# Oxarhodaborane Chemistry: The Formation of [$\mu$-9,9′-O-{5-($\eta^5$-$C_5Me_5$)-*nido*-5-$RhB_9H_{12}$}$_2$] and [7-($\eta^5$-$C_5Me_5$)-10-($NEt_3$)-*nido*-7,12-$RhOB_{10}H_{10}$] from [*nido*-($\eta^5$-$C_5Me_5$)$RhB_{10}H_{13}Cl$]

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Chromatography in air on silica of the *nido* eleven-vertex metallaborane [($\eta^5$-$C_5Me_5$)$RhB_{10}H_{13}Cl$] **2**, yields the $\mu$-9,9′-oxo-bridged bis(*nido*-5-rhodadecaboranyl) species [{($\eta^5$-$C_5Me_5$)$RhB_9H_{12}$}$_2$O] **3**, whereas treatment with $NEt_3$ before exposure to air and chromatography on silica results in the novel contiguous *nido* twelve-vertex oxarhodadecaborane [7-($\eta^5$-$C_5Me_5$)10-($NEt_3$)-*nido*-7,12-$RhOB_{10}H_{10}$] **4**.

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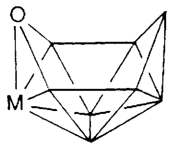
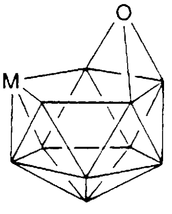
Since the advent of heteroborane cluster chemistry there has been a continual challenge to incorporate the electronegative heteroatom oxygen within the cluster, but examples of such oxaborane clusters are rare, being limited to the *nido* ten-vertex iron compound [2-($\eta^5$-$C_5Me_5$)-*nido*-2,6-$FeOB_8H_{10}$][1] (schematic configuration **I**) and the *nido*-type twelve-vertex species [7-($\eta^5$-$C_5Me_5$)-8-Cl-11-($PMe_2Ph$)-*nido*-7,12-$RhOB_{10}H_9$][2] **1** (schematic configuration **II**). This is due, in part, to the difficulty of achieving cluster oxygenation whilst preventing more extensive nucleophilic attack leading to complete disruption of the cluster. Compound **1** was formed by the interaction of the triply hydrogen-bridged *nido* eleven-vertex species [($\eta^5$-$C_5Me_5$)$RhB_{10}H_{11}Cl(PMe_2Ph)$] with air in the presence of $PMe_2Ph$.[2] Continuing our work in this area we now report the synthesis (and characterization) of further oxarhodaborane products by the action of air on the related quadruply hydrogen-bridged *nido* eleven-vertex species [7-($\eta^5$-$C_5Me_5$)-9-Cl-*nido*-7-$RhB_{10}H_{13}$] **2** (schematic structure **III**). Compound **2** is prepared quantitatively by the reaction between *nido*-$B_{10}H_{14}$ and [{($\eta^5$-$C_5Me_5$)$RhCl_2$}$_2$] in the presence of *N,N,N′,N′*-tetramethyl-1,8-diaminonaphthalene as described elsewhere.[3]

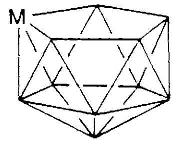
Chromatography of **2** on silica in air results in degradative change to give a variety of substituted and unsubstituted *nido* ten-vertex rhodaboranes, identified by NMR spectroscopy and mass spectroscopy, some of which appear to have oxo- and hydroxo-substituents bound *exo* to boron, demonstrating the ready uptake of oxygen from the components of air. One



I



II



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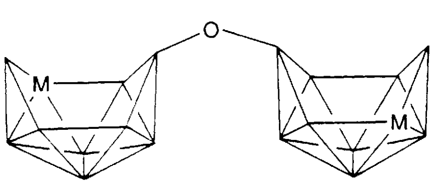

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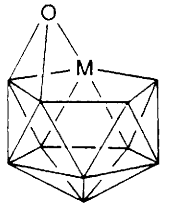

