The first 4,1,10-MC_2B_{10} supraicosahedral metallacarboranes and a route to previously inaccessible 4,1,12-ruthenium arene species

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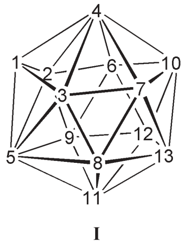
Reduction of 1,12-*closo*-$C_2B_{10}H_{12}$ or its C,C-dimethyl analogue with sodium in liquid ammonia followed by metallation with $\{CpCo\}^{2+}$, $\{(arene)Ru\}^{2+}$ or $\{(dppe)Ni\}^{2+}$ fragments affords the first examples of 4,1,10-MC_2B_{10} species; thermolysis of these yields the appropriate 4,1,12-MC_2B_{10} isomers, unavailable for (arene)Ru metallacarboranes by similar thermolysis of known 4,1,6-MC_2B_{10} compounds.

Following the synthesis of the first supraicosahedral heteroborane, 4-Cp-4,1,6-*closo*-$CoC_2B_{10}H_{12}$, in 1971,[1] of the order of a hundred or so 13-vertex metallacarboranes have been reported. Of these, the vast majority have 4,1,6-MC_2B_{10} docosahedral architectures (see **I** for a line diagram of the docosahedron and its numbering scheme), being obtained by metallation of prior-reduced 1,2-*closo*-$C_2B_{10}H_{12}$ or its derivatives: on 2e reduction the cage C atoms spontaneously separate to give the $[7,9\text{-}nido\text{-}C_2B_{10}]^{2-}$ dianion, which on addition of a suitable metal fragment affords 4,1,6-MC_2B_{10}. The 4,1,6-MC_2B_{10} arrangement is only the kinetic isomer and for some metal fragments, notably {CpCo}, thermolysis easily yields, successively, 4,1,8- and 4,1,12-isomers.[1,2] However, for a number of metal fragments, notably {(arene)Ru}, these progressive thermodynamic isomers are not accessible under standard conditions and the 4,1,8- and 4,1,12-isomers remain unknown. A fourth known isomer of MC_2B_{10} is the 4,1,2-isomer. This is afforded either by the use of tethered carboranes[3] (preventing C atom separation in the reduction step) or by direct insertion of a highly nucleophilic metal fragment into a 1,2-*closo*-C_2B_{10} precursor.[4]



I

No other isomers of MC_2B_{10} have previously been reported but, assuming a docosahedral geometry with the metal atom in the 6-connected vertex 4 and one C atom in the unique four-connected vertex 1 (their preferred sites[5]), the remaining C atom could in principle occupy position 5, 10 or 11. We now report the synthesis and characterisation of the first 4,1,10-MC_2B_{10} species and, upon thermolysis of the Ru(arene) compounds in refluxing toluene, previously inaccessible 4-(arene)-4,1,12-*closo*-RuC_2B_{10} species.

When a THF solution of $Na_2[C_2B_{10}H_{12}]$ (prepared by Na reduction of 1,12-*closo*-$C_2B_{10}H_{12}$ in NH_3)[6] is treated with an excess of $CoCl_2$ and NaCp the red cobaltacarborane 4-Cp-4,1,10-*closo*-$CoC_2B_{10}H_{12}$ (**1**) is formed in *ca.* 5% yield after work-up involving TLC.† Treatment of the reduced carborane with either ½ equiv. of $[(p\text{-cymene})RuCl_2]_2$ or with $(dppe)NiCl_2$ afforded the analogous ruthenacarborane 4-(*p*-cymene)-4,1,10-*closo*-$RuC_2B_{10}H_{12}$ (**2**) or nickelacarborane 4-(dppe)-4,1,10-*closo*-$NiC_2B_{10}H_{12}$ (**3**), but in considerably better yields (*ca.* 40%).† Compounds **1–3** were characterised by mass spectrometry, ^1H and ^{11}B (and, for **3**, ^{31}P) NMR spectroscopies,† and by single-crystal X-ray diffraction studies.‡

A view of a single molecule of **1**, as a typical example, is given in Fig. 1. In all the structural studies of **1–3** the cage C atoms were unambiguously identified on the basis of thermal parameters following initial refinement of all non-metal cage atoms as boron.

