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Polyhedral ruthenaborane chemistry. Approaches to encapsulated boron cores. The isolation and characterisation of the partially encapsulated *isocloso* 10-vertex $\{RuB_9\}$ cluster compound $[(PPh_3)RuB_9H_9\{RuCl_2(PPh_3)_2\}_2]$

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Abstract

$[RuCl_2(Ph_3)_2]$ with $[$*arachno*-$B_9H_{14}]^-$ gives $[(PPh_3)RuB_9H_9\{RuCl_2(PPh_3)_2\}_2]$, which has an *isocloso* 10-vertex $\{RuB_9\}$ core geometry that is partially encapsulated by *exo*-polyhedral $\{RuCl_2(PPh_3)_2\}$ units that cap $\{RuB_2\}$ triangular faces with one $\{RuClRu\}$ and two $\{RuHB\}$ bridges each. The structure engenders focus on the several new compound classes emerging in polyhedral boron-containing cluster chemistry.

Keywords: Metallaboranes; Encapsulated clusters; Cluster categories; Ruthenium-borane cluster; Transition-element hydrides; NMR spectroscopy; X-ray diffraction

Interesting molecular species emerge, and interesting new chemistry is portended, when polyhedral boron cores are surrounded by skins of hydrophilic hydroxy groups, as in the $[B_{12}(OH)_{12}]^{2-}$ anion [1], and by skins of lipophilic organyl groups, such as in the $[B_{12}(CH_3)_{12}]^{2-}$ anion and related species [2,3]. Related to these new structural types are the proposed 'megaloborane' clusters in which a polyhedral boron core is encapsulated by a skin of cross-linked boron hydride units [4–6]. Here we present preliminary results on a structural system that represents an initial step towards the extension of this polyhedral encapsulation concept to the synthesis of species based on polyhedral boron cores surrounded by a skin of units based on transition-element centres, rather than a skin of hydrocarbon or hydroxy ligands.

Reactions of $[RuCl_2(PPh_3)_3]$ with the $[$*nido*-$B_9H_{12}]^-$ or $[$*arachno*-$B_9H_{14}]^-$ anions have been reported to produce the monometallaboranes [6,6,6-$(PPh_3)_2$H-5-(PPh_3)-*nido*-6-RuB_9H_{12}] (compound **1**) and [1,1,1-(PPh_3)HCl-5,6-$(PPh_3)_2$-*isocloso*-1-RuB_9H_7] (compound **2**) [7]. From this same reaction system we now report the isolation of an interesting triple-ruthenium species of formulation $[(PPh_3)RuB_9H_9\{RuCl_2(PPh_3)_2\}_2]$ (compound **3**). Thus, the reaction of $[RuCl_2(PPh_3)_3]$ (961 mg, 1 mmol) and $[NEt_4][$*arachno*-$B_9H_{14}]$ (974 mg, 4 mmol) in CH_2Cl_2 (80 ml) for 18 h gave a red solution. Short-column chromatography on silica using CH_2Cl_2 as liquid phase thence resulted in the isolation of several products, purified by preparative TLC on silica gel G using CH_2Cl_2 as developing solvent. Identified species are: (a) known compound **1** (red, R_F 0.91; 272 mg;

