examples illustrate the utility of the planar thiourea group as a probe in the nature of the metal–sulfur bonding and bridge bonding in particular.

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Supplementary Material Available. Table I, 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, 20X 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-74-2835.

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Structures of Metallocarboranes. IV. Crystal and Molecular Structure of the Nido Metallocarborane Complex 8-η-Cyclopentadienyl-6,7-dicarba-8-cobalta-*nido*-nonaborane(11), 8-η-C_5H_5-8-Co-6,7-$C_2B_7H_{11}$, at −160°[1]

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The crystal and molecular structure of 8-η-C_5H_5-8-Co-6,7-$C_2B_7H_{11}$ has been determined by a complete three-dimensional X-ray diffraction study at −160°. The compound crystallizes in the monoclinic centrosymmetric space group $P2_1/n$ with $a = 6.811$ (2) Å, $b = 15.678$ (2) Å, $c = 10.949$ (5) Å, $\beta = 104.91$ (3)° at −160°, and $Z = 4$. Observed and calculated densities are 1.33 (2) and 1.348 g cm^{-3} at 25°. Diffraction data to $2\theta_{\max} = 50°$ (Mo Kα radiation) were collected on a Syntex $P\bar{1}$ automated diffractometer, and the structure was solved by conventional Patterson, Fourier, and full-matrix least-squares refinement techniques. The final discrepancy index is $R = 3.2\%$ for 1323 independent nonzero reflections. The molecule possesses a decaborane-like geometry, with the three heteroatoms occupying positions in the open face. The carbon atoms are adjacent to each other, one occupying a four-coordinate position and the other a five-coordinate position. The cobalt atom occupies another five-coordinate vertex, being bound to one carbon and three boron atoms and a π-bonded cyclopentadienyl ring. It is further coordinated by a hydrogen atom which bridges the bond between the cobalt atom and an adjacent boron atom occupying the other four-coordinate position. Another hydrogen atom bridges the bond between the four-coordinate boron atom and the adjacent boron atom on the open face. These bridging hydrogen atoms were unambiguously located in difference electron density maps and their coordinates and isotropic thermal parameters were successfully refined. Mechanistic aspects of the synthesis and chemistry of this compound are discussed in light of the atomic arrangement determined in this work.

Introduction

Three synthetic routes to the preparation of metallocarboranes have now been established.[2-4] Polyhedral expansion[5] involves the increase in the number of the vertices of a carborane or metallocarborane polyhedron through the incorporation of a new metallic vertex. The polyhedral subrogation reaction[6] involves the removal of a boron atom vertex from a carborane or metallocarborane by the action of strong base and replacement of this missing vertex with a transition metal ion; the product therefore has the same number of polyhedral vertices as did the starting material. The third synthetic method, termed polyhedral contraction,[7] involves the removal by strong base of a boron atom vertex from a metallocarborane followed by oxidation, which results in cage closure and the formation of a metallocarborane having one vertex less than its precursor. The first two synthetic methods have been widely applied and appear to be relatively general reactions of carboranes and metallocarboranes; polyhedral contraction has been examined to a lesser extent.

The actual mechanism of the polyhedral contraction process is more complex than described above. There is evidence that ligand-substituted metallocarboranes and nido metallocarboranes function as intermediates in this reaction.[7,8] In the polyhedral contraction of the complex 1-η-C_5H_5-1-Co-2,4-$C_2B_8H_{10}$, itself formed by polyhedral contraction of 3-η-C_5H_5-3-Co-1,2-$C_2B_9H_{11}$, a product formulated as $C_5H_5CoC_2B_7H_{11}$ was isolated.[8] Chemical and spectroscopic data indicated that this species possessed bridging hydrogen atoms, but it was impossible uniquely to assign the structure on the basis of these data alone. As a part of an effort to elucidate the mechanism of the polyhedral contraction reaction, a single-crystal X-ray structure determination of this compound was undertaken.

From a set of X-ray diffraction data collected at room temperature the structure was solved and refined to a discrepancy index of $R = 7.4\%$.[9] The overall geometry of the

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[9] $R = [\Sigma||F_o| - |F_c||/\Sigma|F_o|]$; $R_w = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/(\sigma(F))^2$.

Table I. Final Atomic Positions[a]

