Reduction-induced facile isomerisation of metallacarboranes

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Published in:
Dalton Transactions

DOI:
10.1039/c5dt02506k

Publication date:
2015

Document Version
Peer reviewed version

Link to publication in Heriot-Watt University Research Portal

Citation for published version (APA):
One-electron reduction of 3-Cp-3,1,2-closo-CoC2B9H11 followed by heating to reflux in DME (bp 85 °C) induces isomerisation to 4-Cp-4,1,2-closo-CoC2B9H11, a compound previously only synthesised at much higher temperatures (>380 °C). The 4,1,2- isomer has been thoroughly characterised both spectroscopically and crystallographically.

It is exactly 50 years since Hawthorne’s first synthesis of metallacarboranes, specifically the icosahedral anions [Fe(C2B9H11)3]n− (n = 1, 2). Throughout the intervening period metallacarborane chemistry has been very heavily dominated by the icosahedron (reflecting the exceptional stability of closo-C2B10 and closo-CB11 carboranes) with thousands of icosahedral closo-MC2B9 species having been synthesised and characterised.\(^1\)

Cyclopentadienyl cobaltacarboranes can be considered as the archetypal metallacarboranes since (CpCo) is a simple and readily-available fragment isosolobal with (BH), and in fact CpCoC2B9H11 is known for seven of the nine possible isomers shown in Fig. 1, specifically the 3,1,2-, 2,1,7-, 2,1,12-, 4,1,2-, 2,1,8-, 2,1,9- and 9,1,7- isomers. 3-Cp-3,1,2-closo-CoC2B9H11,\(^3\) 2-Cp-2,1,7-closo-CoC2B9H11\(^4\) and 2-Cp-2,1,12-closo-CoC2B9H11\(^5\) are prepared by metallation of the [7,8-nido-C2B9H11]\(^6\), [7,9-nido-C2B9H11]\(^7\) and [2,9-nido-C2B9H11]\(^8\) anions, respectively (which, in turn, are afforded by deboronation of commercially-available 1,2-, 1,7- and 1,12-closo-C2B10H12). Gas-phase thermolysis of 3-Cp-3,1,2-closo-CoC2B9H11 leads to varying amounts of all the other six known isomers of CpCoC2B9H11 dependent on the temperature employed.\(^6\) The two “missing” isomers, 8-Cp-8,1,2-closo-CoC2B9H11 and 9-Cp-9,1,2-closo-CoC2B9H11, both have adjacent cage C atoms (neither of which are directly bound to the metal) and so these isomers would be most unlikely to result from high-temperature thermolysis reactions since thermolysis classically causes C atom separation. However, derivatives of these isomers with the cage C atoms tethered together (via a trimethylene unit) could be obtained by gas-phase thermolysis of the tethered 3,1,2-precursor.\(^6\)

Clearly the syntheses of 4-Cp-4,1,2-closo-CoC2B9H11, 8-Cp-8,1,2-closo-CoC2B9H11 and 9-Cp-9,1,2-closo-CoC2B9H11 (the three isomers of CpCoC2B9H11 apart from 3-Cp-3,1,2-closo-CoC2B9H11 that have adjacent cage C atoms, by conventional chemistry) represent significant challenges. As part of our interest in this area we recently prepared 8-Cp-8,1,2-closo-CoC2B9H11 (and its 2,1,8- analogue) by a low-temperature

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**Fig. 1** The nine isomers of an icosahedral MC2B9 metallacarborane.
route, specifically decapitation of the 13-vertex metallacarborane 4-Cp-4,1,8-closo-CoC₆B₉H₁₂ followed by oxidative closure of the 12-vertex dianion thereby produced.⁷ Both species were characterised spectroscopically and crystallographically, taking to five the number of isomers of CpCoC₆B₉H₁₂ to have been structurally characterised, previously the 3,1,2-⁸ 2,1,7-⁴a,b and 2,1,12-⁴a isomers and now the 8,1,2-⁷ and 2,1,8- isomers.⁷ We now report the synthesis by conventional chemistry of another of these “challenging” isomers.

