REACTIVITY OF SODIUM HEXAETHYL-2,4-DICARBA-*nido*-HEXABORATE(1⁻)

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Dedicated to Dr Stanislav Heřmánek on the occasion of his 70th birthday in recognition of his important contributions to heteropolyborane chemistry.
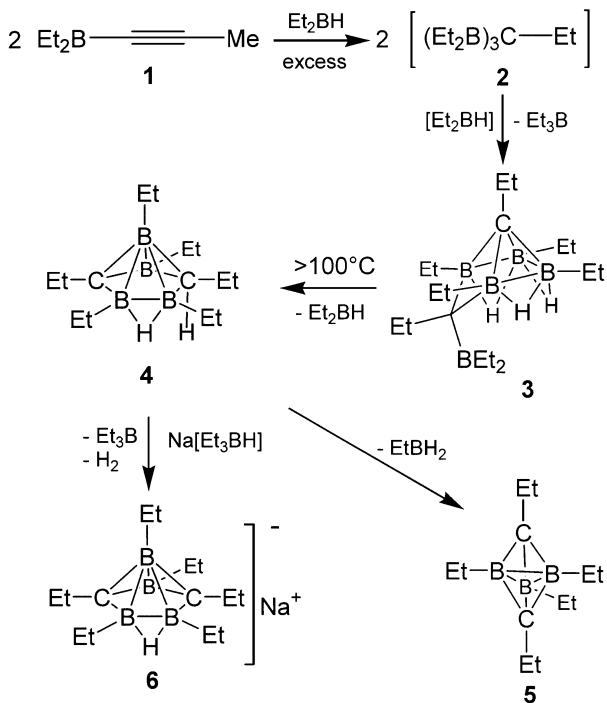
Sodium hexaethyl-2,4-dicarba-*nido*-hexaborate(1⁻) (**6**), available from hexaethyl-2,4-dicarba-*nido*-hexaborane(8) (**4**) by deprotonation, reacts with deuterated methanol, CD_3OD, to give back **4** without H/D exchange of the B–H–B hydrogen atom. The reaction of **6** with diethylboron chloride, Et_2BCl, affords hexaethyl-2,4-dicarba-*closo*-hexaborane(6) (**7**), the first example of a peralkylated carborane of this type. In contrast, the reaction of **6** with boron tribromide, BBr_3, leads mainly to 2,3,4,5,6,7-hexaethyl-2,4-dicarba-*closo*-heptaborane(7) (**8**), together with the corresponding 1-bromo derivative (**9**) and the *closo*-carborane **7** as side products. The reaction of two equivalents of **6** with $FeCl_2$ gives the air-stable sandwich complex bis[hexaethyl-2,4-dicarba-*nido*-hexaborate(1⁻)]iron **10** which was characterised by X-ray structural analysis. All products were characterised by ¹H, ¹¹B and ¹³C NMR spectroscopy, and ⁵⁷Fe Mössbauer spectroscopy was used to study **10**.
Key words: Boranes; Carboranes; Iron; NMR spectroscopy, ¹¹B, ¹³C; X-Ray diffraction; Crystal structure; ⁵⁷Fe Mössbauer spectroscopy; Sandwich complexes.

The synthesis of small carboranes has been an attractive challenge ever since carborane chemistry started[1]. It was found that polyboranes, such as pentaborane(9)[1,2] or tetraborane(10)[1,3,4], react with alkynes to give either complex mixtures of various small carboranes or, in some cases under certain conditions, rather selectively 2,3-dicarba-*nido*-hexaborane(8) derivatives[5]. An alternative route to small carboranes has been explored by studying B–H catalysed condensation reactions of polyborylated alkanes[6]. Recent studies of this route have shown that at first 1-carba-*arachno*-pentaborane(10) derivatives are formed[7–9] (as shown for **3** in Scheme 1), followed

by thermally induced conversion into the *nido*-carborane **4** and the 1,5-dicarba-*closo*-pentaborane(5) **5** (Scheme 1, refs[6,8]).

