Polyhedral azadirhodaborane chemistry. Reaction of [{$RhCl_2$(η^5-C_5Me_5)}$_2$] with [$EtH_2NB_8H_{11}NHEt$] to give contiguous ten-vertex [1-Et-6,7-(η^5-C_5Me_5)$_2$-*closo*-6,7,1-$Rh_2NB_7H_7$]*

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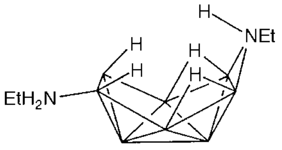
The novel monoazadirhodaborane [1-Et-6,7-(η^5-C_5Me_5)$_2$-*closo*-1,6,7-$NRh_2B_7H_7$], of ten-vertex stretched *closo*-type geometry, has been isolated in 6% yield from the reaction in tetrahydrofuran between [{$RhCl_2$(η^5-C_5Me_5)}$_2$], NaH and [$EtH_2NB_8H_{11}$-NHEt]; the latter azaborane compound therefore exhibits good augury as a potentially interesting and useful azametallaborane synthon.

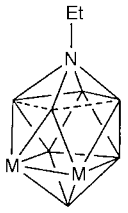
Polyhedral boron-containing cage chemistry based on seven or eight boron atoms is relatively sparsely developed because suitable seven- or eight-boron starting materials are generally only available *via* multistep dismantling or Aufbau reactions from available $B_{10}H_{14}$ or B_5H_9 respectively. A second relatively sparsely developed area is that of the azaboranes and azametallaboranes,[1] which is very poorly represented compared to the carbaborane and carbametallaborane chemistries that dominate the sub-discipline.[2] We surmised that the eight-boron compound [$EtH_2NB_8H_{11}NHEt$] **1** (structure **I**),[3–5] available in reasonable overall yield in a straightforward two-step process from $B_{10}H_{14}$,[3] would constitute a good entry into azaborane chemistry based on clusters with intermediate numbers of boron atoms. This is because it has (*a*) a bridging NHEt group that should be susceptible to more intimate cluster assimilation, (*b*) an *exo* NH_2Et group pendant to a low-connectivity boron atom that should therefore be prone to removal in an eight-boron to seven-boron dismantling, and (*c*) a polyhydrogen *hypho*-type cluster character[5] that should assist redox incorporation of one or more metal centres into the polyhedral matrix. We now report preliminary results from the reaction between [{$RhCl_2$(η^5-C_5Me_5)}$_2$] and [$EtH_2NB_8H_{11}NHEt$] which demonstrate these principles.

Reaction of equimolar quantities (reaction scale *ca.* 100 μmol) of [{$RhCl_2$(η^5-C_5Me_5)}$_2$] and [$EtH_2NB_8H_{11}NHEt$] with 2 equivalents of NaH in tetrahydrofuran for 6 d at room temperature followed by repeated thin-layer chromatography on silica gel G using CH_2Cl_2–hexane mixtures as the liquid phase resulted in the isolation of several coloured solid compounds which have so far been surprisingly difficult to obtain in a form suitable for the single-crystal X-ray diffraction work that is necessary to determine the skeletal arrangement of atoms in polyheteroborane cage compounds. We have now been ultimately successful in obtaining very small crystals of modest quality for one of the products, an air-stable yellow compound of formulation [1-Et-6,7-(η^5-C_5Me_5)$_2$-*closo*-1,6,7-$NRh_2B_7H_7$] **2** (6% yield before repeated recrystallization), and have elucidated its molecular structure by means of results from data gathered on an X-ray diffractometer using as CCD detector,† in conjunction with results from NMR spectroscopy.‡ The X-ray analysis located all the atoms except the methyl hydrogen atoms. The heavier atom structure thus determined (Fig. 1 and structure **II**) is consistent with the NMR properties of the bulk material. In particular, the ^{1}H-{^{11}B} results conform to a structure containing seven BH(*exo*) units.

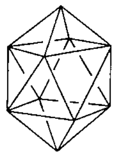
Compound **2** is seen to be of a ten-vertex configuration that is closely related to the closed deltahedral geometry of the ten-vertex binary borane *closo* model $[B_{10}H_{10}]^{2-}$ (structure **III**):[10] a *closo* configuration is compatible with its formal $2n + 2$ cluster-electron count.[11] It has an ethyl-substituted nitrogen atom in an axial position with cluster-connectivity four (*cf.* HNB_9H_9[12]): thus there has been a complete assimilation of a nitrogen vertex into the cluster. Also there is clearly an addition of two metal centres into the cluster to generate an azadimetallaborane: as far as we are aware, no contiguous azadimetallaborane cage compounds have been previously reported; indeed azamonometallaboranes are limited to only five structural types.[13] The loss



I



II



III

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* 1-Ethyl-6,7-bis(η^5-cyclopentadienyl)-*closo*-1,6,7-azadirhodadecaborane(7).

