Preparation of $[(C_5Me_5)_2Rh_2B_{17}H_{19}]$† *via* a Degradative Insertion from *anti*-$B_{18}H_{22}$, and a Possible Mechanism for *anti* → *syn* Macropolyhedral Interconversion‡

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Reaction of $[(C_5Me_5)RhCl_2]_2$ with *anti*-$B_{18}H_{22}$ in the presence of base yields, *via* boron vertex loss, a 19-vertex dirhodanonadecaborane $[(C_5Me_5)_2Rh_2B_{17}H_{19}]$ of which the structure has been confirmed by *X*-ray crystallography; it comprises a 12-vertex *nido* $\{RhB_{11}\}$ subcluster and a 10-vertex *nido* $\{5\text{-}RhB_9\}$ subcluster conjoined with a common triangular $\{B_3\}$ face so as to generate an effective *syn* configuration.

Macropolyhedral metallaborane chemistry involving clusters with more than twelve vertices promises a rich variety of behaviour. However, preparative routes have been limited so far either to serendipitous cluster *aufbau* processes,[1] or to the potentially higher yield addition of metal centres to preformed binary borane macropolyhedral substrates.[2] The latter synthetic route has so far been limited, in effect, to compounds with eighteen boron atoms and one or two metal atoms because of the relative ease of preparation of the starting substrates *syn*- and *anti*-$B_{18}H_{22}$.‡ We have recently found that the reactions of organometallic species such as $[(C_5Me_5)RhCl_2]_2$ and $[(C_6Me_6)RuCl_2]_2$ with *nido* ten-boron substrates readily give good yields of isomers and derivatives of the *nido* ten-vertex nine-boron species $[(C_5Me_5)RhB_9H_{13}]$ and $[(C_6Me_6)RuB_9H_{13}]$ *via* boron-vertex loss.[3] The *BB*-*conjuncto*-(*nido*-decaborano) nature of the $B_{18}H_{22}$ isomers suggests that such degradative insertions should also work with these octadecaboranes to generate new macropolyhedral metallaboranes with less than eighteen boron atoms, and here we report preliminary results on a rhodium system that demonstrates that this is indeed the case.

Reaction of $[NEt_4]_2[anti\text{-}B_{18}H_{20}]$ with $[(C_5Me_5)RhCl_2]_2$ in CH_2Cl_2 solution for 3 days at 21 °C gave air-stable orange-purple $[(C_5Me_5)_2Rh_2B_{17}H_{19}]$§ in a yield of 14%, of which the

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† 7,7′-Bis(η^5-pentamethylcyclopentadienyl)-*nido*-7′-rhodadecaborano-(8′,9′,4′ : 10,11,12)-*nido*-7-rhodadodecaborane.

‡ Throughout this communication we use the descriptors *syn* and *anti* to describe compounds based on the C_2 cluster structure of *nido*-decaborano-(6′,7′:6,7)-*nido*-decaborane and the centrosymmetric cluster structure of *nido*-decarborano-(6′,7′:5,6)-*nido*-decaborane respectively (see Y. M. Cheek, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1982, 80); *syn* and *anti* are preferred to the trivial descriptors '*iso*' and 'normal' which appear in the literature for historical reasons but are structurally uninformative.

§ Satisfactory elemental analyses (C, H, B) were obtained, Found: *m/z* (max.) 681. $C_{20}H_{49}B_{17}Rh_2$ requires: *m/z* (max.) 682 for $^{103}Rh_2$-$^{11}B_{17}$ isotopomer.

