

The First 8-Vertex Monocarbon Metallacarborane with an “Isolated” Boron-Capped Pentagonal Bipyramidal Cage. Synthesis and Molecular Structure of Capped *closo*-2,2-(Ph₃P)₂-2-H-3,6,8-(MeO)₃-RuCB₆H₄

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The electronic and cluster structures of electron-deficient *closo*-metallacarboranes not conforming with Wade's electron counting rules have been of interest for a long time.^{1,2} Among the known *n*-vertex metallacarboranes of this type, which formally possess fewer than $2n + 2$ electrons for skeletal bonding,³ species having an 8-vertex cluster configuration with “isolated” (nonfused) pentagonal bipyramidal polyhedra, to our best knowledge, remained unknown. We now report the first such example of a structurally characterized 8-vertex monocarbon metallacarborane derived from the partially contracted monocarbon carborane [*nido*-B₁₀H₁₂CH]⁻.

We recently reported the synthesis of the two novel hyper-*closo*-type monocarbon RuCB₈ clusters which were formed as main products in the polyhedral contraction reaction of [*nido*-B₁₀H₁₂CH]⁻Cs⁺ promoted by RuCl₂(PPh₃)₃ in hot methanol.⁴ Among those species which were individually isolated from the reaction mixture and identified as having low-coordinate boron atoms, which are usually indicative of specific electronic cluster structures, of particular interest is a pale yellow diamagnetic crystalline solid with the formula (Ph₃P)₂HRuCB₆H₄(OMe)₃ (**1**).⁴ Although the ¹H and ¹¹B/¹¹B{¹H} NMR spectra as well as the FAB mass spectrum⁵ of this latter complex were consistent with its 8-vertex geometry, these data alone were insufficient for an unambiguous assignment of the detailed cluster structure of this

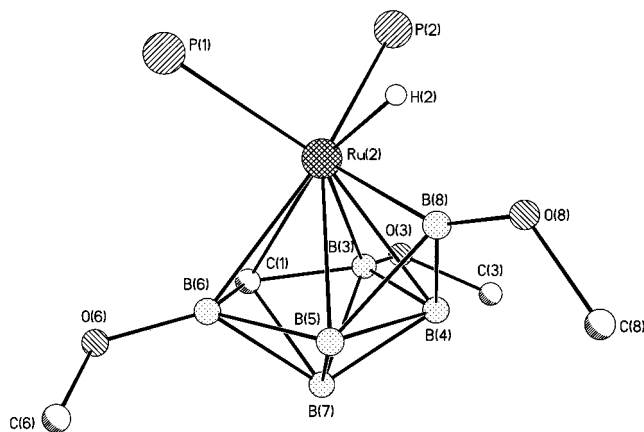


Figure 1. General view of molecule **1**. Selected distances (Å) and bond angles (deg): Ru(2)–P(1), 2.3630(15); Ru(2)–P(2), 2.3617(13); Ru(2)–H(2), 1.40(4); Ru(2)–C(1), 2.301(5); Ru(2)–B(3–6), 2.258(5)–2.336(5); Ru(2)–B(8), 1.961(5); B(8)···H(2), 1.61(4); B(4)–B(8), 1.839(7); B(5)–B(8), 1.838(8); C(1)–B(3), 1.530(7); C(1)–B(6), 1.538(7); P(1)Ru(2)P(2), 99.79(5); P(1)Ru(2)H(2), 85.1(2); P(2)Ru(2)H(2), 77.8(2); H(2)Ru(2)B(8), 54.0(2); H(2)B(8)Ru(2), 45.0(2); Ru(2)H(2)B(8), 81.0(2).

species. An X-ray diffraction study⁶ of **1** was, therefore, undertaken which proved this species to be a small monocarbon ruthenacarborane capped *closo*-2,2-(Ph₃P)₂-2-H-3,6,8-(MeO)₃-RuCB₆H₄ with a number of interesting structural features (Figure 1).

