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Communication

B-frame supported bimetallics. 'Composite cluster' compounds and the structures of $[2,7\text{-}(\eta^5\text{-}C_5Me_5)_2\text{-}nido\text{-}2,7,8,6\text{-}Ir_2CSB_6H_8]$ and its 9-chloro derivative. Synchrotron and conventional X-ray studies ☆

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It is a pleasure and a privilege for the authors to be able to contribute this paper to the Sheldon Shore 70th Birthday Special Edition of the Journal of Organometallic Chemistry, in recognition of Professor Shore's astute contributions to the area of polyhedral boron-containing cluster chemistry that have been, and will continue to be, an omnipresent inspiration and example for successive generations of boron cluster chemists.

Abstract

Reaction of $[IrCl_2(\eta^5\text{-}C_5Me_5)]_2$ with the $[hypho\text{-}CSB_6H_{11}]^-$ anion gives $[2,7\text{-}(\eta^5\text{-}C_5Me_5)_2\text{-}nido\text{-}2,7,8,6\text{-}Ir_2CSB_6H_8]$ and $[2,7\text{-}(\eta^5\text{-}C_5Me_5)_2\text{-}nido\text{-}2,7,8,6\text{-}Ir_2CSB_6H_7\text{-}9\text{-}Cl]$ which exhibit composite cluster features in which the {IrSIrC} string and the $\{B_6\}$ unit occupy separate domains within the overall contiguous *nido*-type ten-vertex $\{Ir_2SCB_6\}$ cluster unit. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: X-ray; Synchrotron; NMR; Metallacarbathiaborane; Borane cluster; Thiaborane cluster; Carbathiaborane cluster; Composite cluster; B-frame bimetallics

Metallaborane and metallaheteroborane chemistry is extensive, and has historically developed largely by the assimilation of one, two or three atoms other than boron into the borane cluster. More rarely, four or more heteroatoms are incorporated [1–7]. There is current interest in the nature of the chemistry that may generally result when the number of metal and non-metal heteroatoms increases to four or more and ultimately approaches the number of boron atoms in the cluster [7–12]. In sulfur-containing cluster compounds such as $[(PPh_3)_3ClRh_2S_2B_7H_7]$ (compound **1**) (schematic **I**) [8], $[\{(PR_3)PdS_2B_6H_8\}_2]$ (compound **2**) (schematic **II**) [9], and $[(C_5H_5)_2Co_2S_2B_2H_2]$ (compound **3**) (schematic **III**) [10,11] there appears to be an interesting tendency for transition-element and *p*-block atoms on one hand, and boron atoms on the other, to group together in separate domains (hatched lines in **I**, **II** and **III**; see also **V** below). Similar clustering is also often a feature of polymetallapolycarbaboranes [13].

☆ IUPAC nomenclature: 2,7-bis(*pentahapto*-pentamethylcyclopentadienyl-*nido*-2,7-diirida-8-carba-6-thiadecaborane and 9-chloro-2,7-bis(*pentahapto*-pentamethylcyclopentadienyl-*nido*-2,7-diirida-8-carba-6-thiadecaborane.

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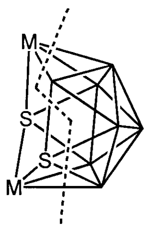
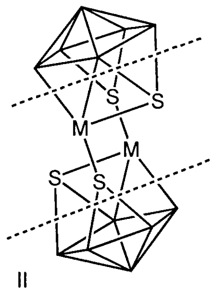


I



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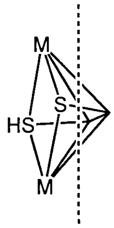


