cule. Figure 2 shows the molecular packing. The positional and thermal vibration parameters are listed in Tables I and II. Bond distances are given in Table III and bond angles in Table IV. There are no abnormal intermolecular contacts.

The corresponding dimensions of the two independent molecules agree throughout to within the uncertainties, thus indicating that both are representative of the inherent, unperturbed structure which the cis isomer might be expected to have when dissolved in a solvent of low polarity.

On nearly all points where comparisons can be made the present structure is closely similar to that of cis-$(\eta^5\text{-}C_5H_5)$-$Fe_2(CO)_4$, 3. Thus, the Fe-Fe distance in 3 is 2.531 (2) Å which is only about 0.015 Å different from the average value for the present case. The iron to bridging carbonyl distances in 3 have an average value of 1.92 Å, while the average of those found here is 1.90 ± 0.02 Å. In 3, the central four-membered ring is folded along the Fe-Fe line to give a dihedral angle of 164°, and angles in the range of 160-164° have been found in other cases. In the present compound the average value of this angle is 159 (1)°. All other bond lengths have values which may be considered normal.

Few accurate crystal structures of compounds containing coordinated triphenyl phosphite have been reported.[23] A

very accurate structure of a presumably representative compound is that of $Cr(CO)_5[P(OPh)_3]$. The mean values of the P-O distance, the O-C distance, and the P-O-C angle are 1.598 Å, 1.399 Å and 127°. These may be compared with the following values for the present compound: 1.61 Å, 1.38 Å, and 125°. Clearly, the dimensions of the $P(OPh)_3$ ligand found here are quite normal.

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, 24X 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 $5.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1407.

(23) H. J. Plastas, J. M. Stewart, and S. O. Grim, *Inorg. Chem.*, 12, 265 (1973), and references therein.

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X-Ray Crystallographic Elucidation of the Structure of (*Pentahapto*cyclopentadienyl)(7,8,9,10,11,12-*hexahapto*dodecahydro-7,9-dicarba-*nido*-dodecaborato)cobalt(III), a Fluxional Molecule Containing a Triangulated 13 Vertex (1,5,6,1) Docosahedral Cage

MELVYN ROWEN CHURCHILL* and BARRY G. DeBOER

The "red" isomer of $(\pi\text{-}C_5H_5)Co(B_{10}C_2H_{12})$, synthesized and found to be "fluxional" by Hawthorne and coworkers, has been subjected to a single-crystal X-ray diffraction study. The species crystallizes as dark red rhombic plates in the non-centrosymmetric orthorhombic space group $Pca2_1$ $[C_{2v}^5$; No. 29] with $a = 13.744$ (4) Å, $b = 7.047$ (2) Å, $c = 13.620$ (3) Å, $\rho_{obsd} = 1.348$ (5) g cm^{-3}, and $\rho_{calcd} = 1.351$ g cm^{-3} for $Z = 4$. X-Ray data complete to $2\theta = 50°$ (Mo Kα radiation) were collected with a Picker FACS-1 diffractometer. All atoms, including hydrogen atoms, have been located, the final discrepancy indices being $R_F = 3.02\%$ and $R_{wF} = 3.81\%$ for 2344 hkl and $\overline{hkl}$ reflections. The π-cyclopentadienyl ligand is bound symmetrically to the cobalt(III) atom, with individual Co-C distances ranging from 2.020 (5) to 2.057 (3) Å and averaging 2.038 Å. The $B_{10}C_2Co$ fragment defines a triangulated (1,5,6,1) 13-apex docosahedron (22-sided figure) in which the equatorial (C-B-C-B-B-B) hexagonal belt is bonded to the cobalt(III) atom, individual distances (taken cyclically) being Co-C(7) = 2.032 (4) Å, Co-C(9) = 2.150 (3) Å, Co-B(10) = 2.093 (3) Å, Co-B(11) = 2.165 (3) Å, and Co-B(12) = 2.203 (4) Å. The linking together of five- and six-membered equatorial rings in forming the (1,5,6,1) 13-apex triangulated cage necessarily causes some severe abnormalities in the environments of individual atoms. Thus, atom C(7) is linked to only five other atoms and is associated with two very short bonds [C(7)-B(8) = 1.429 (10) Å and C(7)-B(12) = 1.527 (6) Å], while atom B(2) is linked to *seven* other atoms and is associated with some very long bonds [B(2)-B(8) = 2.081 (10) Å and B(2)-B(12) = 1.947 (6) Å]. 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 toward open squares.

Introduction

The reduction of the icosahedral $B_{10}C_2H_{12}$ carboranes to produce the $B_{10}C_2H_{12}^{2-}$ dianions[1-4] and the protonation of these species to $B_{10}C_2H_{13}^-$ anions[2-6] are well-known reactions (see Scheme I).

Scheme I

$$B_{10}C_2H_{12} \xrightarrow{+2e^-} B_{10}C_2H_{12}^{2-} \xrightarrow{H^+} B_{10}C_2H_{13}^-$$
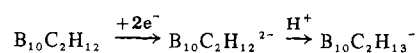
While X-ray crystallographic studies of $[Me_4N^+][B_{10}C_2H_{11^-}$

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(2) L. Zakharkin, V. Kalinin, and L. Podvisotskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2310 (1967).
(3) L. Zakharkin and V. Kalinin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 194 (1969).
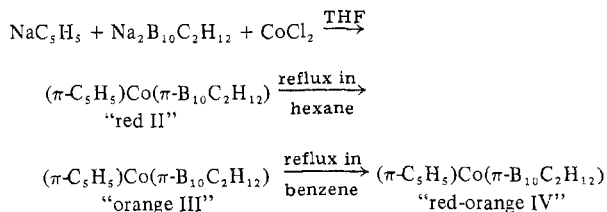
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(5) G. B. Dunks, R. J. Wiersema, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 899 (1972).
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$Ph_2^-]^{7,8}$ and $[Me_4N^+][B_{10}C_2H_{11}Me_2^-]^9$ have revealed the basic geometry of the $B_{10}C_2$ framework in the *protonated* species, there have, as yet, been no reported structural studies of compounds containing isolated $B_{10}C_2H_{12}^{2-}$ ions. Hawthorne and coworkers have, however, prepared transition metal derivatives of $B_{10}C_2H_{12}^{2-}$ ions, including three isomers of $(\pi\text{-}C_5H_5)Co(\pi\text{-}B_{10}C_2H_{12})$.[10,11] Using (here and throughout) the nomenclature of ref 11, these three isomers are formed and interrelated as shown in Scheme II.

Scheme II

$NaC_5H_5 + Na_2B_{10}C_2H_{12} + CoCl_2 \xrightarrow{\text{THF}}$

$(\pi\text{-}C_5H_5)Co(\pi\text{-}B_{10}C_2H_{12}) \xrightarrow[\text{hexane}]{\text{reflux in}}$
"red II"

$(\pi\text{-}C_5H_5)Co(\pi\text{-}B_{10}C_2H_{12}) \xrightarrow[\text{benzene}]{\text{reflux in}} (\pi\text{-}C_5H_5)Co(\pi\text{-}B_{10}C_2H_{12})$
"orange III"　　　　　　　　　　　　　　"red-orange IV"

On the basis of ^1H and ^{11}B nmr spectra taken at room temperature, a structure of C_s symmetry was originally suggested[10] for the "red II" isomer. Subsequent studies (at reduced temperatures) revealed, however, that the molecule is "fluxional" and that the C_s symmetry is an artifact of an intramolecular rearrangement process.[11,12] We have previously published a preliminary account of the crystal structure of the "red II" isomer of $(\pi\text{-}C_5H_5)Co(\pi\text{-}B_{10}C_2H_{12})$;[13] the present paper constitutes a complete description of this structure and (parenthetically) includes an account of the problems encountered in attempting (unsuccessfully) to solve the structures of the remaining two isomers, "orange III" and "red-orange IV" [see Appendix].

Experimental Section

Correction and Treatment of the X-Ray Diffraction Data. Dark red crystals of the "red II" isomer of $(\pi\text{-}C_5H_5)Co(B_{10}C_2H_{12})$, later shown to be $(\pi\text{-}C_5H_5)Co(\pi\text{-}7,9\text{-}B_{10}C_2H_{12})$, were supplied by Professor M. F. Hawthorne of the University of California at Los Angeles. One of these crystals was selected for an X-ray diffraction study and was glued to the tip of a Pyrex glass fiber which itself was fixed into a brass pin on a eucentric goniometer. The crystal was a rhombic plate between {001} faces, 0.21 mm apart, with the rhombus being defined by {110} faces at separations of 0.38 mm. The greatest dimension of the crystal (parallel to a^* and the spindle axis) was reduced to 0.74 mm by a very small (100) face.