The polyhedral cage geometry of **1** is based on a pentagonal bipyramid with one additional boron vertex capping one of its faces. Complex **1** may thus be regarded as the first boron-capped pentagonal bipyramidal metallacarborane. The ruthenium center in the cluster is bonded to one carbon and five boron atoms of the monocarbon carborane cage, of which four are located in the equatorial plane of the bipyramid and the fifth occupies the capping position. The metal atom is additionally coordinated by the two PPh₃ groups and a terminal hydrogen ligand. In contrast to the known bimetalacarboranes [Me₄C₄B₈H₈FeCo(η⁵-Cp)]⁷ and [Me₄C₄B₈H₈FeCo(PEt₃)₂]⁸ consisting of two fused 7-vertex pentagonal bipyramidal *closo* polyhedra with the unique boron atom wedged between both cages, the capping B(8) atom in **1** is

- (1) (a) Nishimura, E. K. *J. Chem. Soc., Chem. Commun.* **1978**, 858. (b) Crook, J. E.; Elrington, M.; Greenwood, N. N.; Kennedy, J. D.; Woollins, J. D. *Polyhedron* **1984**, *1*, 901. (c) Baker, R. T. *Inorg. Chem.* **1986**, *25*, 109. (d) Kennedy, J. D. *Inorg. Chem.* **1986**, *25*, 111. (e) Johnston, R. L.; Mingos, D. M. P. *Inorg. Chem.* **1986**, *25*, 3321. (f) Kennedy, J. D. *Prog. Inorg. Chem.* **1986**, *34*, 211. (g) Johnston, R. L.; Mingos, D. M. P.; Sherwood, P. *New J. Chem.* **1991**, *15*, 831.
- (2) (a) Wade, K. J. *J. Chem. Soc., Chem. Commun.* **1971**, 792. (b) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.
- (3) (a) Gallahan, K. P.; Evans, W. J.; Lo, F. Y.; Strouse, C. E.; Hawthorne M. F. *J. Am. Chem. Soc.* **1975**, *97*, 296. (b) Salentine, C. G.; Hawthorne M. F. *Inorg. Chem.* **1978**, *17*, 1498. (c) Jung, C. W.; Baker, R. T.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1980**, *102*, 5782. (d) Jung, C. W.; Baker, R. T.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1981**, *103*, 810. (e) Crook, J. E.; Greenwood, N. N.; Kennedy, J. D.; McDonald, W. S. *J. Chem. Soc., Chem. Commun.* **1981**, 933. (f) Bould, J.; Greenwood, N. N.; Kennedy, J. D.; McDonald, W. S. *J. Chem. Soc., Chem. Commun.* **1982**, 465. (g) Micciche, R. P.; Briguglio, J. J.; Sneddon, L. G. *Inorg. Chem.* **1984**, *23*, 3992. (h) Crook, J. E.; Elrington, M.; Greenwood, N. N.; Kennedy, J. D.; Thornton-Pett, M.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1985**, 2407.
- (4) Pisareva, I. V.; Chizhevsky, I. T.; Petrovskii, P. V.; Bregadze, V. I.; Dolgushin F. M.; Yanovsky, A. I. *Organometallics*, **1997**, *16*, 5598.
- (5) Complex **1** was prepared in 8% yield as described elsewhere⁴ with some modification of the purification procedure. Characterization data for **1**: ¹H NMR (400.13 MHz, C₆D₆, 22° C) δ 7.51, 6.97, (m + m, 12H + 18H, Ph), 4.17 (s, 3H, MeO), 3.05 (s, 6H, 2 × MeO), 2.99 (s, br, 1H, CH₃), -9.02 (t, br, 1H, H_{Ru}, ²J(H,P) = 20.7 Hz); ³¹P{¹H} NMR (161.98 MHz, C₆D₆) 49.4 (s, P_{Ru}); ¹¹B NMR (128.33 MHz, CD₂Cl₂, J(B,H) (Hz)) +68.9 (s, br, 1B, B(8)), +33.7 (s, 2B, B(3,6)), +12.8 (d, 1B, 140), -31.8 (d, 2B, 150); FAB MS (positive ion, *m/e*) calcd for ¹²C_{40¹H₄₄¹¹B₆¹⁶O₃-³¹P₂¹⁰¹Ru 801.2, found 801.6 [M⁺], 724.4 [M - Ph]⁺, 647.3 [M - 2Ph]⁺, 570.2 [M - 3Ph], 539.4 [M - PPh₃]⁺, 462.4 [M - PPh₃ - Ph]⁺. Anal. Calcd for C₄₀H₄₄B₆O₃P₂Ru: C, 60.00; H, 5.54. Found: C, 59.46; H, 5.63.}

- (6) Crystal data for **1**: RuC₄₀H₄₄B₆O₃P₂Ru·*n*-C₆H₁₄, triclinic, space group P1, *a* = 12.823(3) Å, *b* = 13.125(3) Å, *c* = 14.688(3) Å, α = 86.34(3)°, β = 84.17(3)°, γ = 68.22(3)°, *V* = 2282.8(8) Å³ for *Z* = 2, *d*(calc) = 1.290 g/cm³. Data collection was carried out on a Siemens P3/PC diffractometer (λ(Mo Kα) = 0.71073 Å, *T* = 293(2) K, θ/2θ scan, θ ≤ 25°). The structure was solved by direct methods; 8110 independent reflections (*R*_{int} = 0.0603) were collected and used in the refinement; *R*1 = 0.0597 (on *F* for 5539 observed reflections with *I* > 2σ(*I*)), *wR*2 = 0.1047, and GOF = 1.071 (on *F*² for all data).
- (7) Maxwell, W. M.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1976**, *98*, 3493.
- (8) Barker, G. K.; Garcia, M. P.; Green, M.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1982**, 1679.

