From the cell dimensions, density (>10.6 g/cm^3), and chemical stability (stable toward attack by aqua regia) it is possible that this phase is related to the bronzes but clearly single crystals will have to be obtained to elucidate such a relationship.

Registry No. $CdCO_3$, 513-78-0; $(NH_4)_2PtCl_6$, 16919-58-7; Na_2CO_3, 497-19-8; Pt, 7440-06-4; $NaNO_3$, 7631-99-4; H_2PtCl_6, 16941-12-1; $CaCO_3$, 471-34-1; BaO_2, 1304-29-6; $Cd_xPt_3O_4$, 39394-68-8; $CdPt_3O_6$, 12590-34-0; $NaPt_3O_4$, 50864-26-1; $Na_xPt_3O_4$, 50958-14-0; α-PtO_2, 1314-15-4; $CaPt_2O_4$, 39394-82-6; Pt_3O_4, 12137-40-5; Pt_5O_6, 51021-61-5; $CoPtO_2$, 12516-23-3; $Ni_{0.25}Pt_3O_4$, 37295-01-5; Ag_3PO_4, 7784-09-0; Ag_3AsO_4, 13510-44-6.

(40) M_{20}, the reliability index, is defined by P. M. deWolff, *J. Appl. Crystallogr.*, 1, 108 (1968); 5, 243 (1972).

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Structures of Metallocarboranes. I. Crystal and Molecular Structure of 2,6-Di-η-cyclopentadienyloctahydro-1,10-dicarba-2,6-dicobalta-*closo*-decaborane at −150°, a Bimetallocarborane with a Metal–Metal Bond

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The crystal and molecular structure of 2,6-di-η-cyclopentadienyloctahydro-1,10-dicarba-2,6-dicobalta-*closo*-decaborane, 2,6-(η-C_5H_5)$_2$-2,6-Co_2-1,10-$C_2B_6H_8$, has been determined at −150° by single-crystal X-ray diffraction methods. The molecule crystallizes as green slabs in the monoclinic space group *C*2/*c* with eight molecules per unit cell. At 23° $a = 28.47$ (2) Å, $b = 8.46$ (1) Å, $c = 15.28$ (1) Å, and $\beta = 129.43$ (3)° ($\rho_{\text{calcd}} = 1.61$ g/cm^3, $\rho_{\text{obsd}} = 1.60$ (1) g/cm^3). At −150° $a = 28.101$ (5) Å, $b = 8.351$ (2) Å, $c = 15.154$ (5) Å, and $\beta = 129.28$ (2)° ($\rho_{\text{calcd}} = 1.66$ g/cm^3). The structure was solved by direct methods and refined with 1372 reflections greater than $3\sigma(I)$ collected to $2\theta = 45°$ (Mo Kα radiation) on a Syntex $P\bar{1}$ diffractometer. The final discrepancy indices are $R = 0.034$ and $R_w = 0.043$. The polyhedral framework is a distorted bicapped square antiprism with carbons at the caps and one cobalt in each tropical plane. The cobalt atoms are joined by a 2.489 (1) Å bond, the first confirmed metal–metal bond in a bimetallocarborane.

Introduction

The crystal structures of bimetallocarboranes had been determined prior to this work in only two cases.[1,2] In both cases the complexes contained the same polyhedral framework, {3,6-Co_2-1,2-$C_2B_8H_{10}$}, and they were both prepared by the same method, base degradation of [3,3′-Co(1,2-$C_2B_9H_{11}$)$_2$]$^-$ followed by complexation of another metal. In these complexes the metal atoms are nonadjacent.

Other bimetallocarboranes are known,[3-8] and prior to preliminary disclosure of the results of this work,[9] they were in all cases assigned probable structures in accord with the structural precedents, *i.e.*, nonadjacent metal atoms.[10] However, most of the bimetallics reported since 1970 have been prepared by polyhedral expansion,[7] an entirely different route from that used to prepare the molecules whose structures were determined.[1,2]

Since the known structures were not necessarily good models for the products of polyhedral expansion, the structural investigation of (η-C_5H_5)$_2Co_2C_2B_6H_8$, a polyhedral expansion product,[3] was undertaken. The results described herein provide direct structural information on the stereochemical course of this reaction.

Experimental Section

Very dark green crystals of 2,6-(η-C_5H_5)$_2$-2,6-Co_2-1,10-$C_2B_6H_8$,[12] prepared by Dunks,[3] were used without modification. Despite 2 years of atmospheric storage, no evidence of decomposition was observed.

Precession and Weissenberg photographs were taken of a plate-shaped fragment cut from a long slab. The systematic absence of reflections *hkl* for $h + k \neq 2n$ and *h0l* for $h \neq 2n$, $l \neq 2n$ indicated the space group to be either *Cc* or *C*2/*c*. The space group was assigned as *C*2/*c* based on the successful solution and refinement described herein.