III

This type of grouping generates ‘composite cluster’ species in which individual contiguous-domain subclusters, of boron atoms on one hand, and of metal and main-group atoms on the other, are mutually fused. We think it is useful to draw attention to this as a possible general phenomenon, which we further illustrate here in novel chemistry involving the structures of two two-metal mixed diheteroborane species [2,7-(η^5-C_5Me_5)$_2$-*nido*-2,7,8,6-$Ir_2CSB_6H_8$] (compound **4a**, Fig. 1) (schematic **IV**, X = H) and its 9-chlorinated analogue [2,7-(η^5-C_5Me_5)$_2$-*nido*-2,7,8,6-$Ir_2CSB_6H_7$-9-Cl] (compound **4b**, Fig. 2) (schematic **IV**, X = Cl). In schematics **IVA** and **IVB** unlabelled vertices represent BH(*exo*) units and **C** represents a CH(*exo*) unit. As far as we are aware, the incorporation of a combination of carbon, sulfur and two metal atoms is not previously reported for a boron-containing cluster species.

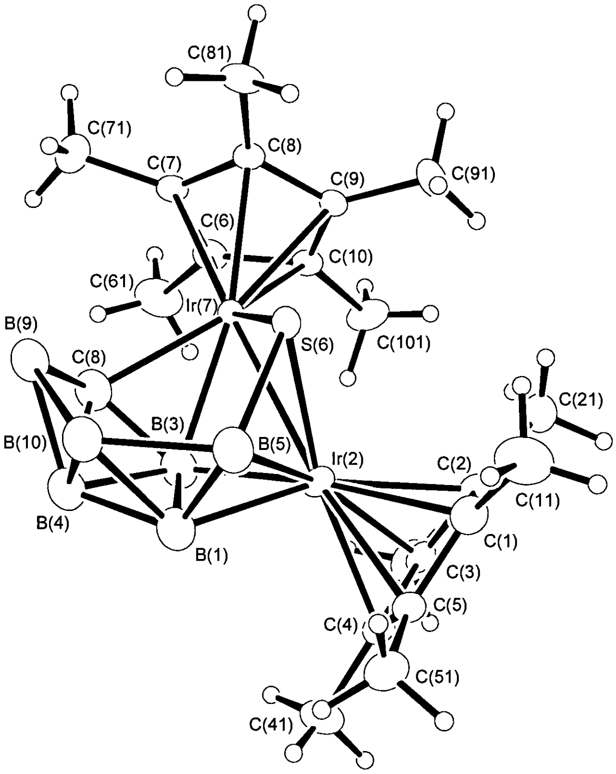


Fig. 1. Crystallographically determined molecular structure of one component of the disordered molecule of [2,7-(η^5-C_5Me_5)$_2$-*nido*-2,7,8,6-$Ir_2CSB_6H_8$] (compound **4a**) (schematic **IV**, where X = H). The disorder arises from a *pseudo* C_2 axis which exchanges the two {Ir(C_5Me_5)} units and also closely juxtapositions the {BH(5)} vertex and the {CH(8)} vertex. The *pseudo* C_2 axis generates two sites for each of the remaining {S} and {BH} vertices. Selected interatomic distances (in Å) are as follows: Ir(2) to B(1) 2.12(2), to B(3) 2.15(2), to B(5) 2.222(11), to S(6) 2.461(4) and to Ir(7) 2.8090(5); Ir(7) to B(1) 2.26(3), to S(6) 2.402(4) and to C(8) 2.187(11); B(9) to C(8) 1.57(2) and to B(10) 1.74(3); note that the *nido*-decaboranyl ‘gunwale’ distance B(5)–B(10) is typically ‘long’ at 1.97(2). All the other interatomic bonding distances are in normal ranges, although those from Ir(2) to B(1) and B(3) are perhaps somewhat towards the shorter end of iridium-to-boron ranges [30] in known polyhedral compounds.

