

A boron–boron linked large metallocarborane cluster: Characterization and X-ray structure of 8,9'-[*closo*-{3-Co(η^5 -C₅H₅)-1,2-C₂B₉H₁₀}]₂

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Received 17 March 2006; received in revised form 25 April 2006; accepted 25 April 2006

Available online 30 April 2006

Abstract

The 8,9'-[*closo*-{3-Co(η^5 -C₅H₅)-1,2-C₂B₉H₁₀}]₂ (**1**) species, in which two large *closo*-CoC₂B₉ sub-clusters are connected by a B–B bond, is unexpectedly obtained from the reaction of *closo*-[3-Co(η^5 -C₅H₅)-1,2-C₂B₉H₁₁] with sulfur in the presence of aluminium chloride under reflux conditions. The solid state conformation of **1** seems to be the result of a pair of intramolecular C–H⋯H–B dihydrogen bonds between the protonic H atoms of the C₅H₅ fragment of a sub-cluster and the hydridic H atoms of the C₂B₉H₁₁ fragment in the other sub-cluster in **1**.

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Keywords: Cobaltacarborane; B–B linkage; DHB; Dihydrogen bond

1. Introduction

Metal complexes having *nido*-[2,3-R₂-2,3-C₂B₄H₄]²⁻ or *nido*-[7,8-R₂-7,8-C₂B₉H₉]²⁻ (dicarbollide) ligands constitute the most widely studied class of metallocarboranes, since they were first reported by Hawthorne in the 1960s [1]. These carborane ligands have planar binding faces and are isolobal and isoelectronic analogues of the cyclopentadienide [C₅H₅]⁻ (Cp) and pyrrolyl [NC₄H₄]⁻ ligands, behaving as 6-electron donors in transition metal complexes (Chart 1, top) [1]. Stable, covalently bonded metallocarboranes are of interest as metal-containing chain polymers, polycluster compounds, and solid-state materials that can be tailored to exhibit useful properties [2]. One interesting class of related compounds is that of multicage systems linked by one direct two-electron two-centre interboron

linkage. Although a number of such boron–boron linked multicage boron clusters (not having carbon) have been synthesized and structurally characterized [3], only three such structures have been reported for small metallocarboranes which correspond to *nido*-[2,3-R₂-2,3-C₂B₄H₄]²⁻ based metallocarborane compounds (see Chart 1 bottom for two examples) [4]. Larger dicarbollide *nido*-[7,8-R₂-7,8-C₂B₉H₉]²⁻ based boron–boron linked metallocarborane compounds have not yet been characterized.

During our ongoing research in polyhedral carboranes as alternatives to the cyclopentadienide ligand in transition metal complexes [5], we became interested in the supramolecular chemistry of these compounds and in particular in that of mercaptane metallocarboranes such as *closo*-[3-Ru(η^6 -C₆H₆)-8-HS-1,2-C₂B₉H₁₀] and *closo*-[3-Co(η^5 -C₅H₅)-8-HS-1,2-C₂B₉H₁₀] [6]. The latter complex, previously reported by Plešek [7], is prepared by treatment of *closo*-[3-Co(η^5 -C₅H₅)-1,2-C₂B₉H₁₁] with sulfur and aluminium chloride (Scheme 1). During the preparation of the mercaptane cobaltacarborane complexes in Scheme 1, we

