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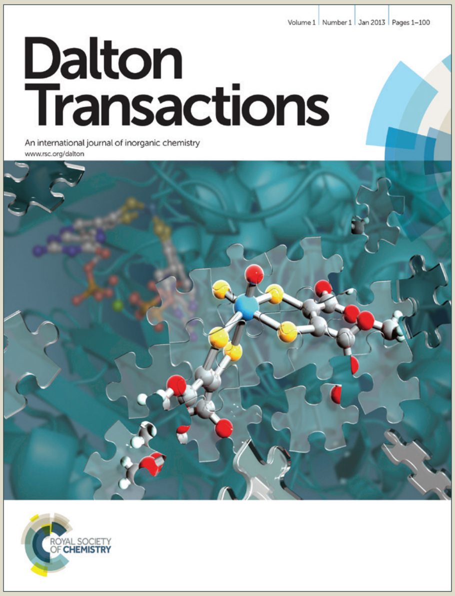

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Reduction-induced facile isomerisation of metallacarboranes: synthesis and crystallographic characterisation of 4-Cp-4,1,2-*closo*-$CoC_2B_9H_{11}$ †

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One-electron reduction of 3-Cp-3,1,2-*closo*-$CoC_2B_9H_{11}$ followed by heating to reflux in DME (bp 85 °C) induces isomerisation to 4-Cp-4,1,2-*closo*-$CoC_2B_9H_{11}$, 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 sandwich anions $[Fe(C_2B_9H_{11})_2]^{n-}$ (n = 1, 2).[1] Throughout the intervening period metallacarborane chemistry has been very heavily dominated by the icosahedron (reflecting the exceptional stability of *closo*-C_2B_{10} and *closo*-CB_{11} carboranes) with thousands of icosahedral *closo*-MC_2B_9 species having been synthesised and characterised.[2]

Cyclopentadienyl cobaltacarboranes can be considered as the archetypal metallacarboranes since {CpCo} is a simple and readily-available fragment isolobal with {BH}, and in fact $CpCoC_2B_9H_{11}$ 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*-$CoC_2B_9H_{11}$,[3] 2-Cp-2,1,7-*closo*-$CoC_2B_9H_{11}$ [4] and 2-Cp-2,1,12-*closo*-$CoC_2B_9H_{11}$ [5] are prepared by metallation of the [7,8-*nido*-$C_2B_9H_{11}]^{2-}$, [7,9-*nido*-$C_2B_9H_{11}]^{2-}$ and [2,9-*nido*-$C_2B_9H_{11}]^{2-}$ anions, respectively (which, in turn, are afforded by deboronation of commercially-available 1,2-, 1,7- and 1,12-*closo*-$C_2B_{10}H_{12}$). Gas-phase thermolysis of 3-Cp-3,1,2-*closo*-$CoC_2B_9H_{11}$ leads to varying amounts of all the other six known isomers of $CpCoC_2B_9H_{11}$ dependent on the temperature employed.[6] The two "missing" isomers, 8-Cp-8,1,2-*closo*-$CoC_2B_9H_{11}$ and 9-Cp-9,1,2-*closo*-$CoC_2B_9H_{11}$, 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]

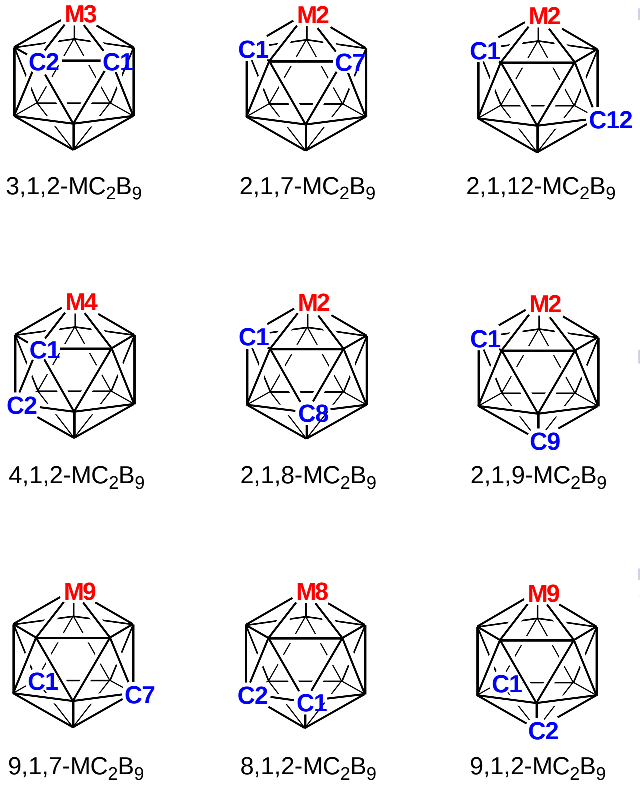

Fig. 1 The nine isomers of an icosahedral MC_2B_9 metallacarborane.