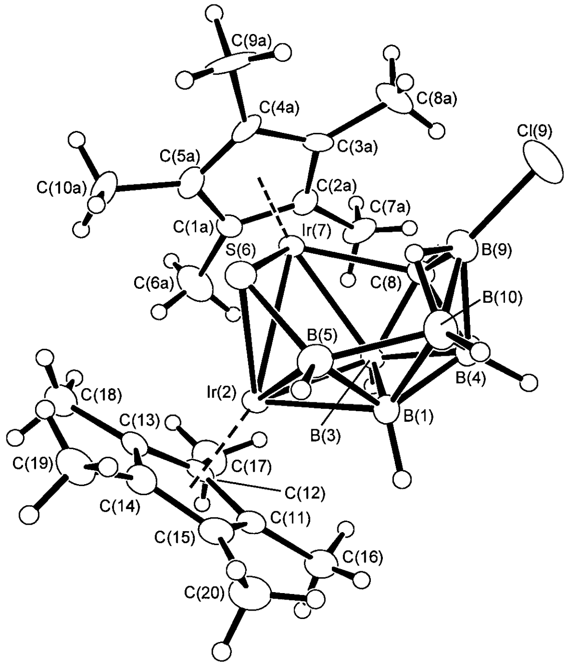
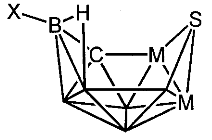
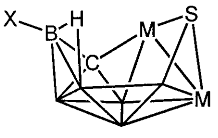


Fig. 2. Crystallographically determined molecular structure of [2,7-(η^5-C_5Me_5)$_2$-*nido*-2,7,8,6-$Ir_2CSB_6H_7$-9-Cl] (compound **4b**) (schematic **IV**, where X = Cl). The {C_5Me_5} group on Ir(7) is disordered equally over two positions rotated at an angle of ca. 36° to each other. In the interests of clarity only one site is shown. Selected interatomic distances (in Å) are as follows: Ir(2) to B(1) 2.177(7), to B(3) 2.243(6), to B(5) 2.217(7), to S(6) 2.3477(15) and to Ir(7) 2.8070(3); Ir(7) to B(3) 2.323(6), to C(8) 2.187(11) and to S(6) 2.3200(16); B(9) to C(8) 1.532(10), to B(10) 1.775(12) and to Cl(9) 1.792(8) Å. Again note that B(5)–B(10) is ‘long’ at 1.915(11) Å (compare compound **4a** in Fig. 1).



IVA



IVB

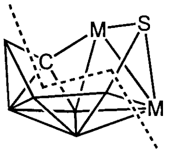
This ‘composite cluster’ chemistry is distinct from the ‘hybrid cluster’ phenomenon [7,12], as noted, for example, in the *hypho*-type species $MeCS_2NB_7H_9$ [12], in which there are mutually exclusive domains of cluster structure and domains of classical two-electron two-centre main-group chain and ring chemistry. It is also distinct from the multicluster assemblies in which individual diverse sub-groupings conjoin with one common metal atom and are non-contiguous, such as {Ru_3}/

$\{RuB_{10}\}$[14], $\{Au_6\}/\{AuB_{10}\}$[15] and $\{C_2B_{10}Mo\}/\{Mo_2S_4\}/\{MoC_2B_{10}\}$[16].

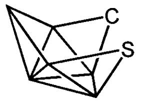
Reaction of [*hypho*-7,8-$CSB_6H_{11}]^-[tmndH]^+$ [17] (42 mg, 130 μmol) (where tmnd = *N*,*N*,*N*′,*N*′-tetramethylnaphthalene-1,8-diamine) with $[IrCl_2$-(η^5-$C_5Me_5)]_2$ (107 mg, 130 μmol) and tmnd (56 mg, 260 μmol) in CH_2Cl_2 (ca. 10 cm^3) for 24 h at room temperature, followed by evaporation and TLC separation on silica gel G (1:1, CH_2Cl_2–hexane), gave an intense red component (R_F 0.62), that was extracted from the silica with CH_2Cl_2 and identified as blood-red $[(C_5Me_5)_2$-*nido*-$Ir_2CSB_6H_8]$ (compound **4a**, 36 mg, 35%) after further TLC purification using CH_2Cl_2–hexane solvent mixtures. Other minor coloured components were present, including trace quantities of compound **4b** (see below).

