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An interesting metallacarborane cage closure and dismantling reaction including the facile halogenation of a cluster carbon atom: Structure of [1,2-(η^5-C$_5$Me$_5$)$_2$-μ-1,2-H-*closo*-1,2,3-Rh$_2$CB$_4$H$_4$-3-I]

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Abstract

Cage closure, together with the loss of two boron vertices, of [2,5-(η^5-C$_5$Me$_5$)$_2$-10-Me-μ-2,5-H-*nido*-2,5,1-Rh$_2$CB$_6$H$_8$] (**1**) using an approximately molar equivalent of elemental iodine and excess triethylamine results in the formation of a new species [1,2-(η^5-C$_5$Me$_5$)$_2$-μ-1,2-H-*closo*-1,2,3-Rh$_2$CB$_4$H$_4$-3-I] (**2**), which is characterized by multinuclear NMR spectroscopy, mass spectrometry, and single-crystal X-ray crystallography. The formation of compound **2** involves the elimination of a {B$_2$CH$_3$} moiety from **1** and an iodination of the single carbon vertex.
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1. Introduction

We have recently reported the formation of a nine-vertex *nido* dimetallamonocarborane [2,5-(η^5-C$_5$Me$_5$)$_2$-10-Me-μ-2,5-H-*nido*-2,5,1-Rh$_2$CB$_6$H$_8$] (compound **1**) from the reaction of the [*hypho*-C$_2$B$_6$H$_{13}$]$^-$ dicarborane anion with [RhCl$_2$(η^5-C$_5$Me$_5$)]$_2$ [1]. The skeletal structure of **1** is shown in Scheme 1 (Structure **I**). Compound **1** is interesting because *nido* nine-vertex metallacarboranes are rare in boron-containing cluster chemistry, and also because it exhibits the rare incidence of a Rh–H–Rh bridging hydrogen atom. There are only a few examples of the latter feature in boron-containing cluster chemistry [2]. In view of this rarity, and in view of the potential of rhodium–hydride complexes for use in hydrogenation catalysis [3], we have become interested in the chemistry associated with this metal-bridging hydrogen atom.

Our initial experiments in this general context were concerned with the evaluation of the acidity and prototropic lability of this Rh–H–Rh bridging hydrogen atom. In our first experiments, compound **1** was therefore treated with the non-nucleophillic deprotonating agent 1,8-bis-(dimethylamino)-naphthalene (also known as 'proton sponge'). However, this led to no molecular change. We thence found that the stronger deprotonating agent, NaH, also did not result in deprotonation, even at the elevated temperature of 68 °C. Treatment of compound **1** with triethylamine and elemental iodine, however, did lead to a molecular change, which was quite unexpected, and which is the subject of this communication.

2. Results and discussion

With an approximately molar equivalent of iodine and excess of triethylamine [2,5-(η^5-C$_5$Me$_5$)$_2$-10-Me-μ-2,5-H-*nido*-2,5,1-Rh$_2$CB$_6$H$_8$] (compound **1**) expels two boron cluster vertices and undergoes a cage-closure reaction, resulting in the formation of a seven-vertex *closo* species

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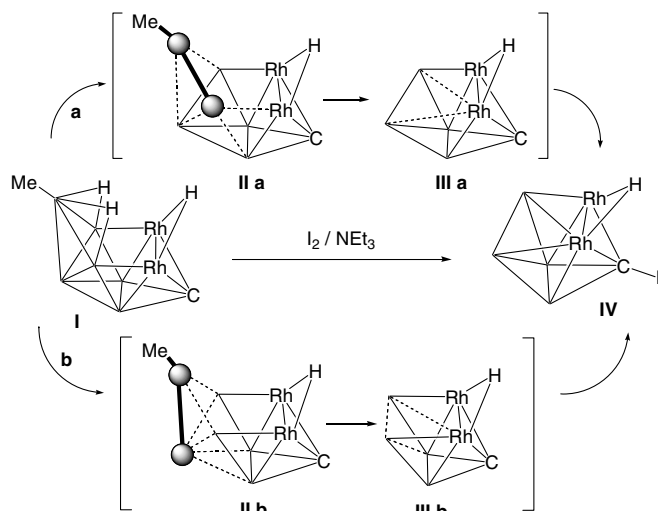
Scheme 1. Two possible routes for the formation of compound **2** (Structure **IV**).

of constitution $[1,2-(\eta^5-C_5Me_5)_2-\mu-1,2-H-closo-1,2,3-Rh_2CB_4H_4-3-I]$ (compound **2**), isolatable in good yield (79%). The molecular structure of **2**, as determined by single crystal X-ray diffraction analysis, is shown in Fig. 1.