Preliminary precession and cone-axis photographs provided approximate cell dimensions, indicated *mmm* (D_{2h}) Laue symmetry, and exhibited the following systematic absences: $h0l$ for $h = 2n + 1$ and $0kl$ for $l = 2n + 1$. These conditions are consistent with two orthorhombic space groups: the centrosymmetric *Pcam* [a nonstandard setting of *Pbcm* (D_{2h}^{11}; No. 57)[14]] or the noncentrosymmetric *Pca2₁* (C_{2v}^5; No. 29).[14] The latter is demonstrated to be the correct choice by the successful solution and refinement of the structure.[15] No

crystallographic symmetry is thereby imposed upon the molecule.

The crystal was transferred to a Picker FACS-1 computer-controlled diffractometer, was accurately centered, and was orientated in such a manner as to place a^* precisely coincident with the instrumental ϕ axis. The apparatus and experimental technique have been described at length previously.[16] Details specific to the present analysis are as follows.

Employing "high-resolution" conditions,[16] the 2θ, ω, and χ settings of the resolved Mo $K\alpha_1$ peaks of 12 high-angle ($2\theta = 35\text{-}50°$) reflections which were well dispersed in reciprocal space were determined automatically.[17] These data were used in a least-squares refinement of cell parameters and orientation parameters,[17] using λ(Mo $K\alpha_1$) 0.70926 Å. The resulting unit cell parameters (at ~25°) and estimated standard deviations are $a = 13.7441$ (41) Å, $b = 7.0465$ (24) Å, and $c = 13.6198$ (33) Å. The unit cell volume is $V = 1319.0$ (7) Å^3. The observed density ($\rho_{\text{obsd}} = 1.348$ (5) g cm^{-3}, by neutral buoyancy in aqueous BaI_2) is in excellent agreement with that calculated for mol wt 268.26 and $Z = 4$ ($\rho_{\text{calcd}} = 1.351$ g cm^{-3}).

Employing a 3.0° takeoff angle to the X-ray tube anode and a niobium β filter (~47% transmission of Mo $K\alpha$ radiation) at the detector aperture (4.0 mm × 4.5 mm, 330 mm from the crystal), intensity data were collected by executing a coupled θ(crystal)–2θ(counter) scan from 0.8° in 2θ below the Mo $K\alpha_1$ peak to 0.8° in 2θ above the Mo $K\alpha_2$ peak, the scan rate being 1.0°/min. Stationary-background counts, each of 40-sec duration, were recorded at the two extremes of the scan. Copper-foil attenuators, whose transmission factors for Mo $K\alpha$ radiation had previously been experimentally determined, were inserted as required to keep the maximum counting rate below ~8000 events/sec, thereby avoiding coincidence losses. All reflections (including systematic absences) of the types hkl and $h\bar{k}l$ with $2\theta < 50°$ (*i.e.*, (sin θ)/$\lambda < 0.596$) were measured. Three "standard reflections" (004, 020, 400) were measured after each batch of 48 reflections in order to monitor the stability of the assembly (*i.e.*, crystal, counter, source, etc.). The first two of these standard reflections remained constant throughout the data collection process (root-mean-square deviations from the mean of 0.8 and 0.6%, respectively). The third standard reflection (400) was constant (±1.0%) for the first 60% of the data set and then steadily declined to approximately 91% of its original intensity, where it remained for the final 15% of the data-collection period. Since this later period of data collection included only high-angle reflections with very few reflections at large χ values (*i.e.*, near $h00$) and we had every reason to be wary of the $h00$ reflections (*vide infra*), we elected to "let the majority rule" and made no (isotropic or anisotropic) "decomposition" correction to the data set. [A careful check at the termination of data collection showed that the crystal *was* still accurately centered and aligned.]

The intensity data were reduced[18] to observed structure factor amplitudes, $|F_o|$, and their estimated standard deviations, $\sigma(|F_o|)$, exactly as described previously.[16] The "ignorance factor" (p) was set to equal to 0.03. Any reflection with a net negative intensity was assigned an intensity of zero and was retained.

All 323 measurements which corresponded to the systematic absences of the space group were found to confirm the rules and were then discarded. The 40 reflections with (sin θ)/$\lambda < 0.155$ were corrected, in the manner described previously,[16] for the effect of the niobium β filter upon their low-2θ background measurements.

Absorption corrections were calculated for all data; with μ(Mo $K\alpha$) = 13.12 cm^{-1}, the maximum and minimum calculated transmission factors were 0.788 and 0.684.[19] However, dark clouds were clearly on the horizon, since the absorption correction was not able to account, *even qualitatively*, for the small intensity variations (~4% from the mean) displayed by the $h00$ reflections as a function of ϕ (at $\chi = 90°$).[20] Indeed, *no* satisfactory explanation for the (repeatedly) observed variation could be found in spite of strenuous efforts to do

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(11) D. F. Dustin, G. B. Dunks, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 95, 1109 (1973).

(12) M. F. Hawthorne and G. B. Dunks, *Science*, 178, 462 (1972).

(13) M. R. Churchill and B. G. DeBoer, *J. Chem. Soc., Chem. Commun.*, 1326 (1972).

(14) "International Tables for X-Ray Crystallography," Vol. 1, 2nd ed, Kynoch Press, Birmingham, England, 1965, pp 115 and 145.

(15) This work was in fact performed using coordinates corresponding to the nonstandard space group *Pbc2₁*, but *all* results reported herein have been transformed by interchanging a and b (or h and k, or x and y) and reversing the sign of c (or l, or z).

(16) M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, 12, 525 (1973).

(17) Diffractometer routines such as crystal orientation, centering of reflections, least-squares refinement of cell dimensions and θ-2θ scan routines were performed by programs described in W. R. Busing and H. A. Levy, *Acta Crystallogr.*, 22, 457 (1967), and adapted by Picker Corp. to the PDP-8/I which forms an integral part of the FACS-1 system.

(18) Data reduction was performed using the Fortran IV program REDUCE, by B. G. DeBoer.

(19) Absorption corrections were calculated using the FORTRAN IV program DRAB, by B. G. DeBoer.

(20) The "ϕ dependence" of the intensities of these reflections was measured by repeated θ-2θ scans at 10° intervals of ϕ from $\phi = 0°$ to $\phi = 350°$.

so.[21] Therefore, uncorrected data were used in this analysis, although the corrected data were tested (*vide infra*).

The final data set consisted of 2345 point group (as opposed to Laue group) independent $|F_o|$ values. Of these, only 3.7% had $I < 3\sigma(I)$. *No reflections were rejected on the basis of being "not significantly above background."*

Solution and Refinement of the Structure. Programs used in determining the structure include FORDAP (Fourier synthesis, by A. Zalkin), SFIX (a much-modified version of SFLS5, by C. T. Prewitt, for structure factor calculations and full-matrix least-squares refinement), STAN1 (distances and angles, with estimated standard deviations, by B. G. DeBoer), PLOD (least-squares planes, by B. G. DeBoer), and ORTEP (thermal-ellipsoid drawings, by C. K. Johnson).

Scattering factors for neutral cobalt, carbon, and boron atoms were taken from the compilation of Cromer and Waber.[22] Both the real and the imaginary components of anomalous dispersion were included in the structure factor calculation, using the values of Cromer and Liberman.[23] For hydrogen atoms, the scattering factors of Mason and Robertson[24] were used. The function minimized during least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, where $w = \sigma^{-2}(|F_o|)$. Discrepancy indices used below are defined as

$$R_F = \frac{\Sigma ||F_o| - |F_c||}{\Sigma |F_o|} \times 100 \ (\%)$$

$$R_{wF} = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w|F_o|^2}\right]^{1/2} \times 100 \ (\%)$$

An "averaged data set" of 1229 Laue group independent members was prepared by averaging the hkl and $hk\bar{l}$ reflections.[25]

Sections of the Patterson synthesis, $P(UVW)$, at $W = 0$ and $\frac{1}{2}$ were calculated and revealed vectors consistent with the cobalt atom lying on the mirror plane at $z = \frac{1}{4}$ in the centrosymmetric space group $Pcam$ or with it having an arbitrarily assignable z coordinate in the polar space group $Pca2_1$. An "observed" Fourier synthesis, phased by the cobalt atom [with its z coordinate fixed at $\frac{1}{4}$], suggested (by the great number of pseudomirror-related peaks which it displayed) that the noncentrosymmetric space group was correct. However, the five-membered π-cyclopentadienyl ring was clearly discernible (well removed from the pseudomirror plane), and its inclusion in the phasing of a second "observed" Fourier synthesis was sufficient to enable the 12 peaks of the $B_{10}C_2$ carborane cage to be distinguished. Several cycles of full-matrix least-squares refinement of positional and isotropic thermal parameters (with all cage atoms assigned boron scattering factors) converged to $R_F = 7.9\%$ and $R_{wF} = 10.5\%$. Anisotropic thermal parameter refinement of the cobalt and carbon atoms of the π-cyclopentadienyl ligand led to $R_F = 6.0\%$ and $R_{wF} = 8.3\%$; refinement of anisotropic thermal parameters for all nonhydrogen atoms led to $R_F = 5.0\%$ and $R_{wF} = 7.0\%$.

