Homobimetallic B-Frame Species: $[\{(PPh_3)_2Ru\}\text{-}(\mu\text{-}MeCO_2)_3\text{-}(\mu\text{-}H)_2\text{-}\{RuB_{10}H_7\}]$,† a Unique Diruthenaborane in which the Metal Atoms are linked by One-, Two-, Three-, and Four-membered Bridges

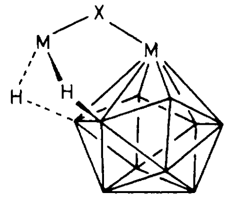
Xavier L. R. Fontaine, Norman N. Greenwood, John D. Kennedy, Mark Thornton-Pett, and Zheng Peiju

School of Chemistry, University of Leeds, Leeds LS2 9JT, U.K.

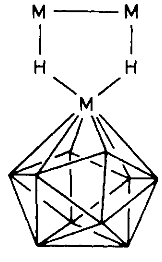
Reaction of $[RuCl_2(PPh_3)_3]$ with *closo*-$[B_{10}H_{10}]^{2-}$ in $MeCO_2H$/tetrahydrofuran (thf) solution forms $[\{(PPh_3)_2Ru\}\text{-}(\mu\text{-}MeCO_2)_3\text{-}(\mu\text{-}H)_2\text{-}\{$*closo*-1-$RuB_{10}H_7\}]$, a unique homobimetallic 'B-frame' complex in which the Ru atom of a *closo*-type 11-vertex $\{RuB_{10}\}$ cluster is joined to a second Ru atom *via* Ru–H–Ru, Ru–B–H–Ru, Ru–O–C–O–Ru, and Ru–B–O–C–O–Ru bridges; other products include the monometallaborane [1-(PPh_3)-1,2;1,6-(μ-MeCOO-*O,O'*)$_2$-3-(OH)-*closo*-1-$RuB_{10}H_7$], which has two exopolyhedral acetate B–Ru bridges and a rare B-terminal OH group.

Closed polyhedral metallaboranes with the 'polar' nine-vertex (C_{2v}), ten-vertex (C_{3v}), and eleven-vertex (C_{2v}) formal geometries do not[1] in general obey the straightforward[2] polyhedral cluster-geometry and electron-counting rules. Of these metallaborane cluster types the eleven-vertex $\{RuB_{10}\}$ system is of particular interest in that it readily supports (mutually unrelated) bimetallic[3] and trimetallic[4] systems represented in (I) and (II) respectively. We now report that the remarkable ability of this cluster type readily to support polymetallic systems extends also to a third category, comprising novel acetate-bridged systems.

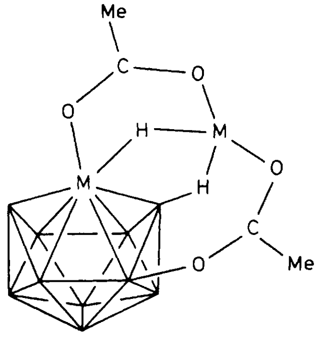
Reaction of $[RuCl_2(PPh_3)_3]$ with *closo*-$[B_{10}H_{10}]^{2-}$ and $MeCO_2H$ in refluxing thf solution, followed by chromatographic separation, yielded the red air-stable crystalline compound $[\{(PPh_3)_2Ru\}\text{-}(\mu\text{-}MeCO_2)_3\text{-}(\mu\text{-}H)_2\text{-}\{$*closo*-1-Ru-$B_{10}H_7\}]$† (**1**) as one of the chromatographically separable metallaborane products (purified yield 1.5%). It was characterized by single-crystal *X*-ray diffraction analysis‡ (Figure 1) and n.m.r. spectroscopy.§ The cluster structure of (**1**) is that of a basic *isocloso* (*hypercloso*) eleven-vertex $\{RuB_{10}\}$ polyhedron, to which a second ruthenium centre is linked by four different types of bridge: two hydrogen bridges (one from boron and one from ruthenium) and two *O,O'*-acetate bridges (one from boron and one from ruthenium) (schematic



(I)



(II)



(III)

---

† [1',1'-$(PPh_3)_2$Ru(1')-1,1'; 1,3; 1',4-(μ-MeCOO-*O,O'*)$_3$-1,1'; 1',2-(μ-H)$_2$-*closo*-1-$RuB_{10}H_7$].

