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Metallacarborane chemistry of the *hypho*-[6,7-C$_2$B$_6$H$_{13}$]$^-$ anion: Reaction with nickelocene and the formation of three multimetallic nickel–boron clusters

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Abstract

The reaction of the *hypho*-[6,7-C$_2$B$_6$H$_{13}$]$^-$ anion (**1**) with nickelocene and an excess of 'proton sponge' (1,8-bis-(dimethylamino-naphthalene)) in boiling acetonitrile leads to the formation of a pair of isomeric trimetallic nickel–boron clusters, [6,7,8-(CpNi)$_3$-1-CB$_5$H$_6$] (**2**) and [6,7,8-(CpNi)$_3$-2-CB$_5$H$_6$] (**3**), in a combined yield of 55%. Isomer (**2**) had been previously prepared from *nido*-2-CB$_5$H$_9$ but in much lower yield. Isomer (**3**) is without precedent and has been characterized using multi-nuclear NMR spectroscopy and mass spectrometry. Isomer (**3**) undergoes conversion to (**2**) via heating in boiling toluene. In addition to this isomeric pair, an interesting *nido* dimetallacarborane of constitution [6,6′-(CpNi)$_2$-7,7′-C$_2$B$_6$H$_8$] (**4**) has been isolated from the same reaction in 5% yield and characterized by single-crystal X-ray diffraction analysis.
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1. Introduction

We have lately become interested in the chemistry of the *hypho* dicarborane anion [6,7-C$_2$B$_6$H$_{13}$]$^-$ (**1**) [1,2], and have recently reported the results from its reaction with the rhodium dimer [RhCl$_2$(C$_5$Me$_5$)]$_2$ [3]. In this last reaction, we found that the eight-vertex *hypho* anion (**1**) incorporates either one or two rhodium centres to form a nine-vertex *arachno* monometallacarborane [5-Cp*-*arachno*-5,4,6-RhC$_2$B$_6$H$_{12}$] and an unusual

nine-vertex *nido* dimetallacarborane [2,5-Cp*-*nido*-2,5,1-Rh$_2$CB$_6$H$_9$], respectively. Here we now report the formation of a pair of isomeric nine-vertex trimetallacarboranes (compounds **2** and **3**) and a ten-vertex dimetallacarborane (compound **4**) from the reaction of anion (**1**) with nickelocene. The isomers (**2**) and (**3**) have formal *nido* electron counts [4], but their actual structural geometries are far more similar to typical nine-vertex *closo* species with a classical tricapped trigonal prismatic architecture. The structure of compound **4** is also atypical. A Ni–Ni localized bond bridges the otherwise regular ten-vertex *nido* shape of (**4**) that generates two open square-faces in its structure.

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2. Results and discussion

The notional addition of {Cp*Rh} fragments into the *hypho*-$[C_2B_6H_{13}]^-$ anion proved to be a facile process [3]. The rhodium-metal moiety contributes three orbitals and two electrons to cluster bonding and may thus be regarded as isolobal and isoelectronic with a {BH} vertex. In this general context it became of interest to us to investigate the insertion of other cluster-stabilizing metal moieties into the *hypho* dicarborane framework of compound (1). In particular we were interested in centres that were isolobal and isoelectronic with a {CH} vertex. An excellent candidate for such an insertion is the {CpNi}$^{3+}$ moiety [5,6] that is readily accessible using reactions involving the twenty-electron species, Ni(Cp)$_2$, commonly known as nickelocene.

Thus, the reaction of anion (1) with a two-molar excess of nickelocene and a five-molar excess of 'proton sponge' in boiling acetonitrile resulted in the formation of a pair of isomeric trimetallic nickel–boron cluster compounds, [6,7,8-(CpNi)$_3$-1-CB$_5$H$_6$] (2) and [6,7,8-(CpNi)$_3$-2-CB$_5$H$_6$] (3), in a combined yield of 55%, and, in a smaller yield of 5%, a ten-vertex dimetallic compound, [6,6′-(Cp)$_2$-*nido*-6,6′,7,7′-Ni$_2$C$_2$B$_6$H$_8$] (4) (see Scheme 1).