At this point the averaged (1229 member) data set was discarded in favor of the full data set (both $+l$ and $-l$; 2345 reflections). Continued refinement, now including the 17 hydrogen atoms (in positions indicated by a difference-Fourier syntheses) with isotropic thermal parameters, gave $R_F = 3.6\%$ and $R_{wF} = 4.4\%$. A majority of the calculated Bijvoet differences were in agreement with those observed, indicating correct chirality for the arrangement of molecules in the noncentrosymmetric space group.

Our attention was now drawn toward the problem of identifying unambiguously the positions of the two carbon atoms in the carborane cage. Position 9 had long been indicated as a carbon atom position by its smaller thermal parameter(s) and shorter intracage distances, but no similar second position was apparent. This, as well as the asymmetrical shape of the cage, was in conflict with the then available ¹H and ¹¹B nmr data,[10] which indicated C_s molecular symmetry and equivalent carbon atoms.

(21) We emphasize that the possibility of recrystallizing the sample (and, thereby, possibly, producing "better" crystals) was rejected because of the ease of isomerization of this species.

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

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

(24) R. Mason and G. B. Robertson, *Advan. Struct. Res. Diffr. Methods*, **2**, 57 (1966).

(25) In the averaging process, only 1.6% of the pairs disagreed by more than twice the combined standard deviation and the single worst disagreement was only 2.92σ (combined). The ordinary and weighted R factors (based on F_o^2) for merging the two sets were 2.73 and 2.34%, respectively. Note, however, that this does *not* permit one to conclude that the centrosymmetric choice of space group is correct (see text).

Table I. Final Positional and Isotropic Thermal Parameters for $(C_5H_5)Co(7,9\text{-}B_{10}C_2H_{12})^a$

Atom	x	y	z	$B,^b$ Å²
Co	0.36169 (2)	0.22904 (4)	$\frac{1}{4}$	2.39
B(1)	0.5422 (3)	0.3335 (5)	0.0500 (3)	3.4
B(2)	0.4175 (3)	0.4038 (6)	0.0433 (3)	4.1
B(3)	0.4587 (3)	0.1526 (6)	0.0319 (3)	4.2
B(4)	0.5529 (3)	0.1141 (5)	0.1127 (3)	3.3
B(5)	0.5824 (2)	0.3299 (5)	0.1749 (3)	3.2
B(6)	0.5079 (3)	0.5150 (5)	0.1296 (3)	3.2
C(7)	0.3186 (3)	0.3562 (8)	0.1234 (3)	4.7
B(8)	0.3414 (4)	0.1673 (13)	0.0931 (4)	5.3
C(9)	0.4392 (2)	0.0600 (4)	0.1444 (2)	3.4
B(10)	0.5088 (2)	0.1573 (7)	0.2353 (3)	4.0
B(11)	0.4854 (2)	0.4191 (5)	0.2488 (4)	3.8
B(12)	0.3851 (3)	0.5004 (5)	0.1733 (3)	3.5
Cp(1)	0.3546 (3)	0.2226 (8)	0.3981 (4)	4.8
Cp(2)	0.2815 (3)	0.3436 (6)	0.3600 (3)	4.6
Cp(3)	0.2213 (3)	0.2346 (6)	0.3007 (4)	4.9
Cp(4)	0.2543 (2)	0.0476 (5)	0.2976 (3)	4.1
Cp(5)	0.3357 (3)	0.0386 (6)	0.3596 (3)	4.5
H(1)	0.589 (3)	0.364 (5)	−0.009 (3)	5.7 (7)
H(2)	0.394 (3)	0.480 (5)	−0.018 (3)	5.8 (8)
H(3)	0.450 (3)	0.070 (5)	−0.029 (3)	5.6 (7)
H(4)	0.601 (2)	−0.008 (5)	0.101 (2)	4.6 (6)
H(5)	0.663 (3)	0.347 (6)	0.198 (3)	5.8 (8)
H(6)	0.530 (2)	0.650 (5)	0.111 (3)	5.2 (7)
H(7)	0.258 (3)	0.395 (7)	0.103 (3)	6.7 (10)
H(8)	0.283 (3)	0.054 (5)	0.057 (3)	5.9 (8)
H(9)	0.429 (3)	−0.081 (5)	0.146 (2)	5.1 (7)
H(10)	0.531 (3)	0.055 (5)	0.287 (3)	5.0 (7)
H(11)	0.496 (3)	0.505 (5)	0.317 (3)	5.2 (7)
H(12)	0.344 (2)	0.643 (5)	0.189 (2)	4.6 (7)
Hp(1)	0.403 (3)	0.247 (4)	0.448 (3)	4.5 (6)
Hp(2)	0.272 (3)	0.487 (7)	0.370 (3)	6.6 (9)
Hp(3)	0.164 (4)	0.295 (7)	0.238 (6)	9.3 (13)
Hp(4)	0.231 (2)	−0.047 (4)	0.258 (3)	5.1 (6)
Hp(5)	0.373 (3)	−0.062 (6)	0.374 (3)	5.5 (8)

^{a} Standard deviations are right adjusted to the last digit of the preceding number and are those derived from the inverse of the final least-squares matrix. ^{b} For nonhydrogen atoms, the "equivalent isotropic temperature factors" are listed. They correspond to a mean-square displacement which is the average of the mean-square displacements along the three principal axes of the anisotropic ellipsoid.

During the refinement of hydrogen atom parameters (*vide supra*), the hydrogen atoms associated with positions 7 and 9 had each refined to within ∼0.5 Å of their respective "boron" atoms and their resulting thermal parameters were *smaller* than those of the "boron" atoms. This seemed to confirm the identity of atom 9 as one carbon atom and indicated that atom 7 was probably the second. Definitive information on the identity of the carbon positions was obtained as follows.

(i) A difference-Fourier synthesis phased by all atoms except those at positions 7, 8, 9, and 12 (the only atoms having anomalous anisotropic thermal parameters and being involved with atypical intracage distances) revealed peaks at these positions with relative heights[26] 5.56:4.54:6.00:5.19, respectively.

(ii) The integrals under these four peaks (approximated as the sum of values found at the 81 points nearest the maximum on a ∼0.28-Å grid) were proportional to[26] 6.00:5.04:5.75:4.98 for atoms 7, 8, 9, and 12.

Atoms 7 and 9 were thus clearly identified as carbon atoms. (Subsequent least-squares refinement, resulting in meaningful anisotropic thermal parameters for all cage atoms, *vide infra*, is consistent with this assignment.) The apparent contradiction with the nmr results was removed by a subsequent nmr study[11] which showed that the ¹¹B nmr spectrum loses its simplicity at low temperatures and that the molecule is fluxional, showing *time-averaged* mirror symmetry in its nmr spectrum at room temperature.

With all atoms now correctly identified, refinement of all positional parameters, anisotropic thermal parameters for nonhydrogen atoms, and isotropic thermal parameters for hydrogen atoms converged with $R_F = 3.06\%$ and $R_{wF} = 4.02\%$ for all 2345 reflections [or $R_F = 3.02\%$ and $R_{wF} = 3.81\%$ upon deletion of the ill-behaved 200 reflection (∼30σ disagreement and $I(\text{obsd}) = 3.43I(\text{calcd})$)]. In

(26) These values are "normalized" to a maximum of 6.00.

