A Double Cluster of Ruthenium and Boron; $[1\text{-}\eta^2\text{-}\{(\eta^6\text{-}C_6Me_6)_2Ru_2H_4\}\text{-}\mathit{isocloso}\text{-}1\text{-}RuB_{10}H_8\text{-}2,3\text{-}(OEt)_2]$

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The novel double cluster compound $[\{(\eta^6\text{-}C_6Me_6)_2Ru_2H_4\}RuB_{10}H_8(OEt)_2]$, obtained in 31% yield as an unexpected product from the reaction between the mononuclear ruthenium complex *arachno*-$[(\eta^6\text{-}C_6Me_6)ClRuB_3H_8]$ and *closo*-$[B_{10}H_{10}]^{2-}$ in ethanol, exhibits a unique (non-carbonyl containing) triangular $\{Ru_3\}$ cluster and a *closo*-type eleven-vertex $\{RuB_{10}\}$ cluster conjoined at a common Ru atom.

Although many metal-cluster and boron-cluster compounds are known, compounds that incorporate both types of cluster are extremely rare, being essentially limited to the gold–boron triple cluster compound $[H_{12}B_{10}Au\{Au(PEt_3)\}_4AuB_{10}H_{12}]$,[1] which comprises two *nido*-type eleven-vertex $\{AuB_{10}\}$ clusters that have their metal vertices in common with opposing vertices of an octahedral $\{Au_6\}$ cluster. We now report the isolation and characterisation of the first example of a further novel structural class, the double cluster species $[\{(C_6Me_6)_2Ru_2H_4\}RuB_{10}H_8(OEt)_2]$. This is an intensely red air-stable crystalline solid, of which the molecular structure (Figure 1)† is based on an '*isocloso*-type' eleven-vertex $\{RuB_{10}\}$ cluster that has its ruthenium vertex in common with a vertex of a triangular $\{Ru_3\}$ cluster. The $\{Ru_3\}$ triangle is unique in being the first such cluster to have no attached carbonyl ligands, the

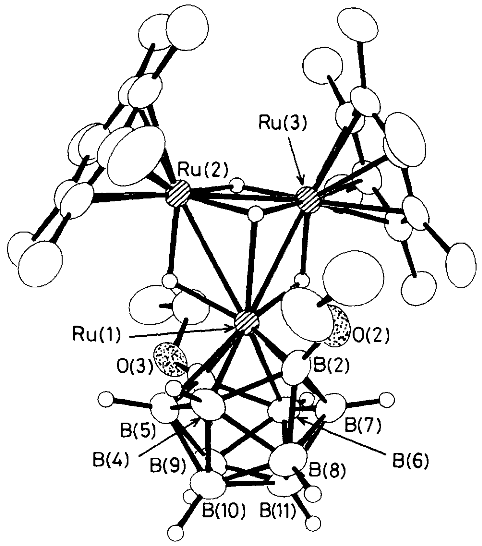

Figure 1. ORTEP drawing of the crystallographically determined molecular structure of $[\{(C_6Me_6)_2Ru_2H_4\}RuB_{10}H_8(OEt)_2]$. Selected interatomic distances are as follows: Ru(1)–Ru(2) 282.7(4), Ru(2)–Ru(3) 268.4(4), and Ru(3)–Ru(1) 279.2(4) pm. The Ru–C distances average at 220.8(5) pm, and the dimensions within the *closo*-type $\{RuB_{10}\}$ cluster are very similar to those reported (ref. 3) for $[(PPh_3)_2RuB_{10}H_8(OEt)_2]$. Ru–H distances are in the caption to Figure 2. The $\{Ru_3\}$ plane is twisted away from the $\{Ru(1)B(10)B(11)\}$ plane by 14.6°, but solution n.m.r. properties show time-averaged C_2 symmetry in solution at ambient temperature. $\delta(^{11}B)$ as follows [with directly bound $\delta(^1H)$ in square brackets]: B(2,3) +88.1 [OEt], B(4,5,6,7) +1.6 [+2.39], B(8,9) +3.6 [+3.11], and B(10,11) −0.1 [+1.93] p.p.m. Bridging H atoms at $\delta(^1H)$ −13.89 (4H), and $\{C_6Me_6\}$ H atoms at $\delta(^1H)$ +2.05 (36H) (CD_3CN solution at 304 K). Note that we use the IUPAC-recommended MB_{10} numbering system here, which differs from that used in our previous papers on this structural type (*e.g.* ref. 3).

