Supporting Information for

Alkylstrontium Diamidoboranes: β-hydride Elimination and Sr-C Insertion

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General Experimental Procedures: All reactions were carried out using standard Schlenk line and glovebox techniques under an inert nitrogen or Argon atmosphere. NMR experiments were conducted in Youngs tap NMR tubes prepared and sealed in a glovebox. NMR spectra were collected on a Bruker AV300 spectrometer operating at 75.5 MHz (^{13}C), 96.3 MHz (^{11}B). Variable-temperature ^{1}H NMR data**,** ^{1}H-^{11}B HMQC and ^{1}H TOCSY were recorded on a Bruker AV400 spectrometer. Solvents (toluene, THF, hexane) were dried by a commercially available solvent purification system (Innovative Technologies), under nitrogen before storage in ampoules over molecular sieves. C_6D_6 and d_8-toluene were purchased from Goss Scientific Instruments Ltd., dried over molten potassium before distillation under nitrogen and storage over molecular sieves. $Me_2NH.BH_3$ was purchased from Sigma-Aldrich Ltd. and used without further purification. $C_4H_8NH.BH_3$[1] and $[Sr\{CH(SiMe_3)_2\}_2(THF)_2]$[2] were synthesised by literature procedures. GCMS data was obtained on an Agilent Technologies 5975C GCMS using 0.5 mg/ml samples in toluene. CHN microanalysis was conducted by Mr. Stephen Boyer of London Metropolitan University.

Synthesis of [({CH(SiMe$_3$)$_2$}(THF)Sr{NMe$_2$}BH$_3$)$_2$], 1

Toluene (ca. 10ml) was added to solid [Sr{CH(SiMe$_3$)$_2$}$_2$(THF)$_2$] (130 mg, 0.23 mmol) and Me$_2$NH.BH$_3$ (0.013 mg, 0.23 mmol) and stirred at room temperature for ca. 18 hours before concentration under vacuum. Compound **1** was crystallised from toluene. Accurate CHN microanalysis was not obtainable due to the extreme air and moisture sensitivity of this species. ^{1}H NMR (d$_8$-tol, 298 K) δ = -1.68 (s broad, 1H, C*H*), 0.04 (s, 18H, Si(C*H*$_3$)$_3$)$_2$), 1.47 (THF), 2.38 (s broad, 6H, N(C*H*$_3$)$_2$), 3.66 (THF). ^{13}C{^{1}H} NMR (d$_8$-tol, 298 K) δ = 6.8 (Si(*C*H$_3$)$_3$)$_2$), 25.9 (THF), 47.6 (N(*C*H$_3$)$_2$), 69.2 (THF). ^{11}B NMR (d$_8$-tol, 298 K) δ = -9.3 (q, *B*H, $^1J_{BH}$ = 81.6 Hz).

Synthesis of [({CH(SiMe$_3$)$_2$}(THF)Sr{NC$_4$H$_8$}BH$_3$)$_2$], 2

Toluene (ca. 10ml) was added to solid [Sr{CH(SiMe$_3$)$_2$}$_2$(THF)$_2$] (130 mg, 0.23 mmol) and C$_4$H$_8$NH.BH$_3$ (20 mg, 0.23 mmol) and stirred at room temperature for ca. 18 hours before concentration under vacuum to provide of an oily residue. Anal. Calc. for C$_{30}$H$_{76}$B$_2$N$_2$O$_2$Si$_4$Sr$_2$: C, 44.74; H, 9.39; N, 3.48 %. Found: C, 44.32; H, 9.11; N, 3.23 %. ^{1}H NMR (C$_6$D$_6$, 298 K) δ = -1.65 (s broad, 1H, C*H*), 0.38 (s, 18H, Si(C*H*$_3$)$_3$)$_2$), 1.40 (THF), 1.78 (s broad, 4H, N(CH$_2$)$_2$(C*H*$_2$)$_2$), 2.80 (s broad, 4H, N(C*H*$_2$)$_2$(CH$_2$)$_2$), 3.60 (THF). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 298 K) δ = 6.76 (Si(*C*H$_3$)$_3$)$_2$), 25.8 (THF), 26.4 (N(CH$_2$)$_2$(*C*H$_2$)$_2$), 56.0 (N(*C*H$_2$)$_2$(CH$_2$)$_2$), 69.1 (THF). ^{11}B NMR (C$_6$D$_6$, 298 K) δ = -10.9 (q, *B*H, $^1J_{BH}$ = 82.3 Hz).

Typical Procedure for Stoichiometric NMR-Scale Reactions

C$_6$D$_6$ or d$_8$-toluene (ca. 0.5 ml) was added to a solid mixture of [Sr{CH(SiMe$_3$)$_2$}$_2$(THF)$_2$] (55 mg, 0.1 mmol) and one molar equivalent of amine borane (Me$_2$NH.BH$_3$ or C$_4$H$_8$NH.BH$_3$) in a glovebox and the solution sealed in a

Youngs tap NMR tube. The reactions were monitored by ^{1}H and ^{11}B NMR spectroscopy. Reactions requiring elevated temperatures were heated using a thermostat-controlled oil bath.

NMR-Scale Synthesis of [{Me_2N}BH{CH($SiMe_3$)$_2$}], 3

D_8-toluene (ca. 0.5 ml) was added to a solid mixture of [Sr{CH($SiMe_3$)$_2$}$_2$(THF)$_2$] (55 mg, 0.1 mmol) and one molar equivalent of $Me_2NH.BH_3$ (5 mg, 0.1 mmol) and the solution sealed in a Youngs tap NMR tube before heating to 80°C for ca. 78 hours. The product proved unstable to concentration under vacuum or by evaporation in a glovebox. GCMS identified a molecular ion M^+ for **3** with m/z of 215.2. ^{1}H NMR (d_8-tol, 298 K) $\delta = -0.36$ (s, 2H, $CH_2(SiMe_3)_2$), 0.04 (s, 18H,$Si(CH_3)_3)_2$), ca. 0.10 (s, 1H, C*H*), 0.12 (s, 18H, $Si(CH_3)_3)_2$), 1.47 (THF), 2.50 (s, 3H, N-CH_3), 2.74 (s, 3H, N-CH_3), 3.55 (THF), 4.52 (d broad, 1H, B*H*, $^1J_{BH}$ ca. 147 Hz). ^{13}C{^{1}H} NMR (d_8-tol, 298 K) $\delta = 1.8$ ($Si(CH_3)_3)_2$), 2.2 ($Si(CH_3)_3)_2$), 4.8 (*C*H), 26.2 (THF), 37.8 (N-CH_3), 45.7 (N-CH_3), 68.2 (THF). ^{11}B NMR (d_8-tol, 298 K) $\delta = 44.8$ (d, *B*H, $^1J_{BH} = 102$ Hz).