Table II. Final Anisotropic Thermal Parameters[a] for $(C_5H_5)Co(7,9-B_{10}C_2H_{12})$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U \rangle^b$
Co	1.90 (1)	2.56 (1)	2.70 (2)	−0.09 (1)	0.44 (2)	0.26 (3)	0.195, 0.178, 0.145
B(1)	2.9 (1)	3.4 (1)	3.8 (1)	0.0 (1)	1.4 (1)	0.6 (1)	0.25, 0.21, 0.15
B(2)	3.5 (2)	5.7 (2)	3.1 (1)	1.2 (1)	0.3 (1)	1.4 (1)	0.29, 0.20, 0.17
B(3)	3.6 (2)	5.7 (2)	3.1 (2)	−0.8 (2)	0.7 (1)	−1.1 (2)	0.29, 0.21, 0.18
B(4)	2.9 (1)	2.8 (1)	4.1 (2)	0.2 (1)	1.0 (1)	−0.2 (1)	0.24, 0.19, 0.16
B(5)	1.7 (1)	3.2 (1)	4.7 (2)	−0.3 (1)	0.4 (1)	0.0 (1)	0.25, 0.20, 0.14
B(6)	2.8 (1)	2.4 (1)	4.4 (2)	−0.2 (1)	0.9 (1)	0.5 (1)	0.25, 0.19, 0.16
C(7)	3.3 (2)	6.8 (2)	4.0 (2)	0.5 (2)	0.2 (1)	1.0 (2)	0.30, 0.22, 0.20
B(8)	3.8 (2)	8.1 (4)	4.1 (2)	−0.3 (3)	−0.3 (2)	−0.6 (3)	0.32, 0.23, 0.21
C(9)	3.0 (1)	2.7 (1)	4.5 (1)	−0.5 (1)	1.0 (1)	−0.6 (1)	0.26, 0.18, 0.17
B(10)	1.7 (1)	6.5 (2)	3.8 (2)	0.6 (1)	0.1 (1)	0.4 (2)	0.29, 0.22, 0.14
B(11)	2.6 (1)	5.1 (1)	3.6 (1)	−1.0 (1)	−0.2 (2)	0.0 (2)	0.26, 0.21, 0.17
B(12)	2.7 (1)	3.0 (2)	4.9 (2)	0.4 (1)	0.7 (1)	1.1 (1)	0.27, 0.18, 0.18
Cp(1)	4.1 (2)	8.5 (3)	1.9 (2)	−1.3 (2)	0.2 (1)	0.2 (1)	0.34, 0.22, 0.15
Cp(2)	4.3 (2)	5.3 (2)	4.2 (2)	−0.1 (2)	2.2 (1)	−0.9 (2)	0.29, 0.25, 0.16
Cp(3)	2.8 (1)	6.2 (2)	5.8 (2)	0.5 (1)	0.8 (1)	0.3 (1)	0.29, 0.27, 0.18
Cp(4)	3.1 (1)	4.6 (2)	4.6 (2)	−1.5 (1)	0.7 (1)	0.2 (1)	0.26, 0.24, 0.16
Cp(5)	4.2 (2)	5.2 (2)	4.2 (2)	−0.7 (1)	0.2 (1)	2.4 (1)	0.30, 0.23, 0.16

[a] In units of Å^2 and for the form $\exp(-0.25\Sigma_i\Sigma_j h_i h_j a_i a_j B_{ij})$; $i, j = 1, 2, 3$, where h_i and a_i are the ith reflection index and reciprocal cell edge, respectively. Standard deviations were derived from the inverse of the final least-squares matrix. [b] These are the root-mean-square amplitudes of vibration (in Å) along the three principal axes of the anisotropic ellipsoid, in order of magnitude. For orientations, see figures.

Table III. Interatomic Distances (with Esd's[a]) for $(C_5H_5)Co(7,9-B_{10}C_2H_{12})$

Atoms	Dist, Å	Atoms	Dist, Å
A. Distances Involving the Cobalt Atom			
Co–C(7)	2.032 (4)	Co–Cp(1)	2.020 (5)
Co–B(8)	2.199 (6)	Co–Cp(2)	2.027 (4)
Co–C(9)	2.150 (3)	Co–Cp(3)	2.049 (4)
Co–B(10)	2.093 (3)	Co–Cp(4)	2.057 (3)
Co–B(11)	2.165 (3)	Co–Cp(5)	2.038 (3)
Co–B(12)	2.203 (4)		
B. Distances within the Cyclopentadienyl Ring			
Cp(1)–Cp(2)	1.416 (7)	Cp(1)–Hp(1)	0.97 (4)
Cp(2)–Cp(3)	1.388 (6)	Cp(2)–Hp(2)	1.03 (5)
Cp(3)–Cp(4)	1.394 (5)	Cp(3)–Hp(3)	1.23 (7)
Cp(4)–Cp(5)	1.403 (5)	Cp(4)–Hp(4)	0.92 (4)
Cp(5)–Cp(1)	1.422 (7)	Cp(5)–Hp(5)	0.90 (4)
C. Distances within the Carborane Cage			
B(1)–B(2)	1.787 (6)		
B(1)–B(3)	1.733 (6)	B(1)–B(6)	1.741 (5)
B(1)–B(4)	1.773 (5)	B(1)–B(5)	1.789 (5)
B(2)–C(7)	1.775 (6)		
B(2)–B(3)	1.865 (6)	B(2)–B(6)	1.881 (6)
B(2)–B(8)	2.081 (10)	B(2)–B(12)	1.947 (6)
B(3)–B(4)	1.720 (6)	B(6)–B(5)	1.770 (5)
B(3)···C(7)	2.705 (6)	B(6)···C(7)	2.834 (6)
B(3)–B(8)	1.818 (7)	B(6)–B(12)	1.792 (5)
B(3)–C(9)	1.686 (5)	B(6)–B(11)	1.786 (6)
B(4)–B(5)	1.788 (5)		
B(4)–C(9)	1.665 (4)	B(5)–B(11)	1.785 (5)
B(4)–B(10)	1.802 (5)	B(5)–B(10)	1.783 (6)
C(7)–B(8)	1.429 (10)	C(7)–B(12)	1.527 (6)
B(8)–C(9)	1.694 (7)	B(12)–B(11)	1.813 (5)
B(8)···B(12)	2.658 (9)		
C(9)–B(10)	1.708 (5)	B(11)–B(10)	1.881 (6)
B(1)–H(1)	1.05 (4)		
B(2)–H(2)	1.05 (4)		
B(3)–H(3)	1.02 (3)	B(6)–H(6)	1.03 (4)
B(4)–H(4)	1.09 (3)	B(5)–H(5)	1.15 (4)
C(7)–H(7)	0.92 (5)		
B(8)–H(8)	1.24 (4)	B(12)–H(12)	1.17 (3)
C(9)–H(9)	1.00 (4)	B(11)–H(11)	1.11 (3)
B(10)–H(10)	1.05 (3)		

[a] Not corrected for thermal motion. Standard deviations (right adjusted, in parentheses) were calculated from the esd's of the atomic coordinates and cell dimensions and include the effect of all positional correlation coefficients of magnitude $\geqslant 0.10$.

the final cycle of refinement, no nonhydrogen parameter shifted by more than 0.14σ and no hydrogen atom parameter by more than 0.4σ. The standard deviation in an observation of unit weight, defined by $[\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, was 2.00, where the number of data (m) was 2344 and the number of parameters refined (n)

was 230 $(m/n = 10.2)$. The function $\Sigma w(|F_o| - |F_c|)^2$ was independent of $|F_o|$ and showed only a modest increase at small $(\sin\theta)/\lambda$, so the weighting scheme was deemed satisfactory. Data were inspected for evidence of secondary extinction (*via* the criterion $|F_o| < |F_c|$ *systematically* for large $|F_o|$) but none was found. A final difference Fourier synthesis had, as its two most significant features, peaks of height 0.6 e Å^{-3} (at −0.02, 0.28, 0.20) and 0.53 e Å^{-3} (at −0.02, 0.28, 0.30) which were interrelated by reflection across the $z = {}^1/_4$ plane.

Finally, two tests of the data were made.

(i) The "absorption-corrected" data were used. No significant $(>1.0\sigma)$ shifts of atomic positions occurred and the final discrepancy indices were each higher, by 0.10%, than for the uncorrected data. These results were rejected.

(ii) The chirality of the molecular arrangement in the crystal was rigorously confirmed by two cycles of refinement of the inverted structure [using the coordinates $(x, y, -z)$ instead of (x, y, z)] which again showed no significant $(>1.0\sigma)$ changes in atomic positional parameters but did give higher discrepancy indices with $R_F = 3.24\%$ and $R_{wF} = 4.15\%$ (*vs.* $R_F = 3.02\%$ and $R_{wF} = 3.81\%$ for the correct chirality).

A table of observed and calculated structure factor amplitudes is available.[27] Final positional and isotropic thermal parameters are listed in Table I; anisotropic thermal parameters and the root-mean-square amplitudes of vibration along their principal axes are collected in Table II.

Discussion of the Molecular Structure

Interatomic distances and their estimated standard deviations (esd's) are shown in Table III; bond angles and their esd's are shown in Table IV. The overall stereochemistry and the labeling of nonhydrogen atoms are illustrated in Figures 1 and 2. [Hydrogen atoms are omitted from these diagrams for the sake of clarity; they are numbered in logical sequence, with H(n) being linked to B(n) or C(n) within the carborane framework and with Hp(n) being linked to Cp(n) within the π-cyclopentadienyl ligand.]