Atom	x	y	z	Atom	x	y	z
I. Heavy Atoms							
Co	0.04048 (8)	0.16936 (3)	0.24433 (5)	B3	−0.0661 (6)	0.2675 (3)	0.1105 (4)
Cp1	0.1727 (6)	0.0595 (2)	0.3283 (4)	B4	−0.2434 (6)	0.2323 (3)	0.1963 (4)
Cp2	0.2906 (6)	0.0927 (2)	0.2510 (4)	B5	−0.0378 (7)	0.3920 (3)	0.2973 (4)
Cp3	0.1634 (7)	0.0972 (2)	0.1279 (4)	C6	0.1653 (6)	0.3549 (2)	0.2950 (4)
Cp4	−0.0304 (7)	0.0659 (3)	0.1280 (4)	C7	0.1617 (5)	0.2858 (2)	0.2061 (4)
Cp5	−0.0243 (7)	0.0423 (2)	0.2528 (4)	B9	−0.1436 (7)	0.2084 (3)	0.3573 (4)
B1	−0.2187 (7)	0.3456 (3)	0.1667 (4)	B10	−0.2442 (7)	0.3104 (3)	0.3146 (4)
B2	0.0187 (6)	0.3739 (3)	0.1477 (4)				
II. Hydrogen Atoms							
CpH1	0.211 (6)	0.054 (3)	0.415 (4)	BH4	−0.384 (6)	0.201 (3)	0.143 (4)
CpH2	0.422 (6)	0.112 (3)	0.284 (4)	BH5	−0.054 (6)	0.453 (3)	0.348 (4)
CpH3	0.199 (6)	0.119 (3)	0.068 (4)	CH6	0.294 (6)	0.382 (3)	0.328 (4)
CpH4	−0.143 (6)	0.063 (3)	0.057 (4)	CH7	0.288 (6)	0.274 (3)	0.178 (4)
CpH5	−0.129 (6)	0.024 (3)	0.286 (4)	BH9	−0.207 (6)	0.170 (3)	0.418 (4)
BH1	−0.364 (6)	0.376 (3)	0.109 (4)	BH10	−0.389 (6)	0.328 (3)	0.341 (4)
BH2	0.052 (6)	0.420 (3)	0.074 (4)	Hb1	0.050 (6)	0.194 (3)	0.369 (4)
BH3	−0.088 (6)	0.252 (3)	0.011 (4)	Hb2	−0.107 (6)	0.290 (3)	0.403 (4)

[a] Estimated standard deviations, shown in parentheses, refer to the last digit of the preceding number.

complex was revealed at this point, as were the positions of the two polyhedral carbon atoms, but the positions of the bridging hydrogen atoms located in a difference electron density map were sufficiently uncertain to warrant collection of new data at −160°. The results of the low-temperature structure determination are discussed in this paper.

Unit Cell and Space Group

A sample of the title compound was kindly furnished by Dr. C. J. Jones. Slow recrystallization from a methylene chloride–hexane mixture afforded crystals suitable for X-ray study. Preliminary room-temperature photographs of the red parallelepiped crystals indicated monoclinic symmetry with systematic absences $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$, indicative of space group $P2_1/n$, an alternate setting of $P2_1/c$ ($C_{2h}{}^5$, No. 14).[10] The room-temperature density, measured by flotation in aqueous potassium iodide, was 1.33 (2) g cm^{-3}, in reasonable agreement with the calculated density (at 25°) of 1.348 g cm^{-3} for $Z = 4$. The calculated density at −160° is 1.380 g cm^{-3}.

Collection and Reduction of X-Ray Data

Intensity data were collected on a Syntex $P\bar{1}$ automated diffractometer equipped with scintillation counter and pulse height analyzer. The low-temperature attachment was locally constructed[11] and maintained the crystal temperature at −160 ± 5° with a temperature stability of ±0.5°. A graphite crystal was employed to produce monochromatic Mo Kα radiation (λ 0.71069 Å). The crystal used for data collection was a parallelepiped bounded by the {100}, {010}, and {001} faces. Crystal dimensions normal to these faces were 0.100, 0.160, and 0.056 mm, respectively. The crystal was glued to a glass fiber parallel to the long axis and enclosed in a borosilicate capillary. Lattice parameters, determined by a least-squares fit of 15 accurately centered, high-angle reflections, were $a = 6.811$ (2) Å, $b = 15.678$ (2) Å, $c = 10.949$ (5) Å, and $\beta = 104.91$ (3)°.

Intensity data were collected with a θ-2θ scan technique to a limit of $2\theta = 50°$ and with a takeoff angle of 4°. The scintillation counter was 19.5 cm from the crystal and equipped with a 1-mm collimator. Reflections were scanned at a rate of 2°/min from 1° below the Kα_1 reflection to 1° above the Kα_2 reflection. Background was measured at each end of the scan. The total time spent counting background radiation was equal to the scan time for each reflection.

The intensities of three standard reflections were remeasured every 97 reflections to monitor the tube efficiency and possible crystal deterioration. No significant deviations were observed. The intensities of 4294 reflections over a hemisphere of data were thus determined.

The reflections were corrected for Lorentz and polarization effects and the intensity of a reflection, $I(hkl)$, and $\sigma[I(hkl)]$, its estimated standard deviation, were calculated according to the equations $I = \mathrm{CT} - (t_c/t_b)(B_1 + B_2)/2$ and $\sigma(I) = [\sigma_s{}^2 + (0.04I)^2]^{1/2}$, where I is the net integrated intensity, CT is the total integrated count, t_c and t_b are the times employed for counting the scan and background, respectively, B_1 and B_2 are the background counts on the low and high sides of the reflection, and σ_s is the standard deviation in the intensity due to counting statistics. Reflections having intensities less than three times their standard deviations were defined as unobserved and not included in subsequent calculations, and the intensities of equivalent observed reflections were averaged.

