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Macropolyhedral boron-containing cluster chemistry. *syn*- and *anti*-$[(C_5Me_5)_2Rh_2S_2B_{15}H_{14}(OH)]$; an interesting nineteen-vertex isomeric pair

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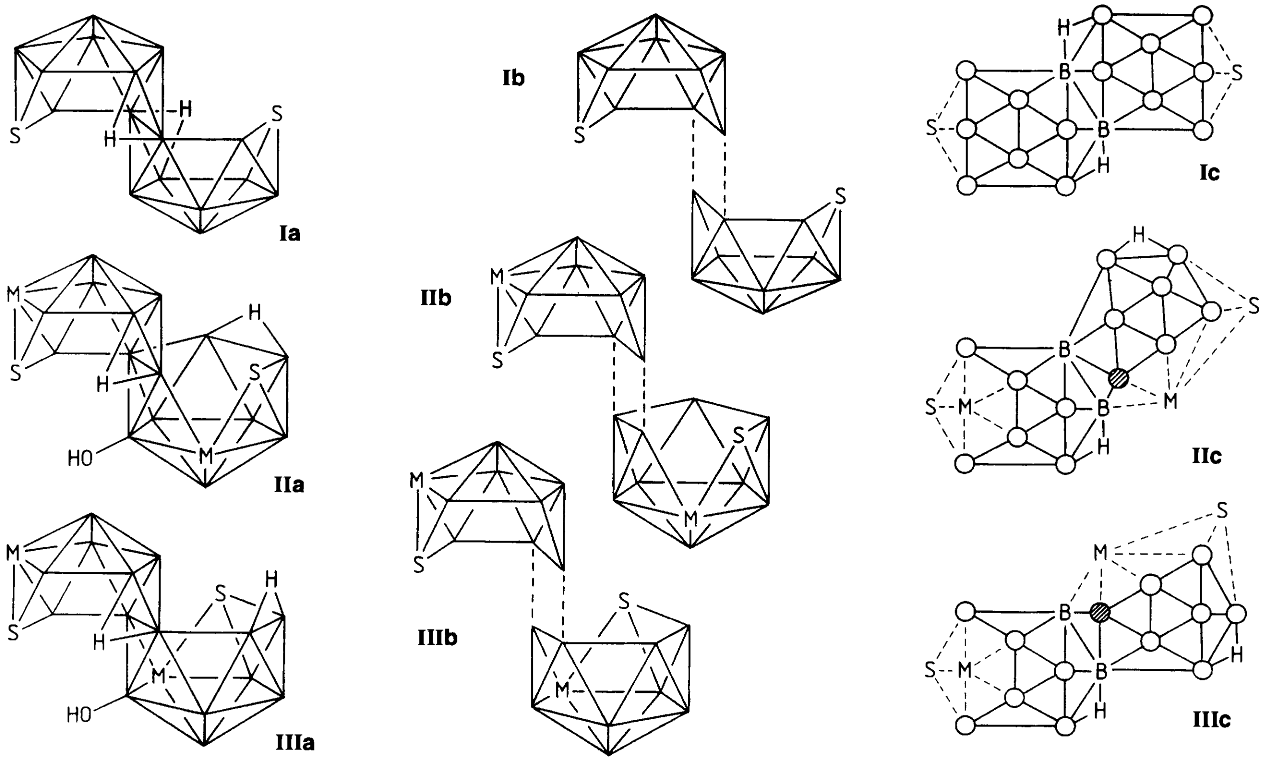
Reaction of *anti*-9,9′-$S_2B_{16}H_{16}$ with $[\{RhCl_2(C_5Me_5)\}_2]$ resulted in two macropolyhedral rhodathiaboranes, *syn* and *anti* isomers of $[(C_5Me_5)_2Rh_2S_2B_{15}H_{14}(OH)]$: each compound consists of a *nido*-shaped $\{RhSB_8H_7\}$ unit and an *arachno*-shaped $\{RhSB_9H_8(OH)\}$ unit conjoined with a B–B edge in common; the isomers differ in the sense of fusion of the two sub-clusters; considerable differential rearrangement has occurred from the starting $S_2B_{16}H_{16}$ substrate.