In a preliminary note[10], we have reported on the isolation of **4** (this alternative and most likely correct structure was proposed later on[11]), and its reaction with Na[Et$_3$BH], leading to sodium hexaethyl-2,4-dicarba-*nido*-hexaborate(1$^-$) (**6**). It proved possible to characterise **6** by X-ray structural analysis as a dimer which crystallises without solvent[10]. In the literature, there is one early report[12] on the parent anion [*nido*-2,4-C$_2$B$_4$H$_7$]$^-$. Later on, C-substituted dianions [*nido*-2,4-R$_2$C$_2$B$_4$H$_4$]$^{2-}$ were prepared by two-electron reduction of *closo*-1,2-R$_2$C$_2$B$_4$H$_4$ carboranes[13]. Although it was possible to convert these dianions into the monoanions [*nido*-2,4-R$_2$C$_2$B$_4$H$_5$]$^-$ by reaction with HCl, the neutral carboranes of the type *nido*-2,4-R$_2$C$_2$B$_4$H$_6$ could not be obtained[14]. Thus, the convenient access to **4** and its readily reversible conversion into the anion **6** deserve attention. In the present work, we

SCHEME 1

Formation of the *arachno*-(**3**), *nido*-(**4**) and *closo*-carboranes (**5**) (ref.[23]), and of the sodium hexaethyl-2,4-dicarba-*nido*-hexaborate(1$^-$) (**6**)

report on the reactivity of **6** towards methanol and electrophiles such as methyl iodide, iodine, Me$_3$SiCl, boron halides and FeCl$_2$.

EXPERIMENTAL

All experiments were carried out in an atmosphere of dry argon excluding oxygen and moisture (if not mentioned otherwise), using carefully dried solvents and oven-dried glassware. The following commercial compounds were used: iodine, methyl iodide, NaBH$_4$, triethylborane, boron tribromide, boron trichloride, and anhydrous FeCl$_2$. The sodium hexaethyl-2,4-dicarba-*nido*-hexaborate(1⁻) (ref.[10]), diethylboron chloride[15], and HBBr$_2$-SMe$_2$ (ref.[16]) were prepared according to literature procedures.

For the characterisation of the compounds and mixtures of compounds the following NMR spectrometers were used: Jeol FX 90Q, Bruker ARX 250, AC 300, DRX 500. Chemical shifts δ are given in ppm, positive values indicate a shift to higher frequency (lower field) with respect to the reference. External references are: tetramethylsilane (δ^{1}H (CHCl$_3$) 7.24, δ^{1}H (C$_6$D$_5$H) 7.15, δ^{13}C (CDCl$_3$) 77.0, δ^{13}C (C$_6$D$_6$) 128.0), boron trifluoride etherate (δ^{11}B 0 for Ξ(^{11}B) 32.083971 MHz). All assignments are based on combinations of 1D heteronuclear double resonance experiments ^{1}H{^{11}B}, 2D ^{1}H/^{1}H COSY, ^{13}C/^{1}H HETCOR and triple resonance experiments ^{13}C{^{1}H,^{11}B} with selective ^{11}B decoupling.

Electron impact (EI) MS spectra: VARIAN MAT CH7 with direct inlet. IR spectra: Perkin–Elmer 983 G, measured in CHCl$_3$ solution at 25 °C. Mössbauer spectrum: measured in transmission mode on a constant acceleration Mössbauer spectrometer at 20 °C; the velocity scale was calibrated relative to a 25 μm α-Fe foil using the positions certified for National Bureau of Standards, standard reference material No. 1541; line widths of 0.28 mm/s for the outer lines of α-Fe were obtained at room temperature. The commercially available fitting program NORMOS (R. A. Brand, Wissenschaftliche Elektronik GmbH, Germany) was used to fit the spectra to Lorentzian lineshapes. The Mössbauer thickness of the sample was approximately 7 mg Fe/cm^2.