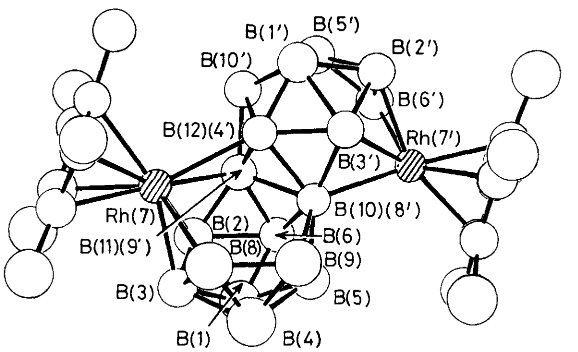
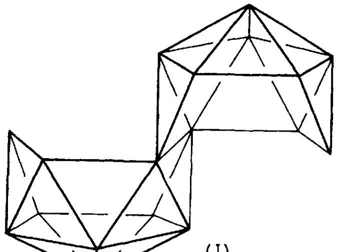
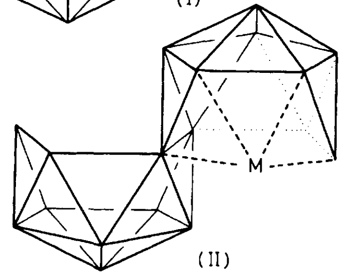


Figure 1. Molecular structure of $[(C_5Me_5)_2Rh_2B_{17}H_{19}]$. Distances from Rh(7) are: to B(2) 229.7(23), to B(3) 223.6(22), to B(8) 228.9(27), to B(11) 225.7(21), to B(12) 243.1(20), and to C(mean) 219.9 pm. Distances from Rh(7') are: to B(2') 220.7(22), to B(3') 218.2(21), to B(6') 216.3(23), to B(10) 231.6(19), and to C(mean) 221.0 pm. B(11)–B(12) is short at 165.1(27), and B(9)–B(10) long at 199.4(30) pm. The dihedral angle between Rh(7)B(8)B(11) and B(8)B(9)B(10)B(11) is 21°, and that between B(6)B(10)B(11) and B(10)B(11)B(12) nearly flat at 177°.

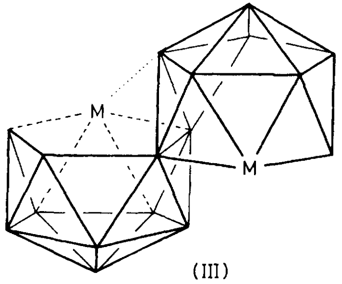
structure has been confirmed by a single crystal *X*-ray diffraction study (see Figure 1).¶ Crystals were obtained by diffusion of hexane into a solution of the compound in dichloromethane; they grow in a very thin habit, and therefore data obtained so far have not been ideal. Hydrogen atoms have not been locatable in crystals examined so far, but n.m.r. spectroscopy ‖ shows that all boron atoms except B(10), B(11), and B(12) have *exo*-terminal atoms associated with them, and that there are five bridging hydrogen atoms, at Rh(7)B(12), B(8)B(9), Rh(7')B(6'), B(5')B(6'), and B(10')B(11).



(I)



(II)



(III)

The molecular structure is seen to be that of a contiguous macropolyhedral $\{Rh_2B_{17}\}$ nineteen-vertex cluster, which can be regarded as consisting of a *nido* twelve-vertex Type 7 (as defined in ref. 10) $\{RhB_{11}\}$ subcluster and a *nido* ten-vertex $\{5\text{-}RhB_9\}$ subcluster conjoined with the triangular B(10)B(11)B(12) [=B(8')B(9')B(4')] face held in common (another related twelve-vertex Type 7 *nido* cluster, $\{RhOB_{10}\}$, has also been reported recently in polyhedral rhodaborane chemistry).[11] It can be seen that Rh(7') has added to the edge of the starting *anti* eighteen-boron skeleton (I), with the elimination of an opposing boron vertex as in (II), to result in an eighteen-vertex $\{RhB_{17}\}$ cluster of effective *syn* configuration [solid lines in (III)]. A movement of a boron vertex between these two sites in an eighteen-boron skeleton would provide a mechanism for *syn* ⇄ *anti* conversion, and in accord with this we have noted[12] that prolonged treatment of $[(PMe_2Ph)_2Pt\text{-}\eta^4\text{-}syn\text{-}B_{18}H_{20}]^2$ with $[PtCl_2(PMe_2Ph)_2]$ under mildly basic conditions gives $[(PMe_2Ph)_4Pt_2(\eta^4,\eta^6)\text{-}anti\text{-}B_{18}H_{16}]^2$ of *anti* eighteen-boron configuration: under these conditions substituted derivatives of $[(PMe_2Ph)_2PtB_{10}H_{12}]$ are known to rearrange by boron-vertex swing mechanisms.[13] In the $\{Rh_2B_{17}\}$ species reported here the second rhodium atom is bound to the other open face in a similar manner to platinum in both *syn* and *anti* isomers of $[(PMe_2Ph)_2Pt\text{-}\eta^4\text{-}B_{18}H_{20}]$ and to the metal atoms in a variety of ten-vertex *nido*-7-metallaundecaboranes [hatched lines in (III)]. Now, however, there is in addition definite Rh(7)–H–B(12) bridge-bonding rather than the lower, probably sterically induced, agostic interaction observed[2] in the platinanonadecaboranes [dotted lines in (III)]; this has the effect of converting the eleven-vertex *nido*-metallaundecaborane subunit into a twelve-vertex metalladodecaborane one. A tendency for rhodium to exhibit

