Fourteen-vertex homo- and heterobimetallic metallacarboranes

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Received (in Cambridge, UK) 7th January 2005, Accepted 25th January 2005
First published as an Advance Article on the web 15th February 2005
DOI: 10.1039/b500236b

Reduction of 4-(*p*-cymene)-4,1,12-*closo*-$RuC_2B_{10}H_{12}$ followed by metallation with {M′} fragments (M′ = {$CpCo^{2+}$}, {(arene)Ru^{2+}} or {(dppe)Ni^{2+}}) affords 14-vertex bimetallic 1,14,2,10-$RuM'C_2B_{10}$ 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*-$CoC_2B_{10}H_{12}$,[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.* $C_2B_xH_{2+x}$ 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 $Me_4C_4B_8H_8$ and subsequent thermolysis Grimes has produced a series of 14-vertex compounds with $Fe_2C_4B_8$ 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_2B_9 and 13-vertex MC_2B_{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, $(CpCo)_2C_2B_{10}H_{12}$, in two isomeric forms (one from reduction and metallation of a 4,1,8-CoC_2B_{10} precursor, the other from similar treatment of the analogous 4,1,12-CoC_2B_{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_2B_{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_2B_{10} species. We now describe the reduction and subsequent metallation of one of these, 4-(*p*-cymene)-4,1,12-*closo*-$RuC_2B_{10}H_{12}$, leading to a series of both homo- and heterobimetallic 14-vertex $MM'C_2B_{10}$ metallacarboranes (the latter reported for the first time) in sufficient yields for complete characterisation and ultimate further polyhedral expansion reactions.

Reduction of 4-(*p*-cymene)-4,1,12-*closo*-$RuC_2B_{10}H_{12}$ with Na in THF followed by treatment with $CoCl_2$–NaCp afforded the 14-vertex ruthenacobaltacarborane {(*p*-cymene)Ru}{CpCo}-$C_2B_{10}H_{12}$ (**1**) in modest yield.†Compound **1** was characterised by microanalysis, mass spectrometry and ^1H and ^{11}B NMR spectroscopies but did not produce crystals suitable for X-ray diffraction study. Treatment of the reduced metallacarborane with $[(\eta\text{-}C_6H_6)RuCl_2]_2$ or $[(p\text{-cymene})RuCl_2]_2$ similarly yielded the diruthenacarboranes {(*p*-cymene)Ru}{(η-C_6H_6)Ru}$C_2B_{10}H_{12}$ (**2**) and {(*p*-cymene)Ru}$_2C_2B_{10}H_{12}$ (**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 ^1H spectrum, and only four resonances (relative integrals 1 : 2 : 1 : 1) in the $^{11}B\{^1H\}$ spectrum. Compound **2** has only five, equally intense, resonances in its $^{11}B\{^1H\}$ 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_2Cl_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}$C_2B_{10}H_{12}$ (**4**) was similarly afforded by addition of (dppe)$NiCl_2$ to the reduced ruthenacarborane, and initially characterised by ^1H, ^{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

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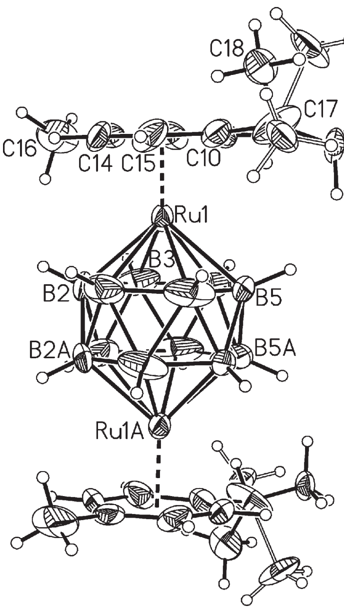
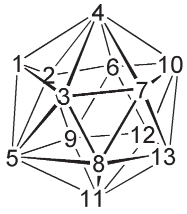


