Synthesis of a silylene–borane adduct and its slow conversion to a silylborane

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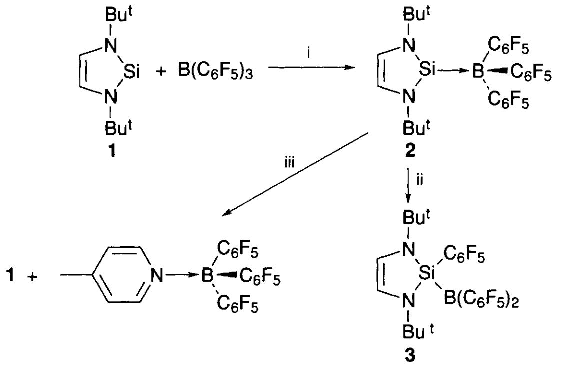
The silylene–borane adduct 2 is formed from the corresponding silylene and tris(pentafluorophenyl)borane and rearranges to silylborane 3 with a half-life of about one month in toluene.

The electronic structure of group 14 compounds with low coordination numbers of the type R_2E^{II} (carbenes, silylenes *etc.*) is still the subject of some controversy in particular with respect to the role of the empty orbital and the lone pair on the central atom E.[1–6] The s-character of the lone pair increases from carbon to lead as was deduced from *ab initio* calculations and photoelectron spectroscopy.[2] This reduces the basicity of the lone pair. Indeed, the purported BF_3 adduct of stannocene $Sn(C_5H_5)_2$ was later shown to have a more complex structure with no Sn–B interaction,[7,8] whereas borane adducts of Arduengo's carbene have been reported.[9] More recently, Tacke *et al.* demonstrated the Lewis acid properties of decamethylsilicocene by preparing the CO adduct thereof.[10] In this work, we show that the bis(amino)silylene **1** can indeed act as a Lewis base towards electron-deficient boranes.

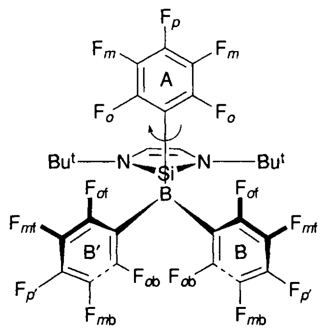
When tris(pentafluorophenyl)borane in toluene is added to a toluene solution of silylene **1**[11] the colour of the resulting solution intensifies to deep yellow within seconds. NMR spectroscopic investigations indicate the formation of one new compound **2**, which can be isolated by removing the solvent and recrystallizing from pentane at −30 °C. **2** was characterized as the Lewis adduct of the silylene **1** by elemental analysis, mass spectroscopy and ^{1}H, ^{11}B, ^{13}C and ^{19}F NMR spectroscopies (Scheme 1).‡ Unfortunately, crystals of **2** were unsuitable for an X-ray structure analysis.

^{11}B NMR spectroscopy clearly indicates tetracoordination of the boron atom, and the high symmetry suggested by the ^{1}H and ^{13}C NMR data rules out B–N coordination as an alternative. Additional proof comes from the variable-temperature ^{19}F NMR spectrum of **2** which indicates hindered rotation around the Si–B bond. At the low temperature limit (< -20 °C) the local symmetry of the borane fragment is reduced from C_3 to C_s: All three C_6F_5 rings are 'locked' between the bulky Bu^t groups but whereas ring A is still rotating freely even at −60 °C (retaining an AA′MM′X spin system), the two rings B are interlocked and give rise to two chemically equivalent sets of five distinct fluorine resonances as is seen in the ^{19}F–^{19}F COSY spectrum (Scheme 2, Fig. 1).



Scheme 1 Formation of **2** and **3**. *Reagents and conditions*: i, toluene, 20 °C; ii, toluene, 20 °C, 3 months; iii, 4-methylpyridine, toluene.

Addition of 4-methylpyridine to a toluene solution of **2** results in the formation of free **1** and the 4-methylpyridine–tris(pentafluorophenyl)borane adduct[12] indicating that the adduct formation of **2** is reversible. To our surprise, reinspection of a [$^{2}H_8$]toluene solution of **2** in a sealed NMR tube after 2 months indicated the formation of a new compound! There was still only one NMR signal for the CH and Bu^t groups, and the ^{19}F NMR spectrum showed two independent rings (**2**: 1 ratio), both rotating freely at −20 °C. This and a new ^{11}B NMR signal at δ 60.4 suggested the formation of silylborane **3** where one



Scheme 2 Steric constraints in **2** at −20 °C and labelling scheme for phenyl rings

