

Hexaethyl-2,4-dicarba-*nido*-hexaborane(8), Deprotonation and Complexation Studied by NMR Spectroscopy and Density Functional Theory (DFT) Calculations

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Deprotonation of hexaethyl-2,4-dicarba-*nido*-borane(8) **2** leads first to the hexaethyl-2,4-dicarba-*nido*-borate(1[−]) **3**, and further deprotonation, using BuLi/KO^tBu, gives the hexaethyl-2,4-dicarba-*nido*-hexaborate(2[−]) **4**. The reaction of **3** with FeCl₂ affords the *commo*-ferracarborane [Fe(Et₆-2,4-C₂B₄H)₂] **5**, and the analogous reaction of **4** leads to the anionic sandwich complex [Fe(Et₆-2,4-C₂B₄H)₂]^{2−} **6** which can be protonated to give **5**. The complex **5** contains two hydrido ligands, each bridging the iron and two boron atoms. Reactions were monitored and the products were characterised by ¹¹B NMR spectroscopy in solution. The geometries of the carboranes, the borates (all unsubstituted and permethyl-substituted) and the iron complexes (all unsubstituted) were optimised by DFT methods [B3LYP/6-311+G(d,p) or B3LYP/6-31+G(d)], and the relevant NMR data [chemical shifts δ¹¹B, δ¹³C, δ⁵⁷Fe, and coupling constants ¹J(¹³C, ¹H), ¹J(¹¹B, ¹H), ¹J(⁵⁷Fe, ¹H), ¹J(⁵⁷Fe, ¹¹B)] were calculated at the same level of theory.

Key words: Carboranes, Iron Complexes, NMR, MO Calculations

Introduction

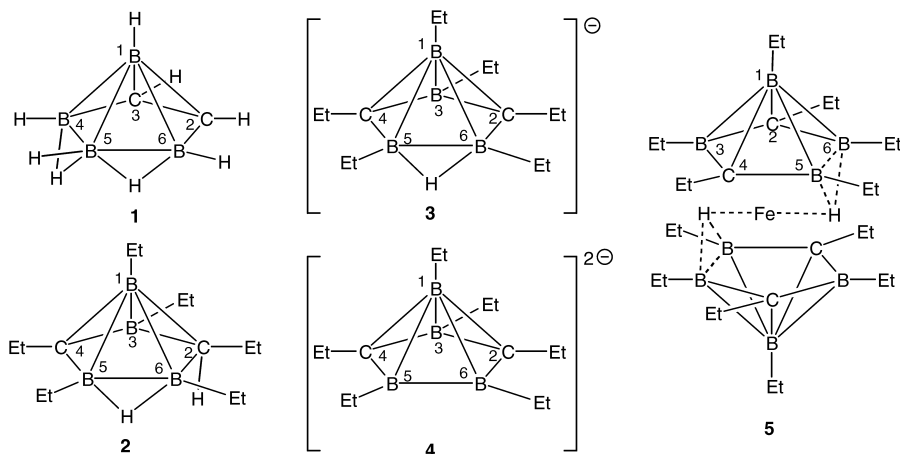
The 2,3-dicarba-*nido*-hexaborane(8) **1** and its C-substituted derivatives are well known [1, 2] and readily accessible by the reaction of pentaborane(9) with alkynes. The chemistry of these carboranes deals mainly with the anions [2,3-R₂C₂-B₄H₅][−] and [2,3-R₂C₂-B₄H₄]^{2−} [3, 4], which are both versatile ligands in the coordination chemistry of s, p, d, and f block elements [5, 6], as one would expect considering the similarity of the open face of the anions with the cyclopentadienyl anion. In contrast, the isomeric parent carborane with non-adjacent carbon atoms, the 2,4-dicarba-*nido*-hexaborane(8), is still unknown, although the parent 2,4-dicarba-*nido*-hexaborate(1[−]) [2,4-C₂B₄H₇][−] has been identified in mixtures by NMR spectroscopy [7]. Some 2,4-C₂-disubstituted (mainly with trimethylsilyl substituents) dianions and monoanions have been prepared, starting from the corresponding 1,6-C₂-disubstituted 1,6-dicarba-*closo*-hexaboranes(6), and were used as ligands [8]. We have shown that the synthesis of the hexaethyl-2,4-dicarba-*nido*-hexaborane(8) **2** can be achieved by BH-catalysed condensation of poly(diethylboryl)alkanes [9, 10]. The *endo*-CH unit of the carborane **2** can be