Whereas a mixture of compounds (2) and (3) was easily separated chromatographically from compound (4) on a silica gel column, separation of (2) from (3) required HPLC.

2.1. Compounds (2) and (3) – a resolution of isomers

The difference in symmetry of (2) and (3) was immediately evident from their ^{11}B NMR spectra – one symmetric and one asymmetric five-boron-atom species. The ^{1}H NMR spectra of the two compounds also suggested the presence of three {CpNi} moieties and one carbon
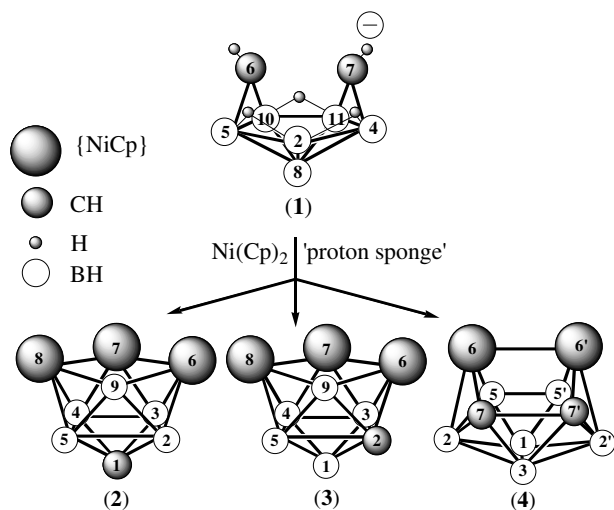
cluster vertex in each. There is only one known example of a trinickel carbaborane compound [5]. It is a nine-vertex symmetrical species containing five boron atoms that, like compound (2), displays three resonances with an intensity ratio 2:2:1 in its ^{11}B NMR spectrum, but of different chemical shift values than compound (2). Concordantly, we concluded that we must have a related but different species that would require a single-crystal X-ray diffraction analysis to fully elucidate its structure. However, these crystallographic results later showed that compound (2) and the trinickel carborane compound reported earlier were identical. This implies that the NMR data for compound (2), which are shown in Section 4 and summarized in Scheme 2, are at variance to that initially reported and should be noted.

The second trinickel compound (3) is, however, without precedent and our attention focussed on its structural elucidation. All attempts to obtain a crystallographic solution to its structure proved unsuccessful as only disordered data were obtained. The analysis however revealed a gross distribution of three nickel atoms and six other cluster atoms as in the structure of (2), but the location of the single carbon atom could not be distinguished from the five cage boron atoms. The isomeric nature of compound (3) was nevertheless confirmed by mass spectrometry and its structural configuration reasonably proposed on the basis of multi-nuclear NMR spectroscopy work.

Thus, the ^{11}B NMR spectrum of (3) contains five doublets of equal intensity indicating an asymmetric compound containing five different {BH} units. The ^{1}H spectrum consists of five broad resonances that represent the five {B–^{1}H} nuclei, which are easily distinguished by a subtraction of the ^{1}H and ^{1}H–{^{11}B} NMR spectra, and are assigned to their adjacent boron nuclei by selectively decoupling at δ^{11}B frequencies. Also present in the ^{1}H spectrum of (3) is a single resonance typical of a cluster {C–^{1}H} proton and three peaks of relative intensity five, which suggest the presence of three {Ni–Cp} moieties. The position of the cage carbon atom in (3), although not apparent from the single-crystal X-ray diffraction

Scheme 1. Reaction summary for the formation of compounds (2), (3) and (4).
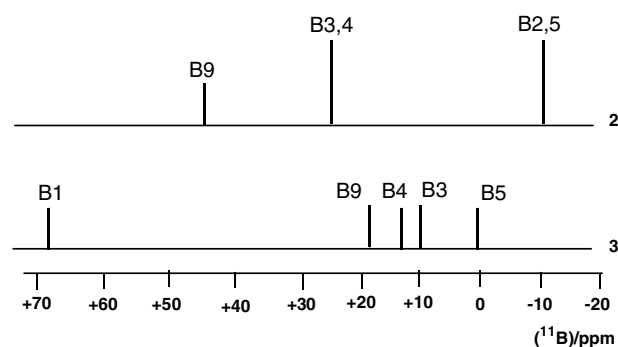
Scheme 2. Stick representation of ^{11}B chemical shifts and relative intensities for compounds (2) and (3).