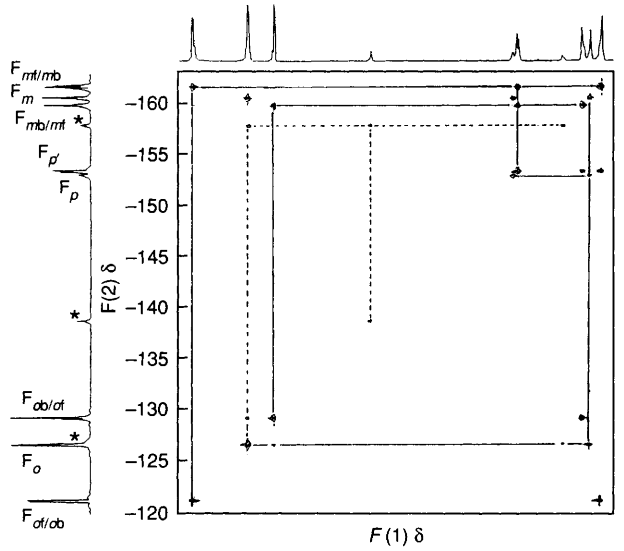


Fig. 1 ^{19}F–^{19}F DQF COSY (phase sensitive, using *z*-gradients). 22 396.4 Hz sweep width at 470.279 MHz, 2048 × 1024 data points after zero-filling in both dimensions, matched squared-sinebell window along *T*1 and *T*2. Relevant expansion only, signals marked with an asterisk indicate a slight excess of $B(C_6F_5)_3$.

C_6F_5 group has moved from B to Si.§ Silylboranes have been prepared before by different routes,[13–15] and Nöth and co-workers reported on the insertion of *in situ* generated dimethylgermylene in B–H bonds.[16] Although predicted from *ab initio* calculations,[17] no silylene adduct of a borane has yet been isolated. ^{29}Si NMR on both **2** and **3** would be highly informative but unfortunately, due to scalar coupling to ^{10}B and ^{11}B as well as fast quadrupolar-induced relaxation of the silicon centre we were unable to detect a ^{29}Si NMR signal even at low temperature. These problems are well documented in the literature[18] and provide strong evidence for a B–Si bond since silylene **1** gave a ^{29}Si NMR spectrum under the same experimental conditions without any difficulty.

Earlier studies which attributed the stability of **1** to electronic rather than steric effects are supported by our finding that despite the steric crowding no less than three strongly electron-withdrawing C_6F_5 groups are necessary to arrive at a stable adduct. Although slightly smaller, an adduct **5** of bis(pentafluorophenyl)phenylborane $BPh(C_6F_5)_2$ **4** with **1** is formed and NMR spectroscopically characterized only at −60 °C and is completely dissociated at 20 °C.¶ No clean reaction was observed with bis(pentafluorophenyl)chloroborane $BCl(C_6F_5)_2$. Neither $BH_3 \cdot$thf nor $AlH_3 \cdot NMe_3$ react with **1** confirming our expectation that **1** is a weaker donor to hard Lewis acids than ethers or amines.

In **2**, electron density must be removed from the silicon atom through donation to the boron centre. It is intriguing to think that Lewis acid adducts of **1** might have at least partial silylenium cation character, bearing in mind that the mere existence of this class of compounds has been questioned.[19] Further theoretical and preparative investigations along these lines are currently in progress.

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Footnotes

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‡ *Selected data* for **2**: NMR ([$^2H_8$]toluene): ^{1}H (−20 °C), δ 0.92 (s, 18 H), 6.16 (s, 2 H). ^{11}B (20 °C), δ −14.3. ^{13}C (−40 °C), δ 30.9, 56.2, 119.1, 142.1 ($C_{mf/mb}$), 142.4 (C_m), 142.7 ($C_{mb/mf}$), 144.1 ($C_{p,p'}$), 151.8 ($C_{of/ob}$), 153.8 ($C_{ob/of}$), 153.9 (C_o), C–B not detected. ^{19}F (−20 °C), δ −121.1 (d, 2 F, $F_{of/ob}$), −126.5 (d, 2 F, F_o), −129.1 (2 F, $F_{ob/of}$), −153.2 (t, 1 F, F_p), −153.7 (t, 2 F, $F_{p'}$), −159.8 (t, 2 F, $F_{mb/mf}$), −160.6 (t, 2 F, F_m), −161.7 (t, 2 F, $F_{mf/mb}$). NMR shifts for F-bonded carbon atoms were taken from a C–F HSQC experiment. MS (EI, 70 eV), *m/z* 512 [$B(C_6F_5)_3$, 11%], 196 (**1**, 100%); no peak for **2** detectable under these conditions. Mp. 96 °C (decomp.), satisfactory elemental analysis.

§ *Selected NMR data* for **3**: NMR ([$^2H_8$]toluene): ^{1}H (20 °C), δ 1.14 (s, 18 H), 5.81 (s, 2 H). ^{11}B (20 °C), δ 60.4. ^{13}C (20 °C, partly from ^{19}F–^{13}C HSQC), δ 30.5, 51.7, 112.2 ($^1J_{CH}$ 150.8 Hz), 137.6 ($C_{m,m'}$), 145.3 ($C_{p'}$), 145.6 (C_p), 148.6 ($C_{o'}$), 148.8 (C_o), C–B not detected. ^{19}F (20 °C), δ −131.2 (d, 2 F, F_o), −131.8 (d, 4 F, $F_{o'}$), −143.2 (t, 1 F, F_p), −144.2 (t, 2 F, $F_{p'}$), −162.8 (m, 2 F, F_m), −163.0 (m, 4 F, $F_{m'}$).

¶ *Selected NMR data* for **5** ([$^2H_8$]toluene, −60 °C): ^{1}H, δ 0.78 (s, 18 H), 5.96 (s, 2 H). ^{19}F, δ −129 (br, 2 F, F_o), −158.7 (1 F, F_p), −165.6 (2 F, F_m).

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