Unit cell parameters were determined by least-squares refinement of 13 reflections which were accurately centered on a Syntex $P\bar{1}$ four-circle diffractometer with Mo Kα radiation and Syntex software. At 23° the lattice parameters are $a = 28.47$ (2), $b = 8.46$ (1), $c = 15.28$ (1) Å, and $\beta = 129.43$ (3)°; at −150° they are $a = 28.101$ (5), $b = 8.351$ (2), $c = 15.154$ (5) Å, and $\beta = 129.28$ (2)°. The calculated densities at 23° and −150° ($Z = 8$) are 1.61 and 1.66 g/cm^3, respectively, while the density determined by flotation in carbon tetrachloride–hexane at 23° is 1.60 (1) g/cm^3.

The structure was first solved with a set of data collected at 23° (1297 reflections with $F_o > 3\sigma(F_o)$, $2\theta \leqslant 50°$). However, check reflections for this set indicated significant decomposition in the X-ray beam, losing from 10 to 90% of their original intensity in 114 hr of exposure. The final structure determined from this set of data had an *R* factor and estimated standard deviations larger than acceptable, so final refinements were based on a set of data collected at −150°.

For the low-temperature data collection a fragment of approximately rectangular dimensions 0.13 × 0.22 × 0.26 mm was cut from

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[2] M. R. Churchill, A. H. Reis, Jr., J. N. Francis, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 92, 4993 (1970).

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[6] V. R. Miller and R. N. Grimes, *J. Amer. Chem. Soc.*, 95, 2830 (1973).

[7] W. J. Evans, G. B. Dunks, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 95, 4565 (1973).

[8] A bimetalloborane has also recently been reported: V. R. Miller and R. N. Grimes, *J. Amer. Chem. Soc.*, 95, 5079 (1973).

[9] (a) M. F. Hawthorne and G. B. Dunks, *Science*, 178, 462 (1972); (b) M. F. Hawthorne, *Pure Appl. Chem.*, 33, 475 (1973).

[10] Most of the bimetallic species reported since preliminary disclosure of this work have proposed structures containing metal–metal bonds[6-8] and in one other case this has now been confirmed.[11]

[11] K. P. Callahan, C. E. Strouse, A. L. Sims, and M. F. Hawthorne, *Inorg. Chem.*, 13, 1397 (1974).

[12] The other enantiomer of this compound, 2,9-(η-C_5H_5)$_2$-2,9-Co_2-1,10-$C_2B_6H_8$, was of course present in equal amount.

a longer slab and mounted, with a^* approximately along the spindle axis, in a glass capillary on a glass fiber with a light mineral oil coat to hold it motionless when cooled. The Syntex diffractometer was equipped with a locally constructed variable-temperature cooling device. The sample temperature was maintained at −150 ± 5°. Temperature stability was better than ±0.5°.

Graphite crystal monochromatized Mo Kα radiation (λ 0.71069 Å) was utilized for data collection. A scan rate of 2.4°/min was employed over a scan interval from 1.0° below Mo Kα_1 to 1.0° above Mo Kα_2 with the θ-2θ scan technique. The ratio of time spent in counting background to time spent in counting the reflection was 0.8. The scintillation counter was 19.5 cm from the crystal and was equipped with a 1-mm collimator. A 4° takeoff angle was employed.

The intensities of 1922 independent reflections with h and k nonnegative were collected to $2\theta = 45°$; of these, the 1372 reflections with $I > 3\sigma(I)$ were used in refinement. Standard deviations were assigned to the intensities by the formula $\sigma(I) = [\sigma_s^2 + (0.04I)^2]^{1/2}$ where σ_s is the standard deviation in the intensity from counting statistics and $I = \mathrm{CT} - (t_c/t_b)(B_1 + B_2)/2$, where CT is the total integrated peak count, t_c and t_b are the times spent in counting the scan and background, respectively, and B_1 and B_2 are the background counts on the low and high sides of the peak. Check reflections for this set of data lost less than 6% of their original intensity in 55 hr of exposure.

The absorption coefficient for the compound with Mo Kα radiation is 24.8 cm^{-1}. The crystal faces were identified as $\{100\}$, $\{\bar{1}00\}$, $\{010\}$, $\{0\bar{1}0\}$, $\{10\bar{1}\}$, $\{\bar{1}01\}$, and $\{\bar{2}01\}$ and from careful measurements an absorption correction was made. The transmission factors ranged from 0.772 to 0.868. The usual Lorentz and polarization corrections were also applied.

