Quantitative Thermal Rearrangement of an Eleven-vertex Metalladicarbaborane to give the Isomeric Cluster *nido*-[2-(η^6-C_6Me_6)-8,10-Me_2-2,8,10-$OsC_2B_8H_8$] with an Unexpected $\overline{\text{BCBCB}}$ Open Face

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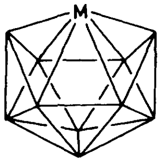
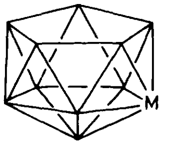
The molecular structure of the title compound exhibits a five-membered $\overline{\text{BCBCB}}$ *open face and is thereby fundamentally different from the closo-nature previously assumed and generally accepted for this type of polyhedral metalladicarbaborane cluster compound.*

It has hitherto been assumed that the eleven-vertex metalladicarbaboranes such as [(C_5H_5)Co$C_2B_8H_{10}$],[1] [(PPh_3)$_2$HIr$C_2B_8H_{10}$],[2] [(C_6H_6)Ru$C_2B_8H_{10}$],[3] *etc.* have straightforward closed deltahedral eleven-vertex geometries like (I) because they have straightforward *closo* electron counts and therefore obey the Williams–Wade cluster-geometry[4] and electron-counting[5] rules.

We now report that the experimentally determined molecular structure of an isomer of the eleven-vertex osmadicarbaundecaborane [(η^6-C_6Me_6)Os$Me_2C_2B_8H_8$] shows that this presumption is not generally valid. The orange air-stable compound is prepared quantitatively by thermal rearrangement (14 min at 400 °C) of its isomer [1-(η^6-C_6Me_6)-2,4-Me_2-1,2,4-Os$C_2B_8H_8$] (provisionally numbered as a *closo*-11-vertex system but not yet structurally characterized; this isomer was itself prepared by reaction of [(η^6-C_6Me_6)OsCl_2]$_2$ and [5,6-$Me_2C_2B_8H_{10}$] in dichloromethane in the presence of bis(dimethylamino)naphthalene). The molecular structure of



(I)



(II)

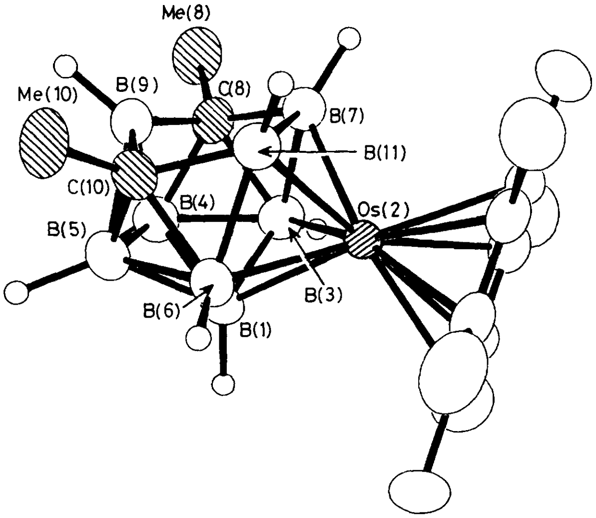


Figure 1. ORTEP drawing of the molecular structure of the title compound. Selected distances from Os(2) are as follows: to B(1) 225.3(7), to B(3) 219.4(7), to B(6) 218.8(7), to B(7) 211.6(7), to B(11) 212.7(7), and to C(aromatic)(mean) 226.1 pm. Distances between open-face atoms are as follows: B(7)–C(8) 157.3(9), C(8)–B(9) 164.6(9), B(9)–C(10) 165.2(9), C(10)–B(11) 157.4(8), B(11)–B(7) 208.4(9) pm.

the 2-osma isomer is shown in Figure 1.† The rhodium analogue [(η^5-C_5Me_5)$RhMe_2C_2B_8H_8$], identified by the extreme similarity of its n.m.r. spectroscopic properties,‡ is prepared similarly.

The metalladicarbaborane cluster (Figure 1) adopts a *nido*-configuration of the $B_{11}H_{14}^-$ structural type with a five-membered $\overline{\mathrm{BCBCB}}$ open face and with the metal atom at a non-open-face five-connected cluster position (structure II). This is clearly fundamentally different from the closed structure (I) expected from its formal [$2n + 2$]-electron *closo*-count, and a rationale analogous to that[6] invoked to account for the 'slipped' structures of certain platinadicarbaboranes does not apply in this case as the osmium centre is fully co-ordinated and does not occupy a position in the open face.

This behaviour is without precedent, and since there is no obvious *a priori* reason for expecting anything other than a straightforward closed structure, it re-emphasizes the importance of backing theoretical deliberations in this area with definitive experimental evidence.[7]

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† *Crystal data:* $C_{16}H_{32}B_8Os$, $M = 501.12$, monoclinic, space group $P2_1/n$, $a = 913.7(1)$, $b = 1340.7(2)$, $c = 1637.1(1)$ pm, $\beta = 95.44(1)^\circ$, $U = 1.9965(3)$ nm^3, $Z = 4$, $\mu = 61.18$ cm^{-1}, $F(000) = 968$. Scans running from 1° below $K_{\alpha1}$ to 1° above $K_{\alpha2}$, scan speeds 2.0—29.3° min^{-1}, and $4.0 < 2\theta < 50.0^\circ$, $T = 290$ K. All crystallographic measurements were made on a Nicolet P3/F diffractometer operating in the $\omega/2\theta$ scan mode using graphite monochromated Mo-K_α radiation following a procedure described elsewhere.[8] The data set was corrected for absorption empirically.[9] The structure was solved by standard heavy atom methods and refined by full-matrix least-squares using SHELX 76.[10] All methyl hydrogen atoms were included in calculated positions and assigned an overall isotropic thermal parameter. The borane hydrogen atoms were located in a Fourier difference map and were freely refined with individual isotropic thermal parameters. The weighting scheme $w = [\sigma^2(F_o) + 0.0003(F_o)^2]^{-1}$ was used at the end of refinement. Final R and R_w values are 0.0239 and 0.0248 (274 parameters, 3129 observed data). Atomic co-ordinates, interatomic distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ *N.m.r. data:* $\delta(^{11}B)$/p.p.m., with respect to $Et_2O{\cdot}BF_3$, [together with $\delta(^1H)$/p.p.m. in parentheses]; tentative assignments by [^{11}B–^{11}B]-COSY, $^1H\{^{11}B\}$, and [^1H–^1H]-COSY n.m.r. experiments. (a) [$(C_6Me_6)OsC_2Me_2B_8H_8$]: BH(1) −15.9(+1.30), BH(3,6) −20.7(+0.91), BH(4,5) +0.3(+2.85), BH(7,11) +40.0(+4.67), and BH(9) −15.9(−0.37). (b) [$(C_5Me_5)RhC_2Me_2B_8H_8$]: BH(1) −8.5(+1.56), BH(3,6) −16.5(+1.50), BH(4,5) +6.9(+2.73), BH(7,11) +36.0(+3.78), and BH(9) −14.9(+0.40).

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