Clearly the syntheses of 4-Cp-4,1,2-*closo*-$CoC_2B_9H_{11}$, 8-Cp-8,1,2-*closo*-$CoC_2B_9H_{11}$ and 9-Cp-9,1,2-*closo*-$CoC_2B_9H_{11}$ (the three isomers of $CpCoC_2B_9H_{11}$ apart from 3-Cp-3,1,2-*closo*-$CoC_2B_9H_{11}$ 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*-$CoC_2B_9H_{11}$ (and its 2,1,8- analogue) by a low-temperature

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† Dedicated to Professor M. Frederick Hawthorne in celebration of 50 years of metallacarboranes (see ref. 1).

Electronic Supplementary Information (ESI) available: Summary of crystal data for the eight crystallographic studies of $CpCoC_2B_9H_{11}$. For 4-Cp-4,1,2-*closo*-$CoC_2B_9H_{11}$; CCDC 1405004. See DOI: 10.1039/x0xx00000x

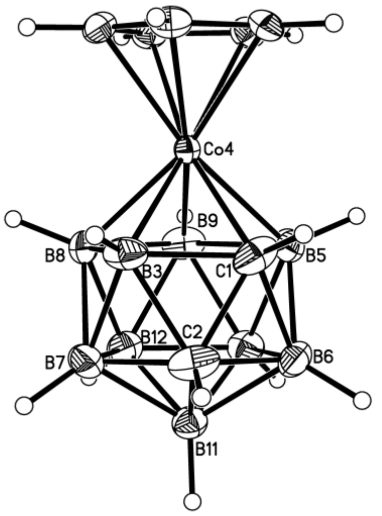

Fig. 2 Perspective view of 4-Cp-4,1,2-*closo*-$CoC_2B_9H_{11}$. Selected interatomic distances (Å): Co4–C1, 2.0115(19); Co4–B3, 2.023(2); Co4–B8, 2.079(2); Co4–B9, 2.102(2); Co4–B5, 2.079(2); Co4–Cp, 2.0655(18)-2.0857(18); C1–C2, 1.657(3).

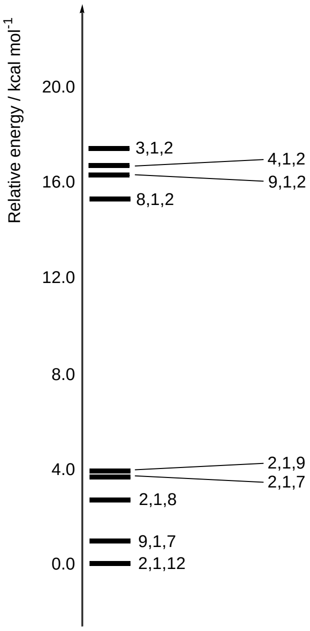

Fig. 3 Relative energies (kcal mol^{-1}) of the nine isomers of $CpCoC_2B_9H_{11}$ (data taken from ref. 17).

route, specifically decapitation of the 13-vertex metallacarborane 4-Cp-4,1,8-*closo*-$CoC_2B_{10}H_{12}$ 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 $CpCoC_2B_9H_{11}$ 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 thermolysis, 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 $CpCoC_2B_9H_{11}$ from 3-Cp-3,1,2-*closo*-$CoC_2B_9H_{11}$.[9a] In repeating this synthesis we have now discovered that a small amount of the compound 4-Cp-4,1,2-*closo*-$CoC_2B_9H_{11}$,‡ which we have fully characterised both spectroscopically and crystallographically,§ 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*-$CoC_2B_9H_{11}$ 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 ^{1}H and ^{11}B NMR spectroscopies against authentic samples (2,1,8-isomer,[7] 8,1,2-isomer [7] and 2,1,7-isomer [4b]). In the ^{1}H spectrum of 4-Cp-4,1,2-*closo*-$CoC_2B_9H_{11}$ 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 $C_{cage}H$ atoms. The ^{11}B NMR spectrum consists of eight resonances between δ 9.1 and –17.5 ppm with integrals in the ratio 1:1:1:2:1:1:1:1 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*-$CoC_2B_9H_{11}$ is the sixth of nine possible isomers of $CpCoC_2B_9H_{11}$ 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 $CpCoC_2B_9H_{11}$ and, somewhat surprisingly, none of these show isomorphism (see ESI).

