Fourteen-vertex homo- and heterobimetallic metallacarboranes

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Reduction of 4-(p-cymene)-4,1,12-$closo$-RuC$_2$B$_{10}$H$_{12}$ followed by metallation with {M′} fragments (M′ = {CpCo^{2+}}, {(arene)Ru^{2+}} or {(dppe)Ni^{2+}}) affords 14-vertex bimetallic 1,14,2,10-RuM′C$_2$B$_{10}$ species having bicapped hexagonal antiprismatic structures.

Supraicosahedral heteroborane chemistry, established nearly 35 years ago with the synthesis of the 13-vertex metallacarborane 4-Cp-4,1,6-$closo$-CoC$_2$B$_{10}$H$_{12}$,[1] continues to be an area of significant research activity: the possible structures of supraicosahedral boranes and heteroboranes attract major interest from computational chemists[2] and, at least in principle, several of the current applications of boron cluster compounds would be enhanced if larger clusters could be prepared.[3] Within carborane chemistry the initial goals are large, supraicosahedral, carboranes, $e.g.$ C$_2$B$_x$H$_{2+x}$ with $x > 10$. Although we were recently successful in preparing the first such compound ($x = 11$)[4] we have always appreciated that valuable lessons could be learned by working first with analogous metallacarboranes in which one or more {BH} fragment was replaced by an isolobal transition metal fragment.[5]

Although there are in excess of a hundred 13-vertex metallacarboranes known there are fewer than ten 14-vertex bimetallacarboranes. From Me$_4$C$_4$B$_8$H$_8$ and subsequent thermolysis Grimes has produced a series of 14-vertex compounds with Fe$_2$C$_4$B$_8$ cores.[6] In these a $closo$ Wadian skeletal electron count[7] results from there being four {CMe} fragments (3e sources) and two {CpFe} fragments (1e sources) per cluster: however, only the final two isomers in the series are actually closed. A 14-vertex bimetallacarborane analogous to Wadian 12-vertex MC$_2$B$_9$ and 13-vertex MC$_2$B$_{10}$ species would have only two {CH/CR} fragments and two 2e {M} fragments, truly isolobal with {BH}. In 1974 Evans and Hawthorne prepared such a compound, (CpCo)$_2$C$_2$B$_{10}$H$_{12}$, in two isomeric forms (one from reduction and metallation of a 4,1,8-CoC$_2$B$_{10}$ precursor, the other from similar treatment of the analogous 4,1,12-CoC$_2$B$_{10}$ species). However, these 14-vertex clusters were only principally characterised by mass spectrometry and low-resolution ^{11}B NMR spectroscopy.[8]

We recently reported the first synthesis of 13-vertex 4,1,10-MC$_2$B$_{10}$ compounds and their facile isomerisation into corresponding 4,1,12-isomers,[9] work which has afforded us gram quantities of a wide range of new 4,1,12-MC$_2$B$_{10}$ species. We now describe the reduction and subsequent metallation of one of these, 4-(p-cymene)-4,1,12-$closo$-RuC$_2$B$_{10}$H$_{12}$, leading to a series of both homo- and heterobimetallic 14-vertex MM′C$_2$B$_{10}$ metallacarboranes (the latter reported for the first time) in sufficient yields for complete characterisation and ultimate further polyhedral expansion reactions.

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Reduction of 4-(p-cymene)-4,1,12-$closo$-RuC$_2$B$_{10}$H$_{12}$ with Na in THF followed by treatment with CoCl$_2$–NaCp afforded the 14-vertex ruthenacobaltacarborane {(p-cymene)Ru}{CpCo}-C$_2$B$_{10}$H$_{12}$ (1) in modest yield.† Compound 1 was characterised by microanalysis, mass spectrometry and ^{1}H and ^{11}B NMR spectroscopies but did not produce crystals suitable for X-ray diffraction study. Treatment of the reduced metallacarborane with [(η-C$_6$H$_6$)RuCl$_2$]$_2$ or [(p-cymene)RuCl$_2$]$_2$ similarly yielded the diruthenacarboranes {(p-cymene)Ru}{(η-C$_6$H$_6$)Ru}C$_2$B$_{10}$H$_{12}$ (2) and {(p-cymene)Ru}$_2$C$_2$B$_{10}$H$_{12}$ (3) respectively, but in much better yields.† Compound 3 is revealed by NMR spectroscopy to be symmetric, with only one set of resonances assigned to the p-cymene ligand and one C$_{cage}$H resonance in the ^{1}H spectrum, and only four resonances (relative integrals 1 : 2 : 1 : 1) in the ^{11}B{^{1}H} spectrum. Compound 2 has only five, equally intense, resonances in its ^{11}B{^{1}H} spectrum, although eventual structural assignment ($vide\ infra$) suggests that these are all 1 + 1 coincidences. One particularly notable feature of the spectra of 2 and 3 is the low frequency of the weighted average ^{11}B chemical shifts, −21.5 and −21.2 ppm, respectively.