Figure S1: ^{1}H NMR spectrum of compound **1** (generated *in situ*) before heating.

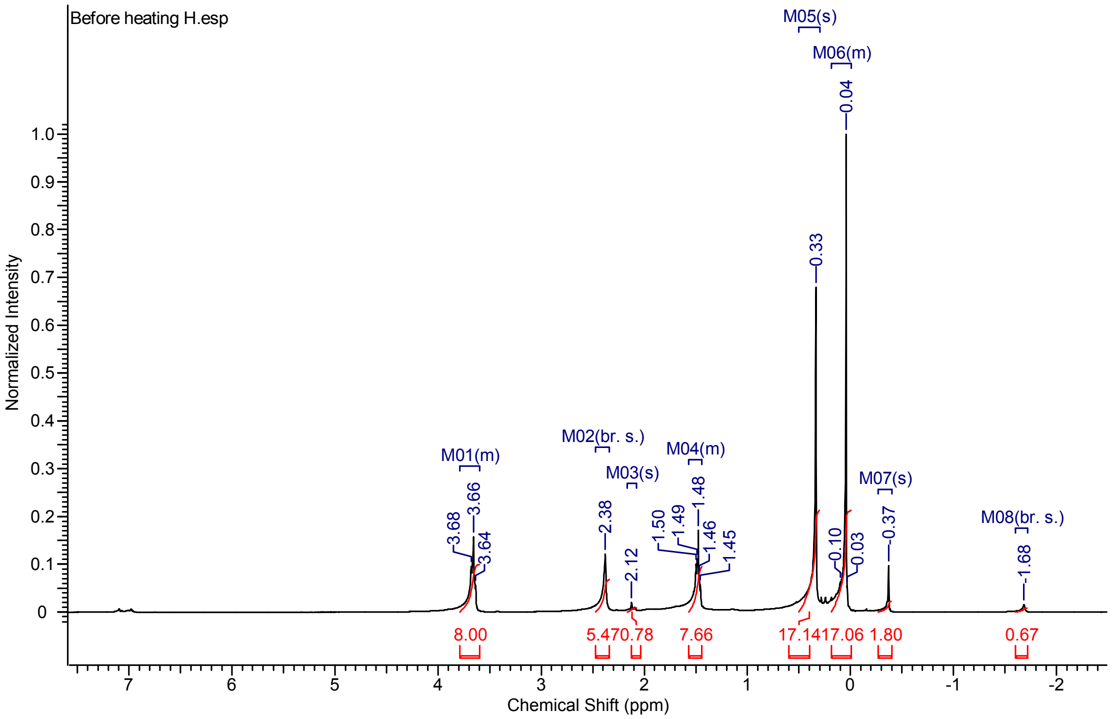


Figure S2: ^{1}H NMR spectrum of compound **1** showing the formation of compound **3** after heating at 80 °C for 78 hours.

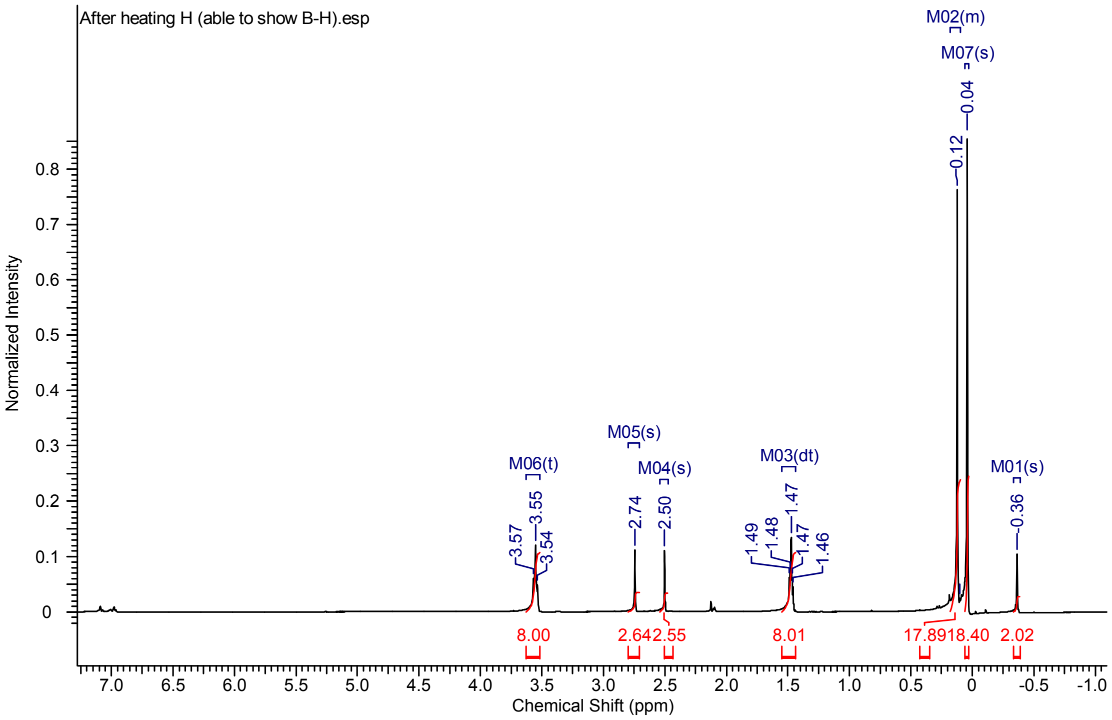


Figure S3: $^{13}C\{^1H\}$ NMR spectrum of compound **1** (generated *in situ*) before heating.

