



The enhanced structural carborane effect

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ARTICLE INFO

Article history:

Received 5 December 2014

Received in revised form

6 January 2015

Accepted 8 January 2015

Available online 19 January 2015

Dedicated to Professor Michael Mingos with very best wishes on the occasion of his 70th birthday and in recognition of his many outstanding contributions to inorganic and organometallic chemistry.

Keywords:

Carborane

Metallacarborane

Synthesis

Structure

X-ray diffraction

Structural carborane effect

ABSTRACT

The structures of 1,2- μ -(C₄H₆)-1,2-*closo*-C₂B₁₀H₁₀ ("dihydrobenzocarborane") and 1,2- μ -(C₄H₄)-1,2-*closo*-C₂B₁₀H₁₀ ("benzocarborane") determined previously (Wade et al., 1996) are analysed. This provides evidence for an *enhanced structural carborane effect*, whereby the cage carbon atoms in the latter bond less strongly with B3 and B6, presumably because their *p*_π orbitals are associated to some degree with the exopolyhedral C₆ ring, affording it a small degree of aromaticity. The corresponding cobaltacarboranes 3-Cp-1,2- μ -(C₄H₆)-1,2-*closo*-CoC₂B₉H₉ (**1**) and 3-Cp-1,2- μ -(C₄H₄)-1,2-*closo*-CoC₂B₉H₉ (**2**) are synthesised, fully characterised by spectroscopic methods and studied crystallographically. Comparison of their molecular structures affords further evidence for the enhanced structural carborane effect in that the C_{cage}–Co3 and C_{cage}–B6 distances in the latter are both significantly longer than those in the former, whilst at the same time the C1–C2 distance significantly decreases on moving from **1** to **2**.

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Introduction

When an indenyl ligand is η^5 -bonded to a transition metal the metal to ring junction carbon atom bonds are weaker than those to the non-junction carbon atoms because the *p*_π atomic orbitals of the junction C atoms are part of both the η -bonded C₅ ring and the free C₆ ring. This gives rise to both a *kinetic indenyl effect* [1] in which rates of ligand substitution in indenyl compounds are orders of magnitude faster than those in analogous Cp compounds, and also a *structural indenyl effect* in which the metal to ring junction C atom distances are measurably longer than those to the non-junction atoms [2] and distinct molecular conformations are adopted [3]. Closely related phenomena are the *kinetic naphthalene effect* [4] and the *structural naphthalene effect* [5].

In 3,1,2-*closo*-MC₂B₉ metallacarboranes the η^5 -bonded carborane ligand face also contains two adjacent atoms that are relatively weakly bound to the metal atom, specifically the cage carbon atoms. This arises because, as Mingos showed many years ago, the

frontier molecular orbitals of a carborane ligand are relatively concentrated on the boron atoms in the ligand face [6]. However, because the atomic radius of C is less than that of B, the C atoms lie closer to the polyhedral centroid [7] and, everything else being equal, M–C distances are actually *shorter* than M–B distances, in spite of the C atoms being less strongly bound. Thus, in the archetypal species 3-Cp-3,1,2-*closo*-CoC₂B₉H₁₁ Co–C distances are 2.005 (2) and 2.009 (2) Å whilst Co–B distances are 2.069(2), 2.106(2) and 2.076 (2) Å [8]. This means that a *structural carborane effect* cannot be measured directly, i.e. by metal–carborane distances. Nevertheless, clear evidence for this effect is available by consideration of metal–exopolyhedral ligand distances and exopolyhedral ligand orientations since the structural trans effect (trans influence) of cage C is less than that of cage B [7].

Given that fusing a {C₄H₄} diene fragment onto a Cp ligand (affording an indenyl ligand) transforms an otherwise evenly bound ligand (in terms of the strength of the M–C links) into an unevenly bound one (the structural indenyl effect) and fusing the same fragment onto a η^6 -C₆H₆ ligand has an analogous result (the structural naphthalene effect) we became interested in the consequences of fusing an exopolyhedral {C₄H₄} fragment onto the C atoms of an MC₂B₉ species. Would this make the cage C atoms even

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less strongly-bonded to the metal atom, resulting in what could be described as an *enhanced structural carborane effect*? In this communication we describe our preliminary results in pursuit of the answer to this question.