Solution and Refinement of Structure

Direct methods were used for the structure determination. A set of normalized structure factors (E's) were calculated from a Wilson plot with an unpublished program of H. S. Maddox and M. L. Maddox.[13] From 296 reflections having E greater than 1.60, two sets of highly consistent signs were obtained with Long's phase determination program.[14] One set was discarded because the electron density map calculated from the signed E's was not chemically reasonable. An electron density map based on the other set of signs yielded the positions of the heavy atoms.

The cobalt atom positions were used to phase the 1297 room-temperature reflections ($R = [\Sigma ||F_o| - |F_c||/\Sigma |F_o|] = 0.64$), but the electron density map constructed from this set of reflections had a false mirror between the cobalt atoms. A new map, constructed from a set of reflections phased on only one cobalt position ($R = 0.55$), located the other cobalt atom and both cyclopentadienyl rings. From a third map, based on reflections phased on both cobalt atoms and both cyclopentadienyl rings, the eight other cage atoms were located.

At this stage all cage atoms other than cobalt were assigned the scattering factor of boron. Full-matrix least-squares refinement of the scale factor, the positional parameters, and the isotropic thermal parameters of the 20 nonhydrogen atoms reduced R to 0.107. With anisotropic thermal parameters for the cobalt atoms and cyclopentadienyl carbon atoms, R was reduced to 0.078. At this point the cage atoms were examined to determine the carbon positions. On the basis of smallest thermal parameters and shortest bond lengths, the carbon atoms were assigned unequivocally to the apical positions, and these atoms were given the scattering factors of carbon in all further refinements.

With all 20 heavy atoms anisotropic, the room-temperature data refined to $R = 0.074$ and $R_w = [\Sigma w ||F_o| - |F_c||^2/\Sigma w |F_o|^2]^{1/2} = 0.094$, where $w = 1/\sigma(F_o)^2$. Estimated standard deviations in bond lengths ranged from 0.02 to 0.03 Å. At this point, the low-temperature data set described above was collected. Starting with the parameters determined at room temperature, the low-temperature structure refined from a first cycle R of 0.40 to convergence at 0.049 ($R_w = 0.065$).

Hydrogen atoms were then included in calculated positions as follows. Hydrogen atoms attached to boron were placed 1.1 Å along a line from the center of the triangular face on the opposite side of the cage through the boron atom. Hydrogen atoms attached to C1 and C10 were placed 1.0 Å from these atoms along a line passing through them from the other apex. The cyclopentadienyl hydrogen atoms were placed 1.0 Å from each carbon atom along a line which passed through the carbon atom from the center of the ring. The hydrogen atoms were all assigned isotropic thermal parameters of 2.0 Å^2. Hydrogen atom parameters were included in the structure factor calculations in subsequent refinements but were not themselves refined.

The refinement of the scale factor and the positional and anisotropic thermal parameters of all nonhydrogen atoms converged to $R = 0.034$ and $R_w = 0.043$. The standard deviation of an observation of unit weight was 1.54.

Scattering factors for least-squares refinement were those of Cromer and Waber[15] for neutral carbon and boron and for cobalt in the +3 oxidation state. The cobalt scattering factor curve was corrected for both real and imaginary components of anomalous dispersion.[16] Hydrogen scattering factors were those of Stewart, Davidson, and Simpson.[17]

Final positional and thermal parameters are listed in Tables I and II. A table of observed and calculated structure factors is available.[18]

Description of the Structure and Discussion

The molecular structure of $2,9\text{-}(\eta\text{-}C_5H_5)_2\text{-}2,9\text{-}Co_2\text{-}1,10\text{-}C_2B_6H_8$[19] shown in Figure 1 is as expected a distorted bicapped square antiprism, in common with other ten-atom polyhedral boranes,[20] carboranes,[21] and metallocarboranes[22] of known structure. However, the structure is not the one originally proposed, which contained nonadjacent metal atoms.[3] Instead, the molecule exhibits the first endopolyhedral metal–metal bond observed in bimetallocarboranes.

The important intramolecular distances and angles are tabulated in Tables III and IV. The idealized molecular symmetry is C_2, and for comparison the bond lengths and angles which are related by the twofold rotation are listed in the same rows in the tables. The deviations from C_2 symmetry are small but statistically significant in a number of cases. These deviations are attributed to crystal packing forces.

Since the cobalt–cobalt bond in $2,6\text{-}(\eta\text{-}C_5H_5)_2\text{-}2,6\text{-}Co_2\text{-}1,10\text{-}C_2B_6H_8$ is the first confirmed metal–metal bond in a polyhedral borane or carborane, comparisons of bond lengths must be made with metal–metal bonds in a different class of compounds. The range of bond lengths for cobalt–cobalt bonds in normal cobalt cluster compounds is about 2.43–2.55 Å.[23,24] The 2.489 (1) Å value found in this work lies in this range.