† Crystallography. All measurements were made at 298 K on a Siemen's SMART CCD detector system with a sealed tube X-ray source (at 50 kV × 40 mA) using Mo-Kα radiation (λ = 0.710 73 Å). Data were reduced using SAINT,[6] structure solution and refinement was carried out using SHELXTL-PLUS (5.03)[7] by minimization of $\Sigma w(F_o^2 - F_c^2)^2$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All of the hydrogen atoms on the cage were located from Fourier-difference maps and were refined with isotropic thermal parameters ($U_H = 1.2 \times U_B$). Crystal data. $C_{22}H_{42}B_7NRh_2$, $M = 602.06$, orange-yellow slab, 0.30 × 0.40 × 0.15 mm, orthorhombic, space group $P2_12_12_1$, $a = 8.4872(1)$, $b = 17.4496(1)$, $c = 18.5529(2)$ Å, $U = 2744.25(5)$ Å^3, $Z = 4$, $D_c = 1.457$ Mg m^{-3}, $\mu = 1.213$ mm^{-1}, T_{min} and $T_{max} = 31.8$ and 72.8%, absorption correction using equivalent reflections,[8] $F(000) = 1224$, $R1 = 0.0558$ for 4627 observed reflections [$F > 4\sigma(F)$], $Rw(F^2) = 0.1297$ for 6637 reflections, and $S = 1.008$ for all data. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/400.

‡ NMR data for compound **2** ($CDCl_3$, 294–297 K); δ(^{11}B) [δ(^{1}H) of directly bound H] (relative intensity) as follows: −16.7 [+0.29] (2 BH), −7.7 [+2.97] (2 BH), −15.0 [+1.64] (1 BH), +36.0 [+3.95] (1 BH) and +85.6 [+8.13] (1 BH); δ(^{1}H) +1.82 (30 H, C_5Me_5), +1.54 (3 H, CH_3) and +3.87 (2 H, CH_2).

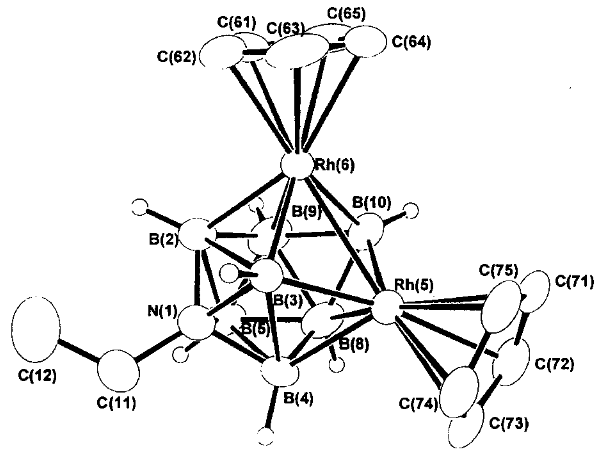

Fig. 1 The ORTEP-type drawing[9] of the crystallographically determined molecular structure of compound **2**, with the C_5Me_5 methyl groups omitted for clarity. Selected interatomic distances (pm): Rh(6)–Rh(7) 274.75(7), N(1)–B(2) 157.5(11), N(1)–B(3) 168.6(10), N(1)–B(4) 161.5(11), N(1)–B(5) 157.0(20), N(1)–Rh(6) 306.5(9), N(1)–Rh(7) 310.8(9), B(2)–B(3) 207.8(13), B(3)–B(4) 203.1(12). The Rh–B distances are in the range 207.8(8)–220.0(9), and the B–B distances within the range 175.0(20)–180.0(14). In solution the compound has effective mirror-plane symmetry (see NMR footnote), through N(1)B(3)B(5)B(10), the mid-point of Rh(6)–Rh(7) and the mid-point of B(8)–B(9)

of a boron vertex has also occurred: in the present instance this is significant because seven-boron systems are relatively difficult to access. Presumably the lost vertex is that initially bound to the pendant NH_2Et moiety of starting compound **1**. An additional interesting feature is the incidence of 'long' interboron distances of *ca.* 208 and 203 pm, for B(2)–B(3) and B(3)–B(4) respectively (hatched lines in structure **II**). This is reminiscent of the initial stretching of one such interboron linkage that occurs *en route* from a *closo* towards the intriguing ten-vertex '*isonido*' type of geometry.[14] It is interesting here that the stretching is exhibited by two pairs of adjacent faces. A simple stoichiometry for the formation of compound **2** can be written as in equation (1), although the actual mechanism is

$$[\{RhCl_2(C_5Me_5)\}_2] + \underset{\mathbf{1}}{[EtH_2NB_8H_{11}NHEt]} + 4NaH \longrightarrow \underset{\mathbf{2}}{[(C_5Me_5)_2Rh_2B_7H_7NEt]} + EtH_2NBH_3 + 4NaCl + 3H_2 \quad (1)$$

probably more complex than this may imply, because several other products are present, and also because the actual reagent stoichiometry in the reaction mixture is 2NaH rather than the 4NaH of equation (1).

Nuclear magnetic resonance spectroscopy and mass spectrometry suggest that other reaction products include azarhodaboranes with other structural features, as well as azarhodaboranes with possible variations and combinations of the features exhibited by compound **2**. These preliminary results augur well for much additional interesting azametallaborane chemistry derived from compound **1** and related species, and we are currently attempting to explore this.

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