Communication

Macropolyhedral boron-containing cluster chemistry. An unusual 'neonido' ten-vertex subcluster configuration in a [(PPh3)2RuB16H20] species ☆

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Abstract

Reaction of $B_{16}H_{20}$ with $[RuCl_2(PPh_3)_3]$ gives a $[(PPh_3)_2RuB_{16}H_{20}]$ species of which the metallaborane cluster configuration consists of a conventional *nido* ten-vertex $\{B_{10}\}$ unit fused via a common $\{B_3\}$ face with a ten-vertex $\{RuB_9\}$ unit of novel 'neonido' ten-vertex shape.
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According to the very useful Williams/Wade cluster-geometry/electron-counting formalisms for 'electron deficient' cluster species [1–4], the classical *nido* ten-vertex cluster configuration **I** is geometrically derived by the removal of the six-connected vertex from the classical *closo* eleven-vertex configuration **II** to generate the six-membered open-faced arrangement of **I**, and this is manifest in very many boron-containing cluster compounds, as exemplified in other contributions to this Edition.
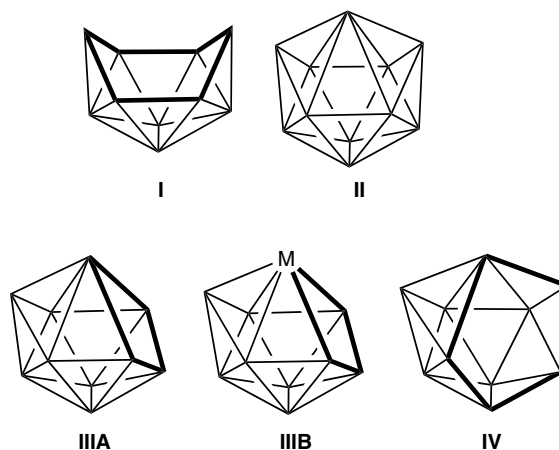

☆ A IUPAC nomenclature for the new species $[(PPh_3)_2RuB_{16}H_{20}]$ **1** would be 9,9-bis(triphenylphosphine)-*nido*-decaborano-⟨5′,6′,2′:7,8,10⟩-*neonido*-9-ruthenadecaborane. This article was freely submitted for publication without royalty. By acceptance of this paper, the publisher and/or recipient acknowledges the right of the authors to retain non-exclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce all or part of the copyrighted paper.

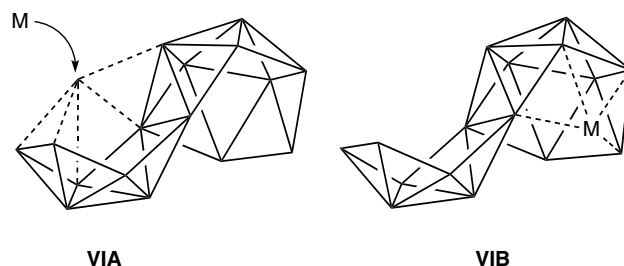* Corresponding author. Tel.: +44 113 343 6414/6401; fax: +44 113 233 6565.

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An alternative ten-vertex open-faced configuration **IIIA** is derived by the removal of a four-connectivity vertex from **II** to give a four-membered open face. This configuration, which has been dubbed 'isonido' [5], tends to be exhibited by $\{MB_9\}$ metallaborane species **IIIB**, in which the open-face position of cluster-connectivity five is occupied by a metal centre that is capable of high connectivities and/or higher metal formal oxidation states [5–8]. Here, we now report preliminary results on a third type of ten-vertex open-face configuration **IV**, that we tentatively describe as 'neonido'. This *neonido* configuration has a five-membered open face, and geometrically results from the removal of one of the three types of five-connectivity sites from the *closo* eleven-vertex geometry **II**. This is manifest in the $\{MB_9\}$ subunit (schematic **VB**) of the previously unreported seventeen-vertex macropolyhedral ruthenaborane $[(PPh_3)_2RuB_{16}H_{20}]$ (compound **1**, Fig. 1), in which the metallaborane unit (schematic **VA**) consists of this novel *neonido* $\{MB_9\}$ subunit **VB** fused to a conventional *nido* $\{B_{10}\}$ unit (schematics **I** and **VC**), with a triangular $\{B_3\}$ face held in common. The incidence of this 'neonido' ten-vertex shape in a fused double-cluster compound is nicely illustrative of the increasingly recognised ability of macropolyhedral species kinetically to arrive at unanticipated new sub-cluster geometries that can thence constitute a target for future single-cluster work [9]. The compound is isolated from the reaction between $B_{16}H_{20}$ and $[RuCl_2(PPh_3)_3]$ in the presence of the non-nucleophilic base 1,8-bis(dimethylamino)naphthalene. Although $B_{16}H_{20}$ has been known for some time, [10,11], its reaction chemistry is essentially unexamined [12].

VA   **VB**   **VC**
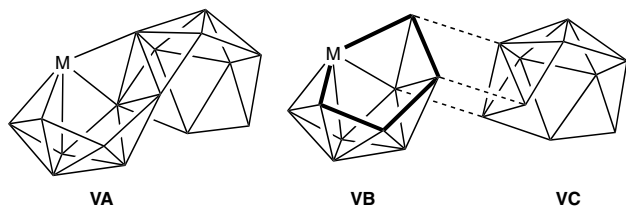
Thus, a small-scale preliminary siting reaction of $[RuCl_2(PPh_3)_3]$ (85 mg; 86 µmol), $B_{16}H_{20}$ (compound **2**, prepared essentially as in reference [10]; 15 mg; 77 µmol) and 1,8-bis(dimethylamino)naphthalene (36 mg; 170 µmol) in solution in refluxing CH_2Cl_2 (ca. 6 ml) for 4 h, followed by repeated TLC separation and purification [silica gel G (Fluka GF$_{254}$), 1 mm layer; CH_2Cl_2/hexane 60/40], resulted in the separation of a pure sample of air-stable orange $[(PPh_3)_2RuB_{16}H_{20}]$ (compound **1**) (R_F 0.75; 12 mg, 14 µmol, 19%), characterised as such by single crystal X-ray diffraction