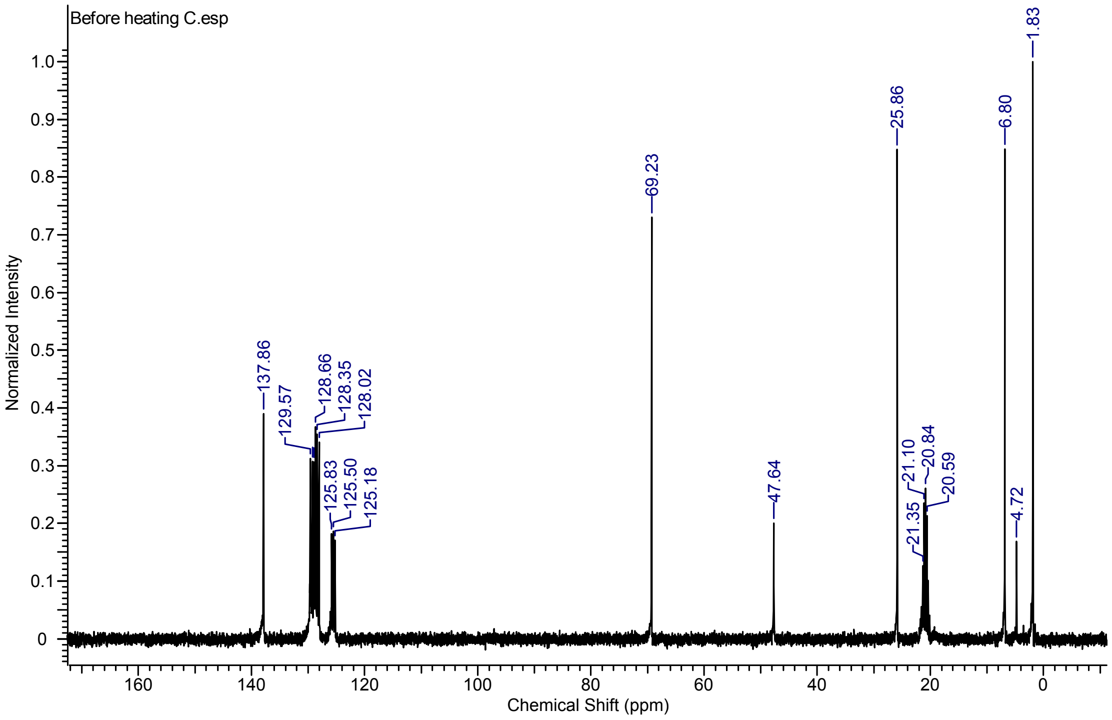


Figure S4: $^{13}C\{^1H\}$ NMR spectrum of compound **1** showing the formation of compound **3** after heating at 80 °C for 78 hours.

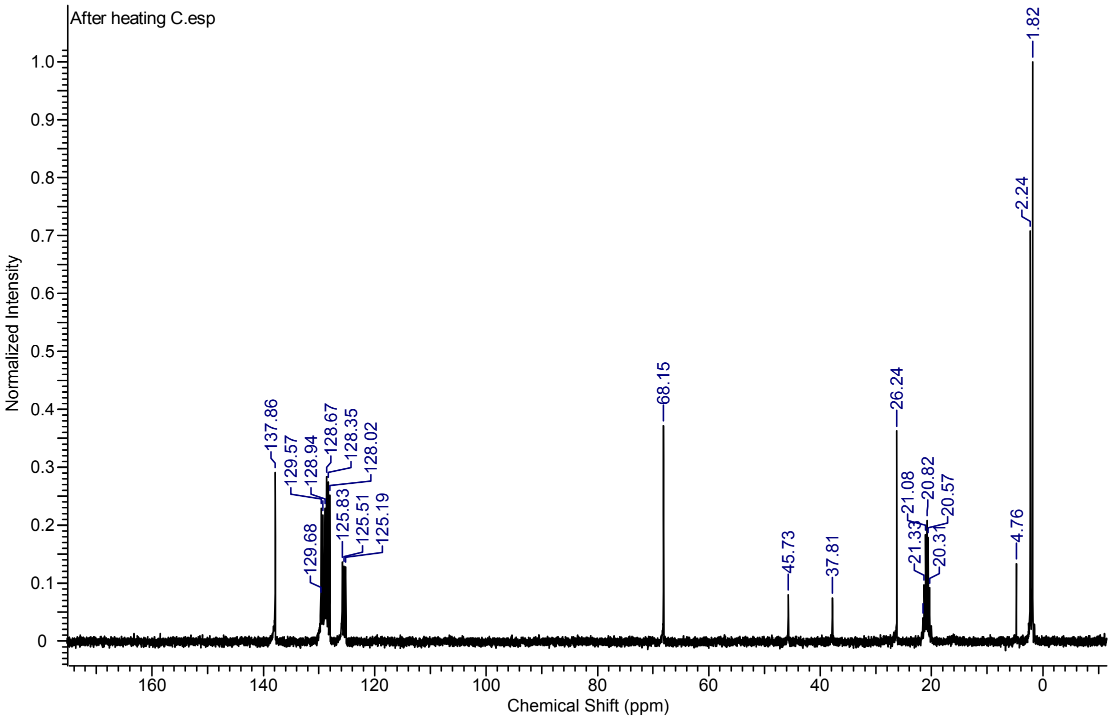


Figure S5: ^{11}B NMR spectrum of compound **1** (generated *in situ*) before heating.