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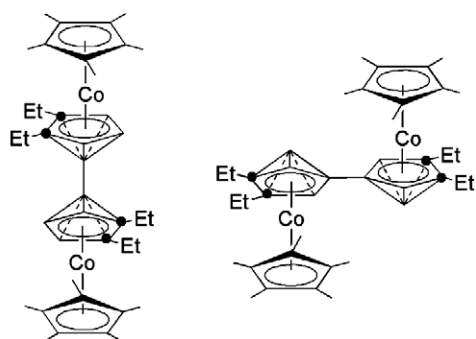
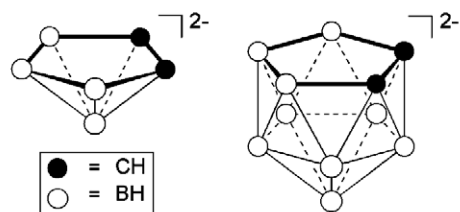
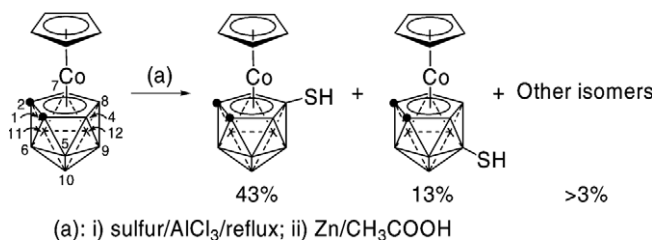


Chart 1. Top: the most common carborane ligands found in metallacarboranes, with formal charges. Bottom: two examples of small B–B linked cobaltacarborane complexes.



Scheme 1. Syntheses of B-substituted mercaptacobaltacarborane complexes.

unexpectedly obtained crystals of a multicage Co system not containing sulfur from the reaction mixture. Herein, we report the structural characterization and NMR data for the first dicobalt species in which two large *closo*- CoC_2B_9 sub-clusters are connected by a B–B bond.

2. Results and discussion

Crystals of the dimer 8,9'-[*closo*-{3-Co(η^5 -C₅H₅)-1,2-C₂B₉H₁₀}]₂ (**1**) were grown from an acetone-*d*₆ solution of the mixture of products in Scheme 1. The compound has been characterized by single crystal X-ray diffraction analysis and NMR spectroscopy. NMR data for **1** indicates an unsymmetrical dimer with inequivalent cluster units in solution and being consistent with the solid structure (Fig. 1). Thus, the ¹H NMR spectrum of **1** shows two different singlets for the C₅H₅ fragments (δ 5.88 and 5.78) and two broad singlets for the cage C–H protons (C_c–H) at δ 4.52 and 4.43, similar to other asymmetric metallacarboranes [5c]. The lack of mirror symmetry in dimer **1** also provoked inequivalency of all B signals in the ¹¹B NMR spectrum so that extensive overlap is observed. Thus, the fully coupled ¹¹B NMR spectrum for **1** displays seven broad resonances with relative intensity 1:1:2:8:4:2. The singlet at δ 18 is diagnostic for one of the substituted B atoms of **1**, which we tentatively assign to B(8) by comparison with other related compounds [4,5,7]. The very small quantities obtained for **1** have precluded completed assignment of other signals by ¹¹B NMR COSY.

The structure for **1** (Fig. 1) shows that the compound consists of two *closo*-[3-Co(η^5 -C₅H₅)-1,2-C₂B₉H₁₀] cobaltacarborane frameworks conjoined by one direct B–B bond of 1.688(10) Å between B(8) and B(9') atoms, which is in the