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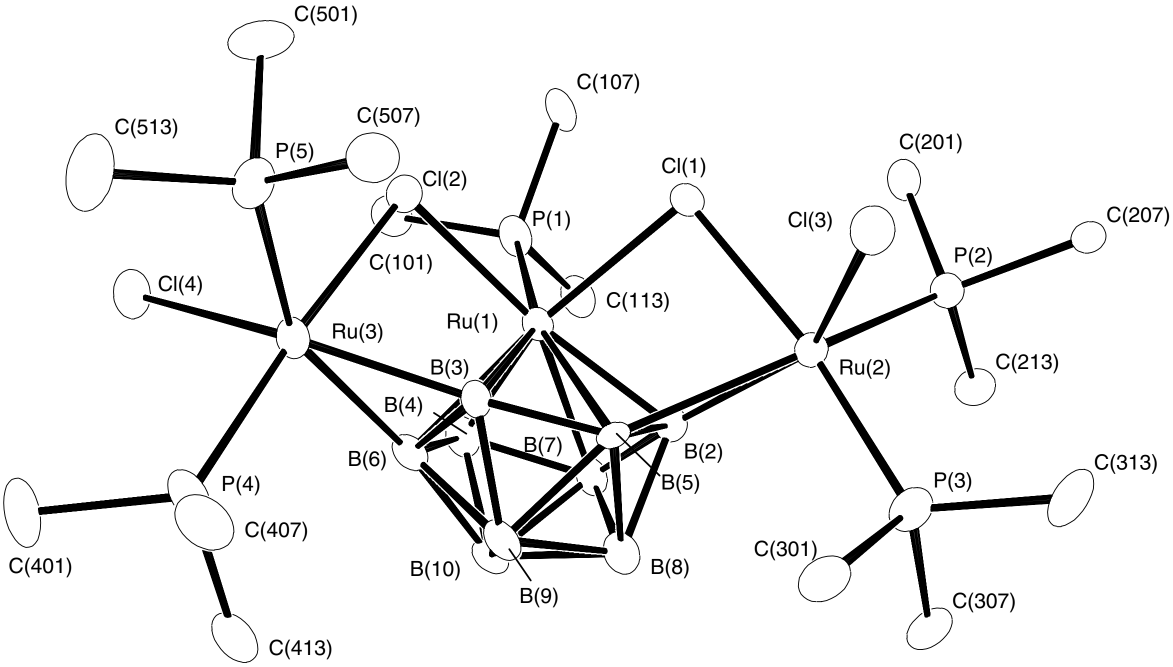

Fig. 1. ORTEP-type drawing of the crystallographically determined molecular structure of $[(PPh_3)RuB_9H_9\{RuCl_2(PPh_3)_2\}_2]$(compound **3**). P-phenyl group atoms, apart from the *ipso* carbon ones, are omitted for clarity. Cluster hydrogen atoms were not reliably locatable from the diffraction analysis, but NMR spectroscopy[2] demonstrates metallaborane hydrogen atoms bridging the Ru(2)B(2), Ru(2)B(5), Ru(3)B(3) and Ru(3)B(6) vectors (schematic structure **I**) and in *exo*-terminal positions on B(4), B(7), B(8), B(9) and B(10). Distances from the Ru(1) atom are: to P(1) 2.468(3), to Cl(1) 2.462(2), to Cl(2) 2.448(3), to B(2) 2.099(11), to B(3) 2.181(11), to B(4) 2.094(12), to B(5) 2.338(11), to B(6) 2.302(11), and to B(7) 2.361(11), distances from the Ru(2) atom are: to P(2) 2.306(3), to P(3) 2.324(3), to Cl(1) 2.497(2), to B(2) 2.231(11), and to B(5) 2.569(10) and distances from the Ru(3) atom are: to P(4) 2.347(3), to P(5) 2.335(3), to Cl(2) 2.480(2), to B(3) 2.237(11), and to B(6) 2.513(11) Å. Interboron distances are within the range 1.67(2)–1.88(2) Å.

27%) [6]; (b) new $[(PPh_3)RuB_9H_9\{RuCl_2(PPh_3)_2\}_2]$ (orange, compound **3**; R_F 0.85; 534 mg; 28%); and (c) known compound **2** (yellow, R_F 0.67; 43 mg; 4%) [6]. Other components, present in smaller quantities, are as yet unidentified. The solid-state molecular structure of compound **3** (Fig. 1)[1] is consistent with the bulk NMR properties.[2] All atoms, including most hydrogen atoms, were located, apart from the four bridging hydrogen atoms and the five terminal hydrogen atoms on the cluster, which, however, were readily confirmed by ^{1}H–^{11}B(selective) NMR experiments.[2]