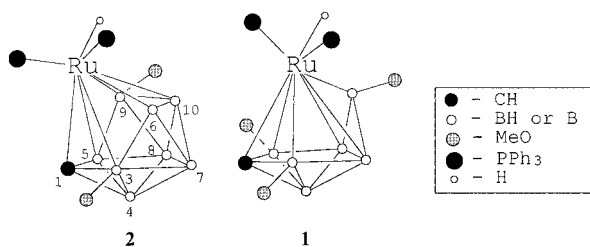


Figure 2. Geometrical and structural relationship between the contracted *hyper-closo-RuCB₈* (**2**) and *hyper-closo-RuCB₆* (**1**) clusters.

located roughly symmetrically over one of the faces of the bipyramid (B(4)–B(5)–Ru) and has a formal cluster connectivity of 3. The single cage carbon atom in the polyhedron framework is in the trans position with respect to the capped BBRu face, so that the complex can be considered as having overall C_s symmetry. Two boron atoms B(3) and B(6) adjacent to the cage carbon as well as the unique B(8) atom in **1** are substituted by methoxy functions. This indicates that **1** is probably formed via methanolic deboronation of *hyper-closo-2,2*-(PPh₃)₂-2-H-3,9-(MeO)₂-2,1-RuCB₈H₇ (**2**), one of the two RuCB₈ clusters isolated as main products from the polyhedral contraction reaction of [*nido*-B₁₀H₁₂CH][−]Cs⁺ with RuCl₂(PPh₃)₃.⁴ It is apparent from the comparison of the cluster geometry of **1** and **2** (Figure 2) that formal removal of both low-connectivity boron atoms, B(6) and B(9), from the RuCB₈ skeleton of **2** would have produced a metallocarborane framework identical to that of complex **1**.⁹

The Ru(2)–B(8) bond 1.961(5) Å happens to be the shortest Ru–B bond ever observed in ruthenium complexes of any boron derivatives. It is about 0.25 Å shorter than the average bond length calculated across all reported Ru–B distances (689 values retrieved from 161 structures with Ru–B bonds of any type found in the Cambridge Structural Database; Release April 2000) and still noticeably shorter than the shortest Ru–B distance of 1.993 Å previously observed in the mixed-metal cluster C₇P₃PAuIr₂Ru₄B(CO)₁₆¹⁰ featuring the interstitial boron atom in the center of the Ir₂Ru₄ octahedron. Interestingly, the shortest ever recorded Fe–B distance is the distance from a similar capping boron vertex to the central iron atom in the electron-deficient complex [Me₄C₄B₈H₈–FeCo(η^5 -Cp)]⁷ mentioned above. All these taken together indicate that the capping boron atom has a rather peculiar electronic environment which allows somewhat closer approach of such boron vertices to the metal centers as compared to boron atoms within any other boron-containing units. The short Ru(2)–B(8) distance in **1** results in the H(2) hydrogen being as close to the B(8) atom as 1.61(4) Å. This close approach of the metal hydride to the capping boron atom is reflected in the unique H(Ru)···B(8) spin–spin interaction observed in the ¹H NMR spectra of **1** (vide infra).

In accord with the overall C_s symmetry, the ¹¹B NMR spectra of **1** revealed the presence of a set of four resonances of relative areas 1:2:1:2 with one of the resonances shifted to extremely low field. This unique signal at $\delta(^{11}\text{B}) + 68.9$ ppm is highly indicative of a low-coordinate boron atom and has been, therefore, tentatively assigned to the capping B(8) atom. Two of the four resonances mentioned above, namely, those at $\delta(^{11}\text{B}) + 68.9$ (1B) and +33.7 (2B) ppm, on proton decoupling collapsed to somewhat broadened and sharp singlets, respectively, supporting their assignment to