The formation of $[1,2-(\eta^5-C_5Me_5)_2-\mu-1,2-H-closo-1,2,3-Rh_2CB_4H_4-3-I]$ may be schematically envisaged as occurring by the loss of a $\{MeB_2H_3\}$ fragment from compound **1**, followed by the formation of new atomic connectivities that close the cluster. In terms of a general mechanism,

two likely routes can be proposed to account for this cluster-dismantling and subsequent cluster-closure. These are shown in Scheme 1 (routes **a** and **b**; hypothetical reaction intermediates in square brackets). Both routes involve the extrusion of two adjacent boron vertices, to give either **II a** or **II b**, which could lead to the intermediate species **III a** or **III b**, respectively. If the reaction were to go by route **a**, then two new connectivities (shown as hatched lines) between one rhodium atom and two boron vertices would lead to the observed product **2** (schematic cluster structure **IV**). Alternatively, if route **b** occurred, then three new connectivities, one rhodium-to-boron and two boron-to-boron, would be required to close the skeleton.

These mechanistic pathways, whilst unproven, are reasonable given that: (a) compound **2** contains no methylated boron vertex, which implies the expulsion of the $\{BMe\}$ vertex, and (b) an unchanged Rh–C–Rh triangular face remains in the skeleton of compound **2**. The latter suggests that no cage rearrangement has occurred and thus that the second expelled boron vertex is most likely to be one that is adjacent to the $\{BMe\}$ vertex in the starting species **1**. The exact roles played by the triethylamine and iodine in this reaction remain speculative, as the overall process must involve a sequence of redox processes. The triethylamine may be involved in a deprotonation at a bridging hydrogen site during the course of the reaction, although it is unlikely to play a role in initiation since compound **1** does not deprotonate with the much stronger base NaH. It is perhaps more likely to be involved in nucleophilic attack at a boron vertex resulting in boron-atom sequestration, this latter being essentially a reductive process. Conversely cluster closure reactions are oxidative in nature, and this stage of the reaction sequence may therefore require iodine.

Compound **2** has a bicapped pentagonal pyramidal structure (Structure **X**, Scheme 2) of the same basic *closo* seven-vertex cluster type that is adopted by the exemplar *closo* binary borane $[B_7H_7]^{2-}$ dianion [4], but distorted from regular by the disparate sizes of the constituent cluster atoms. With respect to this seven-vertex *closo* cluster geometry, compound **2** resembles the dimetallic species $[1,2-(\eta^5-C_5Me_5)_2-(\mu^3-H)_2-closo-1,2-Co_2B_5H_5]$ [5] (Structure **Y**, Scheme 2), which also adopts a 'metals-adjacent' configuration. However, whereas this latter compound contains two $\{Co_2B\}$ face-capping hydrogen atoms, which, under heating [5], are lost to give a capped-*closo* or *pileo* cluster
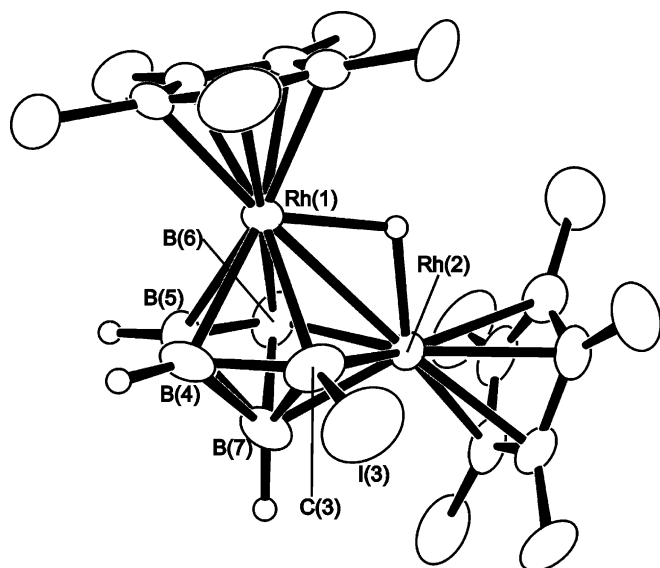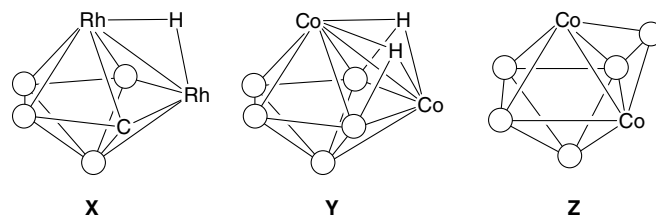