The fusion, with common edges or faces, of polyhedral boron-containing clusters generates large ‘macropolyhedral’ clusters. Such cluster fusion extends considerably[1,2] the extensive variety of chemistry already available to the boron hydrides and their derivatives. The further chemistry of these macropolyhedral species is, however, only sparsely investigated.[2–6] The synthesis[1] of the eighteen-vertex dithiaborane (*anti-nido*:*nido*)-9,9′-$S_2B_{16}H_{16}$ (structure **I**) now constitutes a new convenient entry into macropolyhedral systems. The ready development of some further chemistry is thereby now facilitated.[7] Here we report preliminary results on two interesting isomeric products from the reaction of $S_2B_{16}H_{16}$ with $[\{RhCl_2(\eta^5\text{-}C_5Me_5)\}_2]$. The isomers have the general formulation $[(\eta^5\text{-}C_5Me_5)_2Rh_2S_2B_{15}O_{14}(OH)]$, and they have several features that augur well for much novel macropolyhedral boron-containing cluster chemistry.

The reaction between $S_2B_{16}H_{16}$ (24 mg, 95 μmol) and $[\{RhCl_2(\eta^5\text{-}C_5Me_5)\}_2]$ (65 mg, 105 μmol) in the presence of 1,8-bis(dimethylamino)naphthalene (50 mg, 234 μmol) in refluxing CH_2Cl_2 (25 cm^3) (18 h, N_2), followed by chromatographic separation, reveals several coloured reaction products. Two of these have been isolated by repeated chromatography, and identified as yellow and orange isomers of formulation $[(C_5Me_5)_2Rh_2S_2B_{15}H_{14}(OH)]$. The purified yield of each was *ca.* 3%.† The constitution of both these compounds has been determined by single-crystal X-ray diffraction analysis.‡ They have also been examined by NMR spectroscopy.§