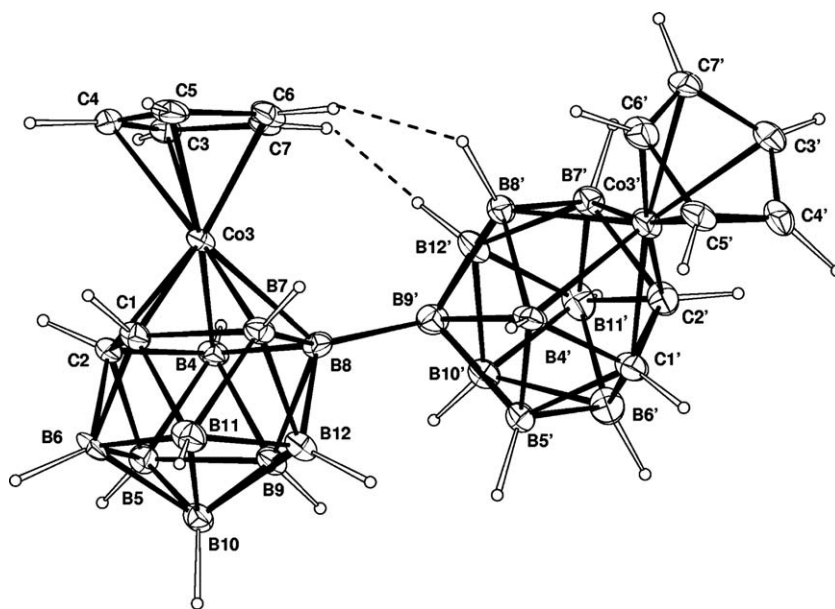


Fig. 1. Molecular structure of **1** (thermal ellipsoids set at 35% probability). Selected interatomic distances (Å): C(1)–C(2) 1.631(9), Co(3)–C(1) 1.991(6), Co(3)–C(2) 2.011(6), Co(3)–B(4) 2.069(7), Co(3)–B(7) 2.071(7), Co(3)–B(8) 2.170(7), C(1')–C(2') 1.650(11), Co(3')–C(1') 2.032(7), Co(3')–C(2') 2.017(7), Co(3')–B(4') 2.102(8), Co(3')–B(7') 2.051(8), Co(3')–B(8') 2.092(8), B(8)–B(9') 1.685(11).

expected range for a single boron–boron bond [4]. The bond lengths in each *closo*-CoC₂B₉ sub-cluster agree well with those in related icosahedral metallocarboranes [5,8]. The crystallographic results show that both cobalt atoms in each sub-cluster are essentially symmetrically located above the C₂B₃ carborane ligand face and that the C₅ ring of the cyclopentadienyl (C₅H₅) ligand is staggered with respect to that face. The connecting bond (B8–B9') in dimer **1** retains the direction corresponding to that of the original terminal H atoms in the corresponding monomer *closo*-[3-Co(η⁵-C₅H₅)-1,2-C₂B₉H₁₁] complex [8]. The mutual orientation of the two frameworks can be defined by the torsion angle Co(3)–B(8)–B(9')–B(8') of 30.33°. The latter conformation seems to be the result of a pair of intramolecular dihydrogen bonds (DHB) between the C₅H₅ ring hydrogens of a sub-cluster and the boron hydride atoms of the other one (C(6)–H···H–B(8') and C(7)–H···H–B(12')); dotted lines in Fig. 1 and Table 1). The contact distance between the two interacting hydrogens is substantially shorter than the sum of their van der Waals radii (2.4 Å) and they qualify as dihydrogen bonds [6,9].

It is noteworthy that the hydridic hydrogens involved in the intramolecular DHB in **1** are those corresponding to the more negative B atoms in the clusters [10]. The DFT [B3LYP/LanL2DZ]-optimized geometry for **1** proved to be the structure shown in Fig. 1 and provides a good reproduction of the experimental results. The calculated torsion angle Co(3)–B(8)–B(9')–Co(3') is 36.116°. The slight difference with the experimental value (~6°) is presumably due to crystal packing. Nevertheless, the geometry permitting the intramolecular C–H···H–B bonds is highly favourable and suggests that the solid state conformation observed in **1** is the result of such DHB. Table 1 shows that there is a reasonable agreement between relevant calculated and X-ray intramolecular DHB distances for the dimer structure of **1**. Moreover, charge analysis also supports the presence of two C–H···H–B DHBs. Atomic charges of the monomer *closo*-[3-Co(η⁵-C₅H₅)-1,2-C₂B₉H₁₁] complex and dimer **1** are listed in Table 2. A necessary criterion for the formation of DHB is the loss of charge of the H atoms involved [11]. As shown in Table 2, this trend is clearly observed in all H atoms involved in the CH···HB DHB (entries 2, 4, 6 and 8).