1,2,3,4,5,6-Hexaethyl-2,4-dicarba-*nido*-hexaborane(8) (**4**) from the Sodium Salt **6** and Methanol

A suspension of **6** (0.2 g, 0.75 mmol) in hexane (10 ml) was cooled to −78 °C and methanol (0.03 ml, slight excess) was injected in one portion. After warming to room temperature, the liquid phase was decanted from insoluble material, and all readily volatile material was removed *in vacuo*, leaving 0.16 g (87%) of **4**, identified by its ^{1}H, ^{11}B and ^{13}C NMR data[10]. The same reaction carried out with deuterated methanol, CD$_3$OD, gave the same result. The ^{1}H NMR spectrum of **4**, obtained from this reaction, did not show the signal of the ^{1}H(C2-H) signal at δ −1.47 (as a result of selective deuteration), whereas the ^{1}H(B-H-B) signal at δ −2.15 remained unchanged, also with respect to its integral intensity.

Hexaethyl-1,6-dicarba-*closo*-hexaborane(6) (**7**)

Iodine (0.38 g, 1.5 mmol) was added to a solution of **6** (0.4 g, 1.5 mmol) in toluene (5 ml), and the mixture was stirred at room temperature for 10 min. The ^{11}B NMR spectrum showed that the carboranes **4** and **7** were present in a ratio of 4 : 1. Exposure of this mixture to air led to oxidation of the carborane **4**, and **7** was then separated and purified by chromatogra-

phy on silica (10 cm column, 2 cm diameter, eluent hexane) which gave 0.073 g of pure **7**. The reaction of **6** with one equivalent of Et$_2$BCl (added at –78 °C) in toluene gave a complex mixture from which **7** could be isolated in the same way. ^{1}H NMR (250.1 MHz, 25 °C, CDCl$_3$): 1.86 q, 4 H (CH$_2$); 1.11 t, 6 H (CH$_2$-CH$_3$); 1.13 q, 8 H (BCH$_2$CH$_3$); 0.99 t, 12 H (BCH$_2$**CH$_3$**). ^{11}B NMR (80.3 MHz, 25 °C, CDCl$_3$): –10.7. ^{13}C NMR (62.9 MHz, –30 °C, CDCl$_3$): 106.2 br (**C**), 18.3 (C-**CH$_2$**), 12.9 (C-CH$_2$**CH$_3$**), 3.5 br (B**CH$_2$**CH$_3$), 14.1 (BCH$_2$**CH$_3$**). EI MS, *m/z* (%): 241 (100) M$^+$.

2,3,4,5,6,7-Hexaethyl-2,4-dicarba-*closo*-heptaborane(7) (**8**) and
1-Bromo-2,3,4,5,6,7-hexaethyl-2,4-dicarba-*closo*-heptaborane(7) (**9**)