The two closely related isomers (Fig. 1),[11] each consist of



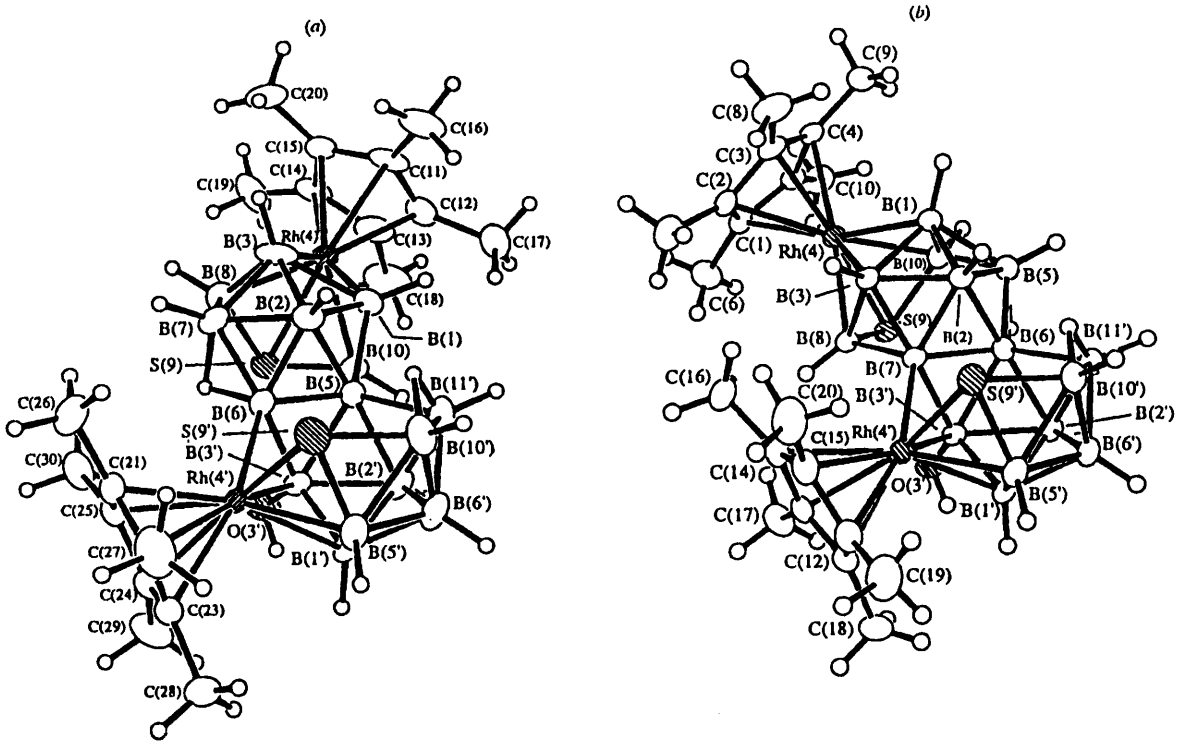


Fig. 1 Molecular structure (ORTEP)[11] of *syn*- (*a*) and *anti*-$[(C_5Me_5)_2Rh_2S_2B_{15}H_{14}(OH)]$ (*b*). Thermal ellipsoids are shown at the 30% level with hydrogen atoms drawn as circles of arbitrary radius. The C_5Me_5 ligand attached to Rh(4′) of the *syn* isomer is disordered over two positions, but, in the interests of clarity, only one of these positions is shown. The compounds are chiral, and in each case both enantiomers are present in the unit cell. The same *syn* enantiomer is represented diagrammatically in (*a*) and in structures **II**. To offer a different perspective, different enantiomers of the *anti* compound are shown in (*b*) and in structures **III**. Selected interatomic distances (pm): Rh(4)–B(8) 221.5(3), Rh(4)–B(10) 223.1(3), B(5)–B(6) 175.4(4), B(7)–B(8) 194.7(5), B(5)–B(10) 190.9(5), S(9)–B(8) 186.2(3), S(9)–B(10) 185.8(3), Rh(4′)–B(6) 213.9(3), Rh(4′)–S(9′) 233.80(8), Rh(4′)–B(3′) 222.6(3), Rh(4′)–B(5′) 227.5(3), S(9′)–B(5′) 189.2(3), S(9′)–B(10′) 191.8(4), B(3′)–O(3′) 141.6(4) (*syn* isomer); Rh(4)–B(8) 220.9(3), Rh(4)–S(9) 232.90(8), Rh(4)–B(10) 219.9(3), B(5)–B(10) 190.2(4), B(7)–B(8) 194.3(4), S(9)–B(8) 187.0(3), S(9)–B(10) 186.8(3), Rh(4′)–B(7) 225.4(3), Rh(4′)–S(9′) 235.26(9), Rh(4′)–B(3′) 225.5(3), Rh(4′)–B(5′) 225.5(3), S(9′)–B(5′) 191.3(3), S(9′)–B(10′) 191.6(3), B(3′)–O(3′) 141.2(3) (*anti* isomer)

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† The reaction mixture was filtered through silica gel (Fluka, TLC grade; GF254) using CH_2Cl_2, and the dark brown filtrate reduced to dryness. Column chromatography (silica gel) using CH_2Cl_2–hexane (50:50) thence gave a dark brown fraction, a change of liquid phase to 100% CH_2Cl_2 then yielding a second dark brown fraction. This second fraction contained several coloured components and was subjected to repeated thin-layer chromatography on silica gel G (Fluka, GF254): ultimately, development with C_6H_6–CH_2Cl_2 (80:20) gave a yellow component (R_f 0.23); extraction with CH_2Cl_2, and evaporation thence yielded a yellow solid identified as *syn*-$[(C_5Me_5)_2Rh_2S_2B_{15}H_{14}(OH)]$; ultimate development with CH_2Cl_2–MeCN (90:10) gave an orange component (R_f 0.80) from which orange *anti*-$[(C_5Me_5)_2Rh_2S_2B_{15}H_{14}(OH)]$ was similarly obtained.