analysis, is assigned to atomic position 2 on the basis of an analysis of the ^{11}B–^{11}B COSY NMR data, which are summarized in Section 4. Theoretically and with respect to the asymmetry of the ^{11}B NMR spectrum, the carbon vertex in compound (**3**) could be located in either position 2 or 3. On the basis that only one ^{11}B–^{11}B COSY correlation was observed that involved B9, the carbon atom was assigned to the 2 position. However, this assignment is tentative. Nevertheless, both isomers share a cluster structure that may be derived from a tricapped trigonal prism by elongation of the Ni7–B9 polyhedral edge. This is an unusual *nido* configuration that is, in this case, strangely favoured to that derived from the elongation of two edges (such as Ni7–B3 and Ni7–B4) to generate a five-membered open face: a geometry adopted by the majority of *nido* nine-vertex species [3,7–10]. Confirmation of the isomeric nature of compounds (**2**) of (**3**) is also in the ready conversion of (**3**) into (**2**) on heating in boiling toluene. The direction of this isomeric conversion is most likely driven by the tendency for carborane structures with cluster carbon atoms with lower coordination numbers to have lower associated internal energies. In this particular case the coordination number of the cluster carbon atoms reduces from five in compound (**3**) to four in compound (**2**).

The formation of isomers (**2**) and (**3**) from the *hypho*-$[C_2B_6H_{13}]^-$ anion is a complex procedure involving the expulsion of one boron and one carbon cluster vertex, accompanied by substantial cluster rearrangement. This is quite different from the route to compound (**2**) described by Hawthorne and coworkers [5], which starts with the *nido* monocarborane species 2-CB$_5$H$_9$ and therefore is a more simple assembly of the three metal centres with no loss of cluster carbon and boron atoms.

2.2. Compound (4) – a possible intermediary species

In the context of the mechanism of formation, compound (**4**) is a model for an intermediate species that links the starting material (**1**) and the isomers (**2**) and (**3**). Within its crystallographically determined ten-vertex structure (Fig. 1) is a pentagonal {B$_6$} pyramid that is also present in (**1**). Two carbon atoms also remain in its cluster structure, although they are now adjacent and mutually connected; a consequence of complexation with the two nickel centres and the overall cluster condensation from *hypho* to *nido* geometry.

It is possible that the addition of a third nickel vertex (the presence of one or more nickel centres in the cage seems to promote the further addition of nickel atoms [6]) could result in the expulsion of one carbon and one boron vertex to form compounds (**2**) and (**3**). Both nickel atoms in compound (**4**) are diamagnetic, and can be regarded as octahedral Ni(IV) centres. In these terms, three orbitals and one electron would be directed from each nickel centre to the external cyclopentadienyl li-
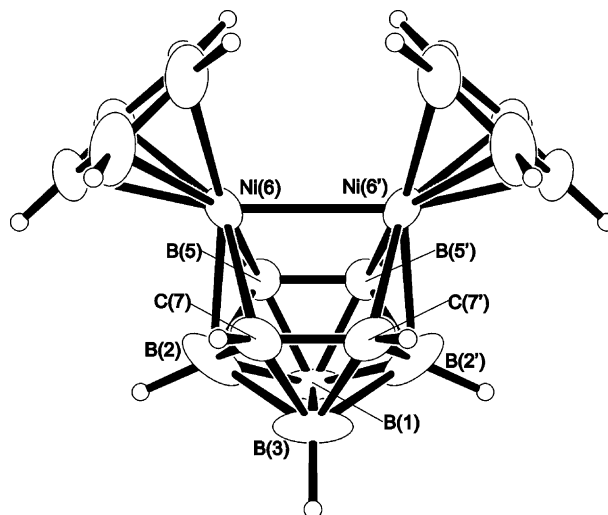