As can conveniently be seen from Table V, the individual molecules of $(C_5H_5)Co(B_{10}C_2H_{12})$ are separated by normal van der Waals distances, there being no H···H contact of less than 2.45 (5) Å.

The X-ray crystallographically determined geometry of this molecule shows it to be (*pentahapto*cyclopentadienyl)·(7,8,9,10,11,12-*hexahapto*dodecahydro-7,9-dicarba-*nido*-dodecaborato)cobalt(III),[28,29] which we will abbreviate to

(27) See paragraph at the end of paper regarding supplementary material.

(28) Note that the molecule may also be named using the equally acceptable closo nomenclature (see ref 29). The correct name is then 1-(*pentahapto*cyclopentadienyl)dodecahydro-1-cobalta-2,4-dicarba-*closo*-tridecaborane.

Table IV. Interatomic Angles for (C₅H₅)Co(7,9-B₁₀C₂H₁₂)[a]

Atoms	Angle, deg	Atoms	Angle, deg
A. Angles within the Cyclopentadienyl Ring			
Cp(1)-Cp(2)-Cp(3)	107.6 (4)	Hp(1)-Cp(1)-Cp(2)	130 (2)
Cp(2)-Cp(3)-Cp(4)	110.3 (4)	Hp(1)-Cp(1)-Cp(5)	123 (2)
Cp(3)-Cp(4)-Cp(5)	106.5 (4)	Hp(2)-Cp(2)-Cp(1)	129 (3)
Cp(4)-Cp(5)-Cp(1)	109.1 (4)	Hp(2)-Cp(2)-Cp(3)	123 (3)
Cp(5)-Cp(1)-Cp(2)	106.5 (4)	Hp(3)-Cp(3)-Cp(2)	126 (3)
		Hp(3)-Cp(3)-Cp(4)	121 (3)
		Hp(4)-Cp(4)-Cp(3)	126 (2)
		Hp(4)-Cp(4)-Cp(5)	127 (2)
		Hp(5)-Cp(5)-Cp(4)	129 (3)
		Hp(5)-Cp(5)-Cp(1)	122 (3)
B. Angles within the Carborane Cage			
B(2)-B(1)-B(3)	64.0 (3)	B(2)-B(1)-B(6)	64.4 (2)
B(3)-B(1)-B(4)	58.8 (2)	B(5)-B(1)-B(6)	60.2 (2)
B(4)-B(1)-B(5)	60.3 (2)		
B(1)-B(2)-B(3)	56.6 (2)	B(1)-B(2)-B(6)	56.6 (2)
B(3)-B(2)-B(8)	54.5 (2)	B(6)-B(2)-B(12)	55.8 (2)
B(3)-B(2)-C(7)	96.0 (3)	B(6)-B(2)-C(7)	101.6 (3)
C(7)-B(2)-B(8)	42.6 (3)	C(7)-B(2)-B(12)	48.2 (2)
B(1)-B(3)-B(2)	59.4 (2)	B(1)-B(6)-B(2)	59.0 (2)
B(1)-B(3)-B(4)	61.8 (2)	B(1)-B(6)-B(5)	61.3 (2)
B(2)-B(3)-B(8)	68.8 (4)	B(2)-B(6)-B(12)	64.0 (2)
B(4)-B(3)-C(9)	58.5 (2)	B(5)-B(6)-B(11)	60.3 (2)
B(8)-B(3)-C(9)	57.7 (3)	B(11)-B(6)-B(12)	60.9 (2)
B(1)-B(4)-B(3)	59.5 (2)	B(1)-B(5)-B(6)	58.6 (2)
B(1)-B(4)-B(5)	60.3 (2)	B(1)-B(5)-B(4)	59.4 (2)
B(3)-B(4)-C(9)	59.7 (2)	B(6)-B(5)-B(11)	60.3 (2)
B(5)-B(4)-B(10)	59.6 (2)	B(4)-B(5)-B(10)	60.6 (2)
C(9)-B(4)-B(10)	58.9 (2)	B(10)-B(5)-B(11)	63.6 (2)
B(2)-C(7)-B(8)	80.3 (4)	B(2)-C(7)-B(12)	71.9 (2)
B(8)-C(7)-B(12)	128.1 (4)		
B(2)-B(8)-B(3)	56.7 (3)	B(2)-B(12)-B(6)	60.2 (2)
B(2)-B(8)-C(7)	57.2 (4)	B(2)-B(12)-C(7)	60.0 (3)
B(3)-B(8)-C(7)	112.3 (6)	B(6)-B(12)-C(7)	117.0 (3)
B(3)-B(8)-C(9)	57.3 (3)	B(6)-B(12)-B(11)	59.4 (2)
C(7)-B(8)-C(9)	118.1 (5)	C(7)-B(12)-B(11)	119.9 (3)
B(3)-C(9)-B(4)	61.8 (2)	B(5)-B(11)-B(6)	59.4 (2)
B(3)-C(9)-B(8)	65.1 (3)	B(6)-B(11)-B(12)	59.7 (2)
B(4)-C(9)-B(10)	64.6 (2)	B(5)-B(11)-B(10)	58.1 (2)
B(8)-C(9)-B(10)	124.4 (4)	B(10)-B(11)-B(12)	112.6 (3)
B(4)-B(10)-B(5)	59.8 (2)		
B(4)-B(10)-C(9)	56.6 (2)	B(5)-B(10)-B(11)	58.2 (2)
C(9)-B(10)-B(11)	111.7 (3)		
C. Angles Involving the Cobalt Atom			
B(8)-C(7)-Co	76.7 (3)	B(12)-C(7)-Co	75.0 (2)
C(7)-B(8)-Co	64.1 (3)	C(7)-B(12)-Co	63.0 (2)
C(9)-B(8)-Co	65.6 (2)	B(11)-B(12)-Co	64.4 (2)
B(8)-C(9)-Co	68.6 (2)	B(12)-B(11)-Co	66.6 (2)
B(10)-C(9)-Co	64.5 (2)	B(10)-B(11)-Co	61.9 (1)
C(9)-B(10)-Co	68.0 (1)	B(11)-B(10)-Co	65.8 (2)
B(2)-C(7)-Co	112.4 (2)		
C(7)-Co-B(8)	39.2 (3)	C(7)-Co-B(12)	42.0 (2)
B(8)-Co-C(9)	45.8 (2)	B(11)-Co-B(12)	49.1 (2)
C(9)-Co-B(10)	47.4 (2)	B(10)-Co-B(11)	52.4 (2)
C(7)-Co-B(10)	107.9 (2)		
B(8)-Co-B(11)	102.4 (3)	C(9)-Co-B(12)	95.2 (1)
D. Angles Involving Cage Hydrogen Atoms			
H(1)-B(1)-B(2)	119 (2)		
H(1)-B(1)-B(3)	117 (2)	H(1)-B(1)-B(6)	119 (2)
H(1)-B(1)-B(4)	120 (2)	H(1)-B(1)-B(5)	123 (2)
H(2)-B(2)-B(1)	118 (2)		
H(2)-B(2)-C(7)	111 (2)		
H(2)-B(2)-B(3)	121 (2)	H(2)-B(2)-B(6)	119 (2)
H(2)-B(2)-B(8)	121 (2)	H(2)-B(2)-B(12)	119 (2)
H(3)-B(3)-B(1)	128 (2)	H(6)-B(6)-B(1)	117 (2)
H(3)-B(3)-B(2)	125 (2)	H(6)-B(6)-B(2)	115 (2)
H(3)-B(3)-B(4)	121 (2)	H(6)-B(6)-B(5)	126 (2)
H(3)-B(3)-B(8)	107 (2)	H(6)-B(6)-B(12)	114 (2)
H(3)-B(3)-C(9)	120 (2)	H(6)-B(6)-B(11)	128 (2)
H(4)-B(4)-B(1)	132 (2)	H(5)-B(5)-B(1)	123 (2)
H(4)-B(4)-B(3)	119 (2)	H(5)-B(5)-B(6)	125 (2)
H(4)-B(4)-B(5)	127 (2)	H(5)-B(5)-B(4)	116 (2)
H(4)-B(4)-C(9)	115 (2)	H(5)-B(5)-B(11)	122 (2)
H(4)-B(4)-B(10)	118 (2)	H(5)-B(5)-B(10)	119 (2)
H(7)-C(7)-B(2)	117 (3)		
H(7)-C(7)-B(8)	113 (3)	H(7)-C(7)-B(12)	119 (3)
H(7)-C(7)-Co	131 (3)		
H(8)-B(8)-B(2)	136 (2)	H(12)-B(12)-B(2)	125 (2)
H(8)-B(8)-B(3)	111 (2)	H(12)-B(12)-B(6)	118 (2)
H(8)-B(8)-C(7)	125 (2)	H(12)-B(12)-C(7)	111 (2)
H(8)-B(8)-C(9)	113 (2)	H(12)-B(12)-B(11)	122 (2)
H(8)-B(8)-Co	127 (2)	H(12)-B(12)-Co	126 (2)
H(9)-C(9)-B(3)	115 (2)	H(11)-B(11)-B(6)	122 (2)
H(9)-C(9)-B(4)	111 (2)	H(11)-B(11)-B(5)	124 (2)
H(9)-C(9)-B(8)	110 (2)	H(11)-B(11)-B(12)	114 (2)
H(9)-C(9)-B(10)	118 (2)	H(11)-B(11)-B(10)	126 (2)
H(9)-C(9)-Co	118 (2)	H(11)-B(11)-Co	116 (2)
H(10)-B(10)-B(4)	114 (2)	H(10)-B(10)-B(5)	128 (2)
H(10)-B(10)-C(9)	112 (2)	H(10)-B(10)-B(11)	131 (2)
H(10)-B(10)-Co	112 (2)		