Fig. 1. An ORTEP-3 [10] illustration of the crystallographically determined molecular structure of $[1,2-(\eta^5-C_5Me_5)_2-\mu-1,2-H-closo-1,2,3-Rh_2CB_4H_4-3-I]$ (compound **2**). *Selected interatomic distances (Å)*. B(4)–B(7) = 1.780(18), B(5)–B(7) = 1.76(2), B(6)–B(7) = 1.88(2), B(4)–B(5) = 1.52(2), B(5)–B(6) = 1.521(19), C(3)–I(3) = 2.152(12), C(3)–B(4) = 1.68(2), C(3)–B(7) = 1.813(19), Rh(1)–Rh(2) = 2.7892(10), Rh(1)–B(6) = 2.279(13), Rh(1)–B(5) = 2.176(12), Rh(1)–B(4) = 2.196(13), Rh(1)–C(3) = 2.256(12), Rh(2)–B(6) = 2.095(13), Rh(2)–B(7) = 2.184(13), Rh(2)–C(3) = 2.115(12). For clarity, the hydrogen atoms on the $\{C_5Me_5\}$ ligands are not shown.

Scheme 2. Structural diagrams of $[1,2-(\eta^5-C_5Me_5)_2-\mu^2-1,2-H-closo-1,2,3-Rh_2CB_4H_4-3-I]$ (**X**), $[1,2-(\eta^5-C_5Me_5)_2-(\mu^3-H)_2-closo-1,2,-Co_2B_5H_5]$ (**Y**), and $[2,3-(\eta^5-C_5Me_5)_2-pileo-2,3-Co_2B_5H_5]$ (**Z**).

framework of sub-*closo* 2n-electron cluster-electron count, viz., [2,3-(η^5-C$_5$Me$_5$)$_2$-*pileo*-2,3-Co$_2$B$_5$H$_5$], (Structure **Z**, Scheme 2), compound **2** retains its bridging hydrogen atom at elevated temperature, undergoing no molecular change even when heated beyond its melting point. In this regard, the general retention of the {RhC$_2$} triangle is of additional interest, and is reminiscent of the 'composite cluster' behaviour exhibited by, for example, [2,7-(η^5-C$_5$Me$_5$)$_2$-*nido*-2,7,8,6-Ir$_2$CSB$_6$H$_8$], in which a tendency of metals and heteroatoms to group together in sub-domains within the boron matrix of metallaheteroboranes is observed [6]. This may be a kinetic phenomenon, as, classically, the thermodynamic stability of heteroborane clusters is generally regarded to be maximised when the heteroatoms are mutually distal. On the other hand, this last perception arose from observations principally on metalladicarborane clusters of the first-row transition elements, and stronger metal-to-heteroelement interactions may engender different behavioural patterns.

Another interesting feature of compound **2** is the presence of the *exo*-terminal {C(3)–I(3)} unit. Halogenation of a C–H bond, especially iodination, and, especially within the coordination sphere of a transition-element atom, is not generally a straightforward synthetic task [7]. Additionally, the reaction of iodine with carborane clusters usually results in iodination of boron atoms, rather than carbon atoms [8]. NMR data, however, confirm the location of the iodine atom on the cage carbon vertex as is also apparent from the crystallographic results (Fig. 1). Thus, four doublets of mutually equal intensity are seen in the ^{11}B spectrum of compound **2**, confirming the presence of four {BH(*exo*)} vertices, thence confirming the position of the iodine on the cluster carbon atom. In the mass spectrum a parent-ion envelope with a high-mass cut-off peak at *m/e* 665 Daltons, corresponding to the ^{103}Rh$_2$^{12}C$_{21}$^{11}B$_4$^{1}H$_{35}$^{127}I molecular ion, is seen. Interestingly, however, the mass spectrum is dominated by a base-peak envelope with a high-mass cut-off peak at 538 Daltons, representing loss of an iodine atom, consistent with cleavage of the carbon–iodine bond.

The carborane core of **2** also merits brief note, because {CB$_4$} polyhedral fragments in coordination with metals are, as far as we are aware, very rare: reported small metallacarboranes with five to seven cluster vertices are dominated by compounds containing {C$_2$B$_3$} or {C$_2$B$_4$} cluster fragments [9]. These species are generally generated from the reaction of small carbaborane substrates with metal precursors [9] and few have arisen from the controlled dismantling of larger single-cluster metallacarbaboranes. In this respect, the synthesis of compound **2,** together with its method of formation in good yield, thence constitute an interesting addition to the growing library of the chemistry of the small metallacarboranes.