Fig. 1. An illustration of the molecular structure as determined by single-crystal X-ray diffraction of [6,6′-(Cp)$_2$-*nido*-6,6′,7,7′-Ni$_2$-C$_2$B$_6$H$_8$] (compound **4**). Selected atomic distances (Å): Ni(6)–Ni(6′) = 2.4407(14), Ni(6)–B(5) = 2.027(6), Ni(6)–C(7) = 2.035(7), Ni(6)–B(2) = 2.173(9) C(7)–C(7′) = 1.492(15), B(5)–B(5′) = 1.516(13), B(3)–C(7) = 1.680(12), B(2)–C(5) = 1.689(10), B(3)–B(1) = 1.739(14), B(3)–B(2) = 1.773(13), B(1)–B(5) = 1.687(11), B(1)–B(2) = 1.767(12), B(2)–C(7) = 1.707(10).

gands, two orbitals and two electrons are directed toward the carborane cluster, and one orbital and one electron contribute to the localized 2-electron, 2-centre bond between metal atoms. This results in a formal 24-electron cluster–electron count which would be consistent with a ten-vertex *nido*-type geometry according to the Williams–Wade paradigm [4]. However the Ni–Ni bond present in (**4**) distinguishes it from other *nido* 6,6′-dimetallaborane compounds such as *nido*-[(Cp*Co)$_2$B$_8$H$_{12}$] [11], which have classical *nido* ten-vertex cluster configurations, and contain metal atoms that are clearly separated from one another and are non-bonding. The Ni–Ni bond in compound (**4**), and the two open faces that result because of this bond, make (**4**) a rather unusual structure. The Ni(6)–Ni(6′) distance is 2.44 Å, which is only marginally larger than that of the average distance between the nickel centres in compounds (**2**) and (**3**) of 2.41 Å. This distance is also significantly smaller than the separation between the B(6) and B(9) vertices in *nido*-decaborane [12], (3.590 Å – non-bonding distance) or the Co(6) and Co(6′) found in *nido*-[(Cp*Co)$_2$B$_8$H$_{12}$] [11,13], (4.225 Å – non-bonding distance).

As {Cp*Ni}$^+$ moieties resemble {CH} vertices in boron cluster chemistry, given that they both contribute three orbitals and three electrons to bonding, then compound (**4**) may be considered as isoelectronic with the tetracarborane [5,6,8,9-C$_4$B$_6$H$_{10}$] (**5**) [14]. Whereas compound (**4**) exhibits an unbroken four-member string of heteroatoms in its cluster open face, compound (**5**)
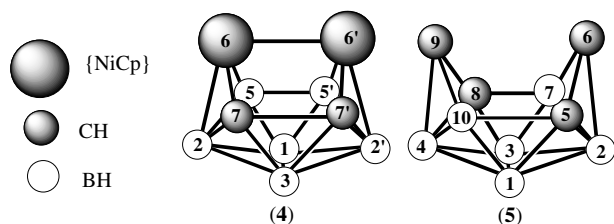
Scheme 3. Comparison of the isoelectronic structural skeletons of *nido*-[6,6′-(CpNi)$_2$-7,7′-C$_2$B$_6$H$_8$] (**4**) and [5,6,8,9-C$_4$B$_6$H$_{10}$] (**5**).

however contains two separated pairs of heteroatoms (Scheme 3).

The NMR spectra of compound (**4**) support the crystallographic data collected for it. A 2:1:1:2 pattern of doublets is seen in the ^{11}B NMR spectrum that is consistent with the crystallographic symmetry of the molecule.

3. Conclusion

The formation of isomers (**2**) and (**3**) by the reaction of *hypho*-[C$_2$B$_6$H$_{13}$]$^-$ with nickelocene has led to an alternative synthesis for the previously described compound (**2**) and the discovery of a different isomer, compound (**3**), which converts to its more symmetrical isomer, essentially quantitatively, on heating. Compound (**4**) from the same reaction represents an interesting variation on the *nido* ten-vertex skeleton.

We continue our investigation into the reactivity of the *hypho* "helmet anion" (**1**).