Solution and Refinement of the Structure

The coordinates of the cobalt atom previously determined from the room-temperature data set by conventional Patterson techniques were used to phase an electron density map from which the coordinates of all the remaining nonhydrogen atoms were obtained.[12] Two cycles of full-matrix least-squares refinement of positional and isotropic thermal parameters (all atoms given boron scattering factors) of the 15 heavy atoms reduced the discrepancy indices R and R_w to 0.091 and 0.100, respectively.[9]

At this point an absorption correction was applied to the original data set ($\mu = 14.71$; maximum and minimum transmission factors were 0.9626 for 1,7,−1 and 0.9284 for 001), and the intensities of all the equivalent reflections were averaged. Those averaged reflections whose intensities were less than 3σ were considered unobserved and not subsequently employed; the remaining 1323 observed reflections were used for further structural refinement.

The positions of the polyhedral carbon atoms were easily recognized by their shorter bond distances and smaller temperature factors and were assigned carbon scattering factors. Further least-squares refinement reduced R to 0.063 and R_w to 0.077, and a difference Fourier synthesis indicated the positions of all the hydrogen atoms. Least-squares refinement of the positional parameters of all the atoms and the anisotropic thermal parameters of the heavy atoms, with anomalous dispersion corrections applied to the scattering of cobalt, resulted in convergence at $R = 0.032$, $R_w = 0.032$. Hydrogen atoms were given isotropic temperature factors of 2.7 Å^2.[13] The standard deviation of an observation of unit weight was 1.09.

Scattering factors for neutral cobalt, carbon, and boron were taken from ref 14; hydrogen scattering factors were obtained from Stewart, Davidson, and Simpson,[15] and the real and imaginary corrections for anomalous scattering of cobalt were taken from Cromer.[16] The function $\Sigma w||F_o| - |F_c||^2$ was minimized in least-squares refinement.

The final observed and calculated structure factors are available.[17]

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(10) "International Tables for X-Ray Crystallography," Vol. 1, Kynoch Press, Birmingham, England, 1962.

(11) C. E. Strouse, to be submitted for publication in *Rev. Sci. Instrum.*

(12) The programs used in this work have been listed previously.[1]

(13) A final least-squares cycle which varied all parameters, including the isotropic thermal parameters of the hydrogen atoms, was calculated; atoms Cp1H and B2H returned negative thermal parameters, while the temperature factors of the other hydrogen atoms were well-behaved.

(14) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962.

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

(16) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

Table II. Anisotropic Thermal Parameters[a]

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Co	68.7 (11)	7.8 (2)	27.9 (4)	−0.8 (5)	11.7 (5)	−0.4 (4)
Cp1	134 (11)	9 (2)	29 (4)	12 (3)	2 (5)	1 (2)
Cp2	77 (10)	7 (2)	76 (5)	7 (3)	34 (6)	−3 (2)
Cp3	233 (14)	5 (2)	56 (5)	16 (4)	61 (7)	2 (2)
Cp4	186 (13)	8 (2)	41 (4)	2 (4)	−6 (6)	−8 (2)
Cp5	124 (11)	8 (1)	52 (4)	−3 (3)	21 (5)	−3 (2)
B1	82 (10)	10 (2)	30 (4)	6 (3)	1 (5)	−5 (2)
B2	86 (11)	11 (2)	23 (4)	3 (4)	−2 (5)	1 (2)
B3	74 (10)	9 (2)	28 (4)	−3 (3)	6 (5)	−2 (2)
B4	61 (10)	10 (2)	31 (4)	1 (3)	7 (5)	−3 (2)
B5	105 (11)	13 (2)	26 (4)	2 (4)	−9 (6)	−4 (2)
C6	76 (10)	12 (2)	33 (4)	−2 (3)	−1 (5)	−2 (2)
C7	59 (9)	10 (2)	41 (4)	2 (3)	17 (5)	3 (2)
B9	75 (11)	21 (2)	33 (4)	−1 (4)	24 (6)	−4 (2)
B10	66 (10)	18 (2)	43 (5)	2 (4)	8 (6)	−8 (2)

[a] See footnote *a* of Table I. The anisotropic temperature factor T is defined as $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Thermal ellipsoids are depicted in the figures.

Atomic fractional coordinates are collected in Table I. Anisotropic thermal parameters are listed in Table II.

The Molecular Structure

Intramolecular distances and their estimated standard deviations (esd's) are listed in Table III. Average bond distances, with their root-mean-square deviations, are collected in Table IV. The individual bond angles and their associated esd's are presented in Table V. The structure of 8-η-C_5H_5-8-Co-6,7-$C_2B_7H_{11}$ is shown in Figure 1, which also illustrates the numbering system employed.[18] It should be noted that the crystal is composed of a mixture of *d* and *l* isomers. Figure 2 shows another view of the molecule, including the positions of the bridging hydrogen atoms. A unit cell packing diagram is presented in Figure 3.

The structure of the complex may be described in terms of a distorted decaborane(14) skeleton comprised of one cobalt, two carbon, and seven boron atoms. The cobalt atom occupies position 8 in the decaborane skeleton and is bound to boron atoms 3, 4, and 9, carbon atom 7, a planar η-cyclopentadienyl ring, and a hydrogen atom which occupies a bridging position between the cobalt atom and boron atom 9. A second bridging hydrogen atom is located between boron atoms 9 and 10. The polyhedral carbon atoms occupy positions 6 and 7 in the icosahedral fragment and are formally four- and five-coordinate, respectively. The overall geometry of the complex is quite similar to that observed in decaborane(14),[19] although certain bond angles and distances differ due to the presence of heteroatoms in the framework; no unusual bond distances or angles were observed.

