Homo- and Hetero-bimetallic B-Frame Compounds: Some Novel Twelve-vertex Ru/Ru, Os/Os, Ru/Os, and Os/Ru Metallaboranes

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The *closo*-type eleven-vertex metallaboranes $[(PPh_3)_2RuB_{10}H_8(OEt)_2]$ and $[(PMe_2Ph)_2OsB_{10}H_8(OEt)_2]$ readily react with a second metal centre $[M'Cl_2(PPh_3)_3]$ (M′ = Ru or Os) to yield the novel mixed-valence bimetallic species $[(PPh_3)_2ClM'ClM(PR_3)B_{10}H_8(OEt)_2]$ in which the second metal centre is bound exopolyhedrally to the original cluster in a remarkable way by converting two terminal $B-H_t$ groups into two two-electron $M'-H_\mu-B$ links and involving one terminal M′–Cl group in a third link to the cluster *via* a four-electron M′–Cl–M bridge; the original cluster metal M remains a sixteen-electron centre but can be readily converted into an eighteen-electron one by replacement of the phosphine ligand by bidentate chelates such as $CH_2(PPh_2)_2$ (dppm).

There is much current interest in molecular bimetallic species, and recently polyhedral borane frameworks have been advocated and exemplified as 'B-frame' substrates suitable for holding two potentially reactive transition-metal sites in specific positions of close proximity.[1,2] We now report preliminary results on a novel type of bimetallic B-frame compound that is readily obtainable in high yield by the reaction of the new eleven-vertex *closo*-type compounds such as $[(PPh_3)_2RuB_{10}H_8(OEt)_2]$[3] (Figure 1) and $[(PMe_2Ph)_2OsB_{10}H_8(OEt)_2]$ with complexes $[M'Cl_2(PPh_3)_3]$ (M′ = Ru or Os) in boiling ethanol solution (equation 1).

$$[(PR_3)_2MB_{10}H_8(OEt)_2] + [M'Cl_2(PPh_3)_3] \rightarrow [(PPh_3)_2ClM'ClM(PR_3)B_{10}H_8(OEt)_2] + PPh_3 + PR_3 \quad (1)$$

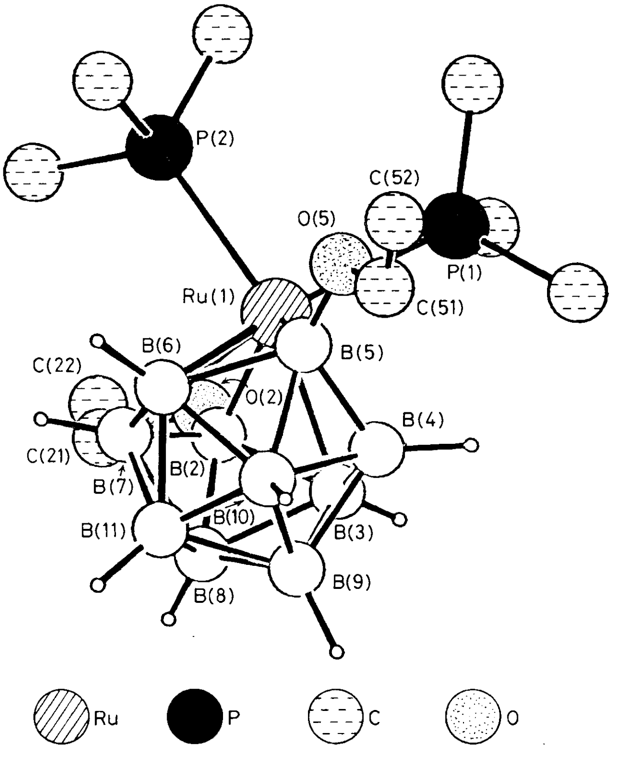

Figure 1. Molecular structure of $[(PPh_3)_2RuB_{10}H_8(OEt)_2]$ with selected organyl group atoms omitted for clarity. Selected distances are as follows: from Ru(1) to B(2) 205.4(8), to B(3) 235.5(8), to B(4) 239.9(8), to B(5) 203.6(8), to B(6) 235.9(8), to B(7) 238.2(8), to P(1) 253.3(4), and to P(2) 251.1(4) pm; B(3)–B(4) and B(6)–B(7) are 168.4(10) and 169.9(11) pm respectively; B(2)–O(2) and B(5)–O(5) average at 137.1 pm. The angles P(1)–Ru(1)–P(2) and B(2)–Ru(1)–B(5) are 97.0 and 118.1(3)° respectively.