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[13] Other programs used in this work include locally written data reduction programs; a phase determination program written by R. E. Long;[14] UCSF, a local structure factor calculator; JBPATT, JBFOUR, and PEAKLIST, modified versions of Fourier programs written by J. Blount; a local version of ORFLS (Busing, Martin, and Levy) for structure factor calculations and full-matrix least-squares refinement; ABSN (Coppens) for absorption corrections; ORTEP (Johnson) for structural drawing; MGTL (Gantzel and Trueblood) for least-squares planes; a local version of ORFFE (Busing, Martin, and Levy) for distance, angle, and error calculations; and PUBLIST (E. L. Hoel) for the table of observed and calculated structure factor amplitudes. All calculations were performed on an IBM 360-91 computer.

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[15] D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 18, 104 (1965).

[16] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 53, 1891 (1970).

[17] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

[18] See paragraph at end of paper regarding supplementary material.

[19] The enantiomer of this compound, $2,6\text{-}(\eta\text{-}C_5H_5)_2\text{-}2,6\text{-}Co_2\text{-}1,10\text{-}C_2B_6H_8$ has the lower numbering by IUPAC rules: R. M. Adams, *Pure Appl. Chem.*, 30, 683 (1972).

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[21] T. F. Koetzle and W. N. Lipscomb, *Inorg. Chem.*, 9, 2279 (1970).

[22] D. St. Clair, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, 11, 377 (1972).

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[24] B. R. Penfold, *Perspect. Struct. Chem.*, 2, 71 (1968).

Table I. Positional and Thermal Parameters for All Atoms except Hydrogens[a,b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co2	0.12434 (3)	0.26812 (8)	0.44554 (6)	7.6 (2)	28 (1)	24.8 (6)	0.8 (3)	8.6 (3)	1.2 (6)
Co9	0.12213 (3)	0.28674 (8)	0.60684 (6)	7.8 (2)	38 (1)	22.8 (6)	0.0 (3)	8.8 (3)	0.4 (6)
C1	0.0833 (2)	0.4693 (6)	0.3846 (5)	8 (1)	36 (8)	31 (5)	0 (2)	9 (2)	5 (5)
C10	0.1778 (3)	0.4636 (6)	0.6734 (5)	11 (1)	53 (9)	34 (5)	1 (3)	14 (2)	−4 (5)
B3	0.1558 (3)	0.5074 (7)	0.4690 (5)	4 (1)	35 (9)	33 (5)	2 (3)	6 (2)	5 (6)
B4	0.0968 (3)	0.6127 (7)	0.4665 (6)	8 (1)	29 (9)	47 (6)	3 (3)	13 (3)	5 (6)
B5	0.0611 (3)	0.4213 (7)	0.4555 (5)	7 (1)	25 (9)	27 (5)	5 (3)	9 (2)	3 (5)
B6	0.1951 (3)	0.3822 (7)	0.6024 (5)	3 (1)	47 (10)	28 (5)	0 (3)	4 (2)	4 (5)
B7	0.1747 (3)	0.5968 (7)	0.5945 (6)	7 (1)	44 (10)	38 (6)	−3 (3)	7 (3)	−9 (6)
B8	0.1093 (3)	0.5382 (8)	0.5903 (6)	11 (2)	41 (10)	42 (6)	−4 (3)	14 (3)	−5 (6)
CP1	0.1452 (2)	0.0255 (6)	0.4607 (5)	11 (1)	40 (8)	27 (5)	−1 (3)	11 (2)	−6 (5)
CP2	0.0824 (3)	0.0543 (6)	0.3616 (5)	10 (1)	47 (8)	33 (5)	−2 (3)	12 (2)	−9 (5)
CP3	0.0831 (3)	0.1588 (7)	0.2890 (4)	16 (2)	57 (9)	22 (4)	3 (3)	13 (2)	−4 (5)
CP4	0.1449 (2)	0.1988 (6)	0.3427 (5)	9 (1)	54 (9)	32 (4)	−1 (3)	12 (2)	−3 (5)
CP5	0.1833 (2)	0.1161 (6)	0.4489 (4)	8 (1)	46 (8)	32 (5)	4 (3)	9 (2)	−5 (5)
CP6	0.0848 (3)	0.0630 (6)	0.5838 (5)	13 (2)	57 (9)	38 (5)	−11 (3)	17 (2)	−3 (5)
CP7	0.1473 (3)	0.0638 (7)	0.6848 (5)	11 (1)	68 (9)	35 (5)	1 (3)	12 (2)	17 (5)
CP8	0.1526 (3)	0.1798 (7)	0.7576 (5)	12 (2)	106 (10)	26 (4)	7 (3)	10 (2)	9 (6)
CP9	0.0944 (3)	0.2520 (7)	0.7023 (5)	16 (2)	93 (10)	44 (5)	−5 (3)	23 (2)	−6 (6)
CP10	0.0524 (2)	0.1806 (7)	0.5943 (5)	7 (1)	93 (10)	42 (5)	1 (3)	11 (2)	18 (5)

[a] The β_{ij}'s have been multiplied by 10^4. The anisotropic temperature factors are of the form $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] The numbers in parentheses are the estimated standard deviations in the last digits.