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† *Crystal data:* $C_{28}H_{58}B_{10}O_2Ru_3$, M = 838.09, monoclinic, a = 1081.7(1), b = 1622.6(3), c = 2120.4(3) pm, β = 102.07(1)°, U = 3.639 nm³, Z = 4, space group $P2_1/c$, D_c = 1.529 g cm^{-3}, μ = 11.29 cm^{-1}, $F(000)$ = 1696, T = 290 K. Scans running from 1° above $K_{\alpha 1}$ to 1° below $K_{\alpha 2}$, scan speeds 2.0—29.3° min^{-1}, $4.0 < 2\theta < 45.0°$. 5108 Data were collected, 4295 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 a procedure described elsewhere.[4] The data set was corrected for absorption empirically.[5] The structure was solved by direct methods and refined by blocked full-matrix least-squares using SHELX76.[6] All non-hydrogen atoms were refined anisotropically. All methyl- and methylene-hydrogen atoms were included in calculated positions and refined with an overall isotropic temperature factor. Borane and ruthenium hydrogen atoms were located in difference maps and freely refined with isotropic temperature factors. The weighting scheme w = $[\sigma^2(F_o)+0.0004(F_o)^2]^{-1}$ was used. Final R values are R = 0.0344, R_w = 0.0396 (458 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.

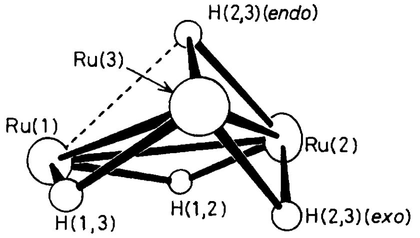

Figure 2. ORTEP drawing of the $\{Ru_3H_4\}$ cluster region of $[\{(C_6Me_6)_2Ru_2H_4\}RuB_{10}H_8(OEt)_2]$. The borane-bound Ru(1) atom is joined to Ru(2) and Ru(3) by one Ru–H–Ru bridge each, whereas Ru(2) and Ru(3) are linked by two such bridges. One of these [H(2,3)(*endo*)] shows some agostic interaction with Ru(1) which gives it some capping (triply bridging) character. The hydrogen atoms are fluxional, all four mutually exchanging at higher temperatures [$\Delta G^{\ddagger}$ *ca.* 46.0 kJ mol^{-1} at 270 K]. At lower temperatures H(2,3)(*endo*) and H(2,3)(*exo*) remain mutually equivalent; presumably each equilibrates between *endo* and *exo* without mutual exchange, and this is accompanied by a flipping of the H(1,2) and H(1,3) atoms across the $\{Ru_3\}$ plane. At 203 K, $\delta(^1H)$ values for these pairs of hydrogen atoms are −10.60 (2H) and −17.67 (2H) (CD_2Cl_2 solution). Ruthenium–hydrogen distances are as follows: Ru(1)–H(1,2) 172(6), Ru(1)–H(1,3) 190(5), Ru(1)–H(2,3)(*endo*) 223(5); Ru(2)–H(1,2) 170(6), Ru(2)–H(2,3)(*endo*) 174(5), Ru(2)–H(2,3)(*exo*) 175(6); Ru(3)–H(1,3) 169(5), Ru(3)–H(2,3)(*endo*) 188(5), and Ru(3)–H(2,3)(*exo*) 156(6) pm. The dihedral angle between the planes Ru(2)Ru(3)H(2,3)(*endo*) and Ru(2)Ru(3)H(2,3)(*exo*) is 179°.

pendant groups being two *hexahapto*-hexamethylbenzene ligands, a *hexahapto*-decaborane group, three edge-bridging Ru–H–Ru hydrogen atoms, and one semi-capping hydrogen atom (Figure 2). The stability of this novel $\{Ru_3\}$ triangular type (which normal electron-counting procedures would suggest is a 44-electron species) presages an extensive and interesting arene–ruthenium cluster chemistry to complement and extend the vast amount of carbonyl-bound ruthenium-cluster chemistry that has been reported during the last decade.

The compound is obtained in the surprisingly high yield of 31% (based on Ru content) as an unexpected product from the reaction between the *closo*-$[B_{10}H_{10}]^{2-}$ anion and the monoruthenium species [2-(η^6-C_6Me_6)-2-Cl-*arachno*-2-RuB_3H_8][2] in refluxing ethanol for three hours. Other products (2—5% yield) are the more straightforward monometallaboranes $[(C_6Me_6)RuB_9H_8(OEt)]$ and $[(C_6Me_6)RuB_{10}H_9(OEt)]$ of previously recognised[3] *isocloso*-type ten- and eleven-vertex configurations. The last-named product suggests that *aufbau*-agglomeration of metal atoms to the borane substrate to give the Ru_3 species may have occurred in a manner similar to that suggested[1] for the formation of the gold compound, and that the $\{B_3H_8\}$ moiety serves as a reducing agent. These factors, in turn, suggest that approaches to polymetallaborane species might now usefully include reductive multiple addition of metal centres to the boron cluster as a general strategy, and that pathways into novel non-boron-containing arene–ruthenium cluster chemistry might usefully use the smaller borane anions as reducing agents.

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