Boron tribromide (0.813 g, 3.24 mmol) was added to a cooled (–78 °C) solution of **6** (0.14 g, 0.53 mmol) in toluene (5 ml). The mixture was stirred for 3 min, warmed to room temperature and stirred for further 20 min. After removing of all the readily volatile material *in vacuo*, the soluble fraction of the residue was taken up in hexane and stirred for further 12 h in air atmosphere. The ^{11}B NMR spectrum showed the presence of **8**, **9** and **7** (ratio 70 : 15 : 5) along with 10% of unidentified boron–oxygen compounds. Fractional distillation gave **8** (0.053 g, 39%; purity >90% according to ^{11}B NMR) as a colourless liquid (b.p. 71–74 °C/0.13 Pa). ^{1}H NMR (500.1 MHz, 25 °C, C$_6$D$_6$): 0.40 br, 1 H, $^1J(^{11}$B,^{1}H) = 170 Hz (B(1)-**H**); 2.26 m, 2 H, 2.22 m 2 H (C(2,4)**CH$_2$**); 0.89 t, 6 H (C(2,4)CH$_2$**CH$_3$**); 0.18 q, 2 H (B(7)**CH$_2$**); 0.65 t, 3 H (B(7)CH$_2$**CH$_3$**); 1.18 q, 2 H (B(3)**CH$_2$**); 0.99 t, 3 H (B(3)CH$_2$**CH$_3$**); 1.32 m, 10 H (B(5,6)**CH$_2$CH$_3$**). ^{11}B NMR (80.3 MHz, C$_6$D$_6$): –23.5 $^1J(^{11}$B,^{1}H) = 170 Hz (B(1)), 12.7 (B(3)), 9.4 (B(5,6)), –10.8 (B(7)). ^{13}C NMR (125.8 MHz, 25 °C, C$_6$D$_6$; assignments based on selective ^{11}B decoupling): 91.9 br (C(2,4)), 19.9 (C(2,4)**CH$_2$**), 14.1 (C(2,4)CH$_2$**CH$_3$**), 10.1 br (B(7)**CH$_2$**), 11.1 (B(7)CH$_2$**CH$_3$**), 2.3 br (B(3)**CH$_2$**), 11.9 (B(3)CH$_2$**CH$_3$**), 3.3 br (B(5,6)**CH$_2$**), 12.7 (B(5,6)CH$_2$**CH$_3$**). EI MS, *m/z* (%): 253 (100) M$^+$. IR, ν(BH) [cm^{-1}]: 2 587 (s). **9** (in mixture with **8**): ^{1}H NMR (500.1 MHz, 25 °C, C$_6$D$_6$): 0.04 q, 2 H (B(7)**CH$_2$**); 0.57 t, 3 H (B(7)CH$_2$**CH$_3$**), other signals overlap with those of **8**, and could not be accurately assigned. ^{11}B NMR (80.3 MHz, C$_6$D$_6$): –21.9 (B(1)), –15.7 (B(7)), 13.9 (B(3)), 13.0 (B(5,6)). ^{13}C NMR (125.8 MHz, 25 °C, C$_6$D$_6$; with selective ^{11}B decoupling): 96.2 br (C(2,4)), 20.3 (C(2,4)**CH$_2$**), 12.3 (C(2,4)CH$_2$**CH$_3$**), 3.1 br (B(5,6)**CH$_2$**), other signals could not be assigned with certainty.

Bis[hexaethyl-2,4-dicarba-*nido*-hexaborate(1$^-$)]iron (**10**)

Iron dichloride (0.104 g, 0.82 mmol) was added to a solution of **6** (0.43 g, 1.64 mmol) in tetrahydrofuran (10 ml), and the mixture was stirred at room temperature for 2 h. Stirring was continued in air for further 10 h. After removing the solvent *in vacuo*, the residue was extracted with hexane. Hexane was removed from the extract *in vacuo*, and the residue (this material was used for ^{57}Fe Mössbauer spectroscopy) was dissolved in a mixture of toluene (1 ml) and acetonitrile (1.5 ml). Cooling of this solution at –78 °C afforded 0.21 g (47%) of **10** as deep-red prism- or irregularly shaped crystals (m.p. 221–225 °C, without decomposition). ^{1}H NMR (250.1 MHz, 25 °C, C$_6$D$_6$): –6.11 br, 2 H (Fe-H-B(5,6)); 1.64 m, 8 H (C(2,2′,4,4′)**CH$_2$**); 0.90 t, 12 H (C(2,2′,4,4′)CH$_2$**CH$_3$**); –0.07 q, 4 H (B(1,1′)**CH$_2$**), 0.56 t, 6 H (B(1,1′)CH$_2$**CH$_3$**); 2.27 q, 4 H (B(3,3′)**CH$_2$**); 1.39 t, 6 H (B(3,3′)CH$_2$**CH$_3$**); 1.48 m, 4 H, 1.12 m, 4 H (B(5,5′,6,6′)**CH$_2$**); 1.37 t, 12 H (B(5,5′,6,6′)CH$_2$**CH$_3$**). ^{11}B NMR (80.3 MHz, C$_6$D$_6$): 12.2 (B(1,1′)), 17.3 (B(3,3′)), –2.2 (B(5,5′,6,6′)). ^{13}C NMR (125.8 MHz, 25 °C, C$_6$D$_6$; assignments based on selective ^{11}B decoupling): 71.2 br (C(2,2′,4,4′)), 23.8 (C(2,2′,4,4′)**CH$_2$**), 14.9