‡ *Crystal data* for $C_{43}H_{50}B_{10}Cl_2O_6P_2Ru_2$, M = 1105.97, triclinic, space group $P1$, a = 1252.9(2), b = 1160.6(2), c = 1787.8(3) pm, α = 95.21(1), β = 83.07(1), γ = 106.18(1)°, U = 2.4738(6) nm^3, Z = 2, μ = 7.39 cm^{-1}, $F(000)$ = 1116. Scan widths 2.0° + α-doublet splitting, scan speeds 2.0—29.3° min^{-1} and $4.0 < 2\theta < 50.0°$. Total data collected = 8960, no. observed = 7726 $[I > 2.0\sigma(I)]$, R = 0.0416, R_w = 0.0486 (g = 0.0002).

Crystal data for $C_{22}H_{29}B_{10}O_5PRu$, M = 613.62, monoclinic, space group $I2/_a$ (=$C2/c$, no. 15), a = 1984.6(2), b = 1442.0(3), c = 1977.6(3) pm, β = 90.48(1)°, U = 5.659(2) nm^3, Z = 8, μ = 5.66 cm^{-1}, $F(000)$ = 2480. Scan widths and speeds and 2θ range as above. Total data collected = 5599, no. observed = 4506, R = 0.0317, R_w = 0.0338 (g = 0.0002).

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.[5] The data sets were corrected for absorption empirically.[6] Both structures were solved by standard heavy atom methods and refined by full-matrix least-squares using SHELX 76.[7] All non-hydrogen atoms were refined anisotropically except for a disordered CH_2Cl_2 molecule in the Ru_2 complex which was refined isotropically. All phenyl rings were treated as rigid bodies with idealised hexagonal symmetry (C–H = 139.5 pm). All phenyl and methyl hydrogen atoms were included in calculated positions (C–H = 108 pm) and refined with an overall isotropic temperature factor while all borane hydrogen atoms were located in Fourier difference maps and freely refined with individual isotropic thermal parameters. The weighting scheme $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ was used at the end of refinement for both complexes.

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.

§ *N.m.r. data*; $\delta(^{11}B)$/p.p.m. [with $\delta(^1H)$ ($CDCl_3$, 294 K) for directly bound H atoms in square brackets]: compound (**1**) [$\delta(^{11}B)$ in $CD_3C_6D_5$ at 373 K]: +110.2 [+1.14 (d of d, $^2J^{31}P^1H$ 15.7 and 47.2 Hz)], +103.3 [OAc substituted], +19.9 [OAc substituted], +15.8 [+4.42], +15.0 [+2.67], *ca.* + 9.2 [+2.93], *ca.* +9.2 [+2.60], *ca.* +9.2 [+1.13], +6.8 [+2.85], +2.30 [+3.70]; $\delta(^1H)$(RuHRu) −7.54 (d of d, $^2J^{31}P^1H$ 47.3 and 30.6 Hz), $\delta(^1H)$(OAc) +2.65, +1.16, and +1.09; compound (**2**) [$\delta(^{11}B)$ in $CDCl_3$ at 294 K] as follows: +99.7 [probably OH-substituted], +88.7 [probably OAc-substituted], +22.5 [OAc-substituted], *ca.* +2.8 [+3.56], *ca.* +2.3 [+2.02], *ca.* +1.8 [+3.59], *ca.* +1.8 [+2.54], *ca.* +1.8 [+1.34], −2.1 [+1.98], −4.0 [+1.67]; $\delta(^1H)$(OAc) +2.04 (d, $^5J^{31}P^1H$ *ca.* 0.35 Hz) and +2.00 (d, $^5J^{31}P^1H$ *ca.* 0.65 Hz), $\delta(^1H)$(OH) +6.43(br.). $\delta(^{11}B)$ and $\delta(^1H)$ in p.p.m. and positive to high frequency (low field) of Ξ 32.083 971 and 100 MHz respectively.