[a] See footnote a of Table III.
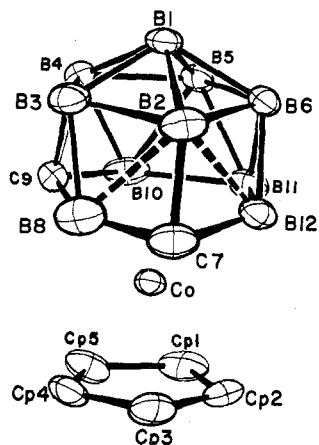
Figure 1. A view of the (π-C₅H₅)Co(7,9-B₁₀C₂H₁₂) molecule, showing the two anomalous four-membered systems B(2)-B(3)-B(8)-C(7) and B(2)-B(6)-B(12)-C(7) (ORTEP diagram, 50% ellipsoids).
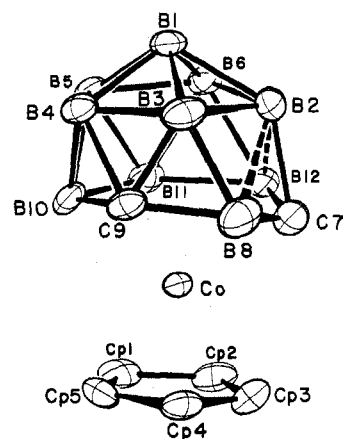
Figure 2. A view of the (π-C₅H₅)Co(7,9-B₁₀C₂H₁₂) molecule, showing nonplanarity in the hexagonal bonding face of the carborane ligand.

(π-C₅H₅)Co(7,9-B₁₀C₂H₁₂) for convenience in future discussions. Note that the molecule is chiral and that the enantiomer will be numbered differently—as (π-C₅H₅)Co(7,11-

(29) *Inorg. Chem.*, **7**, 1945 (1968); *Pure Appl. Chem.*, **30**, 683 (1972).

Table V. Intermolecular H· · ·H Distances (<3.0 Å)[a]

Atoms	Dist, Å	Symmetry transformn of 2nd atom
H(5)· · ·Hp(4)	2.45 (5)	a
H(5)· · ·H(12)	2.49 (5)	$a + (0, 1, 0)$
H(6)· · ·Hp(1)	2.51 (5)	$2_1 + (1, 1, -1)$
H(6)· · ·Hp(3)	2.56 (7)	$a + (0, 1, 0)$
H(4)· · ·H(8)	2.59 (5)	a
H(5)· · ·H(7)	2.59 (6)	$a + (0, 1, 0)$
H(5)· · ·Hp(3)	2.59 (7)	$a + (0, 1, 0)$
H(3)· · ·H(10)	2.68 (5)	$2_1 + (1, 0, -1)$
H(4)· · ·Hp(1)	2.68 (5)	$2_1 + (1, 0, -1)$
H(1)· · ·Hp(5)	2.71 (6)	$2_1 + (1, 0, -1)$
H(2)· · ·H(11)	2.71 (5)	$2_1 + (1, 1, -1)$
H(1)· · ·Hp(2)	2.73 (6)	$2_1 + (1, 1, -1)$
H(2)· · ·Hp(2)	2.73 (6)	$c + (0, 0, -1)$
H(3)· · ·Hp(5)	2.78 (5)	$2_1 + (1, 0, -1)$
H(10)· · ·Hp(4)	2.78 (5)	a
H(1)· · ·H(11)	2.80 (5)	$2_1 + (1, 1, -1)$
H(1)· · ·Hp(1)	2.80 (5)	$2_1 + (1, 1, -1)$
H(4)· · ·Hp(4)	2.81 (5)	a
H(4)· · ·Hp(3)	2.88 (7)	a
H(11)· · ·Hp(3)	2.91 (7)	$a + (0, 1, 0)$

[a] These distances are calculated from the X-ray-determined hydrogen atom positions and are thus likely to be up to ~0.2 Å shorter than the true internuclear separation (see text and ref 38).

$B_{10}C_2H_{12}$). The crystal, although noncentrosymmetric, consists of an ordered racemic array of the 7,9 and 7,11 isomers (since the a and c glides are operations of the second kind).

The Carborane Cage. The $B_{10}C_2Co$ fragment defines a triangulated (1,5,6,1) 13-apex docosahedron (22-sided figure) in which the equatorial hexagonal belt defined by C(7)-B(8)-C(9)-B(10)-B(11)-B(12) is bonded to the cobalt(III) atom. Cobalt-ligand atom distances vary appreciably, with individual values being Co-C(7) = 2.032 (4) Å, Co-B(8) = 2.199 (6) Å, Co-C(9) = 2.150 (3) Å, Co-B(10) = 2.093 (3) Å, Co-B(11) = 2.165 (3) Å, and Co-B(12) = 2.203 (4) Å.

The presence of a 13th atom in the metallocarborane cage has the result of lowering drastically the symmetry of the cage (relative to the possible pseudoicosahedral symmetry of a B_9C_2M fragment). The linking together of the hexagonal and pentagonal equatorial belts necessarily results in non-symmetrical triangulation of the polyhedron and causes some severe abnormalities in the environments of individual cage atoms. Thus, cage atoms in a regular icosahedral carborane have a connectivity of 6 (*i.e.*, are directly linked to five other cage atoms and to one terminal hydrogen atom or substituent). In the present molecule, atom C(7) is linked to only *five* other atoms [Co, B(2), B(8), B(12), H(7)] while atom B(2) is linked to *seven* other atoms [B(1), B(3), B(6), C(7), B(8), B(12), H(2)]. This gives rise to a number of decidedly atypical interatomic distances. Among the most obvious of these are two extremely long boron–boron bond lengths—*i.e.*, B(2)-B(8) = 2.081 (10) Å and B(2)-B(12) = 1.947 (6) Å. These bonds have been drawn with dashed lines in all diagrams, to emphasize that they are abnormally long. Atom B(2) is also involved in a number of other unusually long bonds, *viz.*, B(2)-B(3) = 1.865 (6) Å and B(2)-B(6) = 1.881 (6) Å [a "normal" B-B distance in icosahedral carboranes is ~1.78 Å[30]].

In contradistinction to this are the unusually short intra-cage bonds to C(7), C(7)-B(8) = 1.429 (10) Å and C(7)-B(12) = 1.527 (6) Å [a "normal" distance being ~1.70 Å[30]]; the bond to cobalt, C(7)-Co = 2.032 (4) Å, is also the shortest of the (cage atom)-cobalt distances. These obser-

(30) Typical bond distances within an icosahedral carborane are B-B = 1.78 Å, B-C = 1.70 Å, and C-C = 1.62 Å: M. R. Churchill and A. H. Reis, *J. Chem. Soc., Dalton Trans.*, 1317 (1972), especially Table 6 on p 1320.
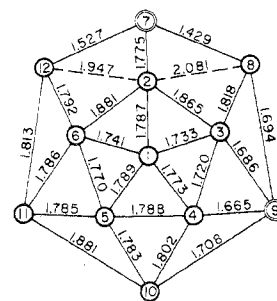

Figure 3. Connectivity diagram and bond lengths for the $B_{10}C_2H_{12}{}^{2-}$ ligand. (For esd's see Table III.)

vations are easily explained qualitatively, since, *omnia paribus*, the average bond length around a cage atom is dependent upon the connectivity of that atom and will increase as the connectivity increases. [We can make little comment on the B(2)-C(7) distance of 1.775 (6) Å since this linkage is between the two abnormal atoms—B(2), which has a high connectivity, and C(7), which has a low connectivity.]