V

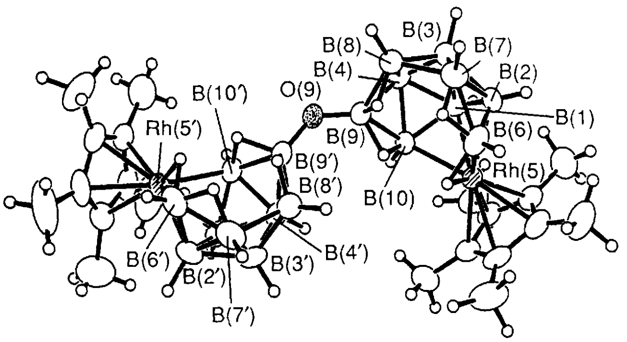

**Fig. 1** Drawing of the molecular structure of [$\mu$-9,9'-O-{5-($\eta^5$-$C_5Me_5$)-*nido*-5-$RhB_9H_{12}$}$_2$] **3**. The distances B(9)–O(9) and B(9')–O(9) are 137.6(8) and 137.4(9) pm respectively and the angle B(9)–O(9)–B(9') is 129.8(5)°. Other salient bond lengths are Rh(5)–C 218.2(7)–221.3(7), Rh(5')–C' 217.9(9)–221.4(8), Rh(5)–B(1) 218.2(8), Rh(5)–B(2) 222.1(8), Rh(5)–B(6) 217.0(8), Rh(5)–B(10) 228.3(7), Rh(5')–B(1') 217.8(8), Rh(5')–B(2') 223.0(9), Rh(5')–B(6') 217.5(9), Rh(5')–B(10') 226.1(9), B(7)–B(8) 199.1(11) and B(7')–B(8') 200.1(13) pm. The use of primes is to distinguish the two different subclusters and has no implications for crystallographic symmetry.

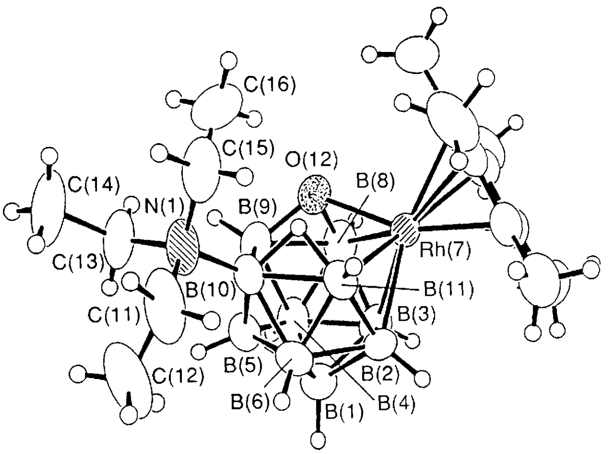

**Fig. 2** Drawing of the molecular structure of [($C_5Me_5$)$RhOB_{10}H_{10}$($NEt_3$)] **4**. Salient interatomic dimensions are Rh(7)–C 216.3(5)–222.6(5), Rh(7)–O(12) 212.2(4), Rh(7)–B(2) 223.5(5), Rh(7)–B(3) 224.3(5), Rh(7)–B(8) 226.4(5), Rh(7)–B(11) 225.1(5), O(12)–B(8) 144.1(5), O(12)–B(9) 152.1(6), B(10)–N(1) 159.6(6), B(8)–B(9) 201.5(7), B(9)–B(10) 198.8(6), B(10)–B(11) 184.7(6) pm, Rh(7)–O(12)–B(8) 76.3(2), Rh(7)–O(12)–B(9) 118.7(3) and B(8)–O(12)–B(9) 85.7(3)° (see ref. 8).

of these products (obtained in 28% yield) has been identified by X-ray crystallography† as a $\mu$-9,9' oxo-linked bis(*nido*-5-rhodadecaboranyl) species **3** of schematic structure **IV**. The molecular structure of **3** is shown in Fig. 1; the compound was formed in equal quantities with its diastereoisomer **3a** from which it was separated by repeated chromatography and fractional crystallisation. The NMR behaviour of **3a** is very similar indeed to that of **3**,‡ differing most noticeably in small changes of proton shielding at sites adjacent to the $\mu$-oxo linkage.

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† *Crystal data* for **3**: $C_{20}H_{54}B_{18}ORh_2 \cdot C_6H_5Cl$, $M$ = 823.62 (includes solvate), monoclinic, space group $P2_1/n$ (= $P2_1/c$, no. 14), $a$ = 1976.6(2), $b$ = 1021.8(2), $c$ = 2165.6(3) pm, $\beta$ = 107.64(1)°, $U$ = 4.1318(11) nm$^3$, $D_c$ = 1.32 g cm$^{-3}$, $Z$ = 4, $F$(000) = 1680, $\mu$ = 7.97 cm$^{-1}$, 4.0 < 2$\theta$ < 45.0°. Final $R(R_w)$ = 0.041(0.043) for 4915 reflections with $F > 4.0\sigma(F)$.

*Crystal data* for **4**: $C_{16}H_{40}B_{10}NORh$, $M$ = 473.52, monoclinic, space group $P2_1/c$, $a$ = 1507.1(5), $b$ = 914.2(3), $c$ = 1896.4(6) pm, $\beta$ = 109.58(2)°, $U$ = 2.4617(14) nm$^3$, $Z$ = 4, $D_c$ = 1.28 g cm$^{-3}$, $F$(000) = 984, $\mu$ = 6.25 cm$^{-1}$, 4.0 < 2$\theta$ < 50.0°. Final $R(R_w)$ = 0.029(0.030) for 3227 reflections with $F > 4.0\sigma(F)$.