Gaines and coworkers[20] have recently reported X-ray crystal structures of several metalloborane complexes which have a gross geometry similar to that observed in this work. These compounds, of the general formula $LB_9H_{12}Mn(CO)_3$, have a $Mn(CO)_3$ group in the 6 position of a decaborane skeleton, the metal being connected to the borane framework by means of a direct Mn–B2 bond and two three-center hydrogen bridge bonds, B5–H–Mn and B7–H–Mn;[21] the bridging hydrogen atoms were observed in difference Fourier maps,

Table III. Interatomic Distances[a]

Atoms	Distance, Å	Atoms	Distance, Å
Distances in the Cyclopentadienyl Ring			
Cp1–Cp2	1.408 (6)	Cp1–CpH1	0.92 (4)
Cp1–Cp5	1.409 (6)	Cp2–CpH2	0.92 (4)
Cp2–Cp3	1.404 (6)	Cp3–CpH3	0.83 (4)
Cp3–Cp4	1.408 (6)	Cp4–CpH4	0.94 (4)
Cp4–Cp5	1.405 (6)	Cp5–CpH5	0.93 (4)
Distances around Cobalt			
Co–Cp1	2.048 (4)	Cp–B3	2.120 (5)
Co–Cp2	2.071 (4)	Co–B4	2.113 (4)
Co–Cp3	2.039 (4)	Co–B9	2.068 (5)
Co–Cp4	2.042 (4)	Co–C7	2.090 (4)
Co–Cp5	2.047 (4)	Co–Hb1	1.40 (4)
Boron–Boron Distances			
B1–B2	1.740 (6)	B2–B3	1.778 (6)
B1–B3	1.813 (6)	B2–B5	1.799 (6)
B1–B4	1.823 (6)	B3–B4	1.797 (6)
B1–B5	1.784 (6)	B4–B9	1.759 (6)
B1–B10	1.761 (6)	B4–B10	1.784 (6)
		B5–B10	1.945 (7)
		B9–B10	1.755 (7)
Carbon–Boron Distances			
C6–B2	1.691 (6)	C7–B2	1.716 (6)
C6–B5	1.507 (6)	C7–B3	1.658 (6)
Carbon–Carbon Distance			
C6–C7	1.452 (5)		
Boron–Hydrogen Distances			
B1–BH1	1.13 (4)	B9–BH9	1.07 (4)
B2–BH2	1.15 (4)	B10–BH10	1.13 (4)
B3–BH3	1.08 (4)	B9–Hb1	1.31 (4)
B4–BH4	1.10 (4)	B9–Hb2	1.37 (4)
B5–BH5	1.12 (4)	B10–Hb2	1.20 (4)
Carbon–Hydrogen Distances			
C6–CH6	0.96 (4)	C7–CH7	1.01 (4)

[a] See footnote *a* of Table I.

Table IV. Average Bond Lengths

Atoms	No.	Range,[a] Å	Av,[b] Å
Co–C	6	2.039 (4)–2.090 (4)	2.06 (2)
Co–B	3	2.068 (5)–2.120 (5)	2.10 (3)
B–B	12	1.740 (6)–1.945 (7)	1.80 (5)
C–B	4	1.507 (6)–1.716 (6)	1.64 (9)
C–C(C_5H_5)	5	1.404 (6)–1.409 (6)	1.407 (2)
B–H(terminal)	7	1.07 (4)–1.15 (4)	1.11 (3)
C–H(C_5H_5)	5	0.83 (4)–0.93 (4)	0.91 (4)

[a] See footnote *a* of Table I. [b] Esd's for average bond lengths were calculated using the equation $\sigma^2 = [\Sigma_{i=1}^{i=N}(\chi_i - \overline{\chi})^2]/(N-1)$, where χ_i is the *i*th bond length and $\overline{\chi}$ is the mean of the N equivalent bond lengths.

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

(18) R. M. Adams, *Pure Appl. Chem.*, 30, 683 (1972).

(19) J. S. Kasper, C. M. Lucht, and D. Harker, *Acta Crystallogr.*, 3, 436 (1950).

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(21) The atom-numbering system employed here is the same positional numbering shown in Figure 1.

Table V. Interatomic Angles[a]

