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 BF₃ adduct of stannocene Sn(C₅H₅)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 ¹H, ¹¹B, ¹³C and ¹⁹F NMR spectroscopies (Scheme 1).‡ Unfortunately, crystals of **2** were unsuitable for an X-ray structure analysis.

¹¹B NMR spectroscopy clearly indicates tetracoordination of the boron atom, and the high symmetry suggested by the ¹H and ¹³C NMR data rules out B–N coordination as an alternative. Additional proof comes from the variable-temperature ¹⁹F 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 C₆F₅ rings are 'locked' between the bulky Bu^t groups but whereas ring A is still rotating freely even at -60 °C



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

(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).

Addition of 4-methylpyridine to a toluene solution of 2 results in the formation of free 1 and the 4-methylpyridinetris(pentafluorophenyl)borane adduct¹² indicating that the adduct formation of 2 is reversible. To our surprise, reinspection of a [²H₈]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 ¹⁹F NMR spectrum showed two independent rings (2:1 ratio), both rotating freely at -20 °C. This and a new ¹¹B 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 ¹⁹F–¹⁹F DQF COSY (phase sensitive, using *z*-gradients). 22 396.4 Hz sweep width at 470.279 MHz, 2048 \times 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(C₆F₅)₃.

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 C_6F_5 group has moved from B to Si.§ Silylboranes have been prepared before by different routes,^{13–15} and Nöth and coworkers 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. ²⁹Si NMR on both **2** and **3** would be highly informative but unfortunately, due to scalar coupling to ¹⁰B and ¹¹B as well as fast quadrupolar-induced relaxation of the silicon centre we were unable to detect a ²⁹Si NMR signal even at low temperature. These problems are well documented in the literature¹⁸ and provide strong evidence for a B–Si bond since silylene **1** gave a ²⁹Si 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 electronwithdrawing 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 BH₃-thf nor AlH₃·NMe₃ 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.

N. M. is grateful to Professor M. L. H. Green and his group for their support of this project and to BASF AG/Studienstiftung des Deutschen Volkes for a fellowship.

Footnotes

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[‡] Selected data for **2**: NMR ([²H₈]toluene): ¹H (-20 °C), δ 0.92 (s, 18 H), 6.16 (s, 2 H). ¹¹B (20 °C), δ -14.3. ¹³C (-40 °C), δ 30.9, 56.2, 119.1, 142.1 (C_{mt/mb}), 142.4 (C_m), 142.7 (C_{mb/mt}), 144.1 (C_{p,p'}), 151.8 (C_{ot/ob}), 153.8 (C_{ob/ot}), 153.9 (C_o), C–B not detected. ¹⁹F (-20 °C), δ -121.1 (d, 2 F, F_{ot/ob}), -126.5 (d, 2 F, F_o), -129.1 (2 F, F_{ob/ot}), -153.2 (t, 1 F, F_p), -153.7 (t, 2 F, F_{p'}), -159.8 (t, 2 F, F_{mb/mt}), -160.6 (t, 2 F, F_m), -161.7 (t, 2 F, F_{mt/mb}). NMR shifts for F-bonded carbon atoms were taken from a C–F HSQC experiment. MS (EI, 70 eV), m/z 512 [B(C₆F₅)₃, 11%], 196 (1, 100%); no peak for 2 detectable under these conditions. Vin Article Online (decomp.), satisfactory elemental analysis.

§ Selected NMR data for 3: NMR ([²H₈]toluene): ¹H (20 °C), δ 1.14 (s, 18 H), 5.81 (s, 2 H). ¹¹B (20 °C), δ 60.4. ¹³C (20 °C, partly from ¹⁹F–¹³C HSQC), δ 30.5, 51.7, 112.2 (¹J_{CH} 150.8 Hz), 137.6 ($C_{m,n'}$), 145.3 ($C_{p'}$), 145.6 (C_{p}), 148.6 ($C_{o'}$), 148.8 (C_{o}), C–B not detected. ¹⁹F (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_{n}), –163.0 (m, 4 F, $F_{m'}$). ¶ Selected NMR data for 5 ([²H₈]toluene, –60 °C): ¹H, δ 0.78 (s, 18 H), 5.96

Selected NMR data for 5 ([²H₈]toluene, -60 °C): ¹H, 8 0.78 (s, 18 H), 5.96 (s, 2 H). ¹⁹F, $\delta - 129$ (br, 2 F, F_o), -158.7 (1 F, F_p), -165.6 (2 F, F_m).

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Received, 27th September 1996; Com. 6/06614C