The connectivity diagram for the $(B_{10}C_2H_{12}{}^{2-})$ ligand, with the twelve terminal hydrogen atoms omitted, is shown in Figure 3. As can be seen from this diagram, the connectivity *framework* has idealized C_s symmetry. In terms of the identity of atoms, the only deviation from C_s symmetry is that atom 9 is a carbon atom, while atom 11 is a boron. However, the deviations from C_s symmetry in terms of bond lengths are really rather large. This is not too surprising for bonds directly involving C(9) and B(11) [which are, taken in pairs, C(9)-B(8) = 1.694 (7) Å *vs.* B(11)-B(12) = 1.813 (5) Å; C(9)-B(3) = 1.686 (5) Å *vs.* B(11)-B(6) = 1.786 (6) Å; C(9)-B(4) = 1.665 (4) Å *vs.* B(11)-B(5) = 1.785 (5) Å; C(9)-B(10) = 1.708 (5) Å *vs.* B(11)-B(10) = 1.881 (6) Å]. It is rather remarkable, however, that differences in bond length as large as ~0.13 Å are maintained even between "pseudo-mirror"-related·distances that involve pairs of atoms of the same chemical identity, *viz.*, B(2)-B(8) = 2.081 (10) Å *vs.* B(2)-B(12) = 1.947 (6) Å (Δ = 0.134 Å), C(7)-B(8) = 1.429 (10) Å *vs.* C(7)-B(12) = 1.527 (6) Å (Δ = 0.098 Å), and B(3)-B(4) = 1.720 (6) Å *vs.* B(6)-B(5) = 1.770 (5) Å (Δ = 0.050 Å). It may well be that the strain(s) inherent within so awkward an object as a 13-vertex polyhedron could cause an unusual sensitivity of the interatomic distances to hetero-atom effects.

While the five-membered equatorial belt, defined by B(2)-B(3)-B(4)-B(5)-B(6), is approximately planar (the root-mean-square deviation from planarity is 0.044 Å—see Table VI), the six-membered ring defined by C(7)-B(8)-C(9)-B(10)-B(11)-B(12) shows pronounced deviations from planarity. (This can conveniently be seen in Figure 3.) The four boron atoms are precisely coplanar, and the carbon atoms are displaced by −0.261 Å [C(7)] and +0.192 Å [C(9)] from this plane—see plane IIa of Table VI. [Note that the minus sign here indicates displacement in the direction of the cobalt(III) atom.] The plane defined by B(8)-C(7)-B(12) makes a dihedral angle of −23.89° with the B(8)· · ·B(10)-B(11)-B(12) plane, while the B(8)-C(9)-B(10) plane makes an angle of +13.96° with the B(8)· · ·B(10)-B(11)-B(12) system.

Consideration of the four-membered systems B(2)-B(3)-B(8)-C(7) and B(2)-B(6)-B(12)-C(7) shows that they are not symmetrically triangulated but are perturbed toward open squares. Thus, while the dihedral angle between adjacent faces of a regular icosahedron is 41.81° (sin⁻¹ (2/3)), the [B(3)-B(2)-B(8)]-[B(8)-B(2)-C(7)] dihedral angle is only 15.16° and the [B(6)-B(2)-B(12)]-[B(12)-B(2)-C(7)] di-

Table VI. Least-Squares Planes,[a,b] Deviations (Å) of Atoms from Planes, and Dihedral Angles

Plane I: $0.5846X + 0.2106Y - 0.7835Z = -1.073$

Co	1.651		
Cp(1)*	0.004	Hp(1)	−0.11
Cp(2)*	0.004	Hp(2)	0.03
Cp(3)*	−0.009	Hp(3)	0.29
Cp(4)*	0.012	Hp(4)	0.11
Cp(5)*	−0.009	Hp(5)	−0.02

Plane IIa: $0.6361X + 0.1856Y - 0.7489Z = 2.254$

B(8)*	0.000	H(8)	−0.29
B(10)*	0.000	H(10)	−0.47
B(11)*	0.000	H(11)	−0.49
B(12)*	0.000	H(12)	−0.34
C(7)	−0.261		
C(9)	0.192	Co	−1.342

Plane IIb: $0.2829X + 0.3442Y - 0.8953Z = 0.598$

C(7)*	0.0	H(7)	0.11
B(8)*	0.0	H(8)	−0.06
B(12)*	0.0	H(12)	−0.01

Plane IIc: $0.5928X + 0.4170Y - 0.6890Z = 2.399$

B(8)*	0.0	H(8)	−0.47
C(9)*	0.0	H(9)	−0.51
B(10)*	0.0	H(10)	−0.60

Plane III: $0.6407X + 0.2197Y - 0.7357Z = 3.919$

B(2)*	−0.052	H(2)	0.48
B(3)*	0.036	H(3)	0.43
B(4)*	−0.004	H(4)	0.34
B(5)*	−0.032	H(5)	0.47
B(6)*	0.052	H(6)	0.64

Plane IVa: $-0.6363X + 0.0879Y - 0.7664Z = -3.853$

B(2)*	0.0	B(8)*	0.0
C(7)*	0.0	B(3)	−0.397

Plane IVb: $-0.4611X - 0.0700Y - 0.8846Z = -3.367$

B(2)*	0.0	B(8)*	0.0
B(3)*	0.0	C(7)	−0.314

Plane Va: $-0.5187X + 0.7463Y - 0.4171Z = -1.099$

B(2)*	0.0	B(12)*	0.0
C(7)*	0.0	B(6)	−0.550

Plane Vb: $-0.1934X + 0.8984Y - 0.3940Z = 1.212$

B(2)*	0.0	B(12)*	0.0
B(6)*	0.0	C(7)	−0.468

Dihedral Angles (deg)

I–IIa	3.83	IVa–IVb	15.16
IIa–IIb	−23.89	Va–Vb	20.71
IIa–IIc	13.96	IVa–Va	44.33

[a] Equations are in cartesian coordinates, *i.e.*, $[X, Y, Z] = [ax, by, cz]$. [b] Planes are derived using unit weights for all atoms marked with an asterisk and zero weights for all other atoms.

hedral angle is only 20.71° (see Table VI). In addition, we may note that the diagonals of the B(2)–B(3)–B(8)–C(7) system are B(2)–B(8) = 2.081 (10) Å and B(3)···C(7) = 2.705 (6) Å, and the diagonals of the B(2)–B(6)–B(12)–C(7) system are B(2)–B(12) = 1.947 (6) Å and B(6)···C(7) = 2.834 (6) Å.

The perturbation of these two four-membered systems toward open squares is particularly interesting in view of Lipscomb's "diamond–square–diamond" mechanism[31] for the intramolecular isomerization of certain triangulated polyhedral boron hydrides and carboranes (see Scheme III).

Scheme III
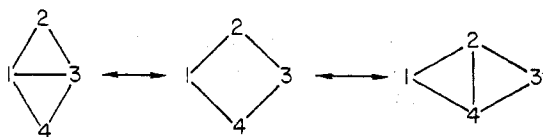
(31) W. N. Lipscomb, *Science*, 153, 373 (1966).

We note here that this mechanism has been specifically invoked to explain the ready intramolecular interconversion of the $(C_5H_5)Co(7,9\text{-}B_{10}C_2H_{12})$ and $(C_5H_5)Co(7,11\text{-}B_{10}C_2H_{12})$ isomers.[11]

Boron–hydrogen distances range from B(3)–H(3) = 1.02 (3) Å to B(8)–H(8) = 1.24 (4) Å, the average of the ten independent values being 1.096 Å. The two carbon–hydrogen distances are C(7)–H(7) = 0.92 (5) Å and C(9)–H(9) = 1.00 (4) Å (average 0.96 Å). These distances are, of course, reduced from the true internuclear distances as a result of the centroid of the electron density around hydrogen not being coincident with its nuclear position but being displaced in the direction of the hydrogen→(other atom) vector.[32]

The *Pentahapto*cyclopentadienyl Ligand. The cyclopentadienyl ligand is bound symmetrically to the cobalt(III) atom, with individual cobalt–carbon distances being Co–Cp(1) = 2.020 (5), Co–Cp(2) = 2.027 (4), Co–Cp(3) = 2.049 (4), Co–Cp(4) = 2.057 (3), and Co–Cp(5) = 2.038 (3) Å. The average of these five values is 2.038 Å. Cobalt–carbon $(\pi\text{-}C_5H_5)$ distances in other molecules are similar, individual values being 2.029 Å in $(\pi\text{-}C_5H_5)Co(S_2C_2(CN)_2)$,[33] 2.080 Å in $(\pi\text{-}C_5H_5)Co(C_5H_5Ph)$,[34] 2.05 Å in $(\pi\text{-}C_5H_5)Co\text{-}(C_5H_5COPh)$,[35] 2.07 Å in $(\pi\text{-}C_5H_5)Co(Me_4C_5O)$,[36] and 2.075 Å in $(\pi\text{-}C_5H_5)Co[(CF_3)_4C_5O]$.[37]

The *pentahapto*cyclopentadienyl ligand has D_{5h} symmetry within the limits of experimental error. The root-mean-square deviation of carbon atoms from the least-squares plane is 0.009 Å (see plane I, Table VI), individual carbon–carbon distances range from Cp(2)–Cp(3) = 1.388 (6) Å to Cp(5)–Cp(1) = 1.422 (7) Å (average 1.405 Å), and C–C–C angles range from Cp(3)–Cp(4)–Cp(5) = 106.5 (4)° to Cp(2)–Cp(3)–Cp(4) = 110.3 (4)° (average 108.0°, as expected for a planar pentagon).