deprotonated to give the hexaethyl-2,4-dicarba-*nido*-hexaborate(1[−]), [Et₆-2,4-C₂B₄H][−] **3**, which has been characterised by X-ray analysis as the sodium salt [10]. Some reactions of **3** with electrophiles have already been reported, including protonation, which leads back to **2**, and the reaction with FeCl₂ to the ferrocene-like sandwich complex the *commo*-ferracarborane [Fe(Et₆-2,4-C₂B₄H)₂] **5** [10, 11]. In the present work, we report on the attempts to obtain the perethylated dianion [Et₆-2,4-C₂B₄]^{2−} **4**, the reaction of **4** with FeCl₂, and on experimental and calculated NMR data of the carboranes **2**, the borates **3** and **4**, and the iron complexes (chemical shifts and coupling constants), including the ⁵⁷Fe NMR data of the iron complex **5**.

Results and Discussion

Deprotonation of 2 and reactions of the anions 3 and 4 with FeCl₂

The anion **3** is accessible by the reaction of **2** with Na[Et₃BH] [10]. An excess of the hydride did not lead to further deprotonation. However, when the sodium salt of **3** [δ¹¹B −39.1(1), +28.9(3), +10.3(5,6)] has been added to BuLi/KO^tBu in hexane/THF [12] the dianion **4** was formed, according to the new ¹¹B NMR



Formulae 1–5.

signals [$\delta^{11}\text{B}$ –48.0(1), +10.5(3), +20.4(5,6)] of the reaction solution. Addition of an excess of methanol to this solution gave back the carborane **2** ($\delta^{11}\text{B}$ –27.8(1), +39.6(3), +17.8(5), +12.3(6)]. After filtration of the reaction mixture containing **4**, and addition of hexane, a colourless, extremely air- and moisture-sensitive powder precipitated. This powder was isolated, dissolved in THF, and it gave the same ^{11}B NMR signals as the reaction solution. After adding FeCl_2 to this THF solution, an orange-red colour developed, and the ^{11}B NMR signal of **4** at lowest frequency disappeared, while three new signals (ratio of 1:1:2) were detected [$\delta^{11}\text{B}$ –19.0(1), +6.5(3), +1.0(5,6)] and assigned to the anionic sandwich complex **6** (Scheme 1). Attempts to remove THF in vacuum left a viscous, red-brown oil. Addition of $[\text{PPh}_4]\text{Br}$ or $[\text{Ph}_3\text{PMe}]\text{Br}$ to the THF solution, in order to exchange the respective cation (Li, Na or K), did not lead to defined products. However, addition of NH_4Cl and hexane to the THF solution, followed by filtration, gave the complex **5** (Scheme 1), readily identified by its known properties [11] [$\delta^{11}\text{B}$ +12.2(1), +17.3(3), –2.2(5,6)]. This reaction could proceed *via* the complex **7**, although we could not detect the ^{11}B NMR signals of **7** in the reaction mixture.