Atoms 1, 2, 3	Angle, deg	Atoms 1, 2, 3	Angle, deg
I. Angles around Cobalt			
A. C_5H_5-Co-C_5H_5			
Cp1-Co-Cp2	40.0 (2)	Cp1-Co-Cp3	67.0 (2)
Cp1-Co-Cp5	40.3 (2)	Cp1-Co-Cp4	67.5 (2)
Cp2-Co-Cp3	39.9 (2)	Cp2-Co-Cp4	67.7 (2)
Cp3-Co-Cp4	40.4 (2)	Cp2-Co-Cp5	67.6 (2)
Cp4-Co-Cp5	40.2 (2)	Cp3-Co-Cp5	67.4 (2)
B. $C_2B_7H_{11}$-Co-$C_2B_7H_{11}$			
B3-Co-B4	50.2 (2)	B4-Co-C7	85.7 (2)
B3-Co-C7	46.4 (2)	B4-Co-B9	49.7 (2)
B3-Co-B9	92.6 (2)	C7-Co-B9	101.1 (2)
C. C_5H_5-Co-$C_2B_7H_{11}$			
Cp1-Co-B3	162.4 (2)	Cp3-Co-C7	96.5 (2)
Cp1-Co-B4	140.6 (2)	Cp3-Co-B9	161.5 (2)
Cp1-Co-C7	132.4 (2)	Cp4-Co-B3	99.3 (2)
Cp1-Co-B9	104.2 (2)	Cp4-Co-B4	99.3 (2)
Cp2-Co-B3	125.3 (2)	Cp4-Co-C7	127.7 (2)
Cp2-Co-B4	166.3 (2)	Cp4-Co-C9	121.7 (2)
Cp2-Co-C7	98.6 (1)	Cp5-Co-B3	134.3 (2)
Cp2-Co-B9	140.4 (2)	Cp5-Co-B4	105.7 (2)
Cp3-Co-B3	95.4 (1)	Cp5-Co-C7	163.7 (2)
Cp3-Co-B4	126.9 (2)	Cp5-Co-B9	95.2 (2)
II. Cyclopentadienyl Ring Angles			
C-C-C Angles			
Cp1-Cp2-Cp3	106.8 (4)	Cp4-Cp5-Cp1	107.8 (4)
Cp2-Cp3-Cp4	109.2 (4)	Cp5-Cp1-Cp2	108.8 (4)
Cp3-Cp4-Cp5	107.4 (4)		
III. $C_2B_7H_{11}$ Cage Angles			
A. B-B-B Angles			
B2-B1-B3	60.0 (2)	B1-B4-B3	60.1 (2)
B2-B1-B4	113.6 (3)	B1-B4-B9	110.8 (3)
B2-B1-B5	61.4 (3)	B1-B4-B10	58.5 (2)
B2-B1-B10	120.3 (3)	B3-B4-B9	116.8 (3)
B3-B1-B4	59.2 (2)	B3-B4-B10	107.2 (3)
B3-B1-B5	102.1 (3)	B9-B4-B10	59.4 (2)
B3-B1-B10	107.5 (3)	B1-B5-B2	58.1 (2)
B4-B1-B5	109.3 (3)	B1-B5-B10	56.2 (2)
B4-B1-B10	59.7 (2)	B2-B5-B10	108.3 (3)
B5-B1-B10	66.6 (3)	B4-B9-B10	61.0 (3)
B1-B2-B3	62.1 (2)	B1-B10-B4	61.9 (2)
B1-B2-B5	60.5 (2)	B1-B10-B5	57.3 (2)
B3-B2-B5	102.9 (3)	B1-B10-B9	114.0 (3)
B1-B3-B2	57.9 (2)	B4-B10-B5	104.1 (3)
B1-B3-B4	60.6 (2)	B4-B10-B9	59.6 (2)
B2-B3-B4	113.0 (3)	B5-B10-B9	112.5 (3)
B. C-B-B Angles			
C6-B2-B1	100.4 (3)	C7-B3-B1	101.2 (3)
C6-B2-B3	97.5 (3)	C7-B3-B2	59.8 (2)
C6-B2-B5	51.1 (2)	C7-B3-B4	111.6 (3)
C7-B2-B1	101.9 (3)	C6-B5-B1	106.1 (3)
C7-B2-B3	56.6 (2)	C6-B5-B2	60.8 (3)
C7-B2-B5	91.2 (3)	C6-B5-B10	115.9 (3)
C. B-C-B Angles			
B2-C6-B5	68.2 (3)	B2-C7-B3	63.6 (2)
D. C-C-B Angles			
C7-C6-B2	65.7 (3)	C6-C7-B2	63.9 (3)
C7-C6-B5	116.2 (3)	C6-C7-B3	113.8 (3)
E. C-B-C Angle			
C6-B2-C7	50.4 (2)		
F. Angles Involving Bridge Hydrogens			
B9-Co-Hb1	38.7 (15)	B10-B9-Hb2	43.2 (17)
Co-B9-Hb1	41.8 (17)	B9-B10-Hb2	51.4 (20)
Hb1-B9-Hb2	92.7 (23)		

[a] See footnote *a* of Table V.

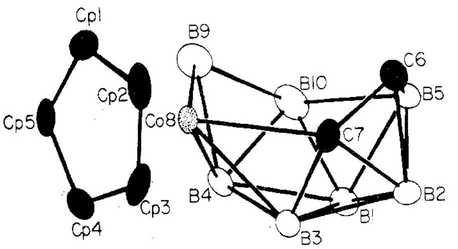

Figure 1. Structure and numbering of 8-η-C_5H_5-8-Co-6,7-$C_2B_7H_{11}$. The terminal and bridge hydrogen atoms are omitted for clarity. Atoms shown as 50% probability ellipsoids.

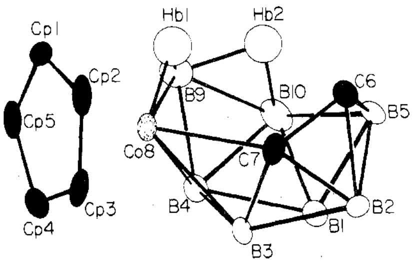

Figure 2. Alternate view of 8-η-C_5H_5-8-Co-6,7-$C_2B_7H_{11}$ showing positions of bridging hydrogen atoms.