Although compound 2 could not be persuaded to crystallise sufficiently well for a diffraction study, good-looking crystals of 3 were obtained by slow evaporation of a CH$_2$Cl$_2$ solution. The results of a crystallographic determination of 3 are shown in Fig. 1.‡ The molecule is located on a crystallographic C_2 axis passing through the mid points of the B2–B2A and B5–B5A connectivities. The dimetallacarborane cluster has a bicapped hexagonal antiprismatic structure with the Ru atoms in the 6-connected (with respect to the polyhedron) capping vertices. Unfortunately it proved impossible to assign the cluster C atoms with certainty and refinement was completed with B atoms occupying all six crystallographically unique 5-connected sites. There is additional minor disorder in the ^{i}Pr group of the p-cymene ligand.

The mixed ruthenium–nickel species {(p-cymene)Ru}-{(dppe)Ni}C$_2$B$_{10}$H$_{12}$ (4) was similarly afforded by addition of (dppe)NiCl$_2$ to the reduced ruthenacarborane, and initially characterised by ^{1}H, ^{11}B and ^{31}P NMR spectroscopies.† For the ruthenanickelacarborane 4 the weighted average ^{11}B chemical shift is −16.9 ppm, essentially the same as that for the ruthenacobaltacarborane 2 (−17.0 ppm), still relatively low frequency but not so low as for the diruthenacarboranes 2 and 3. Although 4 is afforded in poor yield relative to 2 and 3 it formed single crystals which proved to be free of cage atom disorder allowing unequivocal structural determination.‡

A perspective view of a single molecule is given in Fig. 2. The bicapped hexagonal antiprismatic structure observed for 3 is again evident, but this time the cage C atoms were readily distinguished on the twin bases of refined (as B) equivalent isotropic thermal
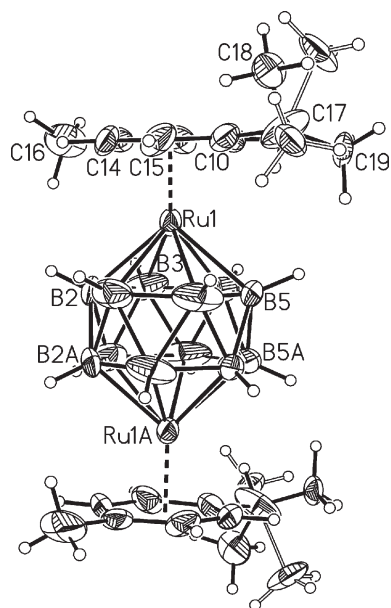
Fig. 1 Perspective view of the diruthenacarborane compound **3**. The molecule bestrides a crystallographic C_2 axis passing through the mid points of the B2–B2A and B5–B5A connectivities. The cage C atoms were not located, all non-Ru cluster vertices being refined as B. Selected interatomic distances (Å) include : Ru1–B2 2.255(6), Ru1–B3 2.251(7), Ru1–B4 2.232(7), Ru1–B5 2.265(6), Ru1–B6 2.251(7), Ru1–B7 2.241(6), Ru1···Ru1A 4.3985(9). The dihedral angle between the least-squares planes through B2B3B4B5B6B7 and B2AB3AB4AB5AB6AB7A is 1.94(16)°.

parameters and interatomic separations. The species is thus identified as 1-(p-cymene)-14-(dppe)-1,14,2,10,-*closo*-RuNiC$_2$-B$_{10}$H$_{12}$. By analogy, compounds **1**–**3** presumably have similar heteroatom patterns, *i.e.* 1,14,2,10-RuCoC$_2$B$_{10}$, 1,14,2,10-Ru$_2$C$_2$B$_{10}$ and 1,14,2,10-Ru$_2$C$_2$B$_{10}$, respectively. These results confirm Hawthorne's proposed structure of 1,14-Cp$_2$-1,14,2,10,-*closo*-Co$_2$C$_2$B$_{10}$H$_{12}$ for the isomer ('isomer I') derived from 4-Cp-4,1,12-*closo*-CoC$_2$B$_{10}$H$_{12}$.[8] With the structure of **4** thus established we looked again at the crystallographic structure of **3** focussing on the 3/3A and 6/6A positions as potential C atom sites (both possibilities would have afforded 1,14,2,10-Ru$_2$C$_2$B$_{10}$ architectures consistent with the crystallographic C_2 symmetry) but neither was convincing and this structure remains disordered.