the cage boron atoms substituted by MeO groups. The ¹H and ³¹P{¹H} NMR spectra of **1**, measured at room temperature, are also consistent with its symmetrical structure. In particular, the terminal hydride resonance appears in the ¹H NMR spectra of **1** as a broadened triplet at $\delta(^1\text{H}) - 9.02$ ppm (line width ca. 22 Hz) exhibiting a coupling of hydrogen to two equivalent PPh₃ groups [²J(H^{Ru},P) = 20.7 Hz] and, apparently, a boron nucleus. Taking into account the essentially short Ru–H···B(8) distance found in the solid-state structure of **1**, the broadening of a high-field triplet resonance is caused either by a unique spin–spin through-space interaction of the metal hydride and the capping B(8) atom or by the long-range coupling ²J(H^{Ru},B⁸). Indeed, in the selective boron-decoupling experiment, when the B(8) resonance at $\delta + 68.9$ ppm was decoupled, the line width of the hydride triplet at $\delta - 9.02$ ppm significantly decreased (from 22 to 12 Hz), indicating the presence of this type of interaction in solution of **1**. The ³¹P{¹H} NMR spectrum of **1** showed one singlet at $\delta(^{31}\text{P}) 49.4$ ppm from the two equivalent PPh₃ groups at the metal vertex. Consequently, decoupling of ³¹P nuclei caused a collapse of the hydride triplet at -9.02 ppm to a singlet with the same line width as the triplet had in the non-boron-decoupled ¹H NMR spectra.

Following the skeletal electron-counting rules² and considering a (Ph₃P)₂HRu group as contributing three orbitals and one electron (8 + 2 × 2 + 1 – 12 = 1) to the monocarbon CB₆ cage for skeletal bonding, cluster **1** has only 16 skeletal electrons, i.e., two electrons fewer than required for a canonical 8-vertex closo cluster. It may therefore be considered as a 2*n* skeletal electron hyper-closo system. At the same time, there is an alternative way for description of such complexes on the basis of the polyhedral skeletal electron pair theory (PSEPT).¹¹ Indeed, in accord with the capping principle,¹² which implies that both the capped and parent uncapped closed polyhedra accommodate the same number of skeletal electrons for cluster bonding, the 2*n* cluster electron count for **1** predicts its capped-closo geometry. Thus, complex **1** may be regarded as a pileo cluster^{1f} which clearly conforms to PSEPT for 8-vertex clusters containing a total of 16 skeletal electrons. Up to now, most of the known capped closo (or pileo) clusters in the field are bimetalla- or trimetallaboranes based on a capped octahedron which involves a BH or metal-containing group capping one of the cluster faces.¹³ The structure of cluster **1** provides the first and a quite unique example of a capped *closo*-metallocarborane based on pentagonal bipyramidal geometry.

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Supporting Information Available: Experimental details for the preparation of **1**. X-ray crystallographic file (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(9) A similar approach has been used for the explanation of an unusual cluster geometry of *isonido*-[IrC(OH)B₈H₆(OMe)](C₆H₄PPh₂)(PPh₃), which is obtained via methanolic deboronation of *closo*-[B₁₀H₁₀]^{2−} in the presence of *trans*-Ir(CO)Cl(PPh₃)₂.^{3c} The removal of a 4-connected rather than the 6-connected vertex from *closo*-[B₁₀H₁₀]^{2−} has been postulated to occur in the reaction.

(10) Galsworthy, J. R.; Hattersley, A. D.; Housecroft, C. E.; Rheingold, A.; Waller, L. A. *J. Chem. Soc., Dalton Trans.* **1995**, 549.

(11) (a) Williams, R. E. *Inorg. Chem.* **1971**, *10*, 210. (b) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311.

(12) (a) Mingos, D. M. P. *Nature Phys. Sci.* **1972**, *236*, 99. (b) Mingos, D. M. P.; Forsyth, M. I. *J. Chem. Soc., Dalton Trans.* **1977**, 610.

(13) See, for instance: (a) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1977**, *12*, 3255. (b) Venable, T. L.; Grimes, R. N. *Inorg. Chem.* **1982**, *21*, 887. (c) Venable, T. L.; Sinn, E.; Grimes, R. N. *Inorg. Chem.*, **1982**, *21*, 904. (d) Bullick, H. J.; Grebenik, P. D.; Green, M. L. H.; Hughes, A. K.; Leach, J. B.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **1994**, 3337. (e) Bould, J.; Rath, N. P.; Barton, L. *Organometallics* **1995**, *14*, 2119. (f) Bould, J.; Rath, N. P.; Barton, L. *J. Chem. Soc., Chem. Commun.* **1995**, 1285. (g) Lei, X.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1999**, *121*, 1275.