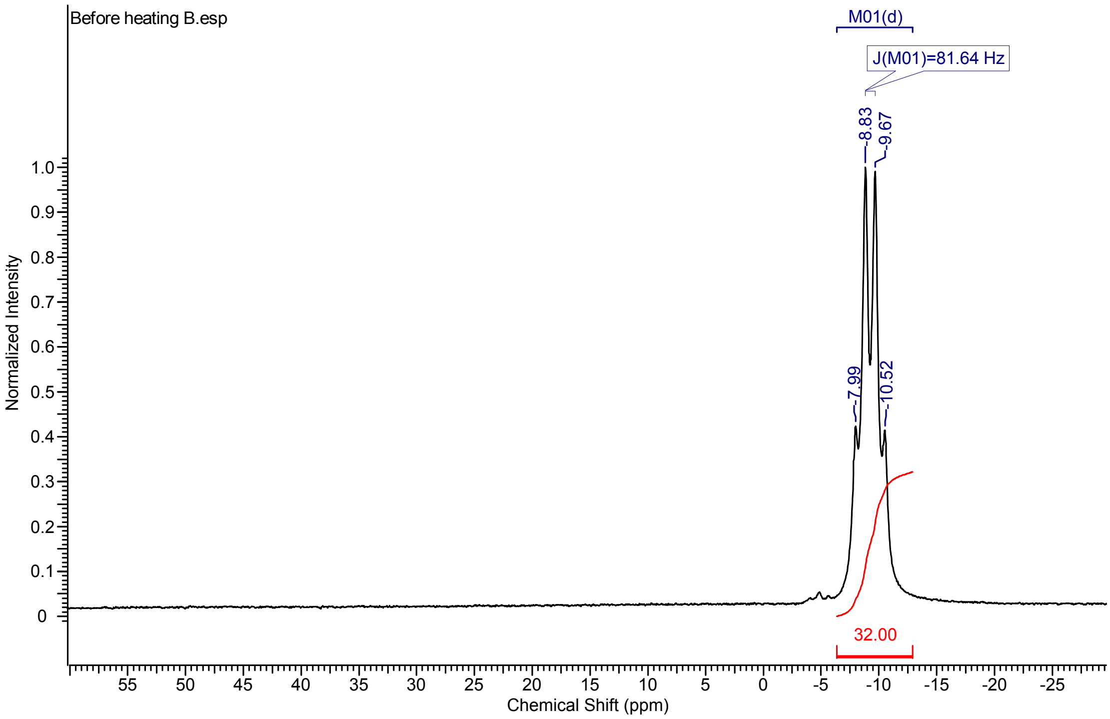


Figure S6: ^{11}B NMR spectrum of compound **1** showing the formation of compound **3** after heating at 80 °C for 78 hours.

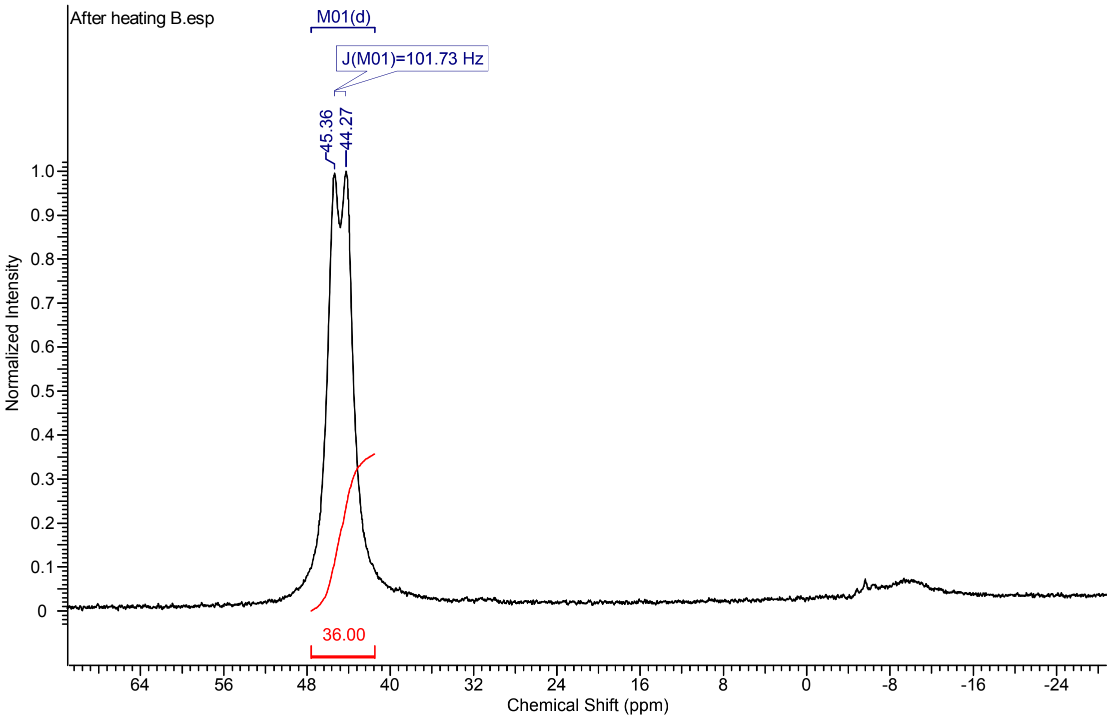


Figure S7: ^{1}H-^{11}B HMQC experiment optimised for long range (ca. 10 Hz) couplings.