Table II. Atomic Parameters for Hydrogen Atoms[a]

Atom	x	y	z
HC1	0.0553	0.4698	0.2989
HC10	0.2067	0.4620	0.7600
HB3	0.1796	0.5456	0.4365
HB4	0.0767	0.7320	0.4326
HB5	0.0131	0.3892	0.4135
HB6	0.2397	0.3227	0.6437
HB7	0.2037	0.7054	0.6313
HB8	0.0896	0.6004	0.6240
HCP1	0.1597	−0.0452	0.5297
HCP2	0.0444	0.0072	0.3458
HCP3	0.0450	0.1990	0.2115
HCP4	0.1595	0.2725	0.3109
HCP5	0.2299	0.1205	0.5064
HCP6	0.0606	−0.0081	0.5141
HCP7	0.1825	−0.0031	0.7021
HCP8	0.1926	0.2060	0.8368
HCP9	0.0846	0.3406	0.7345
HCP10	0.0073	0.2071	0.5342

[a] Hydrogen atoms are in calculated positions with C–H = 1.0 Å and B–H = 1.1 Å.

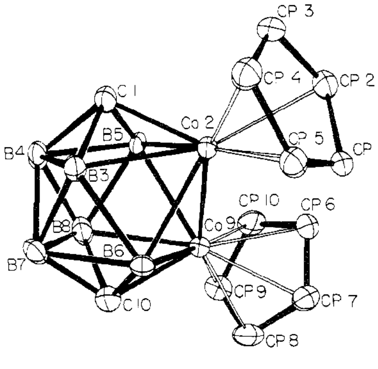

Figure 1. An ORTEP drawing of $2,9\text{-}(\eta\text{-}C_5H_5)_2\text{-}2,9\text{-}Co_2\text{-}1,10\text{-}C_2B_6H_8$ showing the labeling used in this paper and 50% probability ellipsoids for all nonhydrogen atoms. Each atom except cobalt is also bound to a hydrogen atom which has been omitted for clarity.

Table III. Interatomic Distances within $2,6\text{-}(\eta\text{-}C_5H_5)\text{-}2,6\text{-}Co_2\text{-}1,10\text{-}C_2B_6H_8$[a,b]

Atoms	Dist, Å	Atoms	Dist, Å
Distances from Cobalt Atoms			
Co2–Co9	2.489 (1)		
Co2–C1	1.912 (5)	Co9–C10	1.910 (5)
Co2–B3	2.122 (6)	Co9–B8	2.118 (7)
Co2–B5	2.270 (6)	Co9–B6	2.239 (6)
Co2–B6	2.127 (6)	Co9–B5	2.117 (6)
Co2–CP1	2.081 (5)	Co9–CP6	2.062 (5)
Co2–CP2	2.073 (5)	Co9–CP7	2.075 (6)
Co2–CP3	2.080 (5)	Co9–CP8	2.067 (6)
Co2–CP4	2.059 (6)	Co9–CP9	2.051 (6)
Co2–CP5	2.063 (5)	Co9–CP10	2.048 (5)
Carbon–Boron Distances			
C1–B3	1.608 (8)	C10–B8	1.615 (9)
C1–B4	1.588 (8)	C10–B7	1.595 (9)
C1–B5	1.598 (8)	C10–B6	1.587 (8)
Boron–Boron Distances			
B3–B4	1.855 (9)	B7–B8	1.863 (9)
B3–B6	1.891 (8)	B5–B8	1.859 (9)
B3–B7	1.783 (9)	B4–B8	1.788 (9)
B4–B5	1.837 (8)	B6–B7	1.863 (8)
B4–B7	1.787 (9)		
Carbon–Carbon Distances			
CP1–CP2	1.438 (8)	CP6–CP7	1.422 (8)
CP2–CP3	1.414 (8)	CP7–CP8	1.402 (9)
CP3–CP4	1.413 (8)	CP8–CP9	1.416 (8)
CP4–CP5	1.426 (8)	CP9–CP10	1.408 (8)
CP5–CP1	1.413 (8)	CP10–CP6	1.415 (8)

[a] The numbers in parentheses are the estimated standard deviations in the last digits. [b] The distances in the second column are those related by the molecular (noncrystallographic) C_2 axis to those in the first column.