3. Experimental

Reactions were carried out in dry solvents (dichloromethane and hexane) and under a dry argon atmosphere, 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. NMR spectroscopy was performed at 9.4 T (corresponding to 128.3 MHz for ^{11}B and 400 MHz for ^{1}H) on a CD$_3$CN solution at 25 °C. δ (^{11}B) values are given in ppm to high frequency of Et$_2$OBF$_3$.

3.1. Isolation of [1,2-(η^5-C$_5$Me$_5$)$_2$-μ^2-1,2-H-closo-1,2,3-Rh$_2$CB$_4$H$_4$-3-I] (compound **2**) from the reaction of [2,5(η^5-C$_5$Me$_5$)$_2$-10-Me-μ^2-2,5-H-nido-2,5,1-Rh$_2$CB$_6$H$_8$ (**1**)] with I$_2$ and NEt$_3$

To a solution of [2,5-(η^5-C$_5$Me$_5$)$_2$-10-Me-μ-2,5-H-*nido*-2,5,1-Rh$_2$CB$_6$H$_8$] (compound **1**, 110 mg; 190 µmol) in dry CH$_2$Cl$_2$ (15 ml) was added a four-molar excess of NEt$_3$ (0.6 ml, 77 mg, 760 µmol). Tiny crystals of elemental iodine ($\approx$50 mg; 200 µmol) were then added until the solution turned a clear orange colour. This mixture was left to stir at room temperature under dry Argon for a period of one hour. During this period small aliquots of the reaction mixture were taken and TLC measurements performed in order to monitor the progress of the reaction [silica G on aluminium foil {Siluflol (Kavalier, Prague)}, with components being detected by iodine vapour followed by aqueous AgNO$_3$ spray]. Once all the starting compound **1** was consumed, the solution was reduced in volume in vacuo (room temperature, water pump), and filtered through a small amount of silica. The filtrate was subjected to column chromatography (2×25 cm, silica gel, 70–220 mesh) using a 1:1 mixture of hexane and dichloromethane as mobile phase. The major eluted component (orange, R_F 0.6 by analytical TLC, 1:1 hexane:dichloromethane) was collected and thence further purified by preparative TLC (1:1 hexane:dichloromethane R_F = 0.6) and found to be [1,2-(η^5-C$_5$Me$_5$)$_2$-μ-1,2-H-*closo*-1,2,3-Rh$_2$CB$_4$H$_4$-3-I] (compound **2**) (100 mg; 150 µmol, 79%). Orange crystals, m.p. 189–192 °C, suitable for single-crystal X-ray diffraction were grown by slow diffusion of hexane into a concentrated solution of compound **2** in dichloromethane. NMR: δ (^{11}B) +47.3 [d, ^1J(^{11}B–^{1}H) ca. 146 Hz , 1B, B(6)], +22.2 [d, ^1J(^{11}B–^{1}H) ca. 135 Hz , 1B, B(5)], +10.7 [d, ^1J(^{11}B–^{1}H) ca. 165 Hz, 1B, B(7)] and +8.3 (d, ^1J(^{11}B–^{1}H) ca. 143 Hz, 1B, B(4)]; [^{11}B–^{11}B]-COSY cross-peaks were observed for all adjacent boron sites; δ (^{1}H) (from ^{1}H–{^{11}B} experiments) +3.66 [s, 1H, H(6)], +3.04 (s, 1 H, H(5), +1.25 [s, 1H, H(7)], +0.89 [s, 1 H, H(4)] and −15.6 [t, ^1J(^{103}Rh–^{1}H) 32 Hz, 1H, µH(1,2)]. Mass spectrum: *m/e*(max) at 665 Daltons, corresponding to ^{103}Rh$_2$^{12}C$_{21}$^{11}B$_4$^{1}H$_{35}$^{127}I.

3.2. X-ray crystallography

Crystal data for 1,2-(C$_5$Me$_5$)$_2$-closo-1,2,3-Rh$_2$CB$_4$H$_5$-3-I (**2**). Rh$_2$C$_{21}$B$_4$H$_{35}$I: *M* = 663.45, monoclinic, *a* = 15.1581

(3), $b = 9.0151$ (2), $c = 17.9380$ (3) Å, $\beta = 97.234$ (1), $U = 2431.75$ (8) Å^3, $\lambda = 0.71073$ Å, $T = 120(2)$ K, space group $P2_1/c$, $Z = 4$, $\mu(\text{Mo K}\alpha) = 2.632$ mm^{-1}, $R_{int} = 0.0768$ for 4169 reflections and $wR(F^2) = 0.2328$ for all 4735 unique reflections. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 252556 for compound **2**.

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