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¶ *Crystal data:* $C_{20}H_{49}B_{17}Rh_2$, M = 679.37, monoclinic, a = 1031.7(3), b = 2082.6(6), c = 1484.6(3) pm, β = 92.87(2)°, U = 3.186 nm³, space group $P2_1/n$ (=$P2_1/c$, no. 14), Z = 4, D_c = 1.42 g cm⁻³, $\mu(\text{Mo-}K_\alpha)$ = 8.46 cm⁻¹, $F(000)$ = 1360, T = 290 K. Scans running from 1° below $K_{\alpha1}$ to 1° above $K_{\alpha2}$, scan speeds 2.0—29.3° min⁻¹, $4.0 < 2\theta < 45°$. 4902 Data were collected, 3820 were considered observed [$I > 2.0\sigma(I)$]. All crystallographic measurements were made on a Nicolet P3/F diffractometer operating in the ω–2θ scan mode using graphite monochromated Mo-K_α radiation following a procedure described elsewhere in detail.[4] The data set was corrected for absorption empirically once the structure had been solved.[5] The structure was solved *via* standard heavy atom methods and refined by full-matrix least-squares using the SHELX program system.[6] Only the two rhodium atoms were assigned anisotropic thermal parameters while all other atoms were refined isotropically. No hydrogen atoms were locatable in the difference map. The final R value was 0.0772 (unit weights, 167 parameters). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

‖ *N.m.r. data:* $\delta(^{11}B)$ values [with $\delta(^1H)$ values of directly bond *exo*-hydrogens in parentheses] are as follows: B(1) +1.6(+2.80); B(2) +3.1(+2.77); B(3) +13.8(+3.06); B(4) −28.2(+0.59); B(5) +3.8(+3.45); B(6) −19.2(+0.26); B(8) +1.3(+2.24); B(9) −2.2(+2.79); B(10)[=B(8')] −5.6 (−); B(11)[=B(9')] +15.3(−); B(12)[=B(4')] −44.1 (−); B(1') +8.8(+3.07); B(2') −17.8(+0.65); B(3') +12.8(+3.84); B(5') +1.0(+3.20); B(6') +28.0(+4.38); and B(10') −10.8(+2.39). Bridging H atom $\delta(^1H)$ values are: $^1H(7,12)$ −5.50 [$^1J(^{103}Rh\text{–}^1H)$ *ca.* 23 Hz]; $^1H(8,9)$ −1.68; $^1H(5',6')$ −2.57; $^1H(6',7')$ −11.66 [$^1J(^{103}Rh\text{–}^1H)$ *ca.* 32Hz]; and $^1H(10',11)$ +1.27. $\delta(^1H)(C_5Me_5)$ occur at +1.83 and +1.86. $\delta(^{11}B)$ (±0.5) and $\delta(^1H)$ (±0.05) are in p.p.m. to low field (high frequency) of $BF_3(OEt_2)$–$CDCl_3$ and $Si(CH_3)_4$ respectively, values being for CD_2Cl_2 solution at +23 °C. Assignments by $2D[^{11}B\text{-}^{11}B]$COSY,[7] $2D[^1H\text{-}^1H]\{^{11}B\}$ COSY,[8] and $^1H\text{-}\{^{11}B\}$(selective)[9] spectroscopy.

interesting Rh–H–B bridging modes has been noted elsewhere.[14]

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