There are nine examples of 4,1,2-MC_2B_9 compounds in the Cambridge Structural Database,[12] but only one of these is the result of direct metallation of a 2,7-*nido*-C_2B_9 anion.[13] In every other case the initial metallation is of a 7,8-*nido*-C_2B_9 anion followed by isomerisation of the 3,1,2-MC_2B_9 species thus formed (sometimes only transiently) into the 4,1,2-MC_2B_9 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-MC_2B_9 species which isomerise to 4,1,2-MC_2B_9 is that they have a relatively electron-rich metal centre (Ni^{II} or Pd^{II}), perhaps suggesting an analogy with the reduction-induced 3,1,2- to 4,1,2- isomerisation of $CpCoC_2B_9H_{11}$ observed herein.

In Fig. 3 are shown the relative energies of the nine isomers of $CpCoC_2B_9H_{11}$ 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*-$CoC_2B_9H_{11}$ followed by relatively mild heating affords (a small amount of) the isomer 4-Cp-4,1,2-*closo*-$CoC_2B_9H_{11}$, which we have fully characterised including a crystallographic study. This takes to six the number of isomers of $CpCoC_2B_9H_{11}$ 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

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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*-$CoC_2B_9H_{11}$ (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 (R_f = 0.76), two yellow bands, yellow1 (R_f = 0.46) and yellow2 (R_f = 0.28), and unreacted cobaltacarborane starting material (R_f = 0.14). Using ^{1}H and ^{11}B NMR spectroscopies, yellow1 was identified as 2-Cp-2,1,8-*closo*-$CoC_2B_9H_{11}$ with a trace of 8-Cp-8,1,2-*closo*-$CoC_2B_9H_{11}$ 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*-$CoC_2B_9H_{11}$ (R_f = 0.18) and 4-Cp-4,1,2-*closo*-$CoC_2B_9H_{11}$ (R_f = 0.10) in trace amounts. For 4-Cp-4,1,2-*closo*-$CoC_2B_9H_{11}$: ^{1}H NMR ($CDCl_3$, 298 K); δ 5.44 (s, 5H, C_5H_5), 3.36 (s, 1H, $C_{cage}H$), 2.80 (s, 1H, $C_{cage}H$). ^{11}B NMR ($CDCl_3$, 298 K); δ 9.1 (1B), 0.8 (1B), -1.9 (1B), -5.7 (2B), -7.3 (1B), -12.0 (1B), -15.3 (1B), -17.5 (1B). EIMS; *m/z* 256.1(M^+).

§ Crystal data: $C_7H_{16}B_9Co$, M = 256.42, monoclinic, $P2_1/c$, a = 11.6409(12), b = 6.6488(6), c = 16.1299(15) Å, β = 93.823(5)º, V = 1245.6(2) Å^3, Z = 4, D_c = 1.367 Mg m^{-3}, μ = 1.336 mm^{-1}, F(000) = 520. Data to θ_{max} = 32.00º collected at 100(2) K on a Bruker X8 diffractometer using Mo-K_α radiation. 4297 independent reflections out of 29748 measured, R_{int} = 0.0421. S = 1.102 for all data, and R_1 = 0.0377, wR_2 = 0.0803 for 3596 data with $I>2\sigma(I)$. Max. and min. e-density 0.872 and -0.573 eÅ^{-3}, respectively.

1 M. F. Hawthorne, D. C. Young and P. A. Wegner, *J. Am. Chem. Soc.*, 1965, **87**, 1818.

2 R. N. Grimes, *Carboranes*, Academic Press, Oxford, UK, 2nd edn, 2011.

3 M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren and P. A. Wegner, *J. Am. Chem. Soc.*, 1968, **90**, 879.

4 (a) M. E. Lopez, D. Ellis, P. R. Murray, G. M. Rosair, A. J. Welch and L. J. Yellowlees, *Collect. Czech. Chem. Commun.*, 2010, **75**, 853; (b) W. Y. Man, G. M. Rosair and A. J. Welch, *Acta Cryst.*, 2015, E**71**, m141.