Constitution of the iron sandwich complex 5, determined by ^{57}Fe NMR spectroscopy

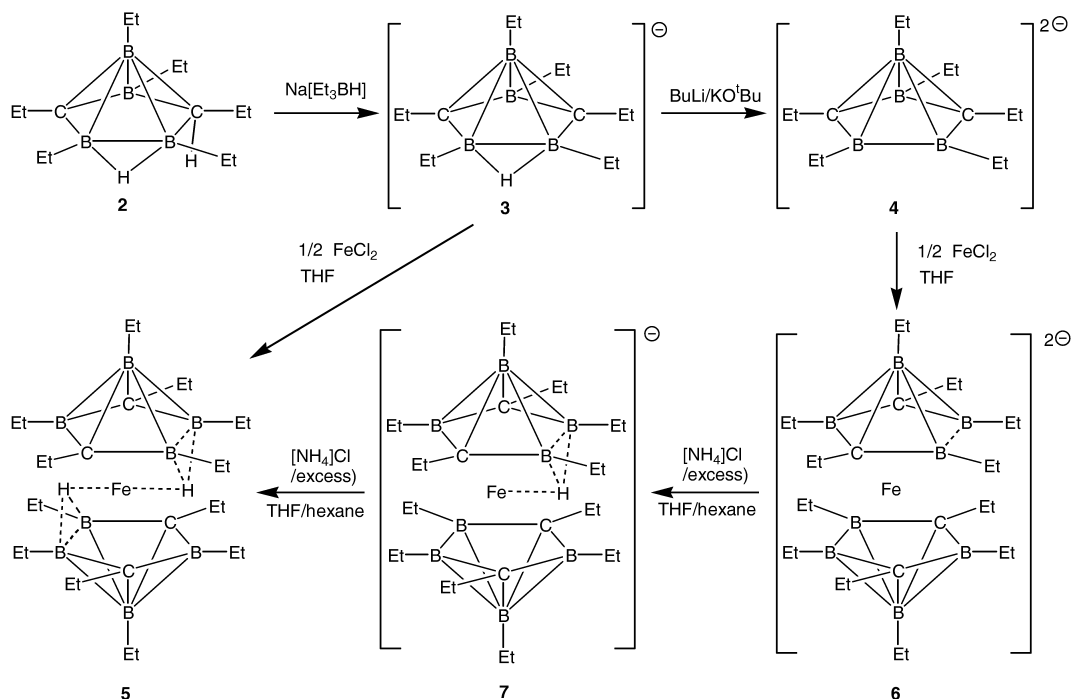
The crystal structures of **5** [11] and also of related iron complexes containing the 2,3- C_2 -substituted borate anion as ligands have been determined [13]. However, the positions of the hydrogen atoms in the vicinity of the iron atom could not be located. The chemical

shifts $\delta^1\text{H}$ in the range between –6 to –10 ppm indicate the presence of Fe–H bonds. However, a selective $^1\text{H}\{^{11}\text{B}(5,6)\}$ heteronuclear decoupling experiment in the case of **5** showed clearly that the boron atoms in 5,6-positions are also attached to this hydrogen atom [11], and therefore, it can be assumed that each of the B–H hydrogen atoms forms a bridge between the iron and the two boron atoms. This assumption is now firmly supported by the ^{57}Fe NMR spectrum of **5** (Fig. 1) which shows a broadened 1:2:1 triplet as a result of ^{57}Fe – ^1H spin-spin coupling [$^1J(^{57}\text{Fe}, ^1\text{H}) = 8\text{ Hz}$] at rather high frequency. The magnitude of $^1J(^{57}\text{Fe}, ^1\text{H})$ is typical for a one-bond coupling [14]. The marked ^{57}Fe nuclear magnetic deshielding by > 3000 ppm relative to ferrocene is qualitatively reflected by the observed [11] significant difference between the Mössbauer spectra of **5** and ferrocene.

The optimised calculated geometry of **5***, the parent derivative of **5** (*vide infra*), confirms the prominent structural features, in particular the hydrogen bridges above the $\text{FeB}(5)\text{B}(6)$ triangular faces. Furthermore, calculated NMR parameters of **5*** (*vide infra*) compare favourably with the experimental data.