(C(2,2′,4,4′)CH$_2$**CH$_3$**), 14.3 br (B(1,1′)**CH$_2$**), 10.6 (B(1,1′)CH$_2$**CH$_3$**), 5.0 br (B(3,3′)**CH$_2$**), 12.8 (B(3,3′)CH$_2$**CH$_3$**), 8.2 br (B(5,5′,6,6′)**CH$_2$**), 12.9 (B(5,5′,6,6′)CH$_2$**CH$_3$**). EI MS, *m/z* (%): 542 (20) M$^+$, 541 (50) M$^+$ – H, 540 (60) M$^+$ – 2 H, 511 (100) M$^+$ – 2 H – Et, 308 (30) M$^+$ – Et$_6$C$_2$B$_4$.

X-Ray Structural Analysis[17]

Compound **10** (C$_{28}$H$_{62}$B$_8$Fe (*M* = 541.1)): dark-red, irregularly shaped crystal, 0.35 × 0.25 × 0.20 mm^3, sealed in a Lindemann capillary; monoclinic, space group *P2$_1$/n* with lattice parameters: *a* = 1 136.2(2), *b* = 1 247.7(2), *c* = 1 202.0(2) pm, β = 92.85(3)°, *Z* = 2, *V* = 1 701.9(5)·10^6 pm^3; *F*(000) = 592; μ = 0.459 mm^{-1}; absorption correction (semiempirical on the basis of Ψ-scans): min/max transmission 0.4376/0.4816; reflection intensities were collected on a Siemens P4 diffractometer (MoKα, λ = 71.073 pm, graphite monochromator) in the range of 2° ≤ 2φ ≤ 55° at 296 K; 5 029 reflections were measured of which 3 853 were independent and 2 409 observed (*F$_o$* ≥ 2σ(*F$_o$*)); after Lorentz and polarisation corrections, the structure was solved by Direct Methods followed by consecutive difference Fourier syntheses (program SHELXTL V4.2); refinement against *F* with all non-hydrogen atoms anisotropic except for the ethyl carbon atoms (ethyl groups are disordered); the hydrogen atom H1A close to the iron atom was located as highest difference peak in the Fourier synthesis, the remaining hydrogen atoms were calculated and refined using the riding model with fixed isotropic temperature factors (*U* = 0.08 Å^2); the refinement with 159 parameters converged at *R* = 0.1101 and *wR* = 0.0771, the max/min residual electron density was 0.52/–0.42·10^{-6} e pm^{-3}.

RESULTS AND DISCUSSION

Syntheses

The reactions of the anion **6** studied in this work are summarised in Scheme 2. Reaction conditions and the stoichiometry of these reactions were not optimised. It was mainly intended to explore some potential changes of the skeleton of the carborane cluster starting from **6**.

Treatment of **6** with methanol or deuterated methanol leads back to **4** without side reactions. Labelling with deuterium occurs only at the *endo*-C(2) position and not in the B–H–B bridge. The reaction of **6** with iodine was originally planned to induce oxidative cage fusion[18] towards *nido*-C$_4$B$_8$ systems[19]. Similarly, the synthesis of the sandwich complex **10** was started in order to give finally *nido*-C$_4$B$_8$ systems by oxidative fusion[19]. However, in the case of the reaction with iodine, the way to the *closo*-1,6-C$_2$B$_4$ cage turns out to be much more favoured. Although, it cannot be excluded that there are traces of *nido*-C$_4$B$_8$ carboranes, the tendency of their formation is apparently very low. In the case of the iron complex **10**, it appears that this product, of which we initially thought as a potential reactive intermediate, is extremely stable. The integration of another boron atom into the cage to give the *closo*-2,4-C$_2$B$_5$-cage in **8** and **9** also came as a sur-

