

Combining carbaboranes with transition-metal clusters; synthesis and X-ray structure analysis of a 1,2,3,4,5-pentamethyl-2,3,4,5-tetracarba-*nido*-hexaborane(6) derivative

Max Herberhold,* Uwe Bertholdt, Wolfgang Milius, Alexandra Glöckle and Bernd Wrackmeyer*

Laboratorium für Anorganische Chemie, Universität Bayreuth, D-95440 Bayreuth, Germany

The 6-bromopentamethyl- and 1,6-dibromo-2,5-dibutyl-3,4-diethyl-2,3,4,5-tetracarba-*nido*hexaboranes(6) (**1** and **2**) react with the tetrahedrane anion $[\text{Fe}_2(\text{CO})_6(\mu\text{-SN})]^-$ **3** to form the *N*-[6-[2,3,4,5-tetracarba-*nido*-hexaborane(6)-yl]]hexacarbonyldiferraazathia tetrahedranes **4** and **5**, respectively, in which two different cages are directly connected through a B–N bond; the X-ray crystal structure of **4** provides the first example of the structure of an ‘undisturbed’ 2,3,4,5-tetracarba-*nido*-hexaborane(6).

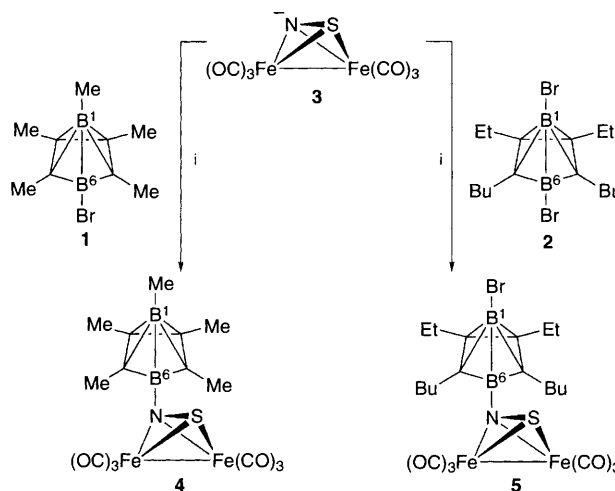
Carbon-rich carbaboranes such as 2,3,4,5-tetracarba-*nido*-hexaboranes(6) are attractive targets both for synthesis and theory, particularly so because they are at the borderline between classical and non-classical structures.¹ The role of transition metals, being either part of the polyhedral system or linked directly or indirectly to the respective polyhedron, is another active research area.² We have now combined the 2,3,4,5-tetracarba-*nido*-hexaborane(6) cage with a metallatetrahedrane, specifically with hexacarbonyldiferraazathia tetrahedrane, by forming a new type of B–N bond.

Although the exceptionally stable peralkylated 2,3,4,5-tetracarba-*nido*-hexaboranes(6) have been known for a long time,³ their chemistry has remained essentially unexplored. Recently, we have succeeded in preparing 6-bromo⁴ (**1**) and 1,6-dibromo derivatives⁵ (**2**) of the alkylated 2,3,4,5-tetracarba-*nido*-hexaboranes(6), opening the way for straightforward derivatization of these carbaboranes. Additionally, we have found that anions of the type $[\text{Fe}_2(\text{CO})_6(\mu\text{-SN})]^-$ **3** are readily accessible,^{6,7} allowing the preparation of various organometal-substituted derivatives of the metallatetrahedrane system.

The anion $[\text{Fe}_2(\text{CO})_6(\mu\text{-SN})]^-$ **3**, generated from $[\text{Fe}_2(\text{CO})_6(\mu\text{-SNH})]$ and DBU (1 : 1) in thf, -78 to $+25$ °C, reacts smoothly (in thf, -78 to $+25$ °C over 2 h) with either **1** or **2** (Scheme 1) to give the compounds **4**[†] and **5**[‡] in high yield (**4** 88%, **5** 76%). The carbaborane cage in both **4** and **5** is linked to the nitrogen atom of the hexacarbonyldiferraazathia tetrahedrane by the B(6)–N bond; in the case of **2**, an excess of **3** does not induce additional substitution at the 1-position. The reactions shown in Scheme 1 were monitored by ¹¹B NMR spectroscopy on the reaction solutions, which showed that the C₄B₂ cage remains intact at all times. The chemical shifts $\delta^{11}\text{B}(1)$ and $\delta^{11}\text{B}(6)$ change from -44.2 and $+13.7$ (**1**), -40.1 and $+15.5$ (**2**) to -43.1 and $+20.7$ (**4**), -39.6 and $+22.2$ (**5**).