5 D. C. Busby and M. F. Hawthorne, *Inorg. Chem.*, 1982, **21**, 4101.

6 M. K. Kaloustian, R. J. Wiersema and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1972, **94**, 6679.

7 W. Y. Man, S. Zlatogorsky, H. Tricas, D. Ellis, G. M. Rosair and A. J. Welch, *Angew. Chem. Int. Ed.*, 2014, **53**, 12222.

8 (a) D. E. Smith and A. J. Welch, *Organometallics*, 1986, **5**, 760; (b) J. G. Planas, C. Viñas, F. Teixidor, M. E. Light and M. B. Hursthouse, *CrystEngComm*, 2007, **9**, 888.

9 e.g. (a) T. P. Hanusa and L. J. Todd, *Polyhedron*, 1985, **4**, 2063, (b) G. G. Thiripuranathar, W. Y. Man, C. Palmero, A. P. Y. Chan, B. T. Leube, D. Ellis, D. McKay, S. A. Macgregor, L. Jourdan, G. M. Rosair and A. J. Welch, *Dalton Trans.*, 2015, **44**, 5628.

10 A. McAnaw, G. Scott, L. Elrick, G. M. Rosair and A. J. Welch, *Dalton Trans.*, 2013, **42**, 645.

11 A. McAnaw, M. E. Lopez, D. Ellis, G. M. Rosair and A. J. Welch, *Dalton Trans.*, 2014, **43**, 5095.

12 C. R. Groom and F. H. Allen, *Angew. Chem. Int. Ed.*, 2014, **53**, 662. For this study we used the CSD version 5.36.

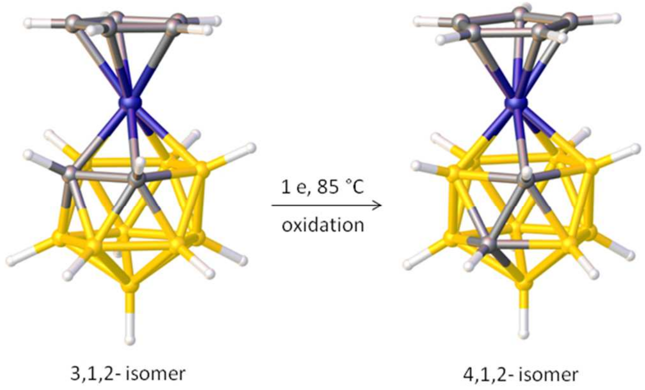
13 M. A. Fox, J. A. K. Howard, A. K. Hughes, J. M. Malget and D. S. Yufit, *J. Chem. Soc. Dalton Trans.*, 2001, 2263.

14 (a) M. R. Churchill and K. Gold, *J. Am. Chem. Soc.*, 1970, **92**, 1180; (b) T. E. Paxson, M. K. Kaloustian, G. M. Tom, R. J. Wiersema and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1972, **94**, 4882; (c) N. Carr, D. F. Mullica, E. L. Sappenfield and F. G. A. Stone, *Inorg. Chem.*, 1994, **33**, 1666; (d) R. M. Garrioch, P. Kuballa, K. S. Low, G. M. Rosair and A. J. Welch, *J. Organomet. Chem.*, 1999, **575**, 57; (e) S. Robertson, D. Ellis, G. M. Rosair and A. J. Welch, *Appl. Organomet. Chem.*, 2003, **17**, 518; (f) S. Robertson, R. M. Garrioch, D. Ellis, T. D. McGrath, B. E. Hodson, G. M. Rosair and A. J. Welch, *Inorg. Chim. Acta*, 2005, **358**, 1485.

15 K. Fallis, D. F. Mullica, E. L. Sappenfield and F. G. A. Stone, *Inorg. Chem.*, 1994, **33**, 4927.

16 e.g. (a) J. A. Doi, E. A. Mizusawa, C. B. Knobler and M. F. Hawthorne, *Inorg. Chem.*, 1984, **23**, 1482; (b) D. R. Baghurst, R. C. B. Copley, H. Fleischer, D. M. P. Mingos, G. O. Kyd, L. J. Yellowlees, A. J. Welch, T. R. Spalding and D. O'Connell, *J. Organomet. Chem.*, 1993, **447**, C14; (c) S. Dunn, G. M. Rosair, Rh. Ll. Thomas, A. S. Weller and A. J. Welch, *Angew. Chem. Int. Ed.,* 1997, **36**, 645.

17 D. S. Perekalin and A. R. Kudinov, *Russ. Chem. Bull.*, 2005, **54**, 1603.



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