The Isolation and Characterisation of the 1- and 2-Isomers of *nido*-[(η^6-C_6Me_6)RuB_9H_{13}]—But is the 1-Isomer *nido* or *arachno*?[1]

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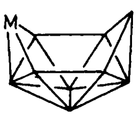
Reaction between [(η^6-C_6Me_6)$RuCl_2$]$_2$ and K[B_6H_{11}] yields a rare example of a 2-metalla *nido*-decaborane derivative, [2-(η^6-C_6Me_6)-*nido*-2RuB_9H_{13}], together with an unprecedented 1-ruthena isomer having the same empirical formula but a more open *arachno*-type structure.

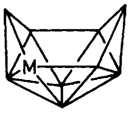
The ten-vertex 6- and 5-metalladecaborane *nido* configurations [(I) and (II) respectively] are well documented,[2] but the 2-configuration (III) is rare, previously being unique to [2-(η^5-C_5Me_5)-*nido*-2-CoB_9H_{13}],[3—5] and the 1-configuration (IV) is previously unreported, having proved to be particularly elusive in spite of a considerable amount of work in areas likely to generate it.[2—4,6] We have now isolated the 1- and 2-isomers of [(η^6-C_6Me_6)RuB_9H_{13}] [compounds (**1**) and (**2**) respectively] from the reaction between the *arachno*-[B_6H_{11}]$^-$ anion and [(η^6-C_6Me_6)$RuCl_2$]$_2$ in tetrahydrofuran (THF)–CH_2Cl_2 at −25 °C. The yields of these air-stable yellow solids were 9 and 5%, respectively. We have also detected these products from the reaction between the *nido*-[B_5H_8]$^-$ anion and [(η^6-C_6Me_6)$RuCl_2$]$_2$. In neither reaction is the mechanism of the cluster expansion process clear.

The structure of compound (**2**) (Figure 1a)† confirms it as a straightforward *nido*-$B_{10}H_{14}$ analogue, as was found[5] in the cobalt analogue [2-(η^5-C_5Me_5)-*nido*-2-CoB_9H_{13}]. The ^{11}B n.m.r. shielding properties (Figure 2a) are consistent with it having an electronic structure analogous to that of *nido*-$B_{10}H_{14}$.

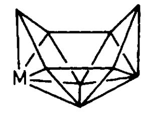
By contrast, although the cluster structure of (**1**) (Figure 1b) exhibits some similarities to the *nido*-$B_{10}H_{14}$ pattern, it is apparent that the interboron distance B(5) · · · B(10) adjacent to the metal is now nonbonding at 249.7 pm, indicating a more



(I)



(II)



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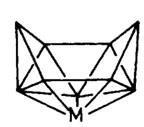
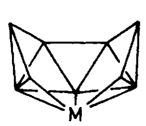


(IV)



(V)

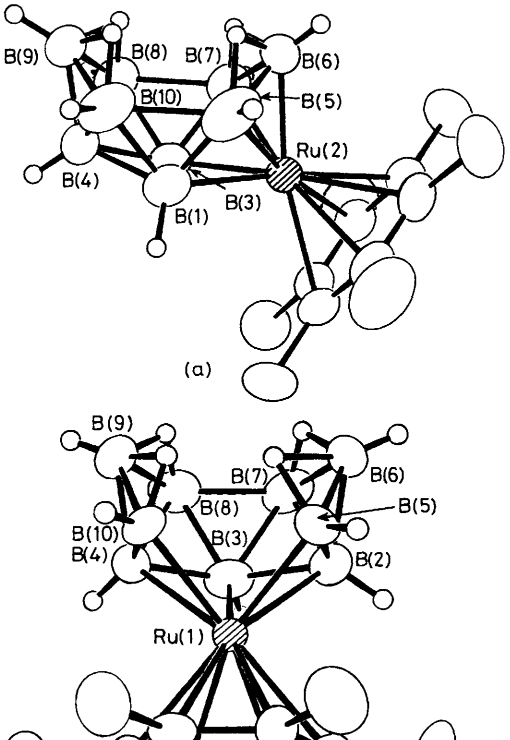


Figure 1. Crystallographically determined molecular structures of (a) [2-(η^6-C_6Me_6)-*nido*-2-RuB_9H_{13}] (**2**) and (b) its ostensible {1-(η^6-C_6Me_6)-1-Ru} analogue (**1**).† The metallaborane subcluster of compound (**2**) has an atomic disposition similar to that of *nido*-$B_{10}H_{14}$. [Selected interatomic distances Ru(2)–B(1) 214.7(8), Ru(2)–B(3) 215.5(7), Ru(2)–B(5) 216.0(8), Ru(2)–B(6) 208.5(8), Ru(2)–B(7) 215.6(8), B(5)–B(10) 196.2(13), and B(7)–B(8) 196.5(11) pm]. In compound (**1**), however, the B(5)–B(10) distance is non-bonding at 249.7 pm [other selected interatomic distances being Ru(1)–B(2) 222.0(9), Ru(1)–B(3) 218.1(9), Ru(1)–B(4) 221.4(7), Ru(1)–B(5) 208.6(7), Ru(1)–B(10) 208.4(8), and B(7)–B(8) 183.5(13) pm].

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† *Crystal data* for (**1**): $C_{12}H_{31}B_9Ru$, M = 373.73, monoclinic, space group $P2_1$ (no. 4), a = 843.3(2), b = 1345.8(3), c = 863.7(2) pm, β = 110.03(2)°, U = 0.9209 nm^3, Z = 2, D_c = 1.347 g cm^{-3}, μ = 7.48 cm^{-1}, $F(000)$ = 378, T = 290 K. 1823 Data were collected ($4.0 < 2\theta < 50.0°$) of which 1768 [$I > 2.0\sigma(I)$] were considered observed.