Because of the high heteroatom content, NMR interboron [18] and interproton [19] correlation methods [20,21] do not reveal the molecular structure, though they do suggest the boron framework.[1] Crystals (from benzene–hexane) were thin (40 μm wafers), and required synchrotron X-radiation [22,23] for sufficient diffraction intensity for single crystal work [24,25].[2] The resultant molecular structure is in Fig. 1. We found that within the crystal there was a disorder about a *pseudo* twofold rotation axis such that the two $\{Ir(C_5Me_5\}$ units were entirely coincident in both contributions, and the atoms in the heteroborane cluster labelled B(5) and C(8) in Fig. 1 were very nearly coincident. Others also had close proximities that also rendered the overall analysis difficult. Although the non-hydrogen atoms refined anisotropically (with the aid of rigid-bond and similarity restraints to the displacement parameters), and hydrogen atoms could be included on the C_5Me_5 ligands (Fig. 1), location of cluster hydrogen atoms was precluded because of the disorder. However, NMR spectroscopy[5] showed terminal hydrogen atoms on the cluster carbon atom C(8) and the six boron atoms, and a bridging hydrogen atom at the open face in the B(9)–B(10) position as shown in schematics **IV**.

Because of these crystallographic problems, recrystallisation was attempted from various solvent systems in the hope of generating a more amenable crystal type. These attempts ultimately gave orange–red crystals, after several months in chloroform–hexane. These, however, were not of **4a**, but of its 9-chlorinated analogue [2,7-(η^5-$C_5Me_5)_2$-*nido*-2,7,8,6-$Ir_2CSB_6H_7$-9-Cl] (compound **4b**), which was also present in the original product mixture in small quantities (TLC R_F 0.55; 1:1, CH_2Cl_2–hexane). X-ray diffraction analysis using a conventional sealed-tube source[6] gave the structure as shown in Fig. 2. In this, there was a 50:50 rotational disorder of the C_5Me_5 group on Ir(5), with one C_5Me_5 ring rotated at approx 36° to the other. This, however, was readily resolved, and did not preclude the location of cluster hydrogen atoms, though these were not refined in the final analysis. For both **4a** and **4b** the NMR properties of the bulk material[5] were consistent with the solid-state structure, indicating that the crystals were representative.



V



VI

The cluster structures of both **4a** and **4b** are seen to adopt a basic *nido* ten-vertex configuration as typified by the *nido*-$B_{10}H_{14}$ model. This observed geometry is in accord with Wade's rules [26–29], which would predict a *nido* ten-vertex constitution. However, because of the disparate sizes of the boron, sulfur, carbon and iridium atoms there is considerable distortion **IVB** from the schematically ideal **IVA** as exemplified by the C_{2v} geometry of *nido*-$B_{10}H_{14}$ itself. Within this structure it is seen that that there is a grouping together of the {MSMC} string and the $\{B_6\}$ unit in separate domains (schematic **V**), well illustrating the phenomenon of 'composite cluster' formation. There appears to be a driving force to achieve this because it is apparent that there has been