analysis (Fig. 1 and schematics **V**),[1] together with NMR spectroscopy, elemental analysis and mass spectrometry.[2] From Fig. 1, it can be seen that the macropolyhedral $\{RuB_{16}\}$ cluster unit consists of a 'neonido' ten-vertex $\{RuB_9\}$ subcluster, as discussed above, fused to a conventional *nido* ten-vertex $\{B_{10}\}$ residue with a $\{B_3\}$ triangular face in common.
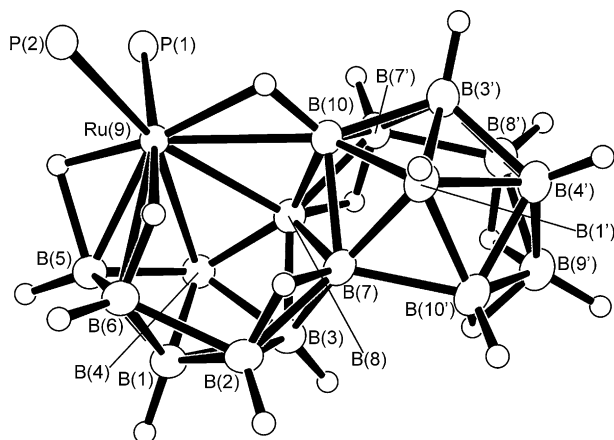

VIA   **VIB**

Fig. 1. Crystallographically determined molecular structure[1] of compound **1**, of formulation [(PPh$_3$)$_2$RuB$_{16}$H$_{20}$], with P-organyl groups omitted for clarity. Selected interatomic distances (in Å) are as follows: from Ru(9) to P(1) 2.3559(5), to P(2) 2.3828(5), to B(4) 2.449(2), to B(5) 2.181(2), to B(8) 2.362(2), to B(10) 2.464(2), to H(5,9) 1.57(2), to H(6,9) 1.77(2) and to H(9,10) 1.88(2); B(2)–B(6) is 1.850(3), B(7)–B(8) is 1.816(3), B(7)–B(10) is 1.852(3), B(7)–B(10′) is 1.869(3), B(7′)–B(8′) is 1.910(3) and B(8)–B(10) in the *conjuncto* link is markedly shorter at 1.694(3); B(5)–H(5,9) is 1.61(2), B(6)–H(6,9) is 1.26(2) and B(10)–H(9,10) is 1.19(2). Selected interatomic angles (in deg) are: P(1)Ru(9)P(2) 99.61(2), P(1)Ru(9)H(5,9) 76.5(8), P(1)Ru(9)H(6,9) 174.9(6), P(1)Ru(9)H(9,10) 98.4(6), P(1)Ru(9)B(4) 94.18(6), P(1)Ru(9)B(5) 108.41(7), P(1)Ru(9)B(8) 96.75(6) and P(1)Ru(9)B(10) 102.94(5); P(2)Ru(9)H(5,9) 85.97, P(2)Ru(9)H(6,9) 75.8(6), P(2)Ru(9)H(9,10) 85.1(6), P(2)Ru(9)B(4) 158.13(6), P(2)Ru(9)B(5) 113.86(6), P(2)Ru(9)B(8) 150.65(6) and P(2)Ru(9)B(10) 110.98(5); H(5,9)–Ru(9)–H(9,10) is nearly linear at 169(1).

In gross geometrical terms, a {Ru(PPh$_3$)$_2$} metal centre has simply added to the *nido*-octaboranyl {B$_8$} subcluster side of the {B$_{16}$} skeleton of **2**, as indicated in schematic **VIA**. However, the actual mechanism is not straightforward, because the molecular constitution of the product [(PPh$_3$)$_2$RuB$_{16}$H$_{20}$] implies an addition of a neutral {Ru(PPh$_3$)$_2$} unit to B$_{16}$H$_{20}$ with no hydrogen loss, whereas the anticipated stoichiometry starting from [RuCl$_2$(PPh$_3$)$_3$] would result in [(PPh$_3$)$_2$RuB$_{16}$H$_{18}$] with loss of two protons as base-sequestered HCl. It should, however, be pointed out that the result reported here arises from a small-scale siting experiment. Other products are present, and we plan to isolate and identify these. In view of the constitution and structure of this first defined species, the constitution and structure of these other products will be of high interest. For example, an additional interesting and unusual feature of the {RuB$_9$} subcluster is the incidence of the edge-bridging hydrogen atom on the Ru(9)B(5) edge, i.e. not on an open-face site, and it will be of interest to see if this type of feature is also mimicked in other macropolyhedral products from this and related systems. It will also be

of interest to ascertain whether products resulting from the addition of the ruthenium centre to the {B$_{10}$} subcluster of B$_{16}$H$_{20}$ also occur. In this last regard, the ruthenaborane **1** reported here contrasts to the only other B$_{16}$H$_{20}$-derived metallaborane reported, [(PMe$_2$Ph)$_2$PtB$_{16}$H$_{17}$Me] (compound **3**) of schematic skeletal configuration **VIB**, obtained using [PtMe$_2$(P-Me$_2$Ph)$_2$] as the cluster-metallating reagent [12]. In this latter platinum compound **3**, the metal atom has added to an alternative open face site on the other, *nido*-decaboranyl, subcluster of the starting B$_{16}$H$_{20}$ substrate (hatched lines in schematic **VIB**).

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