Intensity data for both **3** and **4** were collected on a Nicolet P3/F diffractometer using an $\omega$-2$\theta$ scan mode and graphite monochromated Mo-K$\alpha$ radiation. Both datasets were corrected for absorption empirically.[4] Both structures were solved by Patterson and Fourier methods.[5] Refinement was essentially the same for both compounds; all non-hydrogen were refined anisotropically except for those of a slightly disordered $C_6H_5Cl$ solvate molecule in **3** which were refined isotropically. The methyl and (for **4**) ethyl hydrogen atoms were included in calculated positions and were refined with an overall isotropic thermal parameter. The cluster hydrogen atoms were located experimentally and were freely refined with individual isotropic temperature factors. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors No. 1.

‡ *Selected NMR data* for **3** in $CD_2Cl_2$ solution at 294–297 K, ordered as (assignment) $\delta(^{11}B)$ [$\delta(^1H)$ of directly bound H atom]: (1) +21.1 [+3.69], (2) −19.4 [+0.23], (3) +3.2 [+3.21], (4) −36.4 [+0.89], (5) — [+1.93($C_5Me_5$)], (6) +22.5 [+4.40], (7) +4.7 [+3.72], (8) −7.1 [+2.17], (9) +17.4 [O-linkage position], (10) −13.6 [+2.01]; $\delta(^1H)$ for $H_\mu$ as follows: (5,6) −11.98, (6,7) −1.98, (8,9) −1.02, (9,10) −0.16.

A more interesting example of oxygen atom uptake from air components is obtained when **2**, after formation *in situ*, is treated with $NEt_3$ before chromatography on silica in air. This procedure results in the isolation of the new orange air-stable *nido*-type twelve-vertex oxarhodaborane [7-($\eta^5$-$C_5Me_5$)-10-($NEt_3$)-*nido*-7,12-$RhOB_{10}H_{10}$] **4**, obtained so far in 8% yield (unoptimised). X-Ray crystallography (Fig. 2)† shows that **4** has a contiguous $RhOB_{10}$ cluster structure **V** which differs from that of **1** (schematic structure **II**); the $^{11}B$ and $^1H$ NMR spectra§ also show a different shielding pattern to that of **1**, confirming the differing strucutral type.

The ready formation of this second stable oxarhodaborane suggests that there may well be an extensive chemistry of stable oxaborane clusters awaiting discovery (*cf*. the known potentialities of azametallaborane[6] and thiametallaborane[7] chemistry that are currently also being exploited). The systematic exploration of heteroborane cluster chemistry of this very reactive electronegative heteroatom will be facilitated by the discovery of synthetic routes that involve reliable mild one-oxygen cluster *aufbau* reagents that do not trigger destructive cluster degradation, and we are currently seeking to explore further possibilities in this area.

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7 See, for example, A. R. Kane, L. J. Guggenberger and E. L. Muetterties, *J. Am. Chem. Soc.*, 1970, **92**, 2571; A. R. Siedle, D. M. McDowell and L. J. Todd, *Inorg. Chem.*, 1974, **13**, 2735; T. K. Hilty, D. A. Thompson, W. M. Butler and R. W. Rudolph, *Inorg. Chem.*, 1979, **18**, 2642; G. A. Kukina, M. A. Porai-Koshits, V. S. Sergienko, Yu. V. Zefirov and G. G. Sadikov, *Koord. Khim.*, 1985, **11**, 385.

8 The oxygen atom configuration may be compared with the selenium position in the {$CoSeB_9Se$} cluster compound described by Friesen *et al.*, *Inorg. Chem.*, 1980, **19**, 458.

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§ *Selected NMR data* for **4** in $CDCl_3$ solution at 294–297 K, ordered as (assignment) $\delta(^{11}B)$ [$\delta(^1H)$ of directly bound H atom]: (1) −4.2 [+2.60], (2) −0.6 [+1.83], (3) +12.8 [+3.30 or +3.47], (4) −25.9 [+1.40], (5) −6.5 [+2.04], (6) −32.9 [+0.45], (7) — [+1.76($C_5Me_5$)], (8) +12.8 [+3.30 or +3.47], (9) +2.1 [+3.30], (10) +5.4 [$NCH_2CH_3$ at +3.35 and +1.32 resp., $^3J(^1H-^1H)$ 7.2 Hz], (11) +8.22 [+3.49], $\mu$(10.11) — [−0.65]. In addition: *m/z*(max) (found) 475, $^{12}C_{16}{}^1H_{40}{}^{11}B_{10}{}^{14}N^{16}O^{103}Rh$ requires 475; elemental analyses were satisfactory (C, H, N).