Intramolecular C–H···H–B close contacts are known to be present in aminoboron hydrides or azacyclohexane–borane adducts and seem to be responsible for the stabilization of these molecules against disproportionation or for controlling their conformation in solution, respectively [12,13]. It is therefore surprising that the related

Table 2

Atomic charges (NPA) for the monomer and dimer **1**

Entry	Atom	Dimer charges ^a	Monomer charges ^b	Charges ^c
1	C(6)	–0.233	–0.225	–0.008
2	H(6)	0.254	0.260	–0.006
3	C(7)	–0.204	–0.224	0.020
4	H(7)	0.258	0.260	–0.002
5	B(8')	–0.133	–0.126	–0.007
6	H(8')	–0.022	0.003	–0.025
7	B(12')	–0.147	–0.134	–0.013
8	H(12')	0.010	0.033	–0.023

^a Atomic charges in the dimer structure of **1**.^b Atomic charge for the equivalent atoms in the monomer structure *closo*-[3-Co(η⁵-C₅H₅)-1,2-C₂B₉H₁₁] complex.^c Difference between dimer and monomer atomic charges.

intramolecular DHBs have hardly been reported in icosahedral heteroboranes [9e,9g]. We have now examined the Cambridge Structural Database (Version 1.7, February 2005) for examples of such close contacts from *closo*-[3-X-1,2-C₂B₉] (X = any element) containing structures. 1583 intramolecular C–H···H–B close contacts have been found in 495 structures, with an average H···H distance of 2.214 Å (range, 1.7–2.4 Å). These data clearly suggest that an attractive intramolecular interaction is indeed present in many of these icosahedral heteroboranes.

On the other hand, we have recently shown that, in polyhedral boron clusters, the distance between a substituted B atom and its antipodal boron (*A_d*: Antipodal distance) is significantly affected by the electron-donor or –attracting nature of the substituents attached to boron [5c]. Thus, considering each of the cobaltacarborane sub-clusters in **1** as substituent of the second one, we may compare the relative effect of the cluster cages in their *A_d*, taking the unsubstituted monomer *closo*-[3-Co(η⁵-C₅H₅)-1,2-C₂B₉H₁₁] complex as the reference. The *A_d* values for **1** (Fig. 2) are 3.514 and 3.304 Å for (B6–B8) and (B9'–C2'), respectively, and are around 0.1 Å longer than that for the corresponding monomer [14]. Lengthening of the *A_d* distances in both dimer **1** sub-clusters suggests that there is transference of electron density between them. The significantly shorter *A_d* distance for B9'–C2' than that for B6–B8 is consistent with the former behaving as electron-acceptor and the latter as the donor. The more electronegative carbon atom (C2') withdraws electron density from its antipodal atom (B9') and presumably, from the other sub-cluster through the B9'–B8 bond.

As mentioned above, compound **1** was isolated from the reaction of *closo*-[3-Co(η⁵-C₅H₅)-1,2-C₂B₉H₁₁] with sulfur in the presence of aluminium chloride under refluxing con-

Table 1

Experimental and calculated (in parentheses) values for selected distances (Å) and angles (°) of **1** related to intramolecular DHB

Entry	C–H···H–B	H···H ^a	C···B	C–H···H	H···H–B
1	C(6)–H···H–B(8')	2.097 (2.404)	3.589 (3.797)	114.48 (109.28)	138.89 (142.81)
2	C(7)–H···H–B(12')	1.994 (1.996)	3.534 (3.507)	151.12 (148.73)	110.39 (106.41)

^a Normalised.