‡ Crystals were grown by diffusion of hexane into solutions of the compounds in CH_2Cl_2. All crystallographic measurements were made on a Stoe STADI4 diffractometer using Mo-Kα radiation (λ = 0.710 69 Å) at −73 °C. Both structures were solved by standard heavy-atom methods (SHELXS 86[8]) and were refined by full-matrix least squares (against all the F_o^2 data) (SHELXL 93[9]) with anisotropic displacement parameters for all non-hydrogen atoms. In calculations, methyl and hydroxyl hydrogen atoms were considered as 'rotating' in constrained idealised positions with fixed isotropic displacement parameters of $1.5U_{eq}$ of their parent non-hydrogen atom. All hydrogen atoms bonded to the boron cluster atoms were located on Fourier-difference syntheses and were freely refined.

syn Isomer. $C_{20}H_{45}B_{15}ORh_2S_2$, M_r = 733.65, crystal dimensions 0.45 × 0.30 × 0.28 mm, monoclinic, space group $P2_1/c$, a = 13.1788(13), b = 17.287(2), c = 15.566(2) Å, β = 112.597(7)°, Z = 4, U = 3247.0(7) Å³, D_c = 1.488 g cm⁻³; 5984 reflections collected in the ω–θ scan mode to 2θ = 50°; 5764 unique reflections used in subsequent calculations after Lorentz, polarization and absorption corrections (μ = 1.153 mm⁻¹; azimuthal ψ scans, minimum and maximum transmission factors 0.7449 and 0.9998, respectively). The pentamethylcyclopentadienyl ligand bound to rhodium atom Rh(4′) of the ten-vertex sub-cluster proved to be evenly disordered over two positions. Each group was refined as a variable metric rigid body with rigid-bond restraints applied to the anisotropic displacement components of adjacent bonded atoms. Shift-limiting restraints were applied in the early stages of refinement but were gradually removed later on. Final wR_2 = 0.0844, conventional R = 0.0321 for 5035 reflections with $F_o > 4\sigma(F_o)$. Maximum electron density 1.34 e Å⁻³ [0.32 Å from Rh(4)].

anti Isomer. $C_{20}H_{45}B_{15}ORh_2S_2$, M_r = 733.65, crystal dimensions 0.35 × 0.28 × 0.24 mm, triclinic, space group $P\bar{1}$, a = 10.435(2), b = 12.167(3), c = 14.130(3) Å, α = 70.557(12), β = 87.579(9), γ = 70.014(12)°, Z = 2, U = 1584.6(6) Å³, D_c = 1.538 g cm⁻³; 5836 reflections collected in the ω–θ scan mode to 2θ = 50°; 5604 unique reflections used in subsequent calculations after Lorentz, polarization and absorption corrections (μ = 1.191 mm⁻¹; azimuthal ψ scans, minimum and maximum transmission factors 0.6175 and 0.8762, respectively). Final wR_2 = 0.0644, conventional R = 0.0239 for 4764 reflections with $F_o > 4\sigma(F_o)$. Maximum residual electron density 0.85 e Å⁻³. 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.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/36.

§ Boron-11, ^1H and ^1H-{^{11}B} NMR measurements were made on $CDCl_3$ solutions at *ca.* 9.35 T on a Bruker AM 400 instrument at 294–297 K. Chemical shifts δ are quoted in ppm relative to Ξ 100 MHz ($SiMe_4$) for ^1H and Ξ 32.083 971 MHz (nominally BF_3OEt_2) for ^{11}B, Ξ being defined as in ref. 10. *syn* Isomer: δ(^{11}B) [δ(^1H) of directly bound hydrogen] +40.6 [no terminal H], *ca.* +19.3 [+4.44], *ca.* +19.3 [+4.11], *ca.* +15.8 [+4.25], *ca.* +15.8 [+2.98], *ca.* +14.6 [+3.47], *ca.* +14.6 [no terminal H], +11.9 [+3.62], +9.0 [+2.98], +4.4 [+3.61], −3.4 [no terminal H], −8.5 [+2.51], −12.0 [+2.42], −20.3 [+0.57], −34.8 [+0.69]; δ(^1H) +0.48 [μ-H strongly associated with δ(^{11}B) +4.4] and −0.24 [μ-H strongly associated with δ(^{11}B) −12.0], +1.92 and +1.83 (C_5Me_5); possible δ(^1H)(OH) *ca.* +4.2. *anti* Isomer: δ(^{11}B) +26.0 [no terminal H], +23.2 [δ(^1H) +4.18], +19.8 [+3.94], +16.4 [+3.97], *ca.* +14.7 [+3.79], *ca.* +14.7 [+3.97], *ca.* +14.7 [no terminal H], *ca.* +12.1 [+3.25], *ca.* +12.1 [no terminal H], +8.9 [+2.84], +3.5 [+3.92], −1.8 [+3.30], −3.1 [+2.75], − 25.1 [0.00], −34.4 [+0.82]; δ(^1H) +0.73 [μ-H strongly associated with δ(^{11}B) −1.8 and/or −3.1] and −2.56 [μ-H strongly associated with δ(^{11}B) +14.7], +1.93 and +1.89 (C_5Me_5); δ(^1H)(OH) not yet observed and assigned. In each case ^{11}B linewidths and the small quantities of material have so far precluded the gathering of sufficient interproton or interboron correlation spectroscopic data for spectrum assignment. In each case the 70 eV (1.12 × 10⁻¹⁷ J) electron-impact mass spectrum exhibited a molecular-ion envelope with an m/z_{max} value corresponding to the isotopomer of highest molecular weight.