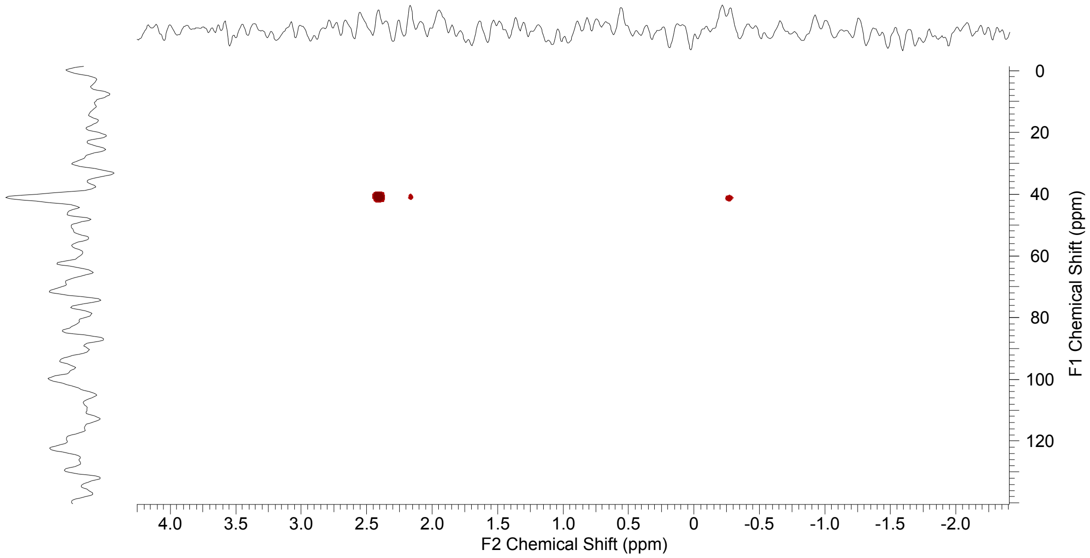
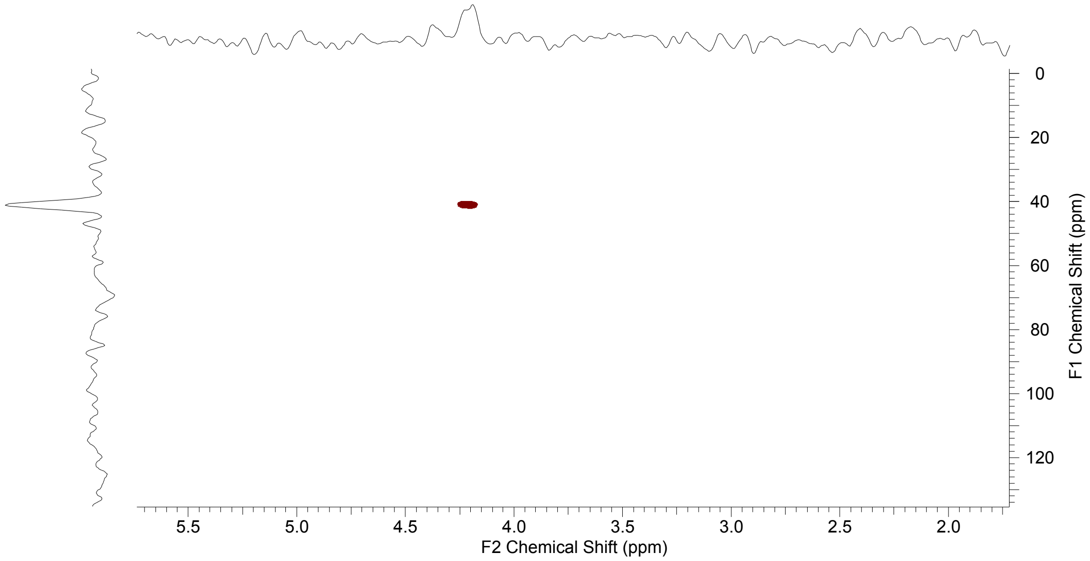


Figure S8: ^{1}H-^{11}B HMQC experiment optimised for short range (ca. 100 Hz) couplings.



The constitution of compound **3** was deduced by a series of ^{1}H NMR experiments. A single 18H silylmethyl resonance was observed at δ 0.04 ppm while two magnetically distinct 3H N-bound methyl signals appeared at δ 2.50 and 2.74 ppm (Figure S2). Although the methine of the -CH(SiMe$_3$)$_2$ group was obscured by the silylmethyl signal, this resonance was identified by means of a ^{1}H-^{11}B HMQC experiment optimised for long range (10 Hz) couplings (Figure S7). This experiment also revealed a correlation between the doublet resonance in the ^{11}B NMR spectrum and both N-methyl groups while a further ^{1}H-^{11}B HMQC experiment optimised for one bond (110 Hz) ^{1}H-^{11}B couplings allowed the identification of a B-H resonance which appeared as an extremely broadened 1H multiplet at δ 4.52 ppm (Figure S8). These data indicated that both the -NMe_2 and -$CH(SiMe_3)_2$ substituents were attached to the same B-H centre and allowed an assignment of compound **3** as the alkylaminoborane, [$HB(NMe_2)\{CH(SiMe_3)_2\}$], in which the appearance of two separate N-methyl resonances is simply a reflection of the co-planarity of the XYB-NMe_2 fragment and restricted rotation about the B-N bond.[1]

Figure S9: Stack plot of ^{11}B NMR spectra of thermolysis of compound **1** recorded at 60 °C after 10 minutes (blue), 1 hour (green), 3 hours (grey) and 6 hours (red).

