C and after 4 days a colorless precipitate was formed. The precipitate was collected and dried *in vacuo* to give compound **6a** (44.0 mg, 0.058 mmol, 36 %) as a colorless powder. Crystals suitable for the X-ray crystal structure analysis were obtained by slow evaporation of a pentane solution of compound **6a** at −32 °C. – $C_{37}H_{28}BF_{10}PSSi$: calcd. C 58.18 H 3.69; found C 58.67 H 3.46. – ^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): $\delta = 7.50$ (m, 2H, *p*-Ph^P), 7.38 (m, 4H, *m*-Ph^P), 7.31 (m, 4H, *o*-Ph^P), 7.27 (m, 2H, *m*-Ph^S), 7.24 (m, 2H, *o*-Ph^S), 7.19 (m, 1H, *p*-Ph^S), 3.12 (m, 2H, CH_2), 2.88 (m, 2H, SCH_2), 0.10 ppm (s, $^2J_{SiH} = 6.7$ Hz, 9H, $SiCH_3$). – ^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2): $\delta = 205.6$ (br, BC=), 147.9 (dm, $^1J_{FC} = \sim 240$ Hz, C_6F_5), 140.0 (dm, $^1J_{FC} = \sim 250$ Hz, C_6F_5), 139.1 (d, $^1J_{PC} = 27.2$ Hz, =CP), 137.3 (dm, $^1J_{FC} = \sim 250$ Hz, C_6F_5), 136.2 (*i*-Ph^S), 132.3 (d, $^2J_{PC} = 9.1$ Hz, *o*-Ph^P), 131.8 (d, $^4J_{PC} = 2.7$ Hz, *p*-Ph^P), 130.1 (*o*-Ph^S), 129.2 (*m*-Ph^S), 129.1 (d, $^3J_{PC} = 10.3$ Hz, *m*-Ph^P), 126.9 (d, $^1J_{PC} = 39.3$ Hz, *i*-Ph^P), 126.7 (*p*-Ph^S), 116.9

(br, *i*-C_6F_5), 40.2 (br d, $^3J_{PC} = 50.0$ Hz, CH_2), 32.8 (SCH_2), 0.1 ppm (d, $^1J_{SiC} = 53.3$ Hz, $^3J_{PC} = 2.2$ Hz, $SiCH_3$). – $^{11}B\{^1H\}$ NMR (160 MHz, 299 K, CD_2Cl_2): $\delta = -6.7$ ppm ($\nu_{1/2} \sim 200$ Hz). – ^{19}F NMR (470 MHz, 299 K, CD_2Cl_2): $\delta = -130.1$ (m, 2F, *o*-C_6F_5), −158.4 (t, $^3J_{FF} = 20.2$ Hz, 1F, *p*-C_6F_5), − 164.9 ppm (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p} = 6.5$]. – $^{29}Si\{^1H\}$ DEPT (99 MHz, 299 K, CD_2Cl_2):$\delta = -10.8$ ppm (d, $^2J_{PSi} = 6.9$ Hz). – $^{31}P\{^1H\}$ NMR (202 MHz, 299 K CD_2Cl_2): $\delta = 14.3$ ppm ($\nu_{1/2} \sim 100$ Hz).