Compound **4** was isolated as a red crystalline solid, and single crystals suitable for X-ray analysis§ were obtained after recrystallization from hexane. The molecular structure is shown in Fig. 1, together with relevant bond lengths and angles. This is the second example after $[\text{Fe}_2(\text{CO})_6\{\mu\text{-SNC}_7\text{H}_7\text{Mo}(\text{CO})_3\}]^7$ confirming the structure of the $\text{Fe}_2(\text{CO})_6(\mu\text{-SN})$ fragment, and the first example of the solid-state structure of an ‘undisturbed’ *nido*-C₄B₂ cage. Previously, the basic structure of the non-classical C₄B₂ system had been confirmed by gas-phase electron diffraction of the hexamethyl derivative Me₆C₄B₂⁸ as well as by microwave spectroscopy of the parent compound C₄B₂H₆.⁹ More recently, the molecular structure of a benzo-

annulated derivative has been reported.¹⁰ The results of the electron diffraction study differ significantly from those of the other structural investigations. In particular, the basal B–C bonds are longer by more than 20 pm, and the bonds between the basal plane and the apical boron atom are shorter by about 20–30 pm. In addition, bending of the methyl groups out of the



Scheme 1 Reagents and conditions: i, thf, -78 to 25 °C, 2 h, evaporation, extraction with hexane; **3** was generated from $[\text{Fe}_2(\text{CO})_6(\mu\text{-SNH})]$ and DBU (1 : 1), thf, -78 °C and used *in situ*

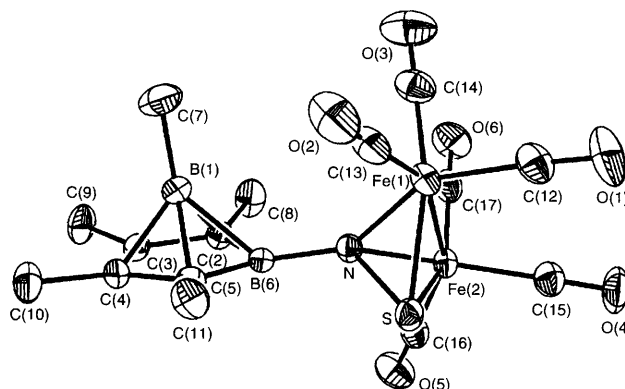


Fig. 1 Molecular structure of **4** (without hydrogen atoms) including thermal ellipsoids with 50% probabilities. Selected bond distances (pm) and angles (°): N–B(6) 148.9(3), B(6)–C(2) 151.2(4), C(2)–C(3) 145.2(3), C(3)–C(4) 141.4(4), C(4)–C(5) 144.8(3), C(5)–B(6) 152.3(2), B(6)–B(1) 183.6(4), C(2)–B(1) 174.3(4), C(3)–B(1) 174.04(4), C(4)–B(1) 172.0(4), C(5)–B(1) 172.2(4), B(1)–C(7) 156.6(4), S–N 169.9(2), Fe(1)–Fe(2) 250.5(1), Fe(1)–N 194.7(2), Fe(2)–N 194.4(2), Fe(1)–S 220.5(1), Fe(2)–S 220.1(1); N–B(6)–C(2) 126.4(2), N–B(6)–C(5) 128.1(2), B(6)–C(2)–C(3) 108.7(2), C(2)–C(3)–C(4) 109.2(2), C(3)–C(4)–C(5) 109.9(2), C(4)–C(5)–B(6) 108.2(2), C(5)–B(6)–C(2) 103.6(2), B(6)–B(1)–C(2) 49.9(1), C(2)–B(1)–C(3) 49.3(1), C(3)–B(1)–C(4) 48.2(1), C(4)–B(1)–C(5) 49.7(1), C(5)–B(1)–B(6) 50.6(1).

basal plane and away from the apical boron has been observed only in the electron diffraction study, in contrast to the present observation. Therefore, the electron diffraction data appear to be unreliable. The bond lengths C(2–5)–B(1) cover only a small range (172.0–174.3 pm), similar to the bond lengths C(2)–C(3) [145.2(3) pm], C(3)–C(4) [141.4(4) pm] and C(4)–C(5) [144.8(3) pm]. Bond lengths and angles of the Fe₂(CO)₆(μ-SN) unit resemble those of the other X-ray structure⁷ published so far. The new B–N bond [148.9(3) pm] between the carbaborane and the Fe₂SN cluster represents a fairly long single bond¹¹ (range *ca.* 146–150 pm).