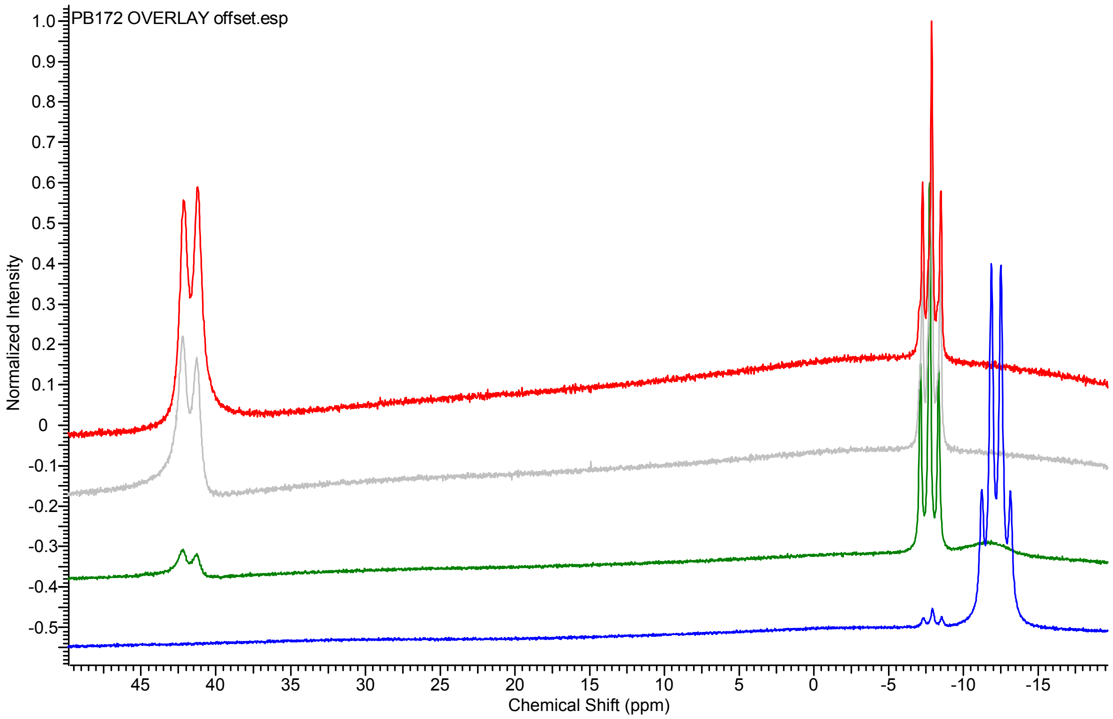
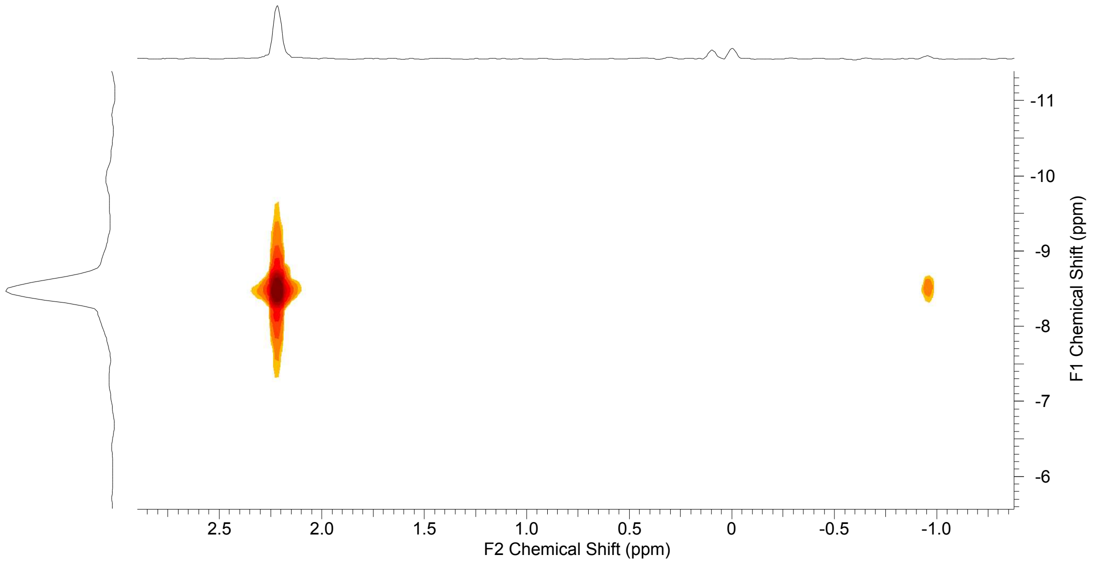


Figure S10: ^{1}H-^{11}B HMQC experiment optimised for long range (ca. 10 Hz) couplings of the thermolysis of compound **1** recorded after 6 hours and showing the correlation between the triplet ^{11}B NMR resonance at 7.9 ppm and ^{1}H resonances proposed to arise from the complex anion $\{N(Me)_2BH_2CH(SiMe_3)_2\}$.



NMR-Scale Synthesis of [{H_8C_4N}BH{CH($SiMe_3$)$_2$}], 4

C_6D_6 (ca. 0.5 ml) was added to a solid mixture of [Sr{CH($SiMe_3$)$_2$}$_2$(THF)$_2$] (55 mg, 0.1 mmol) and one molar equivalent of $C_4H_8NH.BH_3$ (8 mg, 0.1 mmol) and the solution sealed in a Youngs tap NMR tube before heating to 70°C for ca. 12 hours. The product proved unstable to concentration under vacuum or by evaporation in a glovebox. GCMS identified a molecular ion M^+ for 4 with m/z of 241.2. ^{1}H NMR (C_6D_6, 298 K) δ = –0.36 (s, 2H, C*H*$_2$($SiMe_3$)$_2$), 0.04 (s, 18H,Si(C*H*$_3$)$_3$)$_2$), ca. 0.10 (s, 1H, C*H*), 0.18 (s, 18H, Si(C*H*$_3$)$_3$)$_2$), ca. 1.43 (m, 4H, (N(CH$_2$)$_2$(C*H*$_2$)$_2$)), 1.44 (THF), 3.01 (t, 2H, C*H*$_2$, J_{HH} = 13.2 Hz), 3.25 (t, 2H, C*H*$_2$, J_{HH} = 13.2 Hz), 3.57 (THF), 4.84 (d broad, 1H, B*H*, $^{1}J_{BH}$ ca. 136 Hz). $^{13}C\{^{1}H\}$ NMR (C_6D_6, 298 K) δ = 1.8 (Si(*C*H$_3$)$_3$)$_2$), 2.3 (Si(*C*H$_3$)$_3$)$_2$), 4.7 (*C*H), 26.2 (THF), 26.3 (N(CH$_2$)$_2$(CH$_2$)(*C*H$_2$)), 26.6 (N(CH$_2$)$_2$(*C*H$_2$)(CH$_2$)), 47.1 (N(CH$_2$)(*C*H$_2$)(CH$_2$)$_2$), 53.2 (N(*C*H$_2$)(CH$_2$)(CH$_2$)$_2$), 68.2 (THF). ^{11}B NMR (C_6D_6, 298 K) δ = 43.3 (d, *B*H, $^{1}J_{BH}$ = 93.3 Hz).

Figure S11: ^{1}H NMR spectrum of compound **2** (generated *in situ*) before heating.