The core cluster unit of compound **3** is seen to have a characteristic 10-vertex $\{RuB_9\}$ metallaborane *isocloso* geometry which engenders the characteristic 10-vertex *isocloso* $\{MB_9\}$ 3:3:3 ^{11}B relative intensity NMR resonance grouping as typified by the simple models $[1,1,1\text{-}H(PMe_3)_2$-*isocloso*-$1\text{-}IrB_9H_9]$ and $[1\text{-}(\eta^6\text{-}MeC_6H_4CHMe_2)$-*isocloso*-$1\text{-}RuB_9H_9]$ [8,9]. Uniquely, however, there are in addition two exopolyhedral ruthenium atoms, numbered Ru(2) and Ru(3), each encompassed in a $\{RuCl(PPh_3)_2\}$ unit bonded to the central $\{RuB_9\}$ cluster via a $\{RuCl_{\mu}Ru\}$ bridge and two $\{RuH_{\mu}B\}$ bridges to give octahedral bonding geometry about the metal centres in each case (Scheme 1). This type of $\{RuCl_{\mu}Ru\}$ linkage is as in $[(PPh_3)_2ClRuClRu\ (PPh_3)B_{10}H_8(OEt)_2]$ [10], which has only one such $\{RuCl_2(PPh_3)_2\}$ unit bound to a central eleven-vertex *isocloso* $\{RuB_{10}\}$ cluster, rather than two $\{RuCl_2(PPh_3)_2\}$ units bound to a 10-vertex *isocloso* $\{RuB_9\}$ cluster as in compound **3** described here. The binding mode is also related to the metal-to-cluster bonding system in $[\{(PPh_3)_2Ru\}\text{-}\mu,\mu,\mu\text{-}(MeCOO)_3\text{-}\mu,\mu\text{-}H_2\text{-}\{RuB_{10}H_7\}]$, also based on a central

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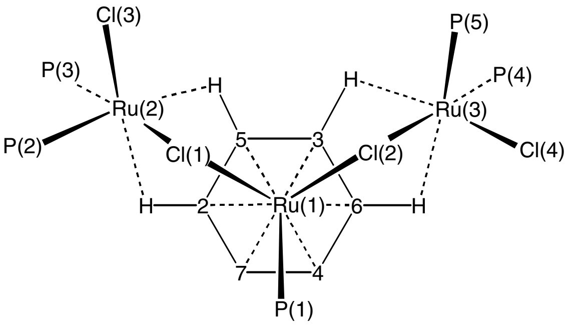
[1] *X-ray diffraction analysis*: $[(PPh_3)RuB_9H_9\{RuCl_2(PPh_3)_2\}_2]\cdot(CH_2Cl_2)_{1.25}(C_6H_6)_{0.5}$, CH_2Cl_2/C_6H_6 solvate of compound **3**, $C_{94.25}H_{89.5}B_9Cl_{6.5}P_5Ru_3$, $M = 2007.93$, orthorhombic, $P2_12_12_1$ (from CH_2Cl_2/C_6H_{12}), $a = 17.9276(5)$, $b = 20.0446(6)$, $c = 26.4539(7)$ Å, $\alpha = \beta = \gamma = 90°$, $U = 9506.3(5)$ Å^3, $D_{calc} = 1.403$ mg m^{-3}, $Z = 4$, Mo Kα, $\lambda = 0.71073$ Å, $\mu = 0.782$ mm^{-1}, $T = 193(2)$ K, $R1 = 0.058$ for 12511 reflections with $I > 2\sigma(I)$, and $wR_2 = 0.115$ for all 19,404 independent reflections; CCDC reference number CCDC 245961. Solution and refinement programs were from the SHELX suite (G.M. Sheldrick, University of Göttingen).

[2] Measured NMR data for compound **3**, $CDCl_3$ solution at 293 K, ordered as assignment $\delta(^{11}B)$/ppm [$\delta(^{1}H)$/ppm in square brackets]: BH(2) and BH(3) +8.73 [−9.12] and +77.4 [−8.38], BH(4) +85.0 [+9.39], BH(5) and BH(6) ca. −29.9 [−1.65, with $^{2}J(^{1}H–^{31}P)$(*trans*) 22 Hz] and ca. −29.9 [−3.55, with $^{2}J(^{1}H–^{31}P)$(*trans*) 47 Hz], −14.6 [−0.45], BH(8) +20.9 [+2.60], BH(9) and BH(10) ca. +27.5 [+2.88] and ca. +27.5 [+2.25]; additionally $\delta(^{1}H)$(Ph) around ca. +7.5 (unresolved multiplets) and, at 233 K, $\delta(^{31}P)$ [with approx $^{2}J(^{31}P–^{31}P)$ values in square brackets]: +49.8 [29 Hz], +46.4 [25 Hz], + 48.4 [25 Hz], +41.6 [29 Hz] and +18.7 (no fine structure observed in $^{31}P–\{^{1}H\}$ spectrum).