Results and discussion

The 1,2-*closo*-C₂B₁₀ carborane with a {C₄H₄} diene fragment fused onto the cage C atoms is the well-known species 1,2-μ-(C₄H₄)-1,2-*closo*-C₂B₁₀H₁₀, generally known as “benzocarborane” (**I**) (Fig. 1) and first prepared by Matteson [9] and studied crystallographically by Wade et al. [10] A fundamental question concerning **I** is the degree of aromatic character associated with the exopolyhedral C₆ ring. Based primarily on ¹H NMR spectroscopy Matteson concluded that the ring has little aromatic character, a view echoed by Wade et al. from their analysis of C–C distances and calculated π-bond orders. Any such aromatic character would require involvement of the *p*_π orbitals of the cage carbon atoms which in turn would lead to an enhanced structural carborane effect. Therefore, if we were able to establish such an effect we would at the same time be able to contribute to the ongoing debate about aromaticity in benzocarborane.

To probe the possibility of an enhanced structural carborane effect in **II**, a metallacarborane derivative of benzocarborane, it is necessary to compare the C_{cage}–M3 distances in **II** with those of a sterically-comparable molecule in which delocalisation in the appended C₄ ring is denied. Such a compound would be **H2-II**, the dihydro analogue. This is a derivative of 1,2-μ-(C₄H₆)-1,2-*closo*-C₂B₁₀H₁₀, “dihydrobenzocarborane” (**H2-I**), also prepared by Matteson [9] and studied structurally by Wade [10]. But in comparing **II** and **H2-II** the C_{cage}–B distances as well as the C_{cage}–M3 distances should be susceptible to any enhanced structural carborane effect. Extending this argument, a comparison of the C_{cage}–B3 and C_{cage}–B6 distances in the parent carboranes **I** and **H2-I** would provide additional evidence for such an effect. Although, as noted, both **I** and **H2-I** have already been studied crystallographically, these C_{cage}–B distances were not discussed [10].

In the dihydro species **H2-I** (two crystallographically-independent molecules per asymmetric unit) there are eight C1/2–B3/6 distances ranging from 1.7153 (15) to 1.7253 (15) Å, average

1.721 (3) Å, and two C1–C2 distances, 1.6608 (15) and 1.6624 (15) Å, average 1.6616 (21) Å. In benzocarborane **I** there are also two molecules per asymmetric unit; the eight C1/2–B3/6 distances range from 1.741 (4) to 1.751 (4) Å, average 1.746 (4) Å, and the two C1–C2 distances are 1.648 (4) and 1.654 (4) Å, average 1.651 (6) Å. The lengthening of the average C–B distance in moving from **H2-I** to **I** is significant [$\Delta = 0.025$ (5) Å] showing that in **I** the C_{cage} atoms are less strongly bound to B3 and B6 and thus demonstrating an enhanced structural carborane effect. This implies that the C_{cage} atom *p*_π orbitals are to some extent involved with the exopolyhedral C₆ unit, affording it a degree of aromaticity. Consistent with this, the average C1–C2 distance shortens in moving from **H2-I** to **I** but less significantly [$\Delta = 0.011$ (6) Å].

Deboronation of **H2-I** and **I** according to the method of Hawthorne et al. [11] and isolation of the anions as trimethylammonium salts afforded [HNMe₃][7,8-μ-(C₄H₆)-7,8-*nido*-C₂B₉H₁₀] and [HNMe₃][7,8-μ-(C₄H₄)-7,8-*nido*-C₂B₉H₁₀] as previously reported by Matteson and Grunzinger [12]. These authors used the latter species to prepare metallacarborane analogues of **I** but none of the products were structurally characterised. Deprotonation of both the above salts with *n*-BuLi in THF followed by treatment with CoCl₂ and NaCp, followed by aerial oxidation, afforded the cobaltacarboranes 3-Cp-1,2-μ-(C₄H₆)-1,2-*closo*-CoC₂B₉H₉ (**1**) and 3-Cp-1,2-μ-(C₄H₄)-1,2-*closo*-CoC₂B₉H₉ (**2**) as yellow and red solids, respectively, in good yields.