The availability of the bromides **1** and **2** is promising for a rich chemistry of combined clusters, including of course the reaction of either **1** or **2** with all types of anionic borane, heteroborane or metallaborane fragments.

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Footnotes

† *Spectroscopic data for 4*: mp 112 °C (decomp.); IR (hexane, cm⁻¹), ν(CO) 2071m, 2029vs, 1991vs, 1984s, 1974m. ¹H NMR (C₆D₆) δ -0.67 (s, BCH₃), 1.22, 1.41 (s, CCH₃); ¹¹B NMR (C₆D₆) δ -43.1 (apical), +20.7 (basal); ¹³C NMR (C₆D₆) δ -18.1 [q, BCH₃, ¹J(¹³C¹H) 91 Hz], 8.6, 8.8 (CCH₃), 86.9 (br, BC-basal), 103.5 (C-basal), 210.0 (CO); MS(EI), *m/z* (fragment relative intensity) 471 (M⁺, 15%), 303 (M⁺ - 6CO, 100%), 287 (M⁺ - 6CO - CH₄, 10%).

‡ *Spectroscopic data for 5*: IR (hexane, cm⁻¹), ν(CO) 2072m, 2031vs, 1993vs, 1977s, 1967m. ¹H NMR (C₆D₆) δ 0.88 (t), 0.96 (t), 1.33 (m), 1.41 (m), 1.61 (m), 1.76 (m), 1.86 (q), 2.21 (m); δ(¹¹B) -39.6 (apical), +22.2 (basal); δ(¹³C), 13.3, 14.2, 17.7, 23.5, 24.3, 33.1 (alkyl), 93.4 (br, BC-basal), 110.3 (C-basal), 210.1 (CO); MS(EI), *m/z* (fragment relative intensity), 649 (M⁺, 8%), 479 (M⁺ - 6CO, 100%), 399 (M⁺ - 6CO - Br, 15%).

§ *Crystal data for 4*: the red crystal was grown from a hexane solution at -2 °C and put into a Lindemann capillary (0.5 mm diameter). C₁₅H₁₅B₂Fe₂NO₆S; *M* = 471; crystal system monoclinic, space group *P*2₁/*c*, *a* = 11.754(2), *b* = 10.065(2), *c* = 17.353(2) Å; β = 105.68(2)°; *U* = 1976.6(6) Å³; *Z* = 4, *F*(000) = 952; *D*_c = 1,582 Mg m⁻³; absorption coefficient μ = 1.603 mm⁻¹; crystal shape, irregular; size, 0.55 × 0.40 × 0.30 mm³. Data collection and processing: Siemens P4 diffractometer (graphite-monochromated Mo-Kα radiation), *T* = 173 K; 2θ range 3.0–55.0°; index ranges -1 ≤ *h* ≤ 15, -3 ≤ *k* ≤ 13, -22 ≤ *l* ≤ 22; 6034 intensities measured, 4516 independent (*R*_{int} = 0.0311); 4516 observed [*F*₀ > 0.0σ(*F*)]. Structure solution and refinement: direct methods (SHELXTL PLUS program package); full-matrix least squares on Σw(*F*_o - *F*_c)²;

isotropic extinction correction $\chi = 0.00029(2)$, where $F^* = F [1 + 0.002 \chi F^2 / \sin(2\theta)]^{-1/4}$, hydrogen atoms refined isotropically with fixed thermal parameters (riding model), all other atoms anisotropic; 245 parameters refined, empirical absorption correction (ψ -scans); min., max. transmission factors 0.4633, 0.5500; data-to-parameter ratio 18.4:1; *R*, *wR* 0.0483, 0.0264 [*w*⁻¹ = σ²(*F*_o)], *S* = 1.22; max., min. residual electron density 1.08, 0.42 e Å⁻³. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/57.

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