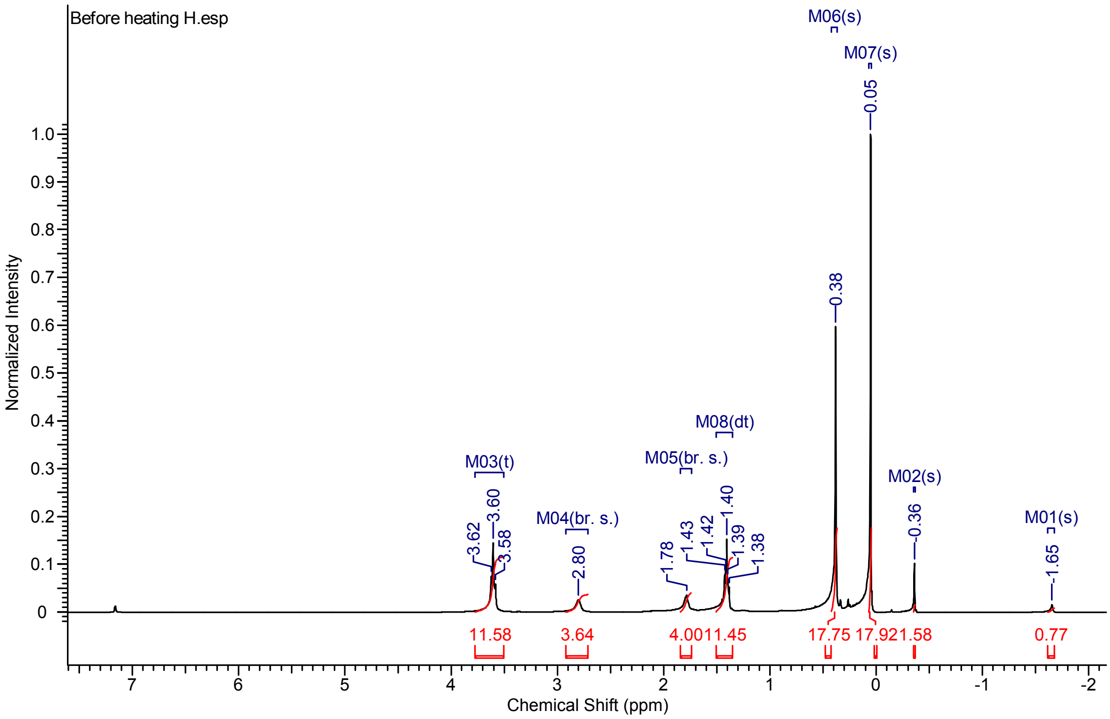


Figure S12: ^{1}H NMR spectrum of compound **2** showing the formation of compound **4** after heating at 70 °C for 12 hours.

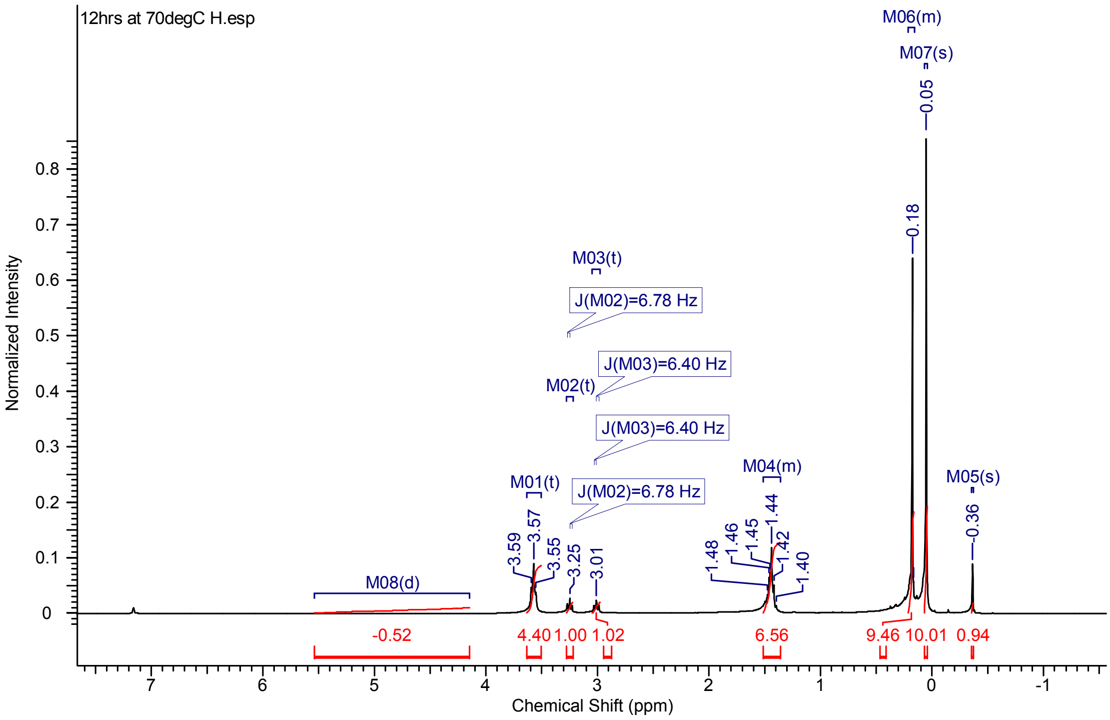


Figure S13: $^{13}C\{^1H\}$ NMR spectrum of compound **2** showing the formation of compound **4** after heating at 70 °C for 12 hours.