4. Experimental

4.1. General

Reactions were carried out in dry solvents (acetonitrile, benzene, toluene, hexane, and dichloromethane) under dry argon, but subsequent manipulatory and separatory procedures were carried out in air. Preparative thin-layer chromatography (TLC) was carried out using 1 mm layers of silica gel G (Fluka, type GF254) made from water slurries on glass plates of dimensions 20 × 20 cm^2, followed by drying in air at 80 °C; components were located visually. Mass spectrometry was performed on an esquire3000-00047 instrument, using an ESI ion source. NMR spectroscopy was performed at 9.4 T in CDCl$_3$ on a Varian MERCURY 400 High Resolution System.

4.1.1. Isolation of compounds [6,7,8-(CpNi)$_3$-1-CB$_5$H$_6$] (**2**), [6,7,8-(CpNi)$_3$-2-CB$_5$H$_6$] (**3**), and [6,6′-(CpNi)$_2$-7,7′-C$_2$B$_6$H$_8$] (**4**) from the reaction of [6,7-C$_2$B$_6$H$_{13}$]$^-$ (**1**) with nickelocene and 'proton sponge'

To a dry CH$_3$CN solution of [C$_2$B$_6$H$_{13}$][NMe$_4$] (0.50 g; 2.8 mmol), Ni(Cp)$_2$ (1.05 g; 5.6 mmol) and 'proton

sponge' (1,8-bis-(dimethylamino-naphthalene)) (1.7 g, 14 mmol) were added. This mixture was stirred and brought to reflux temperature under a stream of argon for a period of approximately 4 hours. The reaction mixture was then allowed to cool and the CH$_3$CN solvent removed to leave a dark solid. This was redissolved in benzene and a small aliquot taken and subjected to TLC [silica G on Al foil {Siluflol (Kavalier, Prague)}, with components being detected by iodine vapour, followed by aqueous AgNO$_3$ spray]. The TLC revealed a single large green spot (R_F = 0.8 in benzene) followed by a fainter green spot (R_F = 0.6 in benzene). This benzene solution was reduced in volume and subjected to column chromatography (2 × 25 cm, silica gel, 70–220 mesh) using benzene as mobile phase. A large, fast-moving, green component was collected and probed via ^{11}B NMR spectroscopy, revealing a mixture of compounds (**1**) and (**2**). HPLC was eventually required to effect the separation of compounds **2** and **3**: (Stainless steel column (250 × 25 mm) packed with Lichrosorb SI 60, Merck (silica gel, 10 μm) by Labio Ltd. Prague (column efficiency more than 16 000 theoretical plates/m for both isomers); mobile phase: dry hexane: CH$_2$Cl$_2$ (4: 1, with 0.3% of CH$_3$CN), flow rate: 27 ml/min, detection UV 253 nm, sensitivity 1.28 A.U.F.S; sample amount ca. 80 mg per single injection dissolved in 4 ml of the mobile phase. Effluent from the baseline resolved peaks of (**2**) and (**3**) was taken from the 10% peak height at the start up to 30% height at the end of the first peak and 30% height to 20% of the second peak. Chromatographic data: Capacity factors (k'), selectivity (α) resolution (R_s) were: (**2**): k'_2 = 2.37, k'_2 = 2.75, α = 1.16, R_s = 1.25.):

[6,7,8-(CpNi)$_3$-1-CB$_5$H$_6$] (**2**) (0.37 g, 0.84 mmol, 30%). Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of a dichloromethane solution of compound (**2**). For (**2**): ^{11}B NMR (128.3 MHz, CDCl$_3$, 25 °C): δ = +44.9 (d, ^1J(B,H) = ~140 Hz, 1B, B9), −11.6 (d, ^1J(B,H) = ~150 Hz, 2B, B2,5), +24.5 (d, ^1J(B,H) = ~150 Hz, 2B, B3,4), strong [^{11}B–^{11}B]-COSY crosspeaks observed for B9–B2,5; ^{1}H{^{11}B} NMR (400 MHz, 25 °C): δ = +2.42 (s, 1H, H9), +2.12 (s, 2H, H2,5), +5.49 (s, 2H, H3,4), +4.28 (s, 1H, H–CH1), +5.37 (s, 10H, H–Cp6,8), +5.31 (s, 5H, H–Cp7).