the same pair of sub-clusters, which are joined with two boron atoms in common, and have several features of interest. One sub-cluster in each compound is an *arachno*-shaped $\{(C_5Me_5)RhSB_9H_8(OH)\}$ eleven-vertex cluster. The other is a *nido*-shaped $\{(C_5Me_5)RhSB_8H_7\}$ ten-vertex cluster. These two sub-clusters are fused *syn* (structure **II**) and *anti* (structure **III**) in a manner analogous to the *syn*- and *anti*-$B_{18}H_{22}$ isomers.[5,12] The *arachno*-shaped eleven-vertex cluster shape has precedent in the cluster geometries of $[6\text{-}(\eta^6\text{-}C_6Me_6)\text{-}6,9,11\text{-}OsC_2Me_2B_8H_8]$[13] and of the $[S_2B_9H_{10}]^-$ anion.[14] Interestingly, these last two species have different formal cluster electron counts,[15] *closo* and *arachno* respectively. It is thence of further interest that the *arachno*-shaped $\{(C_5Me_5)RhSB_9H_8(OH)\}$ sub-clusters of the two $[(C_5Me_5)_2Rh_2S_2B_{15}H_{14}(OH)]$ isomers have a third electron count, formally *nido*. The ten-vertex sub-cluster has the unusual $\{$*nido*-2,6-M(E)$B_8\}$ (E = main-group heteroatom centre) configuration, of which the only precedent, as far as we are aware, is the $\{$*nido*-2,6-FeO$B_8\}$ cluster of the oxaferraborane $[2\text{-}(\eta^6\text{-}C_6H_3Me_3)\text{-}$*nido*$\text{-}2,6\text{-}FeOB_8H_{10}]$.[16] The B-hydroxyl group is also rare in polyhedral borane chemistry.[17] Oxygen take-up is a feature of products of other pentamethylcyclopentadienylrhodaborane reactions that have been worked up in air. However, these other reported oxygen incidences in rhodaboranes are so far manifested in B–O–B intercluster bridge formation or in oxygen cluster assimilation to form contiguous cluster oxarhodaboranes,[18] rather than B-hydroxyl generation.

The reaction itself is also of interest. The pathways for the formation of both *syn*- and *anti*-$[(C_5Me_5)_2Rh_2S_2B_{15}H_{14}(OH)]$ from $S_2B_{16}H_{16}$ are complex: they involve boron-vertex loss, and substantial intracluster rearrangement. The metal centres thereby appear to be embedded in their sub-clusters, rather than being attached to the periphery of the open face of the $S_2B_{16}H_{16}$ starting substrate. Although these two product clusters are isomeric, their contiguous fifteen-vertex boron skeletons (structures **IIc** and **IIIc**) are significantly different not only from the starting borane skeleton (structure **Ic**), but also from each other. This suggests that the rearrangements must be quite different in each case. It is therefore remarkable that the two products differ in their isomerism only in the *syn* and *anti* sense, but are otherwise the same, even down to the detail of the siting of the hydroxyl group. In elucidating pathways it will be useful to know the structures of the several other products from the reaction. It seems coincidental that these first two compounds that we have been able to characterize happen to be so similar. It will also be of interest to see how the products vary when the reaction mixture is separated under anaerobic conditions. We currently continue our investigation of the macropolyhedral thiametallaborane chemistry of this and closely related systems.

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