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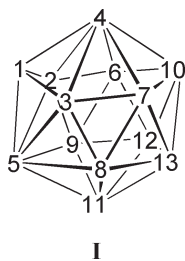
Attempted syntheses of 14-vertex bimetallacarboranes starting from 4-(p-cymene)-4,1,10-*closo*-RuC$_2$B$_{10}$H$_{12}$ were unsuccessful: this isomer of the 13-vertex precursor does not appear to undergo reduction by Na–naphthalene in THF.[10] In cases where reduction *is* successful we believe that the reduced (nido) species is stabilised by the presence of a cage C atom in its open face, since this affords
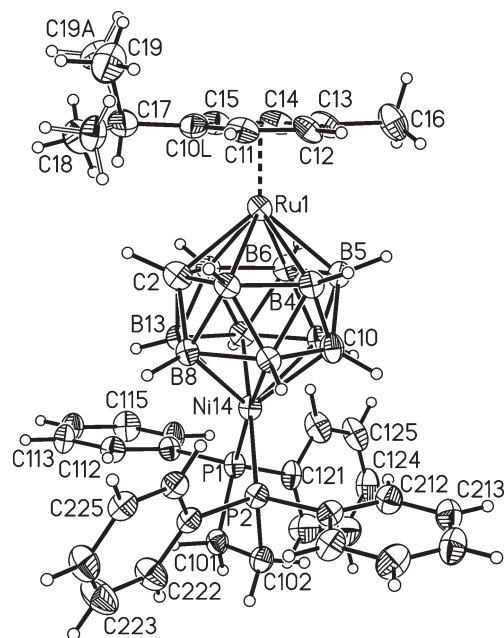

Fig. 2 Perspective view of the ruthenanickelacarborane compound **4**. Selected interatomic distances (Å) include: Ru1–C2 2.257(4), Ru1–B3 2.281(4), Ru1–B4 2.253(4), Ru1–B5 2.261(4), Ru1–B6 2.283(4), Ru1–B7 2.254(4), Ni14–B8 2.198(4), Ni14–B9 2.167(4), Ni14–C10 2.306(4), Ni14–B11 2.244(4), Ni14–B12 2.147(4), Ni14–B13 2.215(4), C–B 1.657(5)–1.733(6), B–B 1.713(6)–1.795(6), Ru1···Ni14 4.3225(6). The upper (C2B3B4B5B6B7) and lower (B8B9C10B11B12B13) hexagonal least-square planes are inclined at a dihedral angle of 0.16(1)°. The ^{i}Pr group of the p-cymene ligand shows partial disorder.

the C atom its preferred low connectivity.[11] Thus 4,1,8-, 4,1,12- and 4,1,11-MC$_2$B$_{10}$ species would seem to be attractive 13-vertex metallacarboranes for further reduction–expansion reactions (see I for numbering) whilst expansion starting from the 4,1,2-, 4,1,6- and 4,1,10-isomers could be more difficult (the remaining 4,1,X-MC$_2$B$_{10}$ isomer, 4,1,5-, is unlikely to yield to synthesis since it contains a high-connected C atom). So far both we and Hawthorne have been successful in reduction–expansion of 4,1,8- and 4,1,12-MC$_2$B$_{10}$ compounds. The 4,1,11-MC$_2$B$_{10}$ isomer has not yet been reported but represents an attractive future target.

These studies establish the first complete characterisation of 14-vertex M$_2$C$_2$B$_{10}$ metallacarboranes and report the first examples of heterobimetallic analogues. They provide a firm basis on which to develop 15-vertex (and possibly beyond) heteroborane chemistry, which is currently without precedent.

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Notes and references

† Experimental procedure. For **1**: 4-(p-cymene)-4,1,12-*closo*-RuC$_2$B$_{10}$H$_{12}$ (0.10 g, 0.26 mmol) was dissolved in dry, oxygen-free THF (30 ml). Sodium