The validity of a comparison of the bonding in polyhedral boranes, carboranes, and metallocarboranes to that in metal clusters has been discussed by several authors.[25-28] These authors observed that the structure of polyhedral boranes, heteropolyhedral boranes, and metal clusters could in most cases be correlated with the number of framework bonding electrons if certain rules for counting electrons were observed. The conclusion of their discussion was that molecules with n polyhedral atoms and $2n + 2$ framework electrons adopt closo deltahedron structures, while those with $2n + 4$ and $2n + 6$ framework electrons adopt nido and arachno structures, respectively. Some theoretical justification for these

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(27) D. M. P. Mingos, *Nature (London), Phys. Sci.*, 236, 99 (1972).

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Table IV. Selected Bond Angles within 2,6-(η-C_5H_5)-2,6-Co_2-1,10-$C_2B_6H_8$[a,b]

Atoms	Angle about atom, deg				
	1	2	3	4	5
		Part A			
		Angle around Three-Membered Rings			
C1, Co2, B3	73.6 (3)	46.6 (2)	59.8 (3)		
C1, B3, B4	71.0 (9)	54.0 (3)	55.0 (3)		
C1, B4, B5	70.4 (4)	55.0 (3)	54.5 (3)		
C1, B5, Co2	80.0 (3)	56.1 (3)	43.9 (2)		
B3, Co2, B6	63.7 (3)	52.8 (2)	63.4 (3)		
B3, B6, B7	60.8 (3)	56.7 (3)	62.4 (3)		
B3, B4, B7	58.8 (4)	58.6 (4)	62.6 (4)		
Co2, Co9, B6	57.4 (2)	53.2 (2)	69.4 (2)		
		Angles around Four-Membered Rings			
Co2, B3, B4, B5	73.7 (2)	99.8 (3)	91.1 (4)	95.2 (3)	
		Angles around Five-Membered Rings			
C1, Co2, B6, B7, B4	120.8 (4)	89.9 (2)	109.1 (4)	104.8 (4)	108.4 (5)
C1, B3, B7, B8, B5	110.6 (4)	107.6 (5)	103.4 (4)	101.1 (4)	106.5 (4)
C1, B4, B8, Co9, Co2	120.8 (4)	110.4 (4)	112.0 (4)	93.1 (2)	92.1 (2)
C1, B5, Co9, B6, B3	110.6 (4)	117.9 (4)	84.7 (2)	107.7 (3)	109.2 (4)
CP1, CP2, CP3, CP4, CP5	107.8 (5)	107.7 (5)	108.3 (5)	108.2 (5)	107.9 (5)
		Part B			
		Angles around Three-Membered Rings			
C10, Co9, B8	73.3 (3)	46.9 (2)	59.7 (3)		
C10, B8, B7	71.0 (4)	54.0 (3)	55.0 (4)		
C10, B7, B6	71.7 (4)	54.0 (4)	54.4 (4)		
C10, B6, Co9	79.0 (3)	56.9 (3)	44.1 (2)		
B8, Co9, B5	63.9 (3)	52.1 (2)	64.0 (3)		
B8, B5, B4	60.4 (4)	57.8 (3)	61.7 (3)		
B8, B7, B4	58.6 (4)	58.6 (4)	62.8 (4)		
Co9, Co2, B5	58.4 (2)	52.6 (2)	69.0 (2)		
		Angles around Four-Membered Rings			
Co9, B8, B7, B6	74.6 (2)	99.6 (4)	90.3 (4)	95.4 (3)	
		Angles around Five-Membered Rings			
C10, Co9, B5, B4, B7	120.4 (4)	89.6 (2)	110.0 (4)	104.9 (4)	108.3 (5)
C10, B8, B4, B3, B6	111.2 (5)	107.3 (5)	103.6 (9)	101.1 (4)	105.4 (4)
C10, B7, B3, Co2, Co9	120.4 (4)	110.2 (4)	112.6 (4)	92.5 (2)	92.6 (2)
C10, B6, Co2, B5, B8	111.2 (5)	118.6 (4)	83.7 (2)	108.2 (3)	109.5 (4)
CP6, CP7, CP8, CP9, CP10	108.7 (5)	107.1 (5)	108.7 (5)	108.2 (5)	107.3 (5)

[a] The numbers in parentheses are the estimated standard deviations in the last digits. [b] The angles in the top half (part A) of the table are those related by the molecular (noncrystallographic) C_2 axis to those in the bottom half (part B).

