# An Unusual Open Twelve-vertex Oxametallaborane Cluster Compound: Synthesis and Structure of [7-($\eta^5$-$C_5Me_5$)-8-Cl-11-($PMe_2Ph$)-*nido*-7,12-$RhOB_{10}H_9$]†

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Eleven-vertex *nido*-[($\eta^5$-$C_5Me_5$)$RhB_{10}H_{11}Cl$($PMe_2Ph$)], when dissolved in $CH_2Cl_2$ solution in the presence of $H_2O$, yields the open twelve-vertex oxametalladodecaborane [($\eta^5$-$C_5Me_5$)$RhOB_{10}H_9Cl$($PMe_2Ph$)],† which is the first non-carbon-containing open twelve-vertex polyhedral boron cluster compound, and the first boron cluster compound that contains an oxygen atom bound solely to boron in a contiguous cluster position.

Treatment of the recently characterised orange eleven-vertex *nido*-7-metallaundecaborane [($\eta^5$-$C_5Me_5$)$RhB_{10}H_{11}Cl$($PMe_2Ph$)][1] (**1**) with $H_2O$ in $CH_2Cl_2$ solution for two days gives a 53% yield of the novel red crystalline compound [($\eta^5$-$C_5Me_5$)$RhOB_{10}H_9Cl$($PMe_2Ph$)] (**2**). This latter compound has a *nido*-type twelve-vertex cluster in which the oxygen-atom vertex is bound solely to three boron atoms and occupies a contiguous cluster position in the open face. The only previously reported open twelve-vertex metal–boron cluster compounds also contain carbon in the cluster,[2] and the sole example of a contiguous polyhedral oxaborane species has the oxygen atom bound to a cluster metal atom (iron) as well as boron.[3]

The structure of the new rhodaoxaborane compound (**2**) was established by single-crystal *X*-ray diffraction analysis and confirmed by n.m.r. spectroscopy. Crystals are air-stable,

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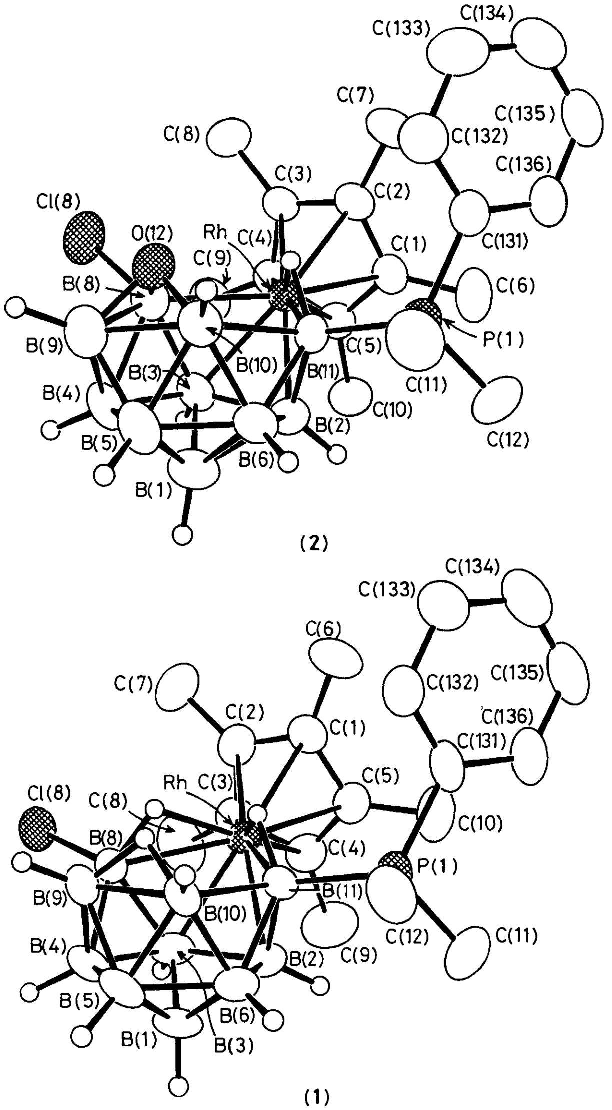
† 7-Pentamethylcyclopentadienyl-8-chloro-11-dimethylphenylphosphine-*nido*-7,12-rhodaoxadodecaborane (type 7 *nido*-type twelve-vertex cluster as delineated in ref. 2, p. 471).