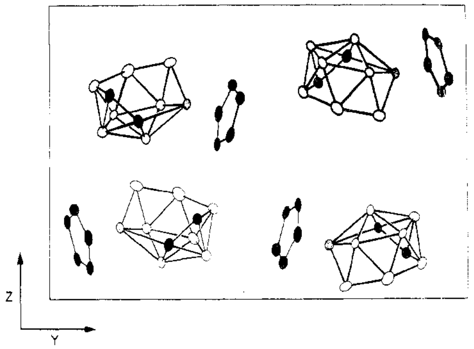

Figure 3. Packing of molecules within the unit cell.

but their positional and thermal parameters were not refined. In general, the bond distances and angles observed by these workers are, when chemically comparable, in good agreement with the values found in this work. One difference, however, exists in the bond distances observed between the bridging hydrogen atoms and the metal. Gaines, *et al.*, have generally found the Mn-H_{bridge} distance to be *ca.* 1.64-1.83 (~10) Å,[20] while our results indicate Co-Hb1 = 1.40 (4) Å. These differences, while still within three standard deviations, may reflect stronger metal interaction with the bridging hydrogen atom in the cobalt complex.[22]

Several authors[23] have recently discussed electron counting methods which allow the prediction of nido or closo structures in boranes, carboranes, and metallocarboranes. It is noteworthy that application of these rules predicts that 24 electrons are available for polyhedral bonding in the pres-

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(22) At the suggestion of a referee, additional refinements of the hydrogen positions were carried out based on only the low-angle data ($2\theta_{max} = 30$ and 40°). The refinement with $2\theta_{max} = 30°$ resulted in a lengthening of the Co-Hb1 bond length to 1.53 (4) Å, a change of about three standard deviations from the distance of 1.40 (4) Å obtained in the refinement with the more complete data set. This bond distance remains shorter than would be expected based on previously observed metal-bridging hydrogen distances [see ref 20 and, for example, L. J. Guggenberger, *Inorg. Chem.*, 9, 367 (1970); R. A. Love and R. Bau, *J. Amer. Chem. Soc.*, 94, 8274 (1972); S. J. Lippard and K. M. Melmed, *ibid.*, 8, 2755 (1969)]. The bond distances of 1.78-1.85 Å obtained in these room-temperature studies all had estimated standard deviations of 0.05-0.10 Å, and therefore the differences between these bond distances and the distance obtained in the present investigation appear to be of marginal significance.

(23) K. Wade, *Chem. Commun.*, 792 (1971); C. J. Jones, W. J. Evans, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 543 (1973); R. W. Rudolph and W. R. Pretzer, *Inorg. Chem.*, 11, 1974 (1972).