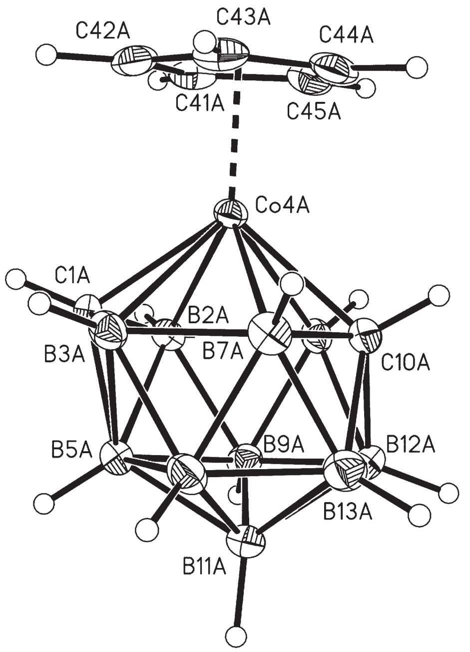


Fig. 1 Perspective view of molecule A of compound **1**. Selected interatomic distances (Å) include [equivalent distances for molecules B and C]: Co4–C1 2.027(2) [2.032(2), 2.025(2)], Co4–B2 2.217(3) [2.215(3), 2.222(3)], Co4–B6 2.167(3) [2.163(3), 2.170(3)], Co4–C10 2.095(2) [2.082(2), 2.093(2)], Co4–B7 2.160(3) [2.142(3), 2.147(3)], Co4–B3 2.216(3) [2.163(3), 2.170(3)].

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The cages are docosahedral with the metal atoms at vertex 4 and carbon atoms at vertices 1 and 10, affording the cages effective C_s symmetry as evidenced by the ^{11}B NMR spectra (assuming free rotation of the *p*-cymene ligand in **2**). In **1** there are three independent molecules in the asymmetric fraction of the unit cell but all are practically superimposable. The cages are characterised by very long B2–B5 and B3–B5 distances [2.004(4)–2.038(4) Å in **1**] and long B5–B8 and B5–B9 distances [1.914(4)–1.934(4) Å in **1**], reflecting the high connectivity of B5. In 4,1,6-MC_2B_{10} metallacarboranes these distances are also very long and long, respectively, but tend to divide such that B2–B5 > B3–B5 and B5–B9 > B5–B8, for reasons that have previously been discussed.[7]

Compound **1** is readily isomerised to the known species 4-Cp-4,1,12-*closo*-$CoC_2B_{10}H_{12}$[2] as evidenced by NMR spectroscopy. Thus, even a freshly prepared room temperature solution of **1** in $CDCl_3$ shows the presence of some 4,1,12 isomer, and the conversion is quantitative after prolonged standing or overnight reflux in THF. As far as we are aware the mechanism of isomerisation of 13-vertex metallacarboranes (the established 4,1,6- → 4,1,8- → 4,1,12-MC_2B_{10} isomerism and, as reported here, 4,1,10- → 4,1,12-MC_2B_{10} isomerism) remains unexplored (both experimentally and computationally) although we would expect that in some way it involves a diamond–square–diamond process. These processes are predicted in the isomerisation of 12-vertex carboranes[8] (supported by experimental observations on analogous metallacarboranes[9]) and have been shown to be relevant to the fluctionality of 13-vertex metallacarboranes.[10,7] The ruthenium species **2** is recovered unchanged from THF reflux, but is similarly isomerised, effectively quantitatively, by 18 hours reflux in toluene. The product of this isomerisation, 4-(*p*-cymene)-4,1,12-*closo*-$RuC_2B_{10}H_{12}$ (**4**), was characterised spectroscopically,† the change from symmetric **2** to asymmetric **4** being clear from inspection of the ^{11}B NMR spectra. However, ^{1}H NMR spectroscopy is an equally diagnostic technique since in **2** the two cage C*H* resonances are well separated (4.1 and 1.7 ppm) but almost converge (3.6 and 3.0 ppm) in **4**. Unfortunately, however, crystallographic confirmation of the structure of **4** was frustrated by disorder. Thermolysis of the nickelacarborane **3** in refluxing toluene also proceeded to the 4,1,12-isomer but was accompanied by significant decomposition. Nevertheless, we were able to characterise the isomerised species, 4-(dppe)-4,1,12-*closo*-$NiC_2B_{10}H_{12}$ (**5**) both spectroscopically† and crystallographically.‡ Compound **5** has a docosahedral cage geometry but suffers from partial disorder of the dppe ligand.