Examples of all four metal combinations ruthenium/ruthenium, osmium/osmium, ruthenium/osmium, and osmium/ruthenium, have been obtained as red-brown (Ru/Ru and Os/Os) or olive-brown (Ru/Os and Os/Ru) air-stable crystalline solids in yields of up to 80%. All are structurally similar as indicated by their mutually very similar ^{31}P, ^{11}B, and ^1H n.m.r. properties, and the structural type is exemplified by the diruthenium species $[(PPh_3)_2ClRuClRu(PPh_3)B_{10}H_8(OEt)_2]$ (Figure 2). The geometry and n.m.r. properties of the central contiguous $\{RuB_{10}H_8(OEt)_2\}$ core are, interestingly, very similar to those of the starting species (Figure 1),

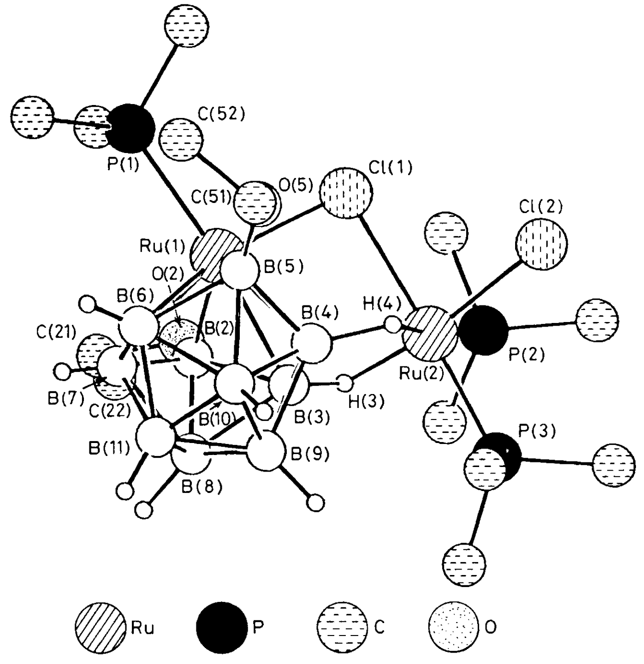

Figure 2. Molecular structure of $[(PPh_3)_2ClRuClRu(PPh_3)B_{10}H_8(OEt)_2]$ with selected organyl group atoms omitted for clarity. Selected distances are as follows: from Ru(1) to B(2) 203.0(11), to B(3) 231.8(12), to B(4) 229.4(13), to B(5) 203.3(12), to B(6) 230.1(12), to B(7) 232.9(10), to P(1) 244.6(5), to Cl(1) 237.7(4), and to Ru(2) 354.0(5) pm; from Ru(2) to H(3) 192.8(49), to H(4) 197.5(44), to B(3) 232.5(11), to B(4) 246.0(12), to Cl(1) 258.9(5), to Cl(2) 240.4(4), and to P(2) 233.7(4) pm; B(3)–B(4) and B(6)–B(7) are 169.0(15) and 164.1(18) pm respectively. The angles P(1)–Ru(1)–Cl(1), B(2)–Ru(1)–B(5), and Ru(1)–Cl(1)–Ru(2) are 95.0(2), 122.3(5), and 90.8(2)° respectively. The bridging H atoms H(3) and H(4) have $\delta(^1H)$ −1.3 and −13.5 (compare footnote b to Table 1). In the direct diosmium analogue they have δ −1.7 and −12.8, in $[(PPh_3)_2ClRuClOs(PMe_2Ph)B_{10}H_8(OEt)_2]$ −0.01 and −14.2, and in $[(PPh_3)_2ClOsClRu(PPh_3)B_{10}H_8(OEt)_2]$ −1.7 and −12.5 (all in $CDCl_3$ solution at + 21 °C).