(**2**): $C_{12}H_{31}B_9Ru$, M = 373.73; monoclinic, space group $P2_1/n$ (=$P2_1/c$, no. 14), a = 866.0(3), b = 1652.2(5), c = 1343.5(3) pm, β = 104.51(2)°, U = 1.861 nm^3, Z = 4, D_c = 1.333 g cm^{-3}, μ = 7.41 cm^{-1}, $F(000)$ = 756, T = 290 K. 2797 Data were collected ($4.0 < 2\theta < 45.0°$) of which 2367 [$I > 2.0\sigma(I)$] were considered observed.

Both data sets were obtained using a Nicolet P3/F diffractometer operating in the ω–2θ scan mode with scan widths of 1.0° below $K_{\alpha1}$ to 1.0° above $K_{\alpha2}$ and scan speeds ranging from 2.0 to 29.3° min^{-1}. Both sets were corrected for absorption empirically.[12] In both cases the structure was solved by heavy-atom and difference Fourier techniques and refined by full-matrix least-squares (SHELX).[13] However, the solution of compound (**1**) was complicated by the presence of a *pseudo* mirror-plane bisecting the C_6Me_6 group (the boron hydrogens were particularly affected) and so a suitable, small, damping factor was included in the least-squares refinement to facilitate their location and refinement. Non-hydrogen atoms were refined with anisotropic thermal parameters for both compounds. The C_6Me_6 group for compound (**1**) was refined as a rigid body [C–C(ring) = 141.8, C–C(methyl) = 152.3 pm]. For both compounds the boron hydrogen atoms were located and refined with individual isotropic thermal parameters. The weighting scheme $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ was used. The final discrepancy indices are R = 0.0352 and R_w = 0.0382 (g = 0.0002, 251 parameters) for compound (**2**) and R = 0.0266 and R_w = 0.0273 (g = 0.0003, 220 parameters) for compound (**1**). Refinement of the enantiomorph of compound (**1**) led to slightly higher discrepancy indices. 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.

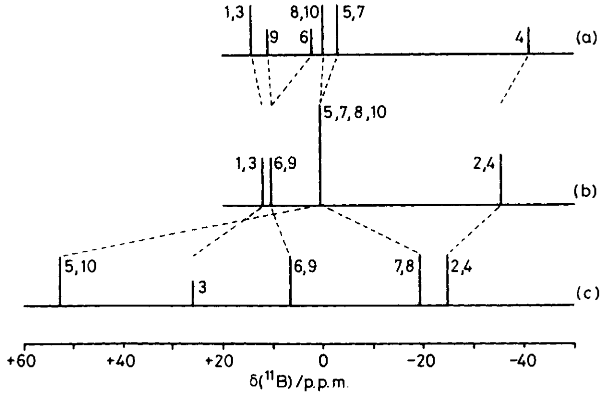

Figure 2. Stick diagrams of the relative intensities and chemical shifts within the ^{11}B n.m.r. spectra of (a) $[2\text{-}(\eta^6\text{-}C_6Me_6)\text{-}$*nido*$\text{-}2\text{-}RuB_9H_{13}]$ (**2**) and (c) its $\{1\text{-}(\eta^6\text{-}C_6Me_6)\text{-}1\text{-}Ru\}$ analogue (**1**). The shielding pattern of the 2-isomer (**2**) is closely related to that of (b) $B_{10}H_{14}$, indicating similar electronic structures, whereas that of the 1-analogue (**1**) is quite different, suggesting a considerably modified electronic structure for this compound.

open structure with a seven-membered open face, rather than the six-membered open face of the straightforward *nido*-$B_{10}H_{14}$ analogues in which B(5)–B(10) is *ca.* 200 pm. (It may be noted that for this compound refinement of the boron-bound hydrogen atoms in the *X*-ray analysis was hampered by *pseudo* mirror symmetry associated with the C_6Me_6 group. It was possible, however, to locate these atoms in chemically sensible positions though the detailed dimensions derived for them may not be particularly accurate.) The cluster ^{11}B n.m.r. shielding behaviour for compound (**1**) (Figure 2c) now deviates widely from that of *nido*-$B_{10}H_{14}$ and its straightforward metalla derivatives.

These factors suggest a considerable deviation from the *nido*-decaborane electronic structure for compound (**1**), and thereby an interesting departure from the simple Williams–Wade[7,8] cluster geometry and electron-counting rules. It would be tempting to speculate that the rupture of the B(5)–B(10) linkage reflects an increased electron contribution from ruthenium to the cluster electron count, though at present there is no experimental evidence as to whether the compound is more accurately described as a Ru^{II} or Ru^{IV} derivative. The more open structure is reminiscent of the anomalous *arachno*-type open structure found[9] for the *nido* eight-vertex binary borane B_8H_{12}, and the high-connectivity metal atom on the open face is reminiscent of that[10] in the '*isonido*' complex $[(PPh_3)(Ph_2P\overline{C_6H_4)IrC(OH)B}_8H_6(OMe)]$. In terms of this latter parallel, compound (**1**) would be an '*isoarachno*' ten-vertex species, the geometry being derived notionally by the removal of two adjacent vertices from a twelve vertex '*isocloso*' cluster geometry such as that observed[11] for the $\{WC_2B_9\}$ cluster in $[Pt(PEt_3)_2(CO)_2WC_2B_9H_8Me_2(CH_2C_6H_4Me)]$.

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