DFT calculations of the geometries and NMR parameters of the carboranes, anions, and commo-ferracarboranes

The geometries of hexamethyl-2,4-dicarba-*nido*-hexaborane(8) (**2Me**₆) and of the anion $[\text{Me}_6\text{C}_2\text{B}_4\text{H}]^-$ **3Me**₆ have already been optimised [MP2(fc)/6-31+G(d)] [15]. We have repeated this procedure at the B3LYP/6-311+G(d,p) level of theory for the parent carborane *nido*-2,4- $\text{C}_2\text{B}_4\text{H}_8$ **2***, **2Me**₆, the an-



Scheme 1. Deprotonation of the carborane **2** takes place stepwise, first to the anion **3**, and then, with a stronger base, to the dianion **4**. Reaction of **4** with FeCl₂ affords the anionic sandwich complex **6** which is protonated by an excess of [NH₄]Cl to give **5**. The proposed intermediate **7** was not observed.

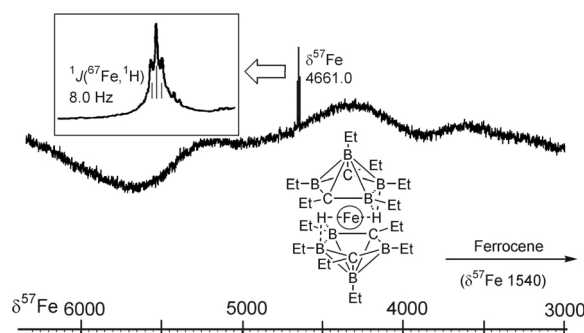


Fig. 1. 16.2 MHz ⁵⁷Fe NMR spectrum of **5** (100 mg in 0.5 ml of C₆D₆; see also Experimental section). The full spectrum as shown was obtained after 30 h of spectrometer time (185000 transients). The rolling baseline is typical of NMR spectra of low-γ nuclei measured by single pulse techniques. The insert shows the splitting of the ⁵⁷Fe NMR signal into a triplet and results from the spectrum after 75 h of measurement time (444000 transients).

ions [2,4-C₂B₄H₇][−] **3*** and 3Me₆, the dianion [2,4-C₂B₄H₆]^{2−} **4*** and 4Me₆. The geometries of the unsubstituted iron complexes **5***, **6*** and **7*** were optimised on the B3LYP/6-31+G(d) level of theory. All structural parameters are in good agreement with those of pre-

vious calculations [8a, 15] or with results from X-ray crystallography if available [10, 11]. In the iron complexes **5*** and **7***, the triply bridging hydrogen is an important structural feature. The structures of **5*** and **6*** possess a centre of symmetry at the iron atom, in agreement with the molecular structure of **5** in the solid state [11], whereas the different anions in **7*** cause a slight distortion of the geometry, as shown by the angle of 171.5° at the iron and the two different apical boron atoms. The energy of **7*** is lower by 53.4 kcal/mol relative to the mean energy of **5*** and **6***. Therefore, **7** can be an intermediate on the reaction of **6** to **5** (Scheme 2). Selected geometrical parameters are listed in Table 1.

The remarkable progress in the quantum chemical treatment of molecular structures at reasonable cost of computing time has opened the access to calculated NMR parameters such as chemical shifts δX and indirect nuclear spin-spin coupling constants $J(\text{X}, \text{Y})$ [16, 17].

Calculated ¹¹B chemical shifts (Table 2) agree well with experimental data, given for the different substituents at boron and carbon, as has been shown previously for numerous examples [15, 18, 19]. In the case

Table 1. Selected calculated^a bond lengths [pm] for the carboranes **2**, the anions **3**, dianions **4**, and the iron complexes **5**–**7**.