Scheme 1.

eleven-vertex *isocloso* $\{RuB_{10}\}$ cluster [11]. There are also parallels in the structure of $[\{Cu(PPh_3)\}_2$-μ,μ-H_2-$\{ReB_9H_7CPh\}]$ that is based on a central eleven-vertex $\{ReCB_9\}$ core [12]. The result in compound **3** is an incipient partial encapsulation of the central $\{RuB_9\}$ core by a developing ruthenium hydride skin.

It is interesting to speculate that this partial encapsulation of the central $\{RuB_9\}$ unit by the other two ruthenium centres may presage a new general structural type based on a more complete encapsulation of a polyhedral boron hydride core by a sheath of linked metal centres. Similarly, encapsulations of carbon hydride cores could also be envisaged, as presaged by species such as $[Ru_6(C_{10}H_6)(PPh)(CO)_{14}]$ [13]. This structural principle contrasts with and complements recently reported earlier-transition-element metallaborane species such as $[(\eta^5\text{-}C_5Me_5)_2Re_2B_7H_7]$, $[(\eta^5\text{-}C_5Me_5)_2W_2B_7H_9]$ and $[(\eta^5\text{-}C_5Me_5)_3W_3HB_8H_8]$ [14], which may conversely presage central polymetal cores encapsulated by boron hydride skins. Experimental approaches to these latter could include the replacement of halides on earlier transition-element polyhalopolymetal anions such as $[Mo_6Cl_{14}]^{2-}$ *via* substitution by anionic boron hydride moieties. These considerations draw attention to other globular borane-based structural principles that are contemporaneously emerging. Thus in addition to species such as the $[B_{12}Me_{12}]^{2-}$, $[B_{12}(OH)_{12}]^{2-}$ and $[B_{12}(OR)_{12}]^{2-}$ dianions that are based on borons-only cores surrounded by hydrocarbon, hydroxy, or organyloxy skins [1,2,14–17], features of species such as $[(CO)(PMe_3)_2Ir B_{26}H_{24}Ir(PMe_3)_2]$, $[(C_5Me_5)_3Ir_3B_{18}H_{15}(OH)]$ and $[(PPh_3)_3(PPh_2)_2Pd_3B_{20}H_{16}Pd(PPh_3)]$ suggest families of very big boranes based on borons-only cores surrounded by boron hydride skins [4,5,18,19]. Species such as $[(CH_2CH_2C_5H_4N)$-*arachno*-$B_{10}H_{10}$ $(NC_5H_4$-*closo*-$C_2B_{10}H_{11})]$ similarly may presage carbons-only cores surrounded by boron hydride skins [21]. Another novel cluster structural principle emerging from a consideration of the structure of $[(PPh_3)_2(PPh_2)Pd_3B_{20}H_{16}Pd(PPh_3)]$ [4] is that consisting of a string of alternating metal and non-metal atoms attached to the borane hydride cluster surface. This last type of *exo*-cluster heteroatom molecular assembly motif contrasts in turn with another emerging new general structural type, exemplified by species such as $[(C_5Me_5)_2Ir_2CSB_6H_8]$, and $[C_6B_6H_6]$ and its derivatives [20,21], which exhibit separate metal and/or heteroatom strings and domains *within* individual boron-containing clusters rather than in *exo*-skeletal positions. This last 'composite cluster' chemistry contrasts in turn to the 'hybrid cluster' phenomenon, as noted, for example, by Sneddon and coworkers in the *hypho*-type species $MeCS_2NB_7H_9$ [22], 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 $\{Ru_3\}/\{RuB_{10}\}$ [23], $\{Au_6\}/\{AuB_{10}\}$ [24] and $C_2B_{10}Mo/\{Mo_2S_4\}/\{MoC_2B_{10}\}$ [25].

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Appendix A. Deposited data

Crystallographic data for compound **3** are deposited at the Cambridge Crystallographic Data Centre, CCDC, deposition no. CCDC 245961. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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