Preparation of compound **7**

Dimesitylvinylphosphane (48.0 mg, 0.162 mmol, 1.0 eq.) and bis(pentafluorophenyl)borane (56.1 mg, 0.162 mmol, 1.0 eq.) were dissolved in pentane (4 mL) and stirred 30 min at room temperature. Then *p*-tolyl[(trimethylsilyl)ethynyl]sulfide (35.7 mg, 0.162 mmol, 1.0 eq.) was added. Immediately the reaction mixture turned yellow, and a colorless solid precipitated. Stirring of the suspension was continued for overnight. Subsequently the supernatant solution was removed, and the resulting residue was washed with pentane (5 mL). The obtained colorless solid was dried *in vacuo* to give compound **7** (65.5 mg, 0.076 mmol, 47 %) as a colorless powder. Crystals suitable for the X-ray crystal structure analysis were obtained from a pentane solution of compound **7** at −32 °C. – $C_{44}H_{42}BF_{10}PSSi$: calcd. C 61.26 H 4.91; found C 59.45 H 4.45. – ^1H NMR (500 MHz, 299 K, C_6D_6): $\delta = 6.82$ (m, 2H, *o*-Tol), 6.65 (d, $^4J_{PH} = 2.3$ Hz, 1H, *m*-Mes^a), 6.43 (m, 2H, *m*-Tol), 6.38 (d, $^4J_{PH} = 2.9$ Hz, 1H, *m*'-Mes^a), 6.08 (s, 1H, *m*-Mes^b), 5.87 (d, $^4J_{PH} = 3.2$ Hz, 1H, *m*'-Mes^b), 2.99 (s, 3H, *o*-$CH_3^{Mes,a}$), 2.89, 2.15 (each m, each 1H, PCH_2), 1.90 (s, 3H, *p*-$CH_3^{Mes,a}$), 1.89 (s, 3H, *p*-CH_3^{Tol}), 1.86 (s, 3H, *o*-$CH_3^{Mes,b}$), 1.85 (s, 3H, *o*'-$CH_3^{Mes,b}$), 1.76, 1.57 (each m, each 1H, BCH_2), 1.66 (s, 3H, *p*-$CH_3^{Mes,b}$), 1.45 (s, 3H, *o*'-$CH_3^{Mes,a}$), 0.39 ppm (s, 9H, $SiCH_3$). – $^{13}C\{^1H\}$ NMR (126 MHz, 299 K, C_6D_6): $\delta = 226.0$ (br, BC=), 144.7 (d, $^2J_{PC} = 7.2$ Hz, *o*-Mes^b), 144.3 (d, $^2J_{PC} = 7.6$ Hz, *o*-Mes^a), 142.4 (d, $^4J_{PC} = 7.9$ Hz, *p*-Mes^b), 142.3 (d, $^4J_{PC} = 7.8$ Hz, *p*-Mes^a), 141.8 (d, $^2J_{PC} = 12.9$ Hz, *o*'-Mes^b), 140.5 (d, $^2J_{PC} = 10.0$ Hz, *o*'-Mes^a), 135.1 (*p*-Tol), 134.4 (*i*-Tol), 132.3 (d, $^3J_{PC} = 10.6$ Hz, *m*-Mes^a), 132.2 (d, $^3J_{PC} = 10.3$ Hz, *m*-Mes^b), 131.9 (d, $^3J_{PC} = 10.8$ Hz, *m*'-Mes^a), 131.7 (d, $^3J_{PC} = 11.2$ Hz, *m*'-Mes^b), 128.5 (*m*-Tol), 127.4 (*o*-Tol), 125.1 (d, $^1J_{PC} = 76.3$ Hz, *i*-Mes^a), 120.5 (d, $^1J_{PC} = 76.6$ Hz, *i*-Mes^b), 117.0 (d, $^1J_{PC} = 58.8$ Hz, PC=)^t, 29.0 (d, $^1J_{PC} = 41.6$ Hz, PCH_2), 24.9 (d, $^3J_{PC} = 5.4$ Hz, *o*'-$CH_3^{Mes,b}$), 24.5 (d, $^3J_{PC} = 3.4$ Hz, *o*-$CH_3^{Mes,b}$), 23.4 (d, $^3J_{PC} = 4.7$ Hz, *o*'-$CH_3^{Mes,a}$), 22.9 (br, *o*-$CH_3^{Mes,a}$), 20.7 (*p*-CH_3^{Tol}), 20.6 (*p*-$CH_3^{Mes,a}$), 20.3 (*p*-$CH_3^{Mes,b}$), 15.5 (br, BCH_2), 3.1 ppm ($SiCH_3$), [C_6F_5 not listed; ^{t} tentative assignment]. – $^{11}B\{^1H\}$ NMR (160 MHz, 299 K, C_6D_6): $\delta = -12.4$ ppm ($\nu_{1/2} \sim 60$ Hz). – ^{19}F NMR (470 MHz, 299 K, C_6D_6): $\delta = -124.0$, −127.0, −128.4, −128.9 (each br, each 1F, *o*-C_6F_5), −160.29 (t), $^3J_{FF} = 20.8$ Hz), −160.34 (t, $^3J_{FF} = 21.1$ Hz) (each 1F, *p*-C_6F_5), −164.1 (2F), −165.3 (1F), − 165.6 ppm (1F) (each br, 4F, *m*-C_6F_5). – $^{29}Si\{^1H\}$ DEPT (99 MHz, 299 K, C_6D_6): $\delta = -3.0$ ppm (dm, $^3J_{PSi} = 25.0$ Hz). – $^{31}P\{^1H\}$ NMR (202 MHz, 299 K, C_6D_6): $\delta = 5.1$ ppm ($\nu_{1/2} \sim 20$ Hz 1 ppm).

Supporting information

Additional experimental and analytical details, crystallographic data and pictures of spectra are given as Supporting Information (33 pages) available online (DOI: 10.5560/ZNB.2014-4190).

CCDC 1020239 to 1020242 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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