	B1-C2	B1-B3	B1-C4	B1-B5/6	C2-B3	B3-C4	C4-B5	B5-B6	B6-C2	Fe-C2	Fe-B3	Fe-C4	Fe-B5/6	Fe-H	B5/6-H
2 ^b	169.8	178.5	170.0	175.8, 171.8	167.4	149.4	155.1	174.3	162.5	–	–	–	–	–	135.8, 130.8
2Me ₆ ^c	172.5	180.8	170.9	176.6, 172.4	167.7	150.1	156.3	174.6	164.6	–	–	–	–	–	136.5, 131.2
3 [*]	171.3	183.0	171.3	175.4	153.3	153.3	154.3	177.6	154.3	–	–	–	–	–	120.5
3Me ₆	171.5	185.4	171.5	176.3	153.8	153.8	154.8	177.1	154.8	–	–	–	–	–	120.6
4 [*]	171.0	181.1	171.0	180.9	154.7	154.7	157.1	167.3	157.1	–	–	–	–	–	–
4Me ₆	173.0	181.7	173.0	181.0	154.9	154.9	157.3	166.6	157.3	–	–	–	–	–	–
5 [*]	171.1	182.0	171.1	176.0	155.0	155.0	154.0	179.0	154.0	212.0	213.4	212.0	226.6	165.9	142.0
^d	171.1	182.1	171.1	176.0	155.4	155.4	154.6	179.3	154.6	212.0	213.4	212.0	226.6	165.9	143.0
6 [*]	172.6	188.6	172.6	182.0	157.5	157.5	158.2	167.7	158.2	211.2	210.7	211.2	216.3	–	–
7 [*]	169.9	184.0	169.9	176.9	156.0	156.0	154.9	177.2	154.9	210.9	209.6	210.9	223.3	163.3	146.0
^d	170.0	183.1	170.0	170.0	155.7	155.7	155.5	168.7	155.5	210.9	211.9	210.9	213.6	–	–

^a Geometries of the unsubstituted **2**^{*}, **3**^{*}, **4**^{*}, and the hexamethyl derivatives **2Me**₆, **3Me**₆, **4Me**₆ were calculated at the B3LYP/6-311+G(d,p) level; the geometries of the unsubstituted iron complexes **5**^{*}, **6**^{*} and **7**^{*} were calculated at the B3LYP/6-31+g(d) level. If not noted otherwise;

^b distance B3-H(CH) 182.6 pm; angle H-C2-B3 79.2°; angle H-C2-B6 98.9°; ^c distance B3-H(CH) 184.4 pm; angle H-C2-B3 80.1°; angle H-C2-B6 94.7°; ^d B3LYP/6-311+G(d,p).

of ⁵⁷Fe chemical shifts, the situation is less favourable, although correct trends can be predicted by using DFT methods [20]. Indeed, the differences in the calculated shielding constants $\sigma^{57}\text{Fe}$ of ferrocene (–4926.8) and **5**^{*} (–7832.5) and Fe(CO)₅ (–2764.8) are close to the differences in the experimental $\delta^{57}\text{Fe}$ data of ferrocene (+1540.0) and **5** (+4661.0), if Fe(CO)₅ is selected as the reference with $\delta^{57}\text{Fe} = 0.0$ [21]. The ⁵⁷Fe nuclear magnetic shielding in the dianionic sandwich complex **6**^{*} is predicted to be similar to that in **5**^{*}, whereas the calculated ⁵⁷Fe shielding in **7**^{*} is increased by about 1300 ppm relative to **5**^{*}. Clearly, the additional B-H-Fe bridges are not responsible for the huge deshielding of ⁵⁷Fe in **5**. The experimental $\delta^{57}\text{Fe}$ value for **5** is the first example for iron as part of a *closo*-structure. Work is in progress in order to show that the ⁵⁷Fe shielding in *nido*-ferraboranes or *nido*-ferracarboranes is much increased relative to that in **5**, and thus similar to that in cyclopentadienyl iron complexes.

The application of DFT hybrid methods such as B3LYP [22], together with a fairly large basis set, *e.g.* 6-311+G(d,p), provides meaningful values for coupling constants $J(\text{X},\text{Y})$ [23], as has been shown already for polyhedral boranes [24], cyclic hydrocarbons [24,26], carbenes [27], and cyclopentadienyl iron complexes [28] to name just a few applications.