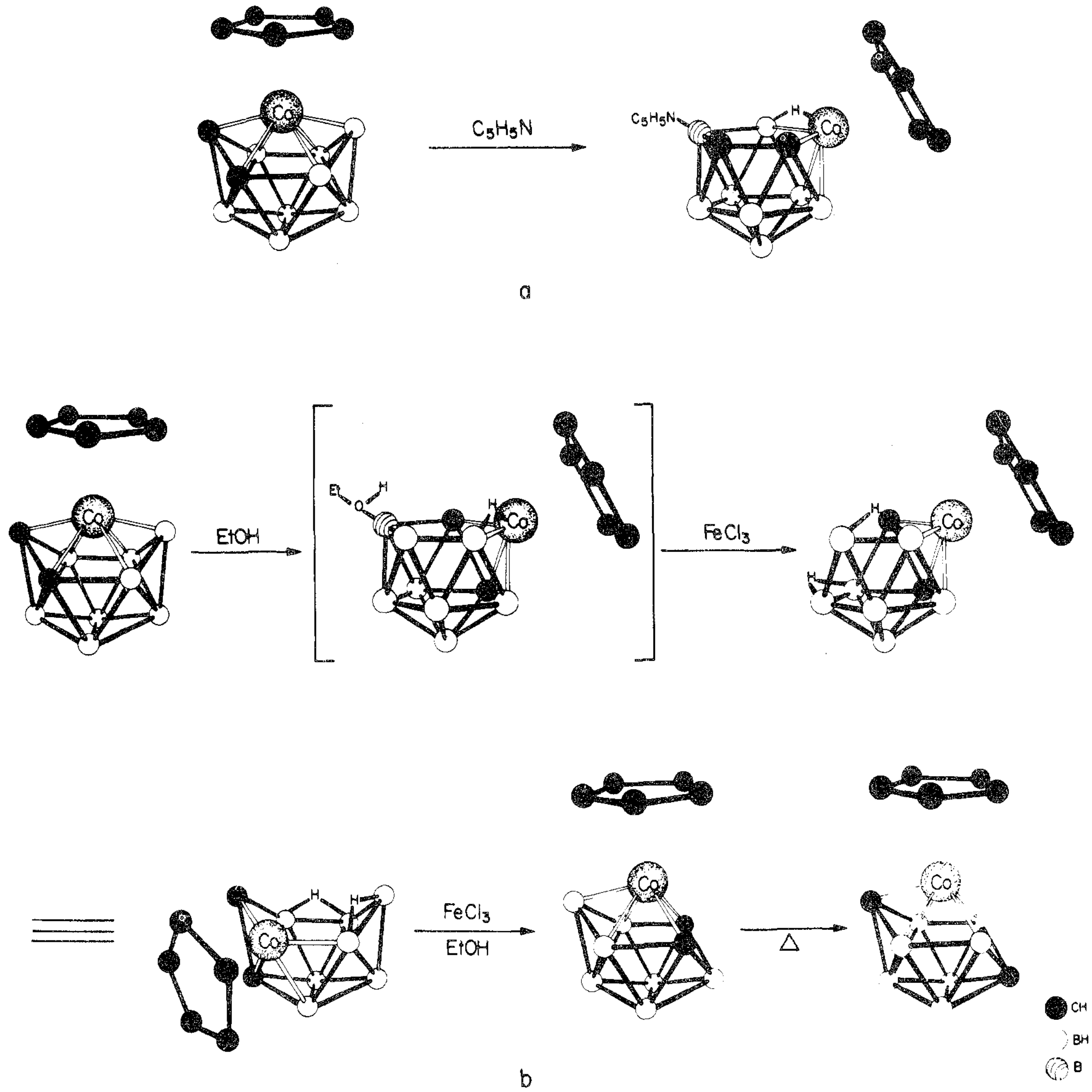

Figure 4. (a) Synthesis of $C_5H_5CoC_2B_8H_{10}NC_5H_5$. (b) Previously proposed mechanism for the formation and reactions of $C_5H_5CoC_2B_7H_{11}$.

ent compound, in $B_{10}H_{14}$, and in $(CO)_3MnB_9H_{12}L$ and that these compounds all exhibit the same gross geometry. The 24 available electrons are two electrons in excess of the $2n + 2$ (n = number of polyhedral vertices) required to form a closo structure, and these compounds are predicted to have nido geometries, as observed.

Chemical Aspects

This crystal structure determination has provided the identity of the major product of polyhedral contraction of 1-η-C_5H_5-1-Co-2,4-$C_2B_8H_{10}$. An earlier structural proposal[8] involved two B-H-B bridge interactions in this new compound, $C_5H_5CoC_2B_7H_{11}$, and two high-field resonances attributable to bridging hydrogen atoms were found in the ^1H nmr spectrum, 4.19 and 18.30 ppm above TMS. The large chemical shift difference of the two bridging hydrogens indicated significant differences in environment around these bridges. Our structural determination of this compound validates the conclusion of highly different bridge hydrogen environments and also validates, in this instance, the suggestions of Grimes[24] and of our group[7] that ^1H nmr resonances of bridging protons in metallocarboranes which appear more than 5 ppm above TMS usually indicate the presence of a hydrogen bridging between metal and boron.

Mechanistic Aspects

It was previously known[7] that 1-η-C_5H_5-1-Co-2,4-$C_2B_8H_{10}$ reacted with pyridine to produce an adduct, $C_5H_5CoC_2B_8H_{10}NC_5H_5$, whose structure, on the basis of ^{11}B nmr and other spectral data, is similar to that crystallographically determined[25] in the anion $(C_2B_9H_{11}CoC_2B_8H_{10}NC_5H_5)^-$, which was synthesized in a similar fashion from $(C_2B_9H_{11}Co\text{-}2,4\text{-}C_2B_8H_{10})^-$ (Figure 4a). It was originally proposed[8] that in the present system the reaction of 1-η-C_5H_5-1-Co-2,4-$C_2B_8H_{10}$ with ethanol in the presence of ferric chloride also produced a ligand adduct in which an alternate geometry was adopted (Figure 4b). The reason for the proposal of a different stereochemistry for the ethanol adduct was the identification of two products resulting from the $FeCl_3$ oxidation of the ethanol adduct. The main product was found to be $C_5H_5CoC_2B_7H_{11}$, which we have structurally characterized in this work. A side product (2% yield) was spectrally identified as 6-η-C_5H_5-6-Co-2,3-$C_2B_7H_9$ (Figure 4b). The observation that traces of this latter compound could be detected during the treatment of $C_5H_5CoC_2B_7H_{11}$ with $FeCl_3$

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[24] L. G. Sneddon and R. N. Grimes, *J. Amer. Chem. Soc.*, 94, 7161 (1972).

[25] M. R. Churchill and K. Gold, *Inorg. Chem.*, 12, 1157 (1973).

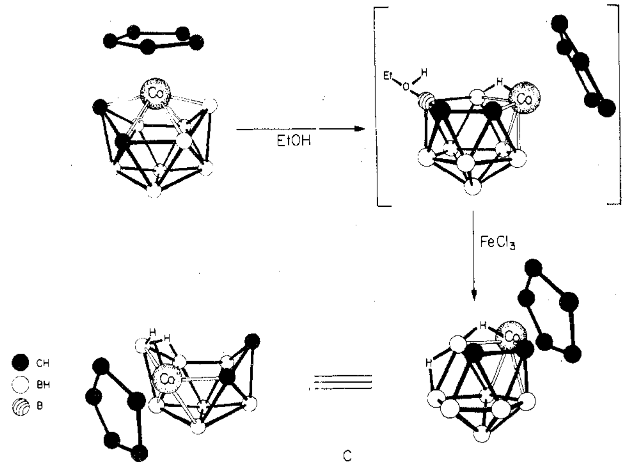

Figure 5. Proposed mechanism of formation of 8-η-C_5H_5-8-Co-6,7-$C_2B_7H_{11}$.