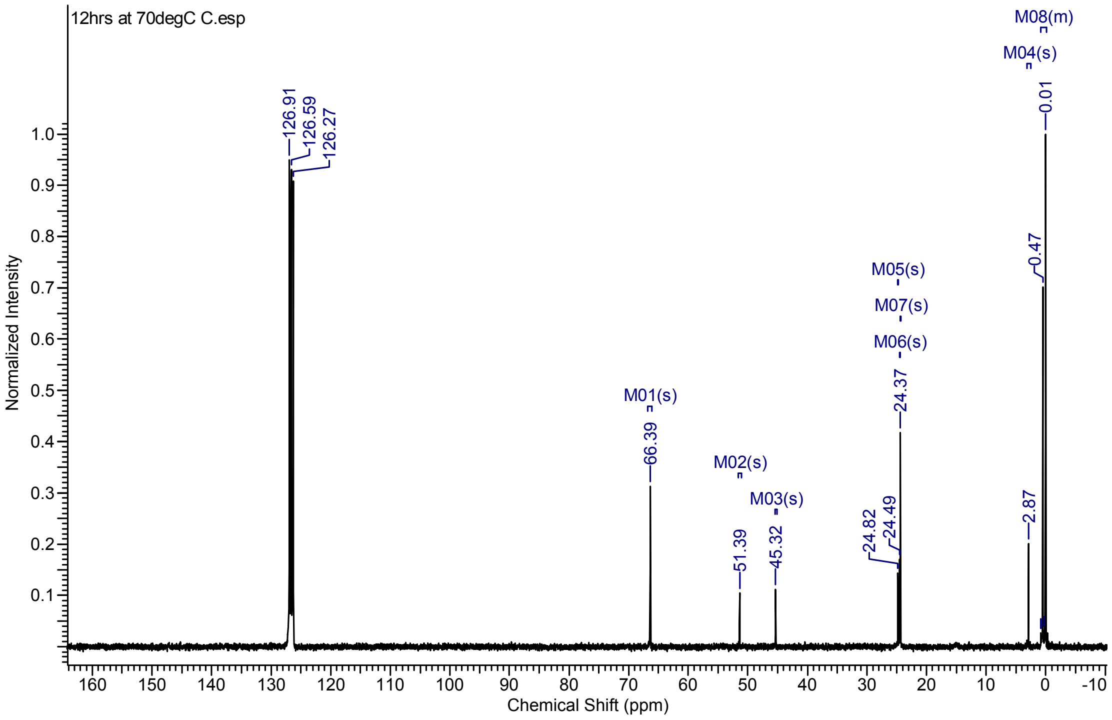
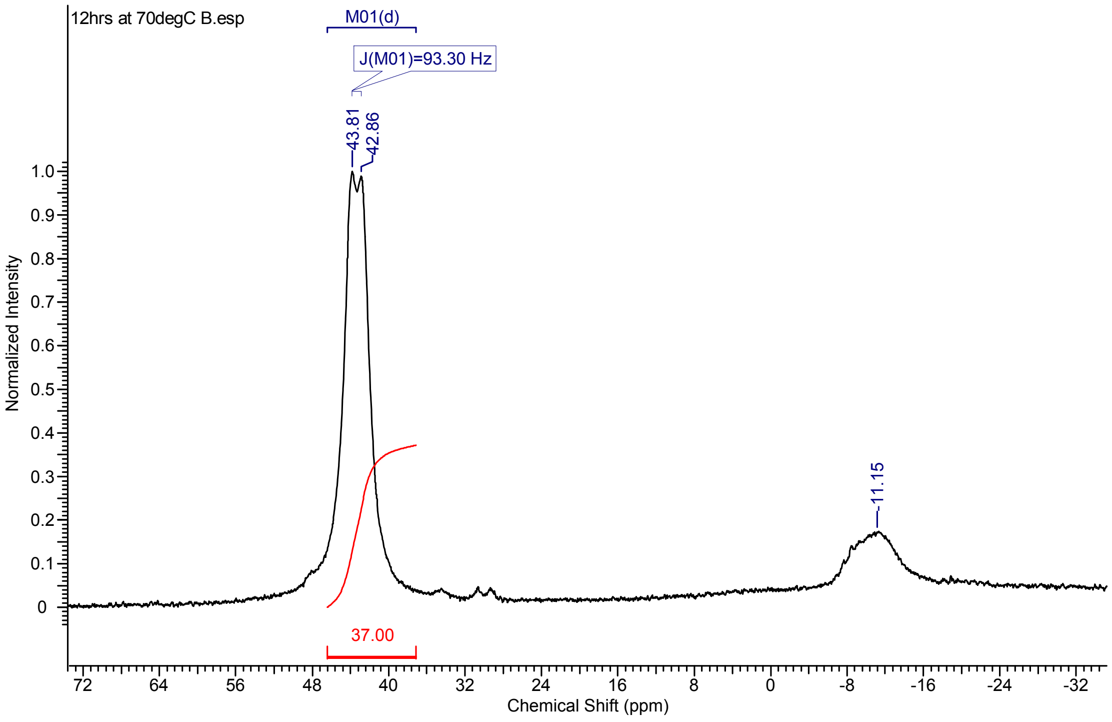


Figure S14: ^{11}B NMR spectrum of compound **2** showing the formation of compound **4** after heating at 70 °C for 12 hours.



Crystallographic data

Data for compound **1** were collected on a Nonius KappaCCD diffractometer equipped with a low temperature device, using graphite monochromated MoKα radiation (λ= 0.71073 Å). Data were processed using the Nonius Software.[4] Structure solution, followed by full-matrix least squares refinement was performed using the programme suite X-SEED throughout.[5] Both THF ligands exhibited disorder of all atoms therein, with the exception of O1, in a 50:50 ratio. Additional disorder (75:25) was modeled for C1-4 and Si1. The hydrogens attached to B1 were included at calculated positions, although all 3 were clearly evident in the penultimate difference Fourier map.

1 C. A. Jaska, K. Temple, A. J. Lough and I. Manners, *J. Am. Chem. Soc*. **2003**, *125*, 9424.

2 A. G. M. Barrett, M. R. Crimmin, M. S. Hill, D. J. MacDougall, M. F. Mahon, P. A. Procopiou, *Chem.-Eur. J.* **2008**, *14*, 11292.

3 See, for example, a) C. Brown, R. H. Cragg, T. J. Miller and D. O. Smith, *J. Organometal. Chem.* 1981, **220**, C25; b) P. A. Barfield, M. F. Lappert and J. Lee, *J. Chem. Soc. (A),* 1968, 554.

4 DENZO-SCALEPACK Otwinowski, Z; Minor, W. " Processing of X-ray Diffraction Data Collected in Oscillation Mode ", Methods in Enzymology, Volume 276: Macromolecular Crystallography, part A, p.307-326, **1997**,C.W. Carter, Jr. & R. M. Sweet, Eds., Academic Press.

5 Barbour, L. J. "X-Seed - A software tool for supramolecular crystallography" *J. Supramol. Chem.* **2001***, 1,* 189-191.