Instead of high-temperature theromolysis, an alternative way to isomerise metallacarboranes is by 1-e reduction, sometimes in conjunction with mild heating,⁹ and Hanusa and Todd used this approach to prepare both the 2,1,7-and 2,1,12-isomers of CpCoC₆B₉H₁₂ from 3-Cp-3,1,2-closo-CoC₆B₉H₁₂.⁹a In repeating this synthesis we have now discovered that a small amount of the compound 4-Cp-4,1,2-closo-CoC₆B₉H₁₂ which we have fully characterised both spectroscopically and crystallographically,⁸ is also afforded. This represents only the second synthesis of this compound and the first at relatively low temperature.

Treatment of 3-Cp-3,1,2-closo-CoC₆B₉H₁₂ with 1.1 equivalents of sodium naphthalenide in DME followed by heating to reflux (85 °C) for 56 hrs and subsequent aerial oxidation resulted in partial isomerisation to a mixture of the 2,1,8-, 8,1,2-, 2,1,7- and 4,1,2- isomers, separated initially by column chromatography and ultimately by thin-layer chromatography. All products were identified by a combination of ¹H and ¹¹B NMR spectroscopies against authentic samples (2,1,8-isomer,⁷ 8,1,2-isomer ⁷ and 2,1,7-isomer ⁴b). In the ¹H spectrum of 4-Cp-4,1,2-closo-CoC₆B₉H₁₂ are observed a sharp integral-5 singlet at δ 5.44 ppm assigned to the Cp protons and two broad integral-1 resonances at δ 3.36 and 2.80 ppm assigned to the Cₙₚₚₚₚₚₚ atoms. The ¹¹B NMR spectrum consists of eight resonances between δ 9.1 and –17.5 ppm with integrals in the ratio 1:1:1:2:1:1:1:2 from high frequency to low frequency, confirming the asymmetric nature of the species.

The precise nature of the compound was established by a crystallographic study (Fig. 2) as part of which the identities of the cage C atoms were unambiguously determined by both the Vertex-to-Centroid Distance ¹⁰ and Boron-Hydrogen Distance ¹¹ methods. Key interatomic distances appear in the legend to Fig. 2. The Cp ligand is essentially parallel to the least-squares planes through atoms C1,B3,B8,B9,B5 [dihedral angle 0.37(8)°] and the plane through atoms C2,B6,B10,B12,B7 [dihedral angle 1.51(8)°].

4-Cp-4,1,2-closo-CoC₆B₉H₁₂ is the sixth of nine possible isomers of CpCoC₆B₉H₁₂ to be structurally studied leaving only the 9,1,2-, 2,1,9- and 9,1,7- isomers remaining. There are two polymorphic forms of each of the 3,1,2- and 2,1,7- isomers, taking to eight the number of crystallographic studies of CpCoC₆B₉H₁₂ and, somewhat surprisingly, none of these show isomorphism (see ESI).

There are nine examples of 4,1,2-MC₂B₉ compounds in the Cambridge Structural Database,¹² but only one of these is the result of direct metallation of a 2,7-nido-C₆B₉ anion.¹³ In every other case the initial metallation is of a 7,8-nido-C₆B₉ anion followed by isomerisation of the 3,1,2-MC₂B₉ species thus formed (sometimes only transiently) into the 4,1,2-MC₂B₉ final product. Although there is evidence that the relief of steric crowding plays a part in several of these 3,1,2- to 4,1,2-isomerisations,¹⁴ this is not obvious in every case.¹⁵ Moreover, in examples where the cage C atoms are not tethered together it is not at all clear why the more common 3,1,2- to 2,1,8-isomerisation ¹⁶ is not observed. On the other hand a common feature of many of the 3,1,2-MC₂B₉ species which isomerise to 4,1,2-MC₂B₉ is that they have a relatively electron-rich metal.

![Fig. 2](image-url) Perspective view of 4-Cp-4,1,2-closo-CoC₆B₉H₁₂. Selected interatomic distances (Å): Co-4C1, 2.0115(19); Co-4B3, 2.023(2); Co-4B8, 2.079(2); Co-4B9, 2.102(2); Co-4B5, 2.079(2); Co-4Cp, 2.0655(18); 2.0857(18); C1-C2, 1.657(3).