[6,7,8-(CpNi)$_3$-2-CB$_5$H$_6$] (**3**) (0.31 g, 0.70 mmol, 25%). For (**3**): M.S.: cut-off at *m/z* 448 corresponding to the ^{12}C$_{16}$^{1}H$_{21}$^{11}B$_5$^{60}Ni$_3^+$ ion. ^{11}B NMR (128.3 MHz, CDCl$_3$, 25 °C): δ = +68.3 (d, ^1J(B,H) = 156 Hz, 1B, B1), +18.3 (d, ^1J(B,H) = ~153 Hz, 1B, B9), +13.2 (d, ^1J(B,H) = ~134 Hz, 1B, B4), +9.8 (d, ^1J(B,H) = ~156 Hz, 1B, B3), +1.45 (d, ^1J(B,H) = ~144 Hz, 1B, B5), strong [^{11}B–^{11}B]-COSY crosspeaks observed for B3–B4, B5–B4 and B5–B9 and weak cross-peaks for B1–B3, B1–B4, and B1–B5; ^{1}H{^{11}B} NMR (400 MHz, 25 °C): δ = ~+8.2 (s, 1H, H1), +4.47 (s, 1H, H9), +3.87 (s, 1H, H4), +3.51 (s, 1H, H5), +2.88 (s, 1H, H3),

+2.81 (s, 1H, H–CH2), +5.47 (s, 5H, H–Cp), +5.44 (s, 5H, H–Cp), +5.38 (s, 5H, H–Cp).

The second green component (R_F = 0.6) from the original column was collected and purified further via preparative TLC using 50:50 CH_2Cl_2:hexane as eluent. A single green band (R_F = 0.45) was collected, found to be pure by ^{11}B NMR, and crystallized via slow diffusion of hexane into a concentrated dichloromethane solution. This resulted in red plate crystals of formula: [6,6′-$(Cp)_2$-nido-6,6′,7,7′-$Ni_2C_2B_6H_8$] (compound **4**) (0.05 g, 0.14 mmol, 5%). For (**4**):^{11}B NMR (128.3 MHz, $CDCl_3$, 25 °C): δ = +3.9 (d, [1]J(B,H) = ~160 Hz, 2B, B5,10), −3.4 (d, [1]J(B,H) = ~161 Hz, 1B, B3), −6.4 (d, [1]J(B,H) = ~153 Hz, 1B, B1), −20.1 (d, [1]J(B,H) = ~152 Hz, 2B, B2,4); strong [^{11}B–[11]B]-COSY crosspeaks observed for B3–B2,4, and B1 and B5–B10; ^{1}H{^{11}B} NMR (400 MHz, 25 °C): δ = +1.54 (s, 2H, H5,10), +1.31 (s, 1H, H1), +0.88 (s, 2H, H2,4), +3.51 (s, 1H, H5), +0.14 (s, 1H, H3), +2.17 (s, 2H, H–CH7,8), +7.36 (s, 10H, H–Cp).

4.1.2. Conversion of isomer (3) into isomer (2)

A sample of [6,7,8-$(CpNi)_3$-2-CB_5H_6] (**3**) (0.20 g, 0.45 mmol) was suspended in dry toluene and heated until reflux under a steady stream of argon. The mixture was kept at reflux for three hours, after which it was allowed to cool to room temperature. The toluene solvent was then removed, the solid residue re-dissolved in dichloromethane and filtered through a small amount of silica. An NMR of the resultant sample showed a complete conversion to symmetrical isomer (**2**) (isolated amount after crystallization 0.16 g, 0.36 mmol).

4.2. X-ray crystallography

4.2.1. Crystal data for [6,6′-$(CpNi)_2$-7,7′-$C_2B_6H_8$] (4)

$C_{12}H_{18}B_6Ni_2$: M = 344.54, monoclinic, a = 6.6666(12), b = 14.450(2), c = 7.6474(13) Å, U = 698.2(2) Å^3, X = 0.71073 Å, T = 120(2) K, space group $P2_1/m$, Z = 2, μ (Mo Kα) = 2.672 mm^{-1}, R_{int} = 0.1005 for 1207 reflections and $wR(F^2)$ = 0.1750 for all unique reflections.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 253168 for compound (**4**).

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