An intriguing feature of the 2,4-dicarba-*nido*-hexaborane(8) **2** is the *endo*-CH hydrogen, since it is supposed to form a C(2)-H-B(3) bridge [15]. Such a bridge can be suggested on the basis of the $\delta^1\text{H}$ value (–1.47) and the magnitude of $^1J(^{13}\text{C}(2), ^1\text{H}_{\text{endo}}) = 100.0$ Hz. The latter evidence is not fully convincing in the case of **2**, because the comparison with $^1J(^{13}\text{C}, ^1\text{H}_{\text{exo}})$ is not possible. However, the calculated coupling constants

Table 2. Chemical shifts $\delta^{11}\text{B}$ and $\delta^{13}\text{C}$ (found^a and calcd.^b) for the carboranes **2**, the anions **3**, dianions **4**, and the iron complexes **5**–**7**.

	$\delta^{11}\text{B}(1)$	$\delta^{11}\text{B}(3)$	$\delta^{11}\text{B}(5,6)$	$\delta^{13}\text{C}(2)$	$\delta^{13}\text{C}(4)$
2 [*]	–42.5	+35.6	+11.9, +3.2	+23.3	+83.7
[MP2/6-31G(d)] ^c	–36.8	+34.2	+12.5, +4.3	+21.0	+67.8
2Me ₆	–26.3	+40.5	+15.5, +10.7	+32.9	+91.7
[MP2/6-31G(d)] ^c	–23.8	+39.3	+16.9, +10.3	+24.1	+72.4
2 (found)	–27.8	+39.6	+17.8, +12.3	+41.3	+91.5
3 [*]	–60.0	+17.5	–3.4	+74.2	+74.2
3 [*] (found) ^d	–51.9	+21.2	+0.8	+75.2	+75.2
3Me ₆	–44.2	+23.3	+12.4	+78.9	+78.9
3 (found)	–39.1	+28.9	+10.3	+86.5	+86.5
4 [*]	–73.9	+3.2	+1.1	+76.8	+76.8
4Me ₆	–55.4	+7.9	+16.4	+83.9	+83.9
4 (found) ^e	–48.0	+10.5	+20.4	n. m.	n. m.
5 [*]	–10.4	+12.6	–12.2	+65.1	+65.1
5 (found)	+12.3	+17.3	–2.2	+71.2	+71.2
6 [*]	–23.9	+3.0	+0.8	+54.1	+54.1
6 (found) ^e	–19.0	+6.5	+1.0	n. m.	n. m.
7 [*]					

^a Taken from ref. [10, 11] if not stated otherwise; ^b see Experimental section; ^c ref. [15]; ^d ref. [7, 19].

$^1J(^{13}\text{C}(2), ^1\text{H}_{\text{exo}}) = 157.9$ Hz and $^1J(^{13}\text{C}(2), ^1\text{H}_{\text{endo}}) = 114.9$ Hz for the unsubstituted **2**^{*} demonstrate the unique properties of the *endo*-CH hydrogen. The reduced magnitude of $^1J(^{13}\text{C}(2), ^1\text{H}_{\text{endo}})$ indicates an activation of the C(2)-H_{endo} bond by the neighbored boron atoms. The calculated value $^1J(^{13}\text{C}(2), ^1\text{H}_{\text{endo}}) = 113.9$ Hz for **2Me**₆ is in reasonable agreement with that found for **2** (100 Hz).

According to the calculated coupling constants $^1J(^{11}\text{B}(5,6), ^1\text{H})$, the nature of the B-H-B bridge in the neutral carboranes **2**^{*} ($^1J(^{11}\text{B}(5,6), ^1\text{H}) = 43.0, 50.9$ Hz) and **2Me**₆ ($^1J(^{11}\text{B}(5,6), ^1\text{H}) = 41.1, 49.8$ Hz), and in the anions **3**^{*} ($^1J(^{11}\text{B}(5,6), ^1\text{H}) = 47.8$ Hz) and **3Me**₆ ($^1J(^{11}\text{B}(5,6), ^1\text{H}) = 47.5$ Hz) does not

change significantly. Therefore, the coupling constant $^1J(^{11}\text{B}(5,6), ^1\text{H})$ in the iron complex of type **5** is of interest, because a significant change in the properties of the B-H bonding is predicted. In the case of **5***, the calculation of the coupling constants was carried out, using the 6-311+G(d,p) basis set and the B3LYP method. The magnitude of $^1J(^{11}\text{B}(5,6), ^1\text{H}) = 31.5$ in **5*** is significantly smaller than for **2** or **3**, as a result of the additional bridge to the iron atom. This mirrors also the changes in the calculated B-H bond lengths (Table 1).