Table 1. Crystallographic data.[a]

	$[Ru(PPh_3)_2B_{10}H_8(OEt)_2]$[b]	$[Ru_2Cl_2(PPh_3)_3B_{10}H_8(OEt)_2]$	$[Ru_2Cl_2(dppm)(PPh_3)_2B_{10}H_8(OEt)_2]$[c]
M	831.91	1 266.39	1 388.50
a/nm	1.309 0(4)	2.170 1(4)	2.073 3(5)
b/nm	2.333 5(4)	1.307 9(3)	1.345 1(5)
c/nm	1.390 2(4)	2.691 8(5)	2.704 0(8)
β/°	93.63(2)	108.87(2)	110.24(2)
U/nm^3	4.238	7.229	7.075
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
Z	4	4	4
No. of observed reflections $[I>2\sigma(I)]$	4 238	7 129	7 437
No. of parameters	479	669	281
R	0.039 2	0.055 9	0.098 4
R_w	0.040 2	0.058 7	0.094 4

[a] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. [b] Preliminary results on this compound have been presented elsewhere.[3] The data have been further refined and are included here for convenience of comparison. [c] The atom-numbering scheme for this compound follows that shown in Figures 1 and 2. H atoms for this compound were not located, but n.m.r. spectroscopy shows that all B atoms except B(2), B(3), B(4), and B(5) have *exo*-terminal H atoms bound to them, and that B(3) and B(4) have B–H–Ru bridging H atoms [at $\delta(^1H)$ −2.5 and −14.8; compare caption to Figure 2]. Selected distances are as follows: from Ru(1) to B(2) 209.9(19), to B(3) 228.3(19), to B(4) 227.0(18), to B(5) 212.6(18), to B(6) 233.7(17), to B(7) 237.7(20), to P(1) 248.3(6), to P(2) 243.8(6), to Cl(1) 243.1(6), and to Ru(2) 355.7(6) pm; from Ru(2) to B(3) 240.8(19), to B(4) 235.5(18), to Cl(1) 253.4(7), to P(3) 235.3(6), and to P(4) 232.9(6) pm. B(3)-B(4) and B(6)-B(7) are 167.6(25) and 177.7(26) pm respectively. The angles B(2)-Ru(1)-B(5) and Ru(1)-Cl(1)-Ru(2) are 122.0(7) and 91.5(2)° respectively and P(1)-Ru(1)-P(2) is 69.6(2)°.

indicating that the electronic structure of this central subcluster is surprisingly little changed by the addition of the second metal centre. The structure of the bimetallic species can be interpreted on the basis that one of the two-electron bonds from the ruthenium atom Ru(1) to a phosphine ligand in the starting species has been replaced by a two-centre two-electron bond to the chlorine atom which is bound to the second metal atom Ru(2); this second metal atom is, in addition, bound to the central $\{Ru(1)B_{10}H_8(OEt)_2\}$ core *via* two two-electron three-centre Ru(2)–H–B bridging bonds, and as such has an eighteen-electron octahedral d^6 ruthenium(II) co-ordination sphere. This μ-H-μ-H-μ-Cl bridged metallaborane linkage seems to be particularly stable in these compounds. It has not previously been encountered in *closo* metallaborane clusters but may be related to that occurring in the smaller *nido-arachno*-type dimanganese cluster compound $[(CO)_6BrMn_2B_3H_8]$.[4]

The other metal centre Ru(1) retains the sixteen-electron d^4 ruthenium(IV) configuration[3] of the starting metallaborane. As such it is readily susceptible to ligand exchange; for example, treatment with the bidentate chelate $Ph_2PCH_2PPh_2$ (dppm) results in the dark-red air-stable complex $[(PPh_3)_2ClRuClRu(dppm)B_{10}H_8(OEt)_2]$ in which both metal centres are now eighteen-electron ones. The molecular structure of this latter species is based on that of the monodentate phosphine complex (Figure 2), except that now the two-fold *exo*-polyhedral co-ordination of the ruthenium atom Ru(1) [to P(1) and Cl(1) in Figure 2] is replaced by a threefold one [to $CH_2(PPh_2)_2$ and Cl(1)]. Some data are in Table 1. Interestingly, again, n.m.r. properties and geometry show that this additional ligand, and the concomitant change from a sixteen- to an eighteen-electron ruthenium(IV) configuration, have little effect on the basic eleven-vertex polyhedral cluster electronic structure.

The electronic unsaturation of the sixteen-electron metal centres Ru(1) [and Os(1)] in these compounds, together with the potential for replacement of the halide and phosphine ligands on both metal centres Ru/Os(1) and Ru/Os(2), augurs well for much interesting further chemistry, as does the possibility of using metal centres other than those of the iron triad in this cluster system.

We thank the S.E.R.C. for support, and Johnson Matthey for the loan of some chemicals.

Received, 19th July 1984; Com. 1051

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