The orientations of the thermal vibration ellipsoids of atoms Cp(1) through Cp(5) (see Figures 1 and 2) are consistent with there being significant libration of the five-membered ring about the cobalt–(center of ring) axis. It is presumably this effect that causes the average carbon–carbon distance to appear shorter than the expected C–C(π-cyclopentadienyl) distance of ~1.43 Å.

The carbon–hydrogen distances range from 0.90 (4) to 1.23 (7) Å, the average value being 1.01 Å (*cf.* ref 38).

Appendix

Crystallographic Data for the "Orange III" and "Red-Orange IV" Isomers of $(C_5H_5)Co(B_{10}C_2H_{12})$. In conjunction with Mr. K.-L. G. Lin of this laboratory, we have examined crystals of the two higher temperature isomers of $(C_5\text{-}$

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

(33) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, 7, 1123 (1968).

(34) M. R. Churchill and R. Mason, *Proc. Roy. Soc., Ser. A*, 279, 191 (1964).

(35) M. R. Churchill, *J. Organometal. Chem.*, 4, 258 (1965).

(36) L. F. Dahl and D. L. Smith, *J. Amer. Chem. Soc.*, 83, 752 (1961).

(37) M. Gerloch and R. Mason, *Proc. Roy. Soc., Ser. A*, 279, 170 (1964).

(38) M. R. Churchill, *Inorg. Chem.*, 12, 1213 (1973).

H_5)Co($B_{10}C_2H_{12}$) referred to by Hawthorne and coworkers as "orange III" and "red-orange IV" (*cf*. ref 11). These two species produce crystals which are isomorphous since they each display apparent *mmm* (D_{2h}) Laue symmetry, identical systematic absences (*hkl* for $h + k = 2n + l$ and *h0l* for $l = 2n + 1$, consistent with the space group *Cmcm*, *Cmc2₁*, or *C2cm*), and very similar cell dimensions. For "orange III," $a = 7.259$ (3) Å, $b = 16.194$ (6) Å, $c = 11.052$ (2) Å, and $\rho_{calcd} = 1.371$ g cm⁻³ for $Z = 4$; for "red-orange IV," $a = 7.249$ (3) Å, $b = 16.258$ (7) Å, and $c = 11.199$ (5) Å, $\rho_{obsd} = 1.340$ (5) g cm⁻³, and $\rho_{calcd} = 1.350$ g cm⁻³ for $Z = 4$. In addition, the species are almost certainly *isostructural* since careful study is required before intensity differences can be found between corresponding photographs.

Diffractometer data for each isomer were collected in a similar manner to that described in the Experimental Section. For each structure the following results were obtained. Routine structure-solving tactics led to marginally acceptable agreement ($R_F \approx 7\%$) only at the price of ridiculous anisotropic thermal parameters and fewer atoms than expected from the (well-established) empirical formulas. Ordinary Wilson-plot analyses of the *hk0* and *0kl* data gave scale factors essentially identical with those resulting from the remaining data, whereas at least one of these zones is expected to have twice the average intensity if the crystals are truly orthorhombic. We are led to believe that the crystals are not truly orthorhombic but are twinned monoclinic with β accidentally 90°. The most probable space group is *Cc*

(since $Z = 4$ and the ¹¹B nmr spectra showed no molecular symmetry¹¹). The hypothesized twinning relation has four equivalent descriptions: either a twofold rotation about, or a mirror perpendicular to, either of the monoclinic *a* or *c* axes. [This would superimpose the *hkl* and *hk̄l* reflections, while preserving the systematic absences for space group *Cc*.]

Our structure-solving efforts made prior to the discovery of twinning, coupled with later work with the *0kl* and *hk0* data (which should not be affected by the twinning), reveal (1) that the principal molecular axis lies nearly parallel to *b* and (2) that the cobalt atoms occupy pseudo special positions (at $y \approx ^1/_4$) such that they define a face-centered lattice and contribute only weakly to data with $h + l = 2n + 1$.

We have not continued with these studies, since it is most unlikely that even the most painstaking effort would enable us to achieve our principal goal, *i.e.*, that of distinguishing which of the cage positions was taken up by carbon and which by boron.

Contribution from the Departments of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680, and Harvard University, Cambridge, Massachusetts 02138

Crystal and Molecular Structure of Cu4Ir2(PPh3)2(C≡CPh)8, a Novel Heteronuclear Octahedral Metal Cluster Complex

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The heteronuclear metal cluster complex bis(triphenylphosphine)octakis(phenylethynyl)tetracopperdiiridium(4*Cu-Cu*)-(8*Cu-Ir*), $Cu_4Ir_2(PPh_3)_2(C≡CPh)_8$, has previously been prepared *via* the reaction of IrCl(CO)(PPh₃)₂ with [PhC≡CCu]$_n$. The complex crystallizes in the noncentrosymmetric monoclinic space group $P2_1$ (C_2^2; No. 4) with $a = 14.86$ (2) Å, $b = 22.04$ (4) Å, $c = 13.62$ (2) Å, and $\beta = 105.04$ (10)°. The observed density (1.59 (3) g cm⁻³) may be compared to the value of 1.52 g cm⁻³ calculated for mol wt 1972 and $Z = 2$. X-Ray diffraction data to sin $\theta = 0.80$ (Cu Kα radiation) were collected with a Supper-Pace diffractometer, using the ω-scan technique. The structure was solved by means of a combination of Patterson, Fourier, and least-squares refinement techniques. All 108 independent nonhydrogen atoms have been accurately located, the final discrepancy index being $R_F = 8.2\%$ for the 4584 independent nonzero (*i.e.*, $I > 3\sigma(I)$) reflections. The six metal atoms define a slightly irregular octahedron in which the two iridium atoms are in mutually trans positions. Interatomic distances are Ir–Cu = 2.776 (4)–2.959 (4) Å [average 2.870 Å] and Cu–Cu = 2.665 (6)–2.823 (5) Å [average 2.739 Å]. Each iridium atom is bonded apically to a triphenylphosphine ligand, with Ir(1)–P(1) = 2.248 (8) Å and Ir(2)–P(2) = 2.268 (7) Å. Four phenylethynyl [PhC≡C–] ligands are σ bonded to each iridium atom, with Ir–C(α) = 1.982 (26)–2.109 (21) Å [average 2.044 Å]. Each acetylenic fragment simultaneously participates in an asymmetric π interaction with a copper atom on the octahedral meridian, such that Cu···C(α) = 1.871 (26)–2.076 (23) Å [average 1.986 Å] and Cu···C(β) = 2.142 (26)–2.254 (28) Å [average 2.185 Å]. Each copper atom is thus bonded to two acetylenic moieties, one above and one below the equatorial plane; the central $Cu_4Ir_2P_2(C≡C)_8$ "core" of the molecule has approximate, but not exact, D_4 symmetry. The eight acetylenic bonds, C(α)–C(β), range from 1.181 (39) to 1.289 (35) Å, averaging 1.226 Å. The Ir–C(α)–C(β)–C(phenyl) dihedral angles range from 114.4 to 171.8° –*i.e.*, the Ir–C≡C–Ph systems adopt non-linear *transoid* configurations, in contrast to the *cis*-bent arrangement of R groups normally observed in species in which R–C≡C–R ligands are coordinated to one (or more) transition metal atom(s).

Introduction

Bruce and coworkers¹ have shown that the reaction of Vaska's compound, IrCl(CO)(PPh₃)₂, with copper phenyl-

acetylide in benzene does not simply result in oxidative addition but, rather, yields the heteronuclear metal cluster complex $Cu_4Ir_2(PPh_3)_2(C≡CPh)_8$, along with other minor

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(1) O. M. Abu Salah, M. I. Bruce, M. R. Churchill, and S. A. Bezman, *J. Chem. Soc., Chem. Commun.*, 858 (1972).