prise. It was unexpected, in particular, that the 1-bromo derivative **9** is only a side product whereas the hexaethyl-2,4-dicarba-*closo*-heptaborane(7) **8** is the major product. An attempt to improve this reaction by using HBBr$_2$–SMe$_2$ instead of BBr$_3$ gave only unidentified products. Peralkylated derivatives with the 2,4-dicarba-*closo*-heptaborane skeleton were obtained previously by dehalogenation of ethylboron halides[20]. It was of interest to prepare a carborane of type **4** without an endocyclic C–H bond. However, various attempts at the methylation of **6** gave only complex mixtures of unidentified products together with varying amounts of the carborane **4** (as indicated by the typical $\delta^{11}B$ values). Similarly, the reaction of **6** with Me$_3$SiCl failed (traces of **7** were found in the reaction mixtures). It is noteworthy, that there is no evidence so far of the existence of carboranes of type **4** in which the unique endocyclic C–H group is replaced by a C–C, C–Si or C–B bond.
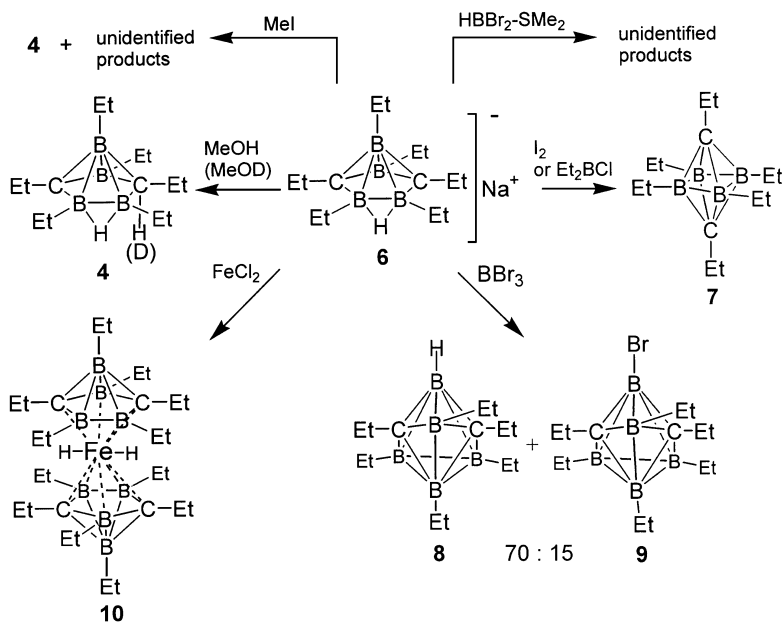
SCHEME 2
Reactivity of sodium hexaethyl-2,4-dicarba-*nido*-hexaborate(1⁻) towards methanol and various electrophiles

NMR Spectroscopic Characterisation

The carborane **7** is readily identified, already in trace amounts in reaction mixtures, by its sharp ($h_{1/2}$ = 40 Hz) ^{11}B NMR signal at δ –10.7 (parent compound 1,6-C$_2$B$_4$H$_6$: δ^{11}B –18.7, ref.[2]). All other NMR data (^{1}H, ^{13}C) support the structural assignment. In the case of **8** and **9**, the δ^{11}B values follow the trend of the data for the parent compound[21] 2,4-C$_2$B$_5$H$_7$, given for the different substitution pattern, and number and relative intensities of signals in the ^{1}H and ^{13}C NMR spectra are in agreement with the proposed structures of **8** and **9**. Since **8** could be obtained in a pure state, the most relevant signals of **9** could be assigned in mixtures of **8** and **9**. In all three cases of **7**–**9**, ^{13}C NMR spectra with broad band ^{1}H and selective ^{11}B decoupling proved very useful for establishing the C–B connectivity in the cages. The δ^{11}B data of the iron sandwich complex **10** are rather different from those of **6** or **4**, as expected[22] for a *closo*-structure in **10**. The fate of the two bridging hydrogen atoms is of particular interest. In solution, a moderately broad ($h_{1/2}$ = 10 Hz) ^{1}H NMR signal at a typically high field (δ^{1}H –6.11) suggests that the protons are in the close neighbourhood of the iron atom, and scalar ^{11}B-^{1}H spin-spin couplings are weak. By selective decoupling of ^{11}B(3), the line width did not change, whereas in the corresponding ^{1}H{^{11}B(5,6)} experiment a sharper ($h_{1/2}$ = 4 Hz) ^{1}H NMR signal was observed. This suggests that in solution the two hydride hydrogen atoms are triply-bridging the iron atom and the boron atoms B(5,6) and B(5′,6′), respectively.
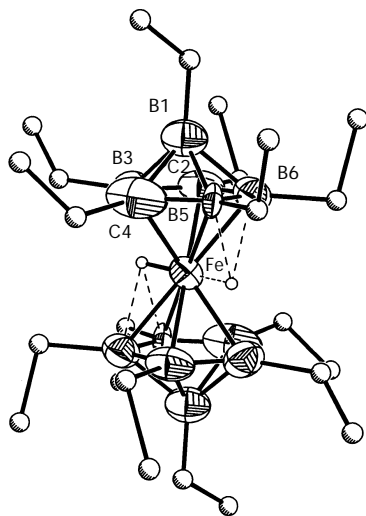