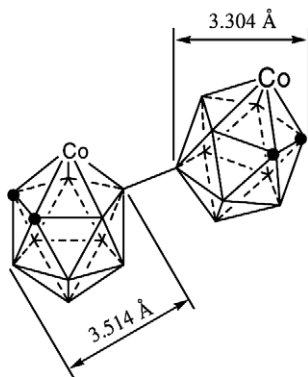


Fig. 2. Relevant antipodal distances (A_d) in **1**.

ditions and following a procedure described by others (Scheme 1) [7]. The fact that only traces of **1** were obtained, and that other major products are present precluded any insights into the mechanism for the formation of this B–B linked cobaltacarborane compound. Nevertheless **1** is, to our knowledge, the first crystallographically characterized metallocarborane dimer involving 12-vertex polyhedra linked by an *exo* B–B bond. It will be of interest to investigate whether other large metallocarboranes could also afford B–B linked products in sufficiently high enough yields to be useful for synthetic purposes.

3. Experimental

3.1. General procedure

All manipulations were carried out under an N_2 atmosphere. Chemicals were used as received. NMR spectra were acquired on Bruker ARX 300 MHz spectrometer and referenced to the solvent (1H , residual acetone- d_6) [15], and $BF_3 \cdot OEt_2$ (^{11}B NMR). Chemical shifts are reported in ppm. Multiplets nomenclature is as follows: s, singlet; br, broad.

In our analysis of the structural data, we have normalised all C–H bonds to a distance of 1.083 Å [16]. As for the boron cage compounds, we have chosen to normalise all cage B–H bonds to a distance of 1.191 Å [16]. Cambridge Structural Database searches for non-bonded contacts were carried out using the programs ConQuest (version 1.7) and VISTA (version 2.1) [17]. The search criteria (CSD dated February 2005) were only error and disorder free structures (organic and organometallic) with R factors less than 0.1 (H normalized). Normalized structures were retrieved from the Cambridge Structural Database as mol2 files and analysed using Mercury (version 1.4) [17].

3.1.1. NMR data for **1**

Selected NMR data are given: 1H NMR (acetone- d_6): δ 5.88 (s, 5H, η^5 -Cp), 5.78 (s, 5H, η^5 -Cp), 4.52 (br s, 2H, C_c-H), 4.43 (br s, 2H, C_c-H). $^{11}B\{^1H\}$ NMR (acetone- d_6): δ 18.0 (br s, 1B, B-8), 8.7 (br s, 1B), 4.1 (br, 2B), -1.9 to -3.6 (br, 8B), -14.3 to -16.1 (br, 4B), -22.0 (br, 2B).

3.2. X-ray diffraction studies of **1**

Bright orange blocks of **1** were obtained from an acetone- d_6 at room temperature. Data were collected on a Bruker Nonius KappaCCD mounted at the window of a Mo rotating anode following standard procedures. The crystals suffered from high anisotropic mosaicity resulting in a higher than desired R factor.

Crystal data for **1** $C_{14}H_{30}B_{18}Co_2$, Mr = 510.82, T = 120(2) K, monoclinic, space group $P2_1/n$, a = 15.1940 (15), b = 10.5240(10), c = 15.7730(13) Å, β = 112.686(4)°, V = 2327.0(4) Å³, ρ_{calc} = 1.458 g cm⁻³, μ = 1.430 mm⁻¹, Z = 4, reflections collected: 34 158, independent reflections: 6539 (R_{int} = 0.1518), final R indices [$I > 2\sigma I$]: R_1 = 0.0935, wR_2 = 0.1802, R indices (all data): R_1 = 0.2039, wR_2 = 0.2277. Despite the moderately high R factor, it was possible to easily distinguish the carbon sites in the cage via consideration of the thermal parameters and analysis of the bond lengths.

Acknowledgements

We thank CICYT (Project MAT2004-01108), Generalitat de Catalunya (2001/SGR/00337), and CSIC (I3P contract to J.G.P.). We also thank the Centro Técnico de Informática (CSIC) and Centre de Supercomputació de Catalunya (CESCA) for computing support. M.B.H thanks the UK EPSRC for continued financial support of the National Crystallography Service at Southampton.

Appendix A. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Center, CCDC No. 602047 for 8,9'-[closo-{3-Co(η^5 -C₅H₅)-1,2-C₂B₉H₁₀}]₂ (**1**). Copies of the data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorgchem.2006.04.031.

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