Seeking a crystallographically-proven 4,1,12-(arene)ruthenium species we prepared 4-(η-C_6H_6)-4,1,10-*closo*-$RuC_2B_{10}H_{12}$ (**6**) and 4-(η-C_6Me_6)-4,1,10-*closo*-$RuC_2B_{10}H_{12}$ (**7**) which were duly characterised.† Both isomerise essentially quantitatively to their respective 4,1,12-isomers **8** and **9** in refluxing toluene but, whilst both species were identified spectroscopically,† they were each unacceptably disordered in crystalline form preventing unambiguous proof of the isomerisation. However, Na/NH_3 reduction of 1,12-Me_2-1,12-*closo*-$C_2B_{10}H_{10}$ followed by metallation with $\{(\eta\text{-}C_6H_6)Ru\}^{2+}$ afforded 1,10-Me_2-4-(η-C_6H_6)-4,1,10-*closo*-$RuC_2B_{10}H_{10}$ (**10**),† which yielded 1,12-Me_2-4-(η-C_6H_6)-4,1,12-*closo*-$RuC_2B_{10}H_{10}$ (**11**)† under toluene reflux. Crucially, the structural study of compound **11**, the C,C-dimethyl analogue of **8**, was free from cage carbon disorder problems although the model refined did include a fractionally disordered Ru atom and there is residual unassigned electron density (*ca.* 2.8 e Å^{-3}) *ca.* 2 Å from a methyl H atom).‡

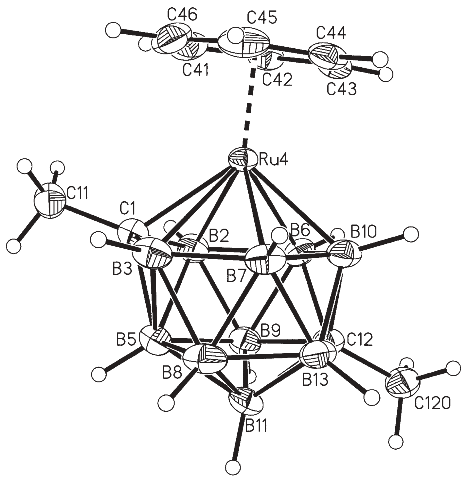

Fig. 2 Perspective view of compound **11**. Selected interatomic distances (Å) include: Ru4–C1 2.160(3), Ru4–B2 2.296(3), Ru4–B6 2.216(3), Ru4–B10 2.203(4), Ru4–B7 2.268(3), Ru4–B3 2.296(5).

The cage of compound **11**, viewed in perspective in Fig. 2, is also docosahedral. C1 remains four-connected and Ru4 six-connected, but the second carbon atom, unambiguously identified by its methyl label, has moved from vertex 10 to the adjacent (but still five-connected) vertex 12. The longest B–B distances are again B2–B5 and B3–B5, 2.005(5) and 2.009(5) Å respectively.