![Fig. 3](image-url) Relative energies (kcal mol⁻¹) of the nine isomers of CpCoC₆B₉H₁₂ (data taken from ref. 17).
centre (NiIII or PdIII), perhaps suggesting an analogy with the reduction-induced 3,1,2- to 4,1,2- isomerisation of CpCoC2B6H12 observed herein.

In Fig. 3 are shown the relative energies of the nine isomers of CpCoC2B6H12 from DFT calculations.17 They fall into two distinct groups, those with the cage C atoms adjacent (3,1,2-, 4,1,2-, 9,1,2- and 8,1,2-) at relatively high energy and those with the cage C atoms separated (2,1,9-, 2,1,7-, 2,1,8-, 9,1,7- and 2,1,12-) at lower energy. This work has demonstrated a low-temperature synthesis of the second-least thermodynamically stable isomer.

Conclusions

In conclusion we have shown that 1-e reduction of 3-Cp-3,1,2-closo-CoC2B6H12 followed by relatively mild heating affords (a small amount of) the isomer 4-Cp-4,1,2-closo-CoC2B6H12 which we have fully characterised including a crystallographic study. This takes to six the number of isomers of CpCoC2B6H12 to be isolated by low-temperature routes, and experiments targeting the remaining isomers yet to be afforded by conventional chemistry (9,1,2-, 2,1,9- and 9,1,7-) are currently in hand. Access to a complete set of isomers of this archetypal metallacarborane will afford a unique opportunity for detailed comparative study which we believe will be of fundamental interest.

Acknowledgement

We thank the EPSRC for support (project EP/I031545/1).

Notes and references

† Experimental procedure: to a freshly prepared solution of sodium naphthalenide (1.1 eq, 0.64 mmol) was added a solution of 3-Cp-3,1,2-closo-CoC2B6H12 (0.15 g, 0.58 mmol) in dry, degassed DME (12 ml). The reagents were heated to reflux for 56 h, oxidised using a water aspirator and the solvent removed in vacuo. Purification of the crude residue using column chromatography in an eluent system of 30:70 dichloromethane:petroleum ether gave naphthalene (Rf = 0.76), two yellow bands, yellow1 (Rf = 0.46) and yellow2 (Rf = 0.28), and unreacted cobaltacarborane starting material (Rf = 0.14). Using 1H and 13C NMR spectroscopies, yellow1 was identified as 2-Cp-2,1,8-closo-CoC2B6H12 with a trace of 8-Cp-8,1,2-closo-CoC2B6H12 whilst re-purification of yellow2 using preparative TLC in an eluent system of 20:80 ethyl acetate:petroleum ether gave 2-Cp-2,1,7-closo-CoC2B6H12 (Rf = 0.18) and 4-Cp-4,1,2-closo-CoC2B6H12 (Rf = 0.10) in trace amounts. For 4-Cp-4,1,2-closo-CoC2B6H12: 1H NMR (CDCl3, 298 K) δ 5.44 (s, 5H, CpH), 3.36 (s, 1H, CpCH3), 2.80 (s, 1H, CpCH3). 13C NMR (CDCl3, 298 K) δ 9.1 (18), 0.8 (18), -1.9 (18), -5.7 (28), -7.3 (18), -12.0 (18), -15.3 (18), -17.5 (18). EIMS: m/z 256.1 (M+).§ Crystal data: C27H22CoM, M = 256.42, monoclinic, P21/c, a = 11.6400(12), b = 6.6488(6), c = 16.1299(15) Å, β = 93.82(3)°, V = 1245.6(2) Å3, Z = 4, D = 1.367 Mg m-3, μ = 1.336 mm-1, f(000) = 520. Data to 32.00° collected at 1002 K on a Bruker X8 diffractometer using Mo-Kα radiation. 4297 independent reflections out of 29748 measured, Rint = 0.0421. S = 1.102 for all data, and R1 = 0.0377, wR2 = 0.0803 for 3596 data with h>2σ(I).