pieces (0.06 g, 2.50 mmol) and naphthalene (*ca.* 0.010 g) were added and the solution was stirred at room temperature for 72 hours. The deep red solution was cooled to 0 °C. NaCp (0.39 ml of a 2 M solution in THF, 0.78 mmol) was added followed by solid $CoCl_2$ (0.13 g, 0.95 mmol) and the reaction mix stirred at room temperature for 18 hours. The purple product isolated by TLC (80% : 20% CH_2Cl_2 : 40/60 petrol, R_f 0.62). Yield 0.010 g (8%). IR (CH_2Cl_2): ν_{max} at 2503 cm^{-1} (B–H). ^{1}H NMR ($CDCl_3$, 298 K): δ 5.00–5.20 (m, 4 H, C_6H_4), 4.79 (s, 5 H, C_5H_5), 2.75 (sept, 1 H, C$H(CH_3)_2$), 1.95 (s, 3 H, CH_3), 1.10 (d, 3 H, CH(CH_3)), 1.06 (d, 3 H, CH(CH_3)), neither cage CH resolved. ^{11}B{^{1}H} NMR ($CDCl_3$, 298 K): δ −11.69 (3B), −15.31 (1B), −17.67 (3B), −20.17 (1B), −23.18 (2B). Mass spectrometry: m/z 503 (M $^+$). Satisfactory microanalytical data were obtained for all compounds reported. For **2**: 4-(*p*-cymene)-4,1,12-*closo*-$RuC_2B_{10}H_{12}$ (0.26 mmol) reduced and treated with [(η-C_6H_6)$RuCl_2$]$_2$ (0.13 mmol). Yield 35%. IR (CH_2Cl_2): ν_{max} at 2492 cm^{-1} (B–H). ^{1}H NMR ($CDCl_3$, 298 K): δ 5.35 (s, 6 H, C_6H_6), 5.05–5.25 (m, 4 H, C_6H_4), 2.60 (sept, 1 H, C$H(CH_3)_2$), 1.95 (s, 3 H, CH_3), 1.75 (br s, 1 H, $C_{cage}H$), 1.15 (d, 3 H, CH(CH_3)), 1.07 (d, 3 H, CH(CH_3)), 0.80 (br s, 1 H, $C_{cage}H$). ^{11}B{^{1}H} NMR ($CDCl_3$, 298 K): δ −16.49 (2B), −20.68 (2B), −21.27 (2B), −22.90 (2B), −25.94 (2B). Mass spectrometry: m/z 560 (M $^+$). For **3**: 4-(*p*-cymene)-4,1,12-*closo*-$RuC_2B_{10}H_{12}$ (0.75 mmol) reduced and treated with [(*p*-cymene)$RuCl_2$]$_2$ (0.38 mmol). Yield 40%. IR (KBr): ν_{max} at 2520 cm^{-1} (B–H). ^{1}H NMR ($CDCl_3$, 298 K): δ 5.15–5.25 (m, 8 H, C_6H_4), 2.65 (sept, 2 H, C$H(CH_3)_2$), 2.00 (s, 6 H, CH_3), 1.70 (br s, 2 H, $C_{cage}H$), 1.05 (overlapping d, 12 H, CH(CH_3)). ^{11}B{^{1}H} NMR ($CDCl_3$, 298 K): δ −16.14 (2B), −20.69 (4B), −23.01 (2B), −25.60 (2B). Mass spectrometry: m/z 615 (M $^+$), 470 (M–$C_2B_{10}H_{12}$). For **4**: 4-(*p*-cymene)-4,1,12-*closo*-$RuC_2B_{10}H_{12}$ (0.26 mmol) reduced and treated with (dppe)$NiCl_2$ (0.26 mmol). Yield 7%. IR (CH_2Cl_2): ν_{max} at 2502 cm^{-1} (B–H). ^{1}H NMR ($CDCl_3$, 298 K): δ 7.2–7.7 (m, 20H, C_6H_5), 5.02–5.19 (m, 4 H, C_6H_4), 2.62 (sept, 1 H, C$H(CH_3)_2$), 2.19 (br s, 2 H, CH_2), 1.90 (s, 3 H, CH_3), 1.77 (br s, 2 H, CH_2), 1.05 (d, 6 H, CH(CH_3)), neither cage CH resolved. ^{11}B{^{1}H} NMR ($CDCl_3$, 298 K): δ −9.34 (2B), −13.40 (2B), −16.72 (2B), −20.34 (1B), −24.80 (1B), −27.78 (1B). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): δ 61.9.

‡ Crystal data. For **3**: $C_{22}H_{40}B_{10}Ru_2$, M_r = 614.78, monoclinic, $C2/c$, a = 16.319(2), b = 16.9323(18), c = 10.3987(12) Å, β = 115.413(5)°, V = 2595.3(5) Å^3, Z = 4 (C_2 symmetry imposed), μ = 1.175 mm^{-1}, $F(000)$ = 1240. Data to θ_{max} = 28.7° collected at 100(2) K on a Bruker AXS X8 diffractometer using Mo-Kα radiation. 14050 reflections, 3319 independent reflections, R_1 = 0.1231, wR_2 = 0.1082, S = 0.961, for all data. For **4**: $C_{38}H_{50}B_{10}NiP_2Ru$, M_r = 836.60, monoclinic, $P2_1/n$, a = 12.7337(9), b = 17.0657(12), c = 17.4612(12) Å, β = 92.338(4)°, V = 3791.3(5) Å^3, Z = 4, μ = 1.009 mm^{-1}, $F(000)$ = 1720. Data collection as for **3** except θ_{max} = 24.6°. 85924 reflections collected, 6348 independent

reflections, R_1 = 0.0670, wR_2 = 0.1175, S = 1.054 for refinement with all data. CCDC 260453 and 260454 for **3** and **4**, respectively. See http://www.rsc.org/suppdata/cc/b5/b500236b/ for crystallographic data in .cif or other electronic format.

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