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A NOVEL CLOSO-TYPE METALLAUNDECABORANE, [1,1-(PPh₃)₂-2,5-(OEt)₂-1-RuB₁₀H₈], AND ITS RELATIONSHIP TO THE 'ISOCLOSO' SERIES OF METALLABORANE CLUSTERS

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(Received 19 March 1984; accepted 9 April 1984)

<u>Abstract</u> - The new ruthenaundecaborane $[(PPh_3)_2 RuB_{10}H_8(OEt)_2]$ may be considered as an eleven-vertex member of a previously unrecognised series of metallaboranes which are formally derived by the single capping of an *arachno*-type (rather than a *nido*-type) cluster geometry with a metal centre which can be thought of as contributing four orbitals to the cluster bonding schemes.

We wish to report preliminary findings about an interesting new eleven-vertex closo-type metallaborane $[(PPh_3)_2 RuB_{10}H_8(OEt)_2]$. The compound, an air-stable yellow solid, is prepared in reasonable yield (at present <u>ca</u>. 40%, unoptimized) by the reaction of the closo-decaborane anion $B_{10}H_{10}^{2-}$ with $[RuCl_2(PPh_3)_3]$ in ethanol/chloroform solution. The structure as determined by single-crystal X-ray diffraction analysis is given in the Figure. ¹ Hydrogen atoms were not locatable in this analysis, but multiple resonance n.m.r. spectroscopy shows that the only cluster hydrogen atoms are the eight *exo*-terminal ones on the non-ethoxy-substituted boron atoms. In particular there are no terminal or bridging hydrogen atoms associated with the metal centre or with the oxygen atoms. The cluster structure conforms closely to an idealized C_{2v} symmetry, and is seen to have the closed deltahedral eleven-vertex 1:2:4:2:2-stack structure as typified by the *closo* binary boron hydride anion $B_{11}H_{11}^{2-}$.

Although this compound is the first structurally characterized polyhedral ruthenaborane, the principal novelty resides in the implications that this structure has for the continuing development of polyhedral skeletal bonding schemes and electroncounting rules.

Two views of the cluster bonding are possible. If the ruthenium atom retains a d^6 core, and contributes three orbitals and two electrons to the cluster bonding in the same manner as presumed for the unique capping neutral {BH} moiety in $B_{11}H_{11}^{2-}$, then it is a formal d^6 ruthenium(II) centre with an overall five-fold bonding-orbital geometry.

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In this case, however, the $\{\operatorname{RuB}_9\}$ cluster would then be deficient by two electrons for a formal *closo* bonding-electron count. An alternative view would be that the ruthenium metal vertex supplies four electrons to the cluster bonding, which would imply a full *closo* electron count: the metal would then have a four-orbital contribution to the cluster resulting in a sixteen electron d^4 ruthenium(IV) centre with a quasi-octahedral or related disposition of six bonding orbitals.



ORTEP drawing of the molecular structure of $[(PPh_3)_2RuB_{10}H_8(OEt)_2]$, with all but the *ipso* carbon atoms of the P-phenyl groups omitted for clarity. Hydrogen atoms were not located by X-ray diffraction but n.m.r. spectroscopy shows that each boron atom except B(2) and B(5) has an *exo* terminal hydrogen atom bound to it, and that there are no other hydrogen atoms associated with the metallaborane cluster. Distances from Ru(1) are as follows, to P(1) 253.6(3) to P(2) 251.3(3), to B(2) 205.7(13), to B(5) 205.2(13), to B(3) 238.5(14), to B(4) 241.5(13), to B(6) 238.3(13) and to B(7) 240.8(13) ppm. B(3)-B(4) and B(6)-B(7) are 170.1(19) and 171.6(18) pm respectively and B(2)-B(3) B(2)-B(7) B(4)-B(5) B(5)-B(6) are in the range 175.2(19)-183.7(18) pm. The angle P(1)-Ru(1)-P(2) is 96.9(1)°.



In terms of this latter interpretation the ruthenaundecaborane reported here would be an eleven-vertex analogue (I) of the previously reported ten-vertex and nine-vertex *isocloso* metallaboranes of the type $[(PR_3)_2HIrB_9H_9]$ (II), and $[(PR_3)_2HIrB_9H_8]$ (III) respectively. ^{2,3} These formally derive geometrically by the capping of an open *arachno*-tupe cluster geometry to produce a closed deltahedron. This contrasts with conventional *closo* structures which are formally derived by the capping of an open *nido*-type geometry with a three-orbital contributor. In the *isocloso* structures, the capping atom would contribute four orbitals to the cluster bonding scheme and, conversely, the *arachno*-type borane fragment would have one more orbital available than the *nido*-type fragment in the metal/borane frontier region. In the present case the *nido* and *arachno* ten-vertex clusters happen to have mutually similar gross geometries, so that the corresponding derived *closo* and *isocloso* eleven-vertex clusters also have mutually similar gross geometries (I). In the ten- and nine-vertex *isocloso* species (II and III), however, the geometries are quite different from those of the straightforward *closo* species.

The overall principles implicit in these considerations may be quite general, for example in the interpretation of the so-called 'hypercloso' metallacarboranes such as $[(C_5H_5)_2Fe_2C_2B_6H_8]^4$ and $[(PPh_3)_2RuC_2B_7H_9]^5$, and in their extension to the interpretation of the 'isonido' clusters typified by $[(Ph_3P)_2(Ph_2PC_6H_4IrC(OH)B_8H_7OMe]^6$ and $[(Ph_3P)_2HIrB_9H_9(PPh_3)]$. The "interstitial" ferraborane $[(CO)_{12}HFe_4BH_2]^8$ may also be interpreted on this basis; the arachno $\{Fe_4\}$ fragment is capped by a $\{BH_2\}$ unit of which all four orbitals are involved in cluster bonding, thus resulting in a *closo* five-vertex trigonal bipyramidal geometry.

We thank SERC for support, Dr D. Reed (Edinbrugh University) for services in high-field n.m.r. spectroscopy, Dr M.A. Beckett for useful discussions, and Johnson Matthey Ltd. for the loan of chemicals.

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- 1. Crystal data: $C_{40}H_{48}B_{10}O_2P_2Ru$, M = 831.94, monoclinic, a = 1.3090(4), b = 2.3335(4), c = 1.3902(4) nm, $\beta = 93.63(2)^\circ$, U = 4.238(2) nm³, Z = 4, $D_c = 1.304$ g cm⁻³, F(000) = 1.712, space group $P2_1/n$, Mo- K_{α} graphite-monochromatised radiation, $\lambda = 71.069$ pm. Atomic coordinates, thermal parameters, interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre.
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