The ready formation of the 4,1,12-RuC_2B_{10} species **4** and its arene and C,C-dimethyl analogues **8**, **9** and **11** by this route is significant because the corresponding 4,1,6-compounds, *e.g.* 4-(*p*-cymene)-4,1,6-*closo*-$RuC_2B_{10}H_{12}$, are recovered unchanged from refluxing toluene after 18 hours.[11] The 13-vertex 4-Cp-4,1,12-*closo*-$CoC_2B_{10}H_{12}$ has been shown[12] to be precursor, following reduction and subsequent metallation, to 14-vertex bimetallic $M_2C_2B_{10}$ supraicosahedra. The current work has demonstrated that we can now access a wide range of (previously inaccessible) 13-vertex 4,1,12-MC_2B_{10} metallacarboranes in significant quantities *via* the appropriate 4,1,10 isomer. We are currently exploring the potential of these 4,1,12 compounds in the further preparation of 14-, 15- and higher-vertex metallacarboranes.[13]

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Notes and references

† Experimental procedure: for **1**: 1,12-$C_2B_{10}H_{12}$ (0.25 g, 1.74 mmol) was treated with sodium metal (0.28 g, 12.2 mmol) in liquid ammonia at −78 °C for 2 hours. The reaction mixture was warmed to room temperature and the dry residue extracted into oxygen-free THF (20 ml). To this was added