Both compounds were initially characterised by elemental microanalysis, mass spectrometry and ¹H and ¹¹B NMR spectroscopies. The ¹H NMR spectrum of **1** contains, in addition to a singlet for the Cp protons, an integral-2 singlet for the CH protons of the tether and two integral-2 doublets for the “upper” and “lower” (with respect to the C₆ plane) protons of the CH₂ groups. In the ¹¹B {¹H} spectrum are six resonances, 1:1:2:2:2:1 from high frequency to low frequency, fully consistent with the expected C_s molecular symmetry. The ¹H spectrum of **2** has two multiplets each of integral 2 for the H atoms of the exopolyhedral ring and an integral-5 singlet for the Cp protons, whilst the ¹¹B{¹H} spectrum again reveals a 1:1:2:2:2:1 pattern of resonances.

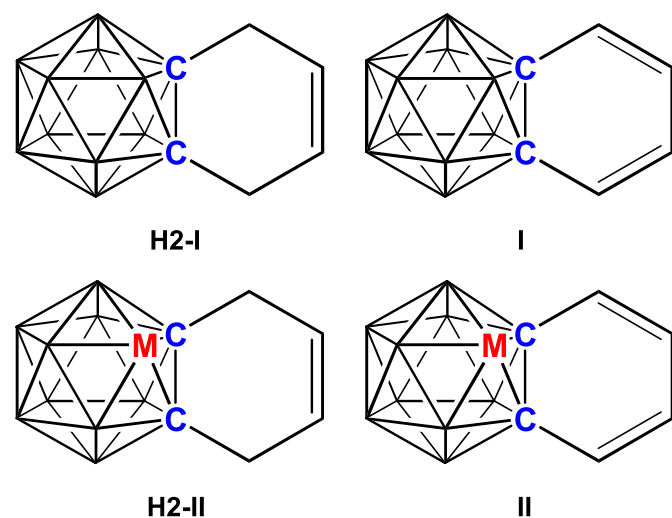


Fig. 1. “Benzocarborane” (**I**), “dihydrobenzocarborane” (**H2-I**) and their respective 3,1,2-MC₂B₉ derivatives **II** and **H2-II**. In these metallacarboranes B6 is the cage atom directly connected to both cage C atoms.

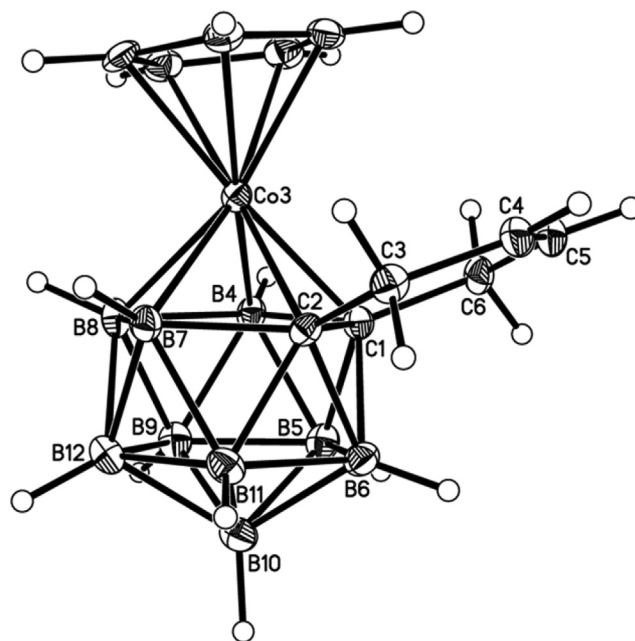


Fig. 2. Perspective view of compound **1** (thermal ellipsoids drawn at 50% probability level except for H atoms). Selected interatomic distances (Å): C1–Co3 2.039 (2), C2–Co3 2.036 (2), C1–B6 1.730 (4), C2–B6 1.724 (4), C1–C2 1.656 (3).

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