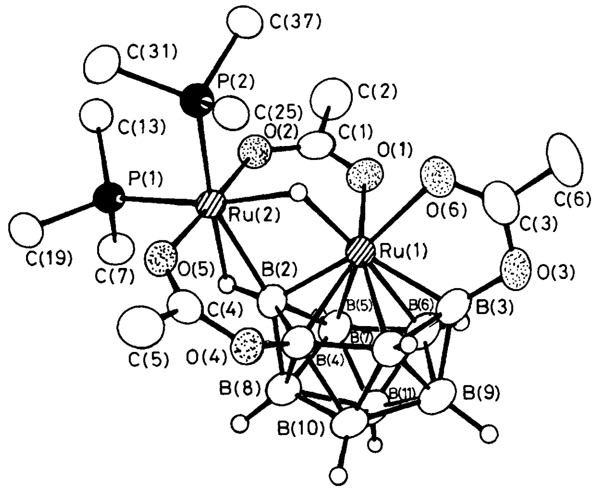


Figure 1. ORTEP drawing for $[\{(PPh_3)_2Ru\}(\mu\text{-}MeCOO)_2(\mu\text{-}H)_2\{RuB_{10}H_7(OCOMe)\}]$ (**1**), with methyl hydrogen and phenyl group atoms other than the *ipso* carbon ones omitted for clarity. Selected interatomic distances are as follows: from Ru(1) to Ru(2) 294.9(1), to B(2) 200.8(6), to B(3) 204.7(6), to B(4) 226.3(6), to B(5) 225.6(7), to B(6) 231.8(7), to B(7) 233.2(6), to O(1) 211.2(5), to O(6) 224.4(5), and to H(1,2) 192(5) pm; from Ru(2) to P(1) 237.1(3), to P(2) 235.3(3), to O(2) 208.5(4), to O(5) 210.5(4), to B(2) 224.0(6), to H(1,2) 172(5), and to H(2,2) 186(5) pm.

structure III). Both metal centres are saturated 18-electron ones. Although a variety of inter-ruthenium acetate and carboxylate linkages are known,[8] nothing like this, involving boron cluster atoms in a metallaborane, has been reported.

A second metallaborane product that has been chromatographically separated in viable yield (3.5%) is the orange-yellow crystalline monometallaborane $[(PPh_3)(MeCO_2)_2$-*closo*-1-$RuB_{10}H_7$-3-$(OH)]$ (**2**), again characterized as such by single-crystal X-ray diffraction analysis‡ (Figure 2) and n.m.r. spectroscopy.§ This also exhibits exopolyhedral borane-to-metal acetate bridging, again to an 18-electron ruthenium centre, but now also exhibits a rare B-hydroxy group, previously reported[9] only in $[6\text{-}(OH)$-*nido*-$B_{10}H_{13}]$.

These novel species presage extensive and unusual monometallaborane and polymetallaborane chemistries involving bridges by acetate and related species.

We thank the S.E.R.C. for support, the Fudan (Shanghai)–Leeds University Exchange Scheme for a Grant (to Z. P.), and Drs. M. Bown and P. MacKinnon for valuable consultations.

Received, 17th July 1987; Com. 1037

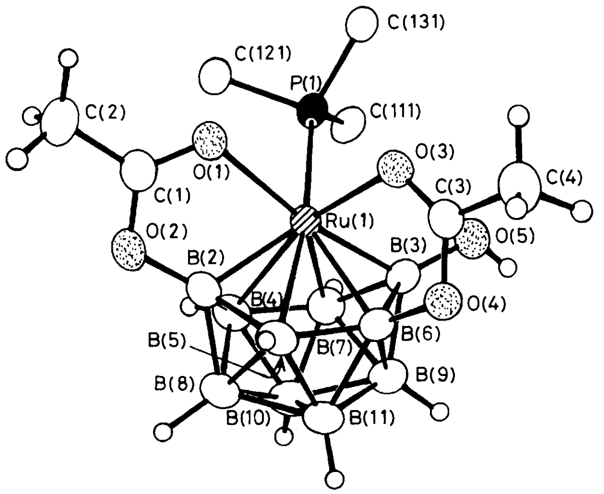


Figure 2. ORTEP drawing for $[(PPh_3)(MeCOO)_2RuB_{10}H_7(OH)]$ (**2**) with methyl hydrogen and phenyl group atoms other than the *ipso* carbon ones omitted for clarity. Selected interatomic distances are as follows: from Ru(1) to P(1) 248.0(3), to O(1) 225.6(4), to O(3) 217.9(4), to B(2) 204.4(5), to B(7) 206.7(5), to B(4) 236.9(5), to B(5) 235.8(5), to B(6) 219.4(5), and to B(7) 230.7(5) pm; B(3)–O(5) is 137.7(5) pm.

References

1 J. E. Crook, M. Elrington, N. N. Greenwood, J. D. Kennedy, and J. D. Woolins, *Polyhedron*, 1984, **3**, 901.

2 R. E. Williams, *Inorg. Chem.*, 1971, **10**, 210; *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 67; K. Wade, *Chem. Commun.*, 1971, 792; *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1.

3 M. Elrington, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1984, 1398.

4 M. Bown, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, P. I. MacKinnon, and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1987, 442.

5 A. Modinos and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1974, 2065.

6 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

7 G. M. Sheldrick, SHELX 76 Program System for X-ray Structure Determination, University of Cambridge, 1976.

8 See, for example T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1966, **28**, 2285; M. Rotem, Y. Shvo, I. Goldberg, and U. Shmueli, *Organometallics*, 1984, **3**, 1758; P. Frediani, M. Bianchi, F. Piacenti, S. Ianelli, and M. Nardelli, *Inorg. Chem.*, 1987, **26**, 1592.

9 N. N. Greenwood, M. J. Hails, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 1985, 953.