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[1] Selected data for $CDCl_3$ solutions at 294–300 K {cluster resonances ordered as: assignment $\delta(^{11}B)$/ppm [$\delta(^1H)$/ppm for directly attached *exo*-hydrogen]}: [2,7-(η^5-$C_5Me_5)_2$-*nido*-2,7,8,6-$Ir_2CSB_6H_8$] (compound **4a**): BH(1) − 1.4 [+ 2.64], BH(3) + 5.8 [+ 2.80], BH(4) − 38.2 [+ 1.13], BH(5) + 11.5 [+ 4.58], BH(9) + 17.2 [+ 4.78] and BH(10) − 12.2 [+ 2.10], with $\delta(^1H)$ values for H(μ-9,10) − 4.18, CH(8) + 3.06 and for C_5Me_5 + 1.93 (both coincident); [2,7-(η^5-$C_5Me_5)_2$-*nido*-2,7,8,6-$Ir_2CSB_6H_7$-9-Cl] (compound **4b**) BH(1) − 3.0 [+ 2.60], BH(3) + 3.8 [+ 3.59], BH(4) − 35.3 [+ 1.60], BH(5) + 10.6 [+ 4.53], BCl(9) + 21.8 [no *exo* H atom, Cl-substituted site] and BH(10) − 16.2 [+ 1.85], with $\delta(^1H)$ values for H(μ-9,10) − 2.78, CH(8) + 2.87 and for C_5Me_5 + 1.94 (both coincident). Cluster ^{11}B and ^1H assignments were by [^{11}B–^{11}B], [^1H–^1H] and ^1H-{^{11}B} correlation experiments [18–21,31–33]. The mass spectrum (70 eV EI) for each compound gave a high mass cut-off corresponding to the highest isotopomer of the molecular ion, but with the highest-mass isotopomer envelope also showing considerable loss of dihydrogen from the molecular ion.

[2] Crystal data for compound **4a** $[C_{21}H_{38}B_6Ir_2S]$, CCDC deposition no. 144020, blood-red wafer, 0.28 × 0.14 × 0.04 mm, from benzene–hexane, $M = 771.83$, monoclinic, space group $P2_1/c$, $a = 15.1838(8)$, $b = 10.1432(6)$, $c = 17.1804(10)$ Å, $\beta = 107.580(2)°$, $U = 2522.4(2)$ Å^3, $Z = 4$, wiggler-generated synchrotron X-radiation ($\lambda = 0.68890$ Å, Station 9.8 [22,23] CCLRC Daresbury Laboratory), $\mu = 10.631$ mm^{-1}, $T = 160(2)$ K, $R_1 = 0.0536$ for 4975 reflections with $I > 2\sigma(I)$, and $wR_2 = 0.1297$ for all 5495 independent reflections. Data were collected on a Bruker AXS SMART CCD diffractometer using the manufacturer's control and integration programs and following a standard procedure, details of which are presented elsewhere [22,23]. Crystal data for compound **4b** $[C_{21}H_{37}B_6ClIr_2S]$, CCDC deposition no. 144021, orange–red prism, 0.56 × 0.22 × 0.10 mm, from chloroform–hexane, $M = 806.28$, monoclinic, space group $P2_1/n$,, $a = 8.4649(2)$, $b = 14.4633(3)$, $c = 20.9099(4)$ Å, $\beta = 94.1430(11)°$, $U = 2553.32(9)$ Å^3, $Z = 4$, Mo–K_α X-radiation, $\lambda = 0.71073$ Å, $\mu = 10.608$ mm^{-1}, $T = 150(2)$ K, $R_1 = 0.0378$ for 4700 reflections with $I > 2\sigma(I)$, and $wR_2 = 0.0976$ for all 5016 independent reflections. Data were collected on a Nonius Kappa CCD diffractometer with the manufacturer's control and integration programs [34,35], using a mixture of area-detector ω- and ϕ-scans. Both structures were solved by direct methods [36] and were refined by full-matrix least-squares (on F^2) using SHELXL-97 [37].

a B-frame rearrangement from the structure **VI** of the *hypho* starting substrate $[CSB_6H_{13}]^-$ to give the product configuration **V**. A possibly related B-frame rearrangement has also been noted in the formation of $[(PPh_3)_3ClRh_2S_2B_7H_7]$ (compound **1**) from its starting substrate 4,6-$S_2B_7H_9$ [8]. This type of phenomenon has interesting implications. For example, the tailoring of compounds allied with crystal engineering and appropriate curing may engender the possibility of fabricating composite sheet structures layered at the sub-nano level. We are currently looking for additional and even more pronounced examples of this phenomenon in a variety of heteroborane systems.

1. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 144020 for compound **4a** and CCDC no. 144021 for compound **4b**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). Crystallographic data are also to be found on http://www.chem.leeds.ac.uk/boronweb/crystal_archive.html

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