The calculated coupling constant $^1J(^{57}\text{Fe}, ^1\text{H}) = 7.8$ Hz for **5*** is in good agreement with the experimental value observed for **5** (Fig. 1). This calculation also provides information on the magnitude of $^1J(^{57}\text{Fe}, ^{11}\text{B})$ [2.0 Hz for B(3), and 0.8 Hz for B(5,6)], which is important with respect to the line width of the ^{57}Fe NMR signal. Since the coupling constants are small and ^{11}B nuclear spin quadrupolar relaxation is fast, broadening of the ^{57}Fe NMR signal owing to unresolved ^{57}Fe - ^{11}B spin-spin coupling will be negligible for most purposes, as can be seen in Fig. 1.

Conclusion

The hexaethyl-2,4-dicarba-*nido*-hexaborate(2[−]), $[\text{Et}_6\text{C}_2\text{B}_4]^{2-}$ **4**, and the correspondingly *commo*-ferracarborate(2[−]), $[\text{Fe}(\text{C}_2\text{B}_4\text{Et}_6)_2]^{2-}$ **6**, were prepared and characterised in solution by ^{11}B NMR spectroscopy. The related known *commo*-ferracarborane, $[\text{Fe}(\text{C}_2\text{B}_4\text{Et}_6\text{H})_2]$ **5**, available from the reaction of hexaethyl-2,4-dicarba-*nido*-borate(1[−]), $[\text{Et}_6\text{C}_2\text{B}_4\text{H}]^-$ **3** with FeCl_2 or from protonation of **6**, was characterised by ^{57}Fe NMR, by which the presence of triply bridging hydrido ligands could be firmly established. The bonding situation in the 2,4-dicarba-*nido*-boranes(8) of type **2**, the borate anions of type **3** and **4**, and the *commo*-ferraboranes **5** and **6** was also studied by DFT calculations with respect to their geometry and NMR parameters (chemical shifts and coupling constants). The coupling constants reflect the nature of the *endo*-CH hydrogen in **2**, the B-H-bridges in **2** and **3**, and the triple bridging in **5**.

Experimental Section

The preparative work was carried out using carefully dried solvents, oven-dried glass ware, and taking all precautions to exclude traces of oxygen. The carborane **2** and the anion **3** were prepared as described [10]. The reaction of **3** with FeCl_2 in THF was used [11] to obtain a sufficient amount of the complex **5** for the ^{57}Fe NMR measurement. ^{11}B NMR