Table V. Comparison of C-B and B-B Bonds in Ten-Atom Polyhedra[a]

Molecule	Polar C-B	Tropical B-B	Equatorial B-B	Ref
2,9-(η-C_5H_5)-2,9-Co_2-1,10-$C_2B_6H_8$	1.587 (8)-1.615 (9)	1.837 (8)-1.863 (9)	1.783 (9)-1.788 (9)[b]	c
2,2′-Co(1,6-$C_2B_7H_9$)$^-$	1.57 (2)-1.64 (2)	1.87 (2)-1.89 (2)	1.79 (2)-1.90 (2)[d]	22
1,6-$(CH_3)_2$-1,6-$C_2B_8H_8$	1.588 (7)-1.611 (6)	1.808 (7)-1.861 (7)	1.787 (7)-1.828 (7)	21
$Cu_2B_{10}H_{10}$		1.80 (3)-1.90 (3)	1.78 (3)-1.84 (3)	20a
$B_{20}H_{18}NO^{3-}$		1.81 (4)-1.92 (4)	1.79 (4)-1.86 (4)	20b

[a] "Polar" bonds are those to the apices; "tropical" bonds are those in the square base of an apex; "equatorial" bonds are those between the two squares (according to ref 22). Bond length ranges are in angstroms. [b] Does not include bonds between atoms bonded to cobalt; if these are included, the range is 1.783 (9)-1.891 (8) Å. [c] This work. [d] Does not include bonds between atoms bonded to cobalt, which in this study were disordered B-B and B-C.

empirical concepts has been advanced.[29] In the particular case of cobaltacarboranes, the {(η-C_5H_5)Co} unit has been proposed to be electronically equivalent to the {BH} unit in that both are two-electron, three-orbital donors to the polyhedral bonding. This concept is supported by the stability of mono- and bimetallic cobaltacarboranes in various polyhedral arrangements. In the present case, the adjacency of the cobalt atoms is another example of the formal equivalence of {(η-C_5H_5)Co} and {BH}, since this bimetallic complex is formally related to 1,10-$C_2B_8H_{10}$ by the replacement of {BH} at two positions. The cobalt-cobalt bond length suggests that the metal-metal bonding is similar to that in $2n + 2$ electron cobalt clusters. Another way to view the equivalence of {BH} and {(η-C_5H_5)Co} is that both require four electrons to achieve an inert gas configuration.

The other bond lengths within the cage correlate well in general with the analogous bonds in [2,2′-Co(1,6-$C_2B_7H_9$)$_2$]$^-$,[22] 1,6-$(CH_3)_2$-1,6-$C_2B_8H_8$,[21] $Cu_2B_{10}H_{10}$,[20a] and [$B_{20}H_{18}NO$]$^{3-}$ [20b] (Table V). The most significant deviations are (1) the B-B bonds between boron atoms bonded to cobalt (B3-B6 and B5-B9) average 1.875 Å, which is 0.09 Å longer than the average of the other three equatorial[30] B-B bonds, and (2) the Co2-B5 and Co9-B6 bonds average 2.255 Å, which is 0.10 Å longer than the 2.15 Å typical for Co-B bonds in both ten- and twelve-atom polyhedra.[1,2,22]

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[29] R. W. Rudolph and W. R. Pretzer, *Inorg. Chem.*, 11, 1974 (1972).

[30] See footnote *a*, Table V.

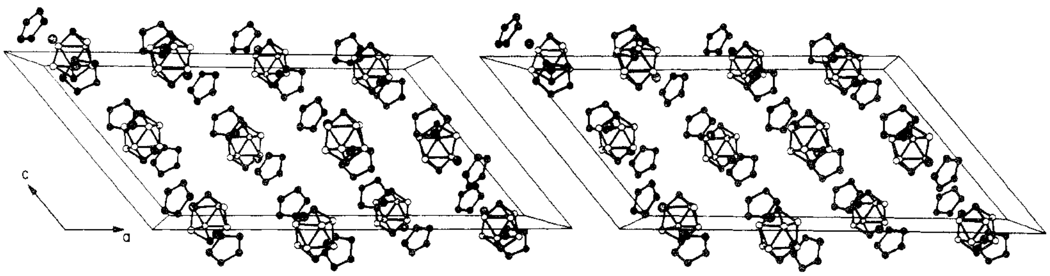

Figure 2. Steropair showing the crystal structure of 2,9-(η-C_5H_5)$_2$-2,9-Co_2-1,10-$C_2B_6H_8$ (and its enantiomer[19]) viewed down the *b* axis. Black circles are carbon, open circles are boron, and stippled circles are cobalt. Hydrogens are omitted for clarity.