(2)

(1)

**Figure 1.** Molecular structures of (top) [($\eta^5$-$C_5Me_5$)$RhOB_{10}H_9Cl$-($PMe_2Ph$)] (**2**), and (bottom) the starting substrate [($\eta^5$-$C_5Me_5$)$RhB_{10}H_{11}Cl(PMe_2Ph)$] (**1**)[1] for comparison. In compound (**2**) the rhodium–boron distances to B(2), B(3), B(8), and B(11) are 218.9(6), 218.9(6), 232.8(6), and 220.9(6) pm respectively, compared to 225.2(7), 222.1(7), 231.0(7), and 243.0(7) pm respectively for the corresponding distances in compound (**1**). The distances B(8)–B(9) and B(9)–B(10) in (**2**) [199.9(9) and 191.7(10) respectively] are comparable to those in (**1**) [192.3(9) and 187.8(9) pm respectively]. Distances from O(12) to B(8), B(9), and B(10) are 152.1(7), 147.6(7), and 153.5(7) pm respectively.

monoclinic, space-group $P2_1/n(=P2_1/c$, No. 14), $a$ = 867.7(2), $b$ = 1984.4(4), $c$ = 1551.8(3) pm, $\beta$ = 102.08(2)°, $U$ = 2.6129 nm$^3$, $Z$ = 4, $D_c$ = 1.38 g cm$^{-3}$, $F(000)$ = 1120, $\mu$(Mo-$K_\alpha$) = 7.43 cm$^{-1}$. The structure was solved by heavy atom methods and refined to $R$ = 0.0407, $R_w$ = 0.0441 by full-matrix least-squares using 4258 observed reflections [$I > 2.0\sigma(I)$] out of a total of 5212 collected.‡ A drawing of the molecular structure, together with that of the starting substrate [($\eta^5$-$C_5Me_5$)$RhB_{10}H_{11}Cl(PMe_2Ph)$] (**1**) for comparison, is given in Figure 1.

The presence of oxygen at position O(12) in compound (**2**) is inferred from: (i) the very short interatomic distances to the adjacent boron atoms B(8), B(9), and B(10); (ii) unacceptably low thermal parameters when the atom was refined as carbon or boron; and (iii) the absence of any significant electron density about the cluster atom (12), in the Fourier difference synthesis, which might have corresponded to hydrogen atoms expected if atom (12) were boron or carbon (all other hydrogen atoms being located in the structure). This inference is supported by n.m.r. spectroscopy which shows the presence of only ten boron atoms, eight *exo*-BH protons, and one bridging BHRh proton.§

It can be seen from Figure 1 that the cluster geometries of (**1**) and (**2**) are very similar, with a formally divalent oxygen atom in compound (**2**) essentially replacing two of the open-face bridging hydrogen atoms of the starting eleven-vertex compound (**1**) (formally equation 1). The replacement appears not to be accompanied by any major changes in the interboron distances among the B(8), B(9), and B(10) atoms that become bound to oxygen in (**2**), although the differences in cluster-atom n.m.r. shielding parameters between the two compounds (compare ref. 1) suggest that there may be significant cluster electronic differences.

$$\underset{\textbf{(1)}}{[(\eta^5\text{-}C_5Me_5)RhB_{10}H_{11}Cl(PMe_2Ph)]} + H_2O \longrightarrow$$

$$\underset{\textbf{(2)}}{[(\eta^5\text{-}C_5Me_5)RhOB_{10}H_9Cl(PMe_2Ph)]} + 2H_2 \qquad (1)$$

This very ready addition of an oxygen vertex to a boron cluster structure is unprecedented and remarkable, and suggests the use of other appropriate reagents for this type of novel cluster-expansion process, both to explore novel heteroatom chemistry and to functionalise these types of metallaborane cluster.

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## References

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ N.m.r. data for (**2**): $^{11}B$ $\delta$ values with $^1H$ $\delta$ values of directly bound H atoms in parentheses: B(1) +5.9 (+3.06), B(2) −4.9 (+1.34), B(3) + 10.8 (+2.96), B(4) −6.7 (+2.69), B(5) −1.3 (+3.40), B(6) −3.9 (+2.23, doublet, $^3J[^{31}P\text{–}B\text{–}B\text{–}^1H]$ 24 Hz), B(8) +5.5 (Cl-substituted), B(9) + 12.1 (+3.28), B(10) −12.8 (+1.94), and B(11) +21.2, {doublet, $^1J(^{31}P\text{–}^{11}B)$ 120 Hz} (−8.21, doublet of doublets, $^1J[^{103}Rh\text{–}^1H]$ and $^2J[^{31}P\text{–}B\text{–}^1H]$ 31.2 and 7.0 Hz); $CD_2Cl_2$ solution at 21 °C; assignments by substituent positions, homonuclear $^{11}B$ COSY, heteronuclear $^1H\{^{11}B(\text{selective})\}$, and homonuclear $^1H$ COSY n.m.r. spectroscopy; $\delta(^{11}B)$ with respect to $BF_3(OEt)_2$–$CDCl_3$, $\Xi$ = 32.083971 MHz, taken as standard.