NaCp (2.6 ml of a 2.5 M solution in THF, 5.2 mmol) and $CoCl_2$ (0.83 g, 6.4 mmol). The reaction mixture was stirred for 18 hours, and the brick-red product isolated by TLC (60% : 40% CH_2Cl_2 : 40/60 petrol, R_f 0.47). Yield 0.024 g (5%). IR (KBr): v_{max} at 2530 cm^{-1} (B–H). ^1H NMR ($CDCl_3$, 298 K): δ 5.40 (s, 5H, C_5H_5), 4.52 (br, 1H, C*H*), 1.87 (br, 1H, C*H*). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 3.71 (2B), 1.84 (2B), −4.09 (1B), −6.89 (2B), −9.40 (1B), −12.62 (2B). Mass spectrometry: *m*/*z* 269 (M^+), 124 (M − $C_2B_{10}H_{12}$). Satisfactory microanalytical data were obtained for all compounds reported. For **2**: IR (KBr): v_{max} at 2525 cm^{-1} (B–H). ^1H NMR ($CDCl_3$, 298 K): δ 5.7–5.6 (m, 4H, C_6H_4), 4.10 (br s, 1H, C*H*), 2.75 (sept, 1H, C*H*(CH_3)$_2$), 2.25 (s, 3H, CH_3), 1.68 (br s, 1H, C*H*), 1.25 (d, 6H, CH(CH_3)$_2$). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 298 K): δ −2.23 (2B), −4.43 (2B), −8.69 (1B), −10.61 (1B), −14.83 (2B), −16.72 (2B). Mass spectrometry: *m*/*z* 378 (M^+), 232 (M − $C_2B_{10}H_{12}$).For **3**: IR (KBr): v_{max} at 2538 cm^{-1} (B–H). ^1H NMR ($CDCl_3$, 298 K): δ 7.6–7.3 (m, 20H, C_6H_5), 4.1 (br s, 1H, C*H*), 2.2 (s, 2H, CH_2), 2.1 (s, 2H, CH_2), one cage CH not resolved. $^{11}B\{^1H\}$ NMR ($CDCl_3$, 298 K): δ −0.57 (br 4B), −4.38 (br 1B), −8.42 (br 5B). $^{31}P\{^1H\}$ NMR (C_2D_6CO), 298 K): δ 60.6. Mass spectrometry: *m*/*z* 398 (M − $NiC_2B_{10}H_{12}$), 144 (M − Nidppe).For **4**: IR (KBr): v_{max} at 2520 cm^{-1} (B–H). ^1H NMR ($CDCl_3$, 298 K): δ 5.75–5.55 (m, 4H, C_6H_4), 3.63 (br s, 1H, C*H*), 3.00 (br s, 1H, C*H*), 2.76 (sept, 1H, C*H*(CH_3)$_2$), 2.20 (s, 3H, CH_3), 1.20 (d, 6H, CH(CH_3)$_2$). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 2.84 (1B), −0.61 (1B), −2.37 (1B), −4.70 (1B), −10.19 (br, 2B), −13.73 (1B), −14.89 (1B), −23.22 (2B). Mass spectrometry: *m*/*z* 380 (M^+), 233 (M − $C_2B_{10}H_{12}$).For **5**: IR (CH_2Cl_2): v_{max} at 2537 cm^{-1} (B–H). ^1H NMR ($CDCl_3$, 298 K) δ 7.9–6.9 (m, 20H, C_6H_5), 2.3–2.1 (m, 4H, CH_2), neither cage CH resolved. $^{11}B\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 1.88 (2B), −2.75 (3B), −8.72 (2B), −11.58 (1B), −13.59 (1B), −16.86 (1B). $^{31}P\{^1H\}$ NMR (C_2D_6CO, 298 K): δ 64.4. Mass spectrometry: *m*/*z* 398 (M − $NiC_2B_{10}H_{12}$), 144 (M − Nidppe).For **6**: IR (CH_2Cl_2): v_{max} at 2531 cm^{-1} (B–H). ^1H NMR (C_2D_6CO, 298 K): δ 6.22 (s, 6H, C_6H_6), 4.18 (br s, 1H, C*H*), 1.95 (b. s, 1H, C*H*). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 298 K): δ −3.27 (2B), −5.42 (2B), −9.05 (1B), −11.02 (1B), −15.74 (2B), −17.34 (2B). Mass spectrometry: *m*/*z* 324 (M^+).For **7**: IR (KBr): v_{max} at 2516 cm^{-1} (B–H). ^1H NMR ($CDCl_3$, 298 K): δ 3.60 (br s, 1H, C*H*), 2.09 (s, 18H, CH_3), 1.00 (br s, 1H, C*H*). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 298 K): δ −0.58 (2B), −4.07 (2B), −10.44 (2B), −15.33(2B), −16.88 (2B). Mass spectrometry: *m*/*z* 408 (M^+).For **8**: IR (CH_2Cl_2): v_{max} at 2528 cm^{-1} (B–H). ^1H NMR (C_2D_6CO, 298 K): δ 6.09 (s, 6H, C_6H_6), 3.60 (br s, 1H, C*H*), 2.95 (br s, 1H, C*H*). $^{11}B\{^1H\}$ NMR (C_2D_6CO, 298 K): δ 1.79 (1B), −1.52 (1B), −3.25 (1B), −5.50 (1B), −11.07 (2B), −14.07 (1B), −15.42 (1B), −23.67(1B), −24.14 (1B). Mass spectrometry: *m*/*z* 324 (M^+).For **9**: IR (KBr): v_{max} at 2511 cm^{-1} (B–H). ^1H NMR (C_2D_6CO, 298 K): δ 3.55 (br s, 1H, C*H*), 2.05 (s, 18H, CH_3), 2.90 (br s, 1H, C*H*). $^{11}B\{^1H\}$ NMR (C_2D_6CO, 298 K): δ 4.43 (1B), 0.51 (1B), −2.61 (1B), −4.66 (1B), −9.04 (1B), −13.36 (1B), −14.28 (1B), −15.81 (1B), −24.16 (1B), −24.71 (1B). Mass spectrometry: *m*/*z* 408 (M^+).For **10**: IR (CH_2Cl_2): v_{max} at 2522 cm^{-1} (B–H). ^1H NMR (CD_2Cl_2, 298 K): δ 5.95 (s, 6H, C_6H_6), 2.02 (br s, 3H, CH_3), 1.21 (br s, 3H, CH_3). $^{11}B\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 1.60 (2B), −2.05 (2B), −6.22 (1B), −7.08 (1B), −10.61 (2B), −14.74 (2B). Mass spectrometry: *m*/*z* 352 (M^+).For **11**: IR (CH_2Cl_2): v_{max} at 2522 cm^{-1} (B–H). ^1H NMR (CD_2Cl_2, 298 K): δ 5.86 (s,6H, C_6H_6), 1.95 (br s, 3H, CH_3), 1.68 (br s, 3H, CH_3). $^{11}B\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 2.30 (2B), −0.10 (1B), −2.99 (1B), −5.81 (1B), −6.95 (1B), −7.78 (1B), −10.73 (1B), −19.76 (1B), −21.03 (1B). Mass spectrometry: *m*/*z* 352 (M^+).