spectra (80.3 and 160.6 MHz) were recorded, using Bruker ARX 250 and DRX 500 spectrometers. The ^{57}Fe NMR spectra (16.2 MHz) were measured using a Bruker DRX 500 spectrometer, equipped with a tunable low frequency triple resonance probehead for 5 mm tubes (fixed ^1H and ^{31}P frequencies), for which the duration of the 90° pulse for ^{57}Fe NMR was 80 μs . The ^{57}Fe 90° pulses were calibrated using the ^{73}Ge NMR signal of GeCl_4 , since this signal is readily observed with a single transient, and the resonance frequency of ^{73}Ge (17.45 MHz) is reasonably close to that of ^{57}Fe . A concentrated solution of **5** (100 mg in 0.5 ml of C_6D_6) was filtered twice through silica immediately before the measurement was started (444000 transients; acquisition time 0.6 s; 75 h of spectrometer time; 23 ± 1 °C; digital resolution 1.3 Hz; spectral window 7000 ppm, pulse length 20 μs , corresponding to a pulse angle of 22.5°; repetition delay 2 ms; without ^1H decoupling). All calculations were performed using the Gaussian 03 package [29]. The stationary points related to the respective geometries were found to be minima by the absence of imaginary frequencies. Experimental chemical shifts are given relative to external $\text{BF}_3\text{-OEt}_2$ ($\delta^{11}\text{B} = 0$ for $\Xi(^{11}\text{B}) = 32.083971$ MHz), and $\text{Fe}(\text{CO})_5$ [$\delta^{57}\text{Fe} = 0$ for $\Xi(^{57}\text{Fe}) = 3.237798$]. Calculated $\delta^{11}\text{B}$ data are derived from the $\sigma(^{11}\text{B})$ values using the relationship $\delta^{11}\text{B} = \sigma(^{11}\text{B}, \text{B}_2\text{H}_6) - \sigma(^{11}\text{B}, \text{calcd.}) + \delta^{11}\text{B}(\text{B}_2\text{H}_6)$, where $\sigma(^{11}\text{B}, \text{B}_2\text{H}_6) = +84.2$ [B3LYP/6-311+G(d,p)] or $+94.2$ [B3LYP/6-31+G(d)] and $\delta^{11}\text{B}(\text{B}_2\text{H}_6) = +18.0$. The calculated $\delta^{13}\text{C}$ values are directly related to $\delta^{13}\text{C}(\text{Me}_4\text{Si}) = 0$, using the calculated $\sigma(^{13}\text{C})$ values and $\sigma(^{13}\text{C}, \text{Me}_4\text{Si}) = 184.0$ [B3LYP/6-311+G(d,p)] or 203.1 [B3LYP/6-31+G(d)].

Synthesis of the hexaethyl-2,4-dicarba-*nido*-hexaborate(2[−]) **4**

A solution of $\text{BuLi/KO}^t\text{Bu}$ (1.5 mmol / 1.5 mmol) in hexane/THF (5 ml / 5 ml) was prepared at -100 °C, and the sodium salt of the anion **3** (40 mg, 1.5 mmol) was added in one portion. The reaction mixture was allowed to reach room temperature, and stirring was continued for 2 h. The absence of the ^{11}B NMR signals of **3** and the appearance of three new signals ($\delta^{11}\text{B} = -48.0, +10.5, +20.4$; ratio 1:1:2) indicated that the reaction was complete. After addition of hexane (10 ml) at room temperature, insoluble materials were filtered off, and the solution was kept for 5 d at -78 °C, until a colourless precipitate was formed. This powder was isolated, dissolved in THF, checked by ^{11}B NMR, and used for further reactions.

Attempted synthesis of the iron complex **6**

The THF solution of **4**, as described above, containing about 1 mmol of **4** in 20 ml of THF, was cooled to -78 °C, and FeCl_2 (0.5 mmol) was added in one portion. When the mixture was warmed to room temperature, an orange-red colour developed, and stirring was continued for 2 h.

^{11}B NMR spectra showed that **4** was completely consumed and that a new species was present ($\delta^{11}\text{B} -19.0, +6.5, +1.0$; ratio 1:1:2; the integral intensity of other signals was less than 30% of the total intensity). The reaction solution was divided into three equal portions. Removing the THF in a vacuum left a red-brown viscous oil which could be redissolved in THF. Addition of $[\text{Ph}_4\text{P}]\text{Br}$ or $[\text{Ph}_3\text{PMe}]\text{Br}$ did not give any defined materials. The remaining part of the reaction solution was given into 50 ml of hexane, and an excess

of $[\text{NH}_4]\text{Cl}$ (1.5 g) was added. After 24 h at room temperature, all insoluble materials were filtered off, volatile materials were removed in a vacuum, and finally 25 mg of a deep-red solid was left, identified as **5** [11] [28%; m. p. 222 – 225 °C; $\delta^{11}\text{B} +12.2(1)$; $+17.3(3)$, $-2.2(5,6)$].

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