Discovery of a Triangulated Thirteen Vertex (1,5,6,1) Docosahedron from an *X*-Ray Diffraction Study of $(\pi\text{-}C_5H_5)Co(\pi\text{-}7,9\text{-}B_{10}C_2H_{12})$

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Summary $(\pi\text{-}C_5H_5)Co(\pi\text{-}7,9\text{-}B_{10}C_2H_{12})$ contains a thirteen vertex docosahedron in which an apical cobalt(III) atom is linked directly to a six-atom B_4C_2 hexagon; the irregularity of the docosahedron leads to atoms having connectivities of 5, 6, and 7, and to a wide range of distances between adjacent atoms within the polyhedron.

Hawthorne and his co-workers have described three isomers of $(\pi\text{-}C_5H_5)Co(\pi\text{-}B_{10}C_2H_{12})$.[1] On the basis of ^1H and ^{11}B n.m.r. spectra taken at room temperature, a structure of C_s symmetry was suggested for the isomer referred to as 'red I' (see Figure 1).

We have undertaken a single-crystal *X*-ray diffraction study of this complex and find the true structure to be different from that originally suggested.

Crystal data: $C_7H_{17}B_{10}Co$, $M = 268{\cdot}26$, orthorhombic, $a = 7{\cdot}0465(24)$, $b = 13{\cdot}7441(41)$, $c = 13{\cdot}6198(33)$ Å, $U = 1319{\cdot}0(7)$ Å^3, $D_c = 1{\cdot}351$, $D_m = 1{\cdot}348$ g cm^{-3}, $Z = 4$, space group $Pbc2_1$ (C^5_{2v}; No. 29).

Diffraction data ($2\theta_{max} = 50°$; Mo-K_α radiation) were collected with a Picker FACS-1 diffractometer and the structure solved by Patterson and Fourier methods. All atoms, including the 17 hydrogens, have been located and their positional and thermal parameters (anisotropic for Co, C, B; isotropic for H) optimized by full-matrix least-squares refinement. The final discrepancy index is R 3·06% for the 2344 *hkl* and *hkl* reflections. The molecular geometry of C_1 symmetry is illustrated in Figure 2. The crystal contains an ordered racemic array of π-cyclopentadienyl-π-dodecahydro-7,9-dicarba-*nido*-dodecaboratocobalt(III)† and the enantiomeric 7,11-dicarba-isomer.

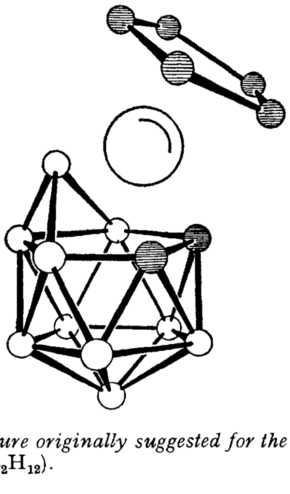

Figure 1. *Structure originally suggested for the "red* I" *isomer of* $(\pi\text{-}C_5H_5)Co(\pi\text{-}B_{10}C_2H_{12})$.

The $B_{10}C_2Co$ fragment defines a triangulated (1,5,6,1) thirteen-apex docosahedron in which an equatorial (C–B–C–B–B–B) hexagonal belt is bonded directly to the cobalt(III) atom, individual distances being Co–C(7) = 2·032(4), Co–B(8) = 2·199(6), Co–C(9) = 2·150(3), Co–B(10) = 2·093(3), Co–B(11) = 2·165(3), and Co–B(12) = 2·203(4) Å.

The linking together of five- and six-membered equatorial rings in a (1,5,6,1) thirteen-apex cage necessarily causes some severe irregularities in the environments of individual atoms. Principal among these are two abnormal connectivities—atom C(7) is linked to only five other atoms [terminal H, Co, B(2), B(8), B(12)], while B(2) is linked to seven other atoms [terminal H, B(1), B(3), B(6), C(7), B(8), B(12)].

Certain bond distances involving C(7) are abnormally short,‡ with C(7)–B(12) = 1·527(6) and C(7)–B(8) = 1·429(10) Å, the latter distance being indicative of multiple bond character. Similarly, certain distances involving B(2) are abnormally long, with B(2)–B(12) = 1·947(6) and B(2)–B(8) = 2·081(10) Å.

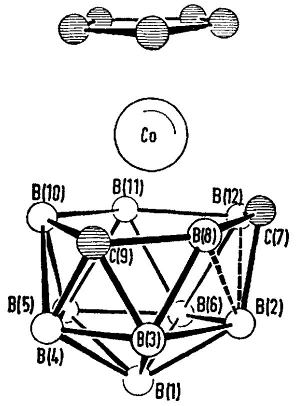

Figure 2. *Molecular geometry* (*with* 17 *terminal hydrogen atoms omitted*) *as determined by the present* X-*ray structural analysis.*

This last observation is particularly important since the four-membered systems B(2)–B(3)–B(8)–C(7) and B(2)–B(6)–B(12)–C(7) are not symmetrically triangulated but are perturbed towards open squares. This lends direct support to Lipscomb's[4] 'diamond–square–diamond' mechanism for the intramolecular isomerization of certain triangulated polyhedral boron hydrides and carboranes. Hawthorne[5] has recently shown that the ^{11}B n.m.r. spectrum of the present complex loses its symmetry at reduced temperatures; a mechanism is suggested whereby intramolecular interconversion of the enantiomeric 7,9- and 7,11-dicarba-isomers occurs *via* a diamond–square–diamond rearrangement involving mainly the two distorted diamond-shaped faces.

Other bonding distances in the carborane cage are in the ranges: B–B = 1·720(6)—1·881(6) and B–C = 1·665(4)—1·708(5) Å. Within the $\pi\text{-}C_5H_5Co$ system, Co–C = 2·020(5)

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† Using the equally acceptable *closo* nomenclature (ref. 2), this molecule is 1-(π-cyclopentadienyl)dodecahydro-1-cobalta-2,4-dicarba-*closo*-tridecaborane.

‡ In icosahedral metallo-carborane complexes, typical distances are B–B = 1·78, B–C = 1·72, C–C = 1·61 Å (see ref. 3).

—2·057(3), C–C = 1·388(6)—1·422(7), and C–H = 0·90(4)—1·23(7) Å.

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[1] G. B. Dunks, M. M. McKown, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1971, **93**, 2541.

[2] *Inorg. Chem.*, 1968, **7**, 1945.

[3] M. R. Churchill and A. H. Reis, *J.C.S. Dalton*, 1972, 1317, see, especially, Table 6 on p. 1320.

[4] W. N. Lipscomb, *Science*, 1966, **153**, 373.

[5] M. F. Hawthorne, personal communication.