Fig. 1

Molecular structure of the sandwich complex **10** as determined by X-ray structural analysis[16]. Selected bond lengths (pm) and angles (°): Fe–C(2) 209.3(7), Fe–B(3) 216.8(8), Fe–C(4) 216.7(9), Fe–B(5) 211.8(7), Fe–B(6) 211.3(8), B(1)–B(3) 177.7(12), B(1)–B(5) 175.1(13), B(1)–B(6) 179.5(12), B(1)–C(2) 171.5(11), B(1)–C(4) 174.3(13), C(2)–B(3) 154.2(11), C(2)–B(6) 156.2(11), B(3)–C(4) 175.4(13), C(4)–B(5) 150.3(12), B(5)–B(6) 152.4(10); C(2)–B(3)–C(4) 101.2(6), B(3)–C(2)–B(6) 113.7(6), C(2)–B(6)–B(5) 106.1(6), C(4)–B(5)–B(6) 113.2(7)

X-Ray Structural Analysis of *10*

The molecular structure of **10** is shown in Fig. 1; selected data of bond lengths and angles are given in the caption. In spite of some disorder of the ethyl groups[17], the important structural features are evident. The two carborane units are arranged parallel, the deviation of the five atoms C(2)B(3)C(4)B(5,6) from a plane is small (mean deviation 0.7 pm), and the iron atom lies on the inversion centre of symmetry. The distances Fe–B(5,6) (211.8(7), 211.3(8)) and Fe–C(2) (209.3(7)) are almost identical within experimental error, whereas the distances Fe–C(4) (216.7(9) pm) and Fe–B(3) (216.8(8)) are slightly larger. The bridging hydrogen atoms were located, and their positions are closer to the iron atom than to B(5,6) and B(5′,6′), respectively. This is in agreement with the NMR data for the solution (*vide supra*).

^{57}Fe Mössbauer Spectroscopy of *10*

The Mössbauer spectrum of the isolated raw material shows two doublets with the following hyperfine parameters: δ_1 (relatively to α-Fe) = 0.231(5) mm/s; Δ_1 = 2.25 mm/s; Γ_1 = 0.24(1) mm/s; area$_1$ = 75%; δ_2 (relatively to α-Fe) = 0.16(2) mm/s; Δ_2 = 0.77(2) mm/s; Γ_2 = 0.27(4) mm/s; area$_2$ = 25%. The major doublet corresponds to iron in the environment of **10**, the minor doublet indicates the presence of an additional iron-containing phase (arising from incomplete conversion of the starting material) which could not be isolated in pure state. The linewidths are narrow, implying that the environments are well defined and discrete. The quadrupole splitting of the dominant doublet is similar to the value for ferrocene, while the centre shift is significantly less (ferrocene parameters are δ (relatively to α-Fe) = 0.53 mm/s; Δ_1 = 2.37 mm/s, ref.[24]). This may indicate a similar symmetry of the charge distribution around the iron atom in **10** when compared with ferrocene; however, the overall charge at the iron atom and its redistribution towards the ligands appears to be different from the situation encountered in ferrocene.

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