‡ *Crystal data*: for **1**: $C_7H_{17}B_{10}Co$, M_r = 268.24, monoclinic, $P2_1/c$, a = 11.026(3), b = 21.411(7), c = 15.908(5) Å, β = 90.127(12)°, V = 3756(2) $Å^3$, Z = 12 (3 independent molecules), D_c = 1.423 Mg m^{-3}, μ = 1.331 mm^{-1}, $F(000)$ = 1632. Data to θ_{max} = 30.2° collected at 100(2) K on a Bruker AXS X8 diffractometer using Mo-K_α radiation. 54012 reflections collected, 11108 independent reflections, R_1 = 0.0909, wR_2 = 0.1351, S = 1.010 for refinement with all data.For **2**: $C_{12}H_{26}B_{10}Ru$, M_r = 379.50, monoclinic, $P2_1/c$, a = 8.3795(10), b = 15.0106(17), c = 14.1747(15) Å, β = 95.718(6)°, V = 1774.0(3) $Å^3$, Z = 4, D_c = 1.421 Mg m^{-3}, μ = 0.870 mm^{-1}, $F(000)$ = 768. Data collection as for **1** except θ_{max} = 36.2°. 43732 reflections, 8441 independent reflections, R_1 = 0.0318, wR_2 = 0.0626, S = 1.036, for all data. For **3**: $C_{28}H_{36}B_{10}NiP_2 \cdot CH_2Cl_2$, M_r = 686.24, monoclinic, $P2_1/n$, a = 9.8421(8), b = 17.7252(16), c = 19.8235(18) Å, β = 102.911(3)°, V = 3370.8(5) $Å^3$, Z = 4, D_c = 1.352 Mg m^{-3}, μ = 0.851 mm^{-1}, $F(000)$ = 1416. Data collection as for **1** except θ_{max} = 24.7°. 126892 reflections, 5686 independent reflections, R_1 = 0.0971, wR_2 = 0.1887, S = 1.042, for all data. For **5**: $C_{28}H_{36}B_{10}NiP_2$, M_r = 601.32, monoclinic, $P2_1/c$, a = 14.3005(5), b = 13.3956(5), c = 16.4077(5) Å, β = 104.343(2) °, V = 3045.15(18) $Å^3$, Z = 4, D_c = 1.312 Mg m^{-3}, μ = 0.762 mm^{-1}, $F(000)$ = 1248. Data collection as for **1** except θ_{max} = 30.9°. 84185 reflections, 9551 independent reflections, R_1 = 0.0879, wR_2 = 0.1471, S = 0.956, for all data. For **11**: $C_{10}H_{22}B_{10}Ru$, M_r = 351.45, orthorhombic, $Pna2_1$, a = 15.418(3), b = 12.509(3), c = 7.9793(16) Å, V = 1538.9(5) $Å^3$, Z = 4, D_c = 1.517 Mg m^{-3}, μ = 0.997 mm^{-1}, $F(000)$ = 704. Data collection as for **1** except θ_{max} = 36.6°. 74038 reflections, 7338 independent reflections, R_1 = 0.0484, wR_2 = 0.1024, S = 1.005, for all data. CCDC 255165–255169. See http://www.rsc.org/suppdata/cc/b4/b416646a/ for crystallographic data in .cif or other electronic format.

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