These long bonds and the 5.5° dihedral angle between the planes formed by atoms B3, B4, B5 and B6, B7, B8 (Table VI) are all distortions consistent with the spatial requirements of the relatively longer metal-metal bond in the polyhedron. The Co-C bond lengths in the cage average 1.911 Å, in good agreement with 1.93 (1) Å for the equivalent bond in [2,2′-Co(1,6-$C_2B_7H_9$)$_2$]$^-$,[22] but significantly shorter than the 2.06 (1) Å bond length found in icosahedral systems.[1,2]

Both cyclopentadienyl rings possess D_{5h} symmetry within experimental error. The average C-C bond length is 1.417 Å, which is just slightly shorter than the accepted value of 1.43 Å.[31] Similar results in other systems have been attributed to librational motion in the ring.[31] The cobalt-cyclopentadienyl carbon distances average 2.066 Å, typical of those observed in other cyclopentadienyl cobalt complexes.[32]

The crystal packing of the unit cell is shown in stereoview in Figure 2. The shortest intermolecular contacts are 2.205 Å between HB5 and HCP3, 2.271 Å between HCP9 and HC1 and 2.273 Å between HCP6 and HCP10. All other contacts are greater than 2.34 Å. As Figure 2 shows, the molecules are arranged in planes parallel to the *bc* plane, with offsets to minimize interplanar contacts. The plane of molecules between $x = 0$ and $x = {}^1/_4$ is shown in Figure 3 projected onto the *bc* plane. An interesting feature of the packing in this plane is the face-to-face stacking of the cyclopentadienyl rings. Closest contacts between cyclopentadienyl carbons in these rings range from 3.478 Å for CP5-CP8 and CP4-CP7 to 3.703 Å for CP3-CP10. These may be compared to the shortest interplanar carbon-carbon separation in graphite of 3.40 Å[33] and to the closest known separation of aromatic rings, in [2.2]paracyclophane, of 3.09 Å.[34] Of course, the intermolecular contacts at −150° are somewhat reduced from the room temperature contacts as indicated by the unit cell parameters.

The results of this and related work[11] show that metallocarboranes produced by polyhedral expansion reactions can contain metal-metal bonds between metal atoms on adjacent vertices of the polyhedra. Such species have not yet been produced by other methods of bimetallocarborane synthesis.

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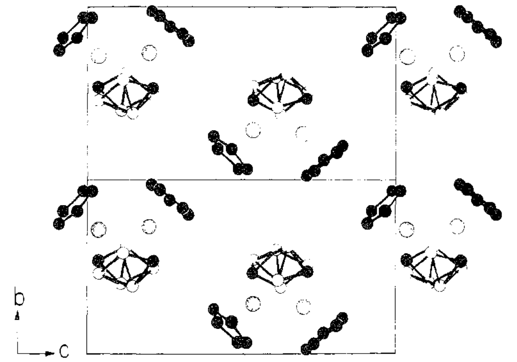

Figure 3. Projection of one plane of molecules (those with $0 \leqslant x \leqslant {}^1/_4$) onto the *bc* plane, showing face-to-face stacking of cyclopentadienyls. Black circles are carbon, open circles are boron and stippled circles are cobalt. Hydrogens are omitted for clarity.

Table VI. Selected Least-Squares Planes within 2,6-(η-C_5H_5)$_2$-2,6-Co_2-1,10-$C_2B_6H_8$$^{a-c}$

Atom	Dev from plane, Å	Atom	Dev from plane, Å
Plane I:	$-0.0468X - 0.0544Y + 0.9974Z - 5.2625 = 0$		
B3*	0.000	B5*	0.000
B4*	0.000	Co2	−0.135
Plane II:	$-0.0385X + 0.0407Y + 0.9984Z - 7.1966 = 0$		
B6*	0.000	B8*	0.000
B7*	0.000	Co9	0.100
Plane III:	$-0.4363X + 0.7784Y + 0.4513Z - 2.761 = 0$		
CP1*	−0.007	CP4*	0.004
CP2*	0.009	CP5*	0.002
CP3*	−0.008	Co2	1.682
Plane IV:	$-0.6081X - 0.6867Y + 0.3983Z - 4.3178 = 0$		
CP6*	0.006	CP9*	0.002
CP7*	−0.005	CP10*	−0.005
CP8*	0.002	Co9	−1.674

[a] Planes are defined as $C_1X + C_2Y + C_3Z + d = 0$, where X, Y, Z are cartesian coordinates related to the monoclinic fractional coordinates x, y, z by the transformation $[X, Y, Z] = [xa + zc \cos \beta, yb, zc \sin \beta]$. Dihedral angles between two planes are then given by $\cos^{-1} [C_1C_1' + C_2C_2' + C_3C_3']$, and the deviation of an atom at X', Y', Z' from a plane is $[C_1X' + C_2Y' + C_3Z + d]$ Å. [b] Least-squares planes were calculated with unit weights for all atoms marked with an asterisk and zero weights for all other atoms. [c] The dihedral angle between planes I and II is 5.5°.

Registry No. 2,6-(η-C_5H_5)$_2$-2,6-Co_2-1,10-$C_2B_6H_8$, 39475-08-6; $(C_5H_5)_2Co_2C_2B_6H_8$, 11077-53-5.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1388.

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