Fig. 1 Perspective view of the diruthenacarborane compound **3**. The molecule bestrides a crystallographic C_2 axis passing through the mid points of the B2–B2A and B5–B5A connectivities. The cage C atoms were not located, all non-Ru cluster vertices being refined as B. Selected interatomic distances (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_2B_{10}, 1,14,2,10-$Ru_2C_2B_{10}$ and 1,14,2,10-$Ru_2C_2B_{10}$, respectively. These results confirm Hawthorne's proposed structure of 1,14-Cp_2-1,14,2,10,-*closo*-$Co_2C_2B_{10}H_{12}$ for the isomer ('isomer I') derived from 4-Cp-4,1,12-*closo*-Co$C_2B_{10}H_{12}$.[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-$Ru_2C_2B_{10}$ 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*-Ru$C_2B_{10}H_{12}$ 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 the C atom its preferred low connectivity.[11] Thus 4,1,8-, 4,1,12- and 4,1,11-MC_2B_{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_2B_{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_2B_{10} compounds. The 4,1,11-MC_2B_{10} isomer has not yet been reported but represents an attractive future target.

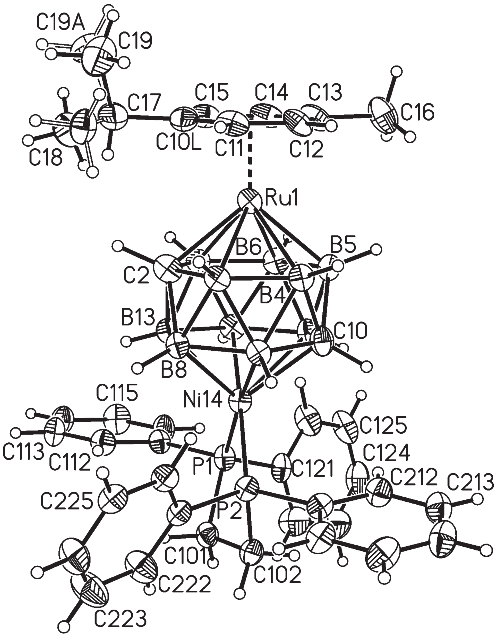

Fig. 2 Perspective view of the ruthenanickelacarborane compound **4**. Selected interatomic distances (Å) include: Ru1–C2 2.257(4), Ru1–B3 2.281(4), Ru1–B4 2.253(4), Ru1–B5 2.261(4), Ru1–B6 2.283(4), Ru1–B7 2.254(4), Ni14–B8 2.198(4), Ni14–B9 2.167(4), Ni14–C10 2.306(4), Ni14–B11 2.244(4), Ni14–B12 2.147(4), 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.

These studies establish the first complete characterisation of 14-vertex $M_2C_2B_{10}$ 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.

We thank the EPSRC (DE, MEL) and the Carnegie Trust (RMcI) for support, Dr R. Ferguson and Mr G. P. Smith for mass spectrometry, Dr A. F. S. Boyd for NMR spectroscopy and Ms C. Graham for microanalysis.

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Notes and references

† Experimental procedure. For **1**: 4-(*p*-cymene)-4,1,12-*closo*-Ru$C_2B_{10}H_{12}$ (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). ^1H 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, $CH(CH_3)_2$), 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. $^{11}B\{^1H\}$ 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 $[(\eta\text{-}C_6H_6)RuCl_2]_2$ (0.13 mmol). Yield 35%. IR (CH_2Cl_2): ν_{max} at 2492 cm^{-1} (B–H). ^1H 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, $CH(CH_3)_2$), 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, $C_{cage}H$). $^{11}B\{^1H\}$ 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 $[(p\text{-cymene})RuCl_2]_2$ (0.38 mmol). Yield 40%. IR (KBr): ν_{max} at 2520 cm^{-1} (B–H). ^1H NMR ($CDCl_3$, 298 K): δ 5.15–5.25 (m, 8 H, C_6H_4), 2.65 (sept, 2 H, $CH(CH_3)_2$), 2.00 (s, 6 H, CH_3), 1.70 (br s, 2 H, $C_{cage}H$), 1.05 (overlapping d, 12 H, $CH(CH_3)_2$). $^{11}B\{^1H\}$ 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 ($M\text{–}C_2B_{10}H_{12}$). 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). ^1H 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, $CH(CH_3)_2$), 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, $CH(CH_3)_2$), neither cage CH resolved. $^{11}B\{^1H\}$ NMR ($CDCl_3$, 298 K): δ −9.34 (2B), −13.40 (2B), −16.72 (3B), −20.34 (1B), −24.80 (1B), −27.78 (1B). $^{31}P\{^1H\}$ 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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