in ethanol led to the conclusion that 6-η-C_5H_5-6-Co-2,3-$C_2B_7H_9$ was produced upon dehydrogenation of $C_5H_5CoC_2B_7H_{11}$, and the structure proposed for this latter compound was that which would readily close to produce the observed isomer of closo geometry. To rationalize the structure of $C_5H_5CoC_2B_7H_{11}$ thus generated, an alternate site of ligand attack in the reaction of 1-η-C_5H_5-1-Co-2,4-$C_2B_8H_{10}$ with ethanol and $FeCl_3$ was proposed. This proposed reaction sequence is shown in Figure 4b.

The structural results presented here indicate that there is no evidence to support a mode of attachment of ethanol to 1-η-C_5H_5-1-Co-2,4-$C_2B_8H_{10}$ different from that observed for pyridine. Instead, we envision the reaction to proceed in a manner similar to that observed with pyridine. Ferric chloride oxidation would remove the ligand-substituted boron atom from the polyhedron and thus generate the *nido*-8-η-C_5H_5-8-Co-6,7-$C_2B_7H_{11}$ geometry found here (Figure 5c).

Dehydrogenation of this compound would not produce 6-η-C_5H_5-6-Co-2,3-$C_2B_7H_9$, however. Closure would instead produce the presently unknown species 3-η-C_5H_5-3-Co-1,2-$C_2B_7H_9$. This compound would be expected to undergo rapid thermal polyhedral rearrangement[26] to produce, in turn, the 1,6 and 1,10 isomers (carbon positions numbered only), and, in fact, 2-η-C_5H_5-2-Co-1,10-$C_2B_7H_9$ is the major product isolated from the reaction of 8-η-C_5H_5-8-Co-6,7-$C_2B_7H_{11}$ with ethanolic ferric chloride (only traces of 6-η-C_5H_5-6-Co-2,3-$C_2B_7H_9$ were noticed in the reaction mixture). It therefore appears that the side product, 6-η-C_5H_5-6-Co-2,3-$C_2B_7H_9$, is not an intermediate in the reaction sequence 1-η-C_5H_5-1-Co-2,4-$C_2B_8H_{10}$ $\rightarrow$ $C_5H_5CoC_2B_7H_{11}$ $\rightarrow$ 2-η-C_5H_5-2-Co-1,10-$C_2B_7H_9$. The origin of this side product still remains obscure. It could arise in the initial reaction solution by oxidative removal of boron atom 8 from 1-η-C_5H_5-1-Co-2,4-$C_2B_8H_{10}$ followed by polyhedral closure, but its production from $C_5H_5CoC_2B_7H_{11}$ must involve substantial polyhedral rearrangement.

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Supplementary Material Available. Observed and calculated structure factors for 8-η-C_5H_5-8-Co-6,7-$C_2B_7H_{11}$ 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-74-2842.

(26) M. F. Hawthorne, K. P. Callahan, and R. J. Wiersema, *Tetrahedon*, **30**, 1795 (1974), and references therein.

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Description of a Monovalent Nickel Complex. Crystal and Molecular Structure of Iodo[1,1,1-tris(diphenylphosphinomethyl)ethane]nickel(I)

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The complex of nickel(I) with the terdentate ligand 1,1,1-tris(diphenylphosphinomethyl)ethane (p_3), having the formula $Ni(p_3)I$, has been studied by X-ray analysis using diffractometric data. The crystals are orthorhombic, space group $Pn2_1a$, with cell dimensions $a = 20.439$ (6), $b = 17.143$ (7), and $c = 10.359$ (3) Å. The structure has been solved by three-dimensional Patterson and Fourier syntheses and refined by least-squares techniques to a final conventional R factor of 0.051, for the 2357 independent observed reflections. The structure consists of discrete $Ni(p_3)I$ molecules. The nickel atoms are four-coordinate, linked to the three phosphorus atoms of the p_3 ligand and to the iodine atom. The coordination polyhedron can be described as a distorted tetrahedron. Bond lengths and angles in the coordination polyhedron are Ni–I = 2.546 (2), Ni–P(1) = 2.222 (4), Ni–P(2) = 2.224 (4), Ni–P(3) = 2.217 (4) Å; I–Ni–P(1) = 125.0 (1), I–Ni–P(2) = 125.3 (1), I–Ni–P(3) = 116.2 (1), P(1)–Ni–P(2) = 91.8 (1), P(1)–Ni–P(3) = 94.1 (1), P(2)–Ni–P(3) = 96.9 (1)°.

Introduction

By reaction of the potentially terdentate tripod ligand 1,1,1-tris(diphenylphosphinomethyl)ethane, $CH_3C(CH_2PPh_2)_3$ (p_3), with NiI_2 and CoI_2 in alcoholic solution, nickel(I) and cobalt(I) complexes having the general formula $M(p_3)I$ are formed.[1] This reaction can be attributed to the reducing

(1) L. Sacconi and S. Midollini, *J. Chem. Soc., Dalton Trans.*, 1213 (1972).