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(6) Tetracarbon Metallocarboranes. 6. Stereochemical Relationships Between $Co_2^{II}C_4^{II}B_6^{II}$ Cage Isomers Formed by Oxidative Fusion. Crystal Structure of $(\eta^5\text{-}C_5^{II}H_5^{II})_2^{II}Co_2^{II}(CH_3)_4^{II}C_4^{II}B_6^{II}H_6^{II}$, Isomer V.

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Tetracarbon Metallocarboranes. 6.[1] Stereochemical Relationships Between $Co_2C_4B_6$ Cage Isomers Formed by Oxidative Fusion. Crystal Structure of $(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_4C_4B_6H_6$, Isomer V

J. Robert Pipal and Russell N. Grimes*

Abstract. The crystal and molecular structure of the title compound was determined from X-ray diffraction data and found to consist of two pentagonal pyramidal $(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_3H_3$ units which are partially fused together along their C_2B_3 faces, such that the pairs of carbon atoms on the two pyramidal units are separated by nonbonding distances. The molecule resembles a severely distorted icosahedron with a large opening on one side, and its central cage system is very similar to that previously reported for the monocobalt complex $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_6\text{-}OC_2H_5$. From ^{11}B and ^1H NMR data, the title compound is isostructural with isomer V of the $(\eta^5\text{-}C_5H_5)_2Co_2C_4B_6H_{10}$ system, which was previously obtained together with two other isomers (VI and VII) in the oxidative fusion of 1,2,3-$(\eta^5\text{-}C_5H_5)CoC_2B_3H_7$ in ethanolic KOH. These three isomers adopt different types of cage geometry, as determined from the present study, from an X-ray investigation of VII, and from NMR data on isomer VI. A structure is proposed for isomer VI, and a mechanism is suggested to account for the formation of the three $(\eta^5\text{-}C_5H_5)_2Co_2C_4B_6H_{10}$ species from $(\eta^5\text{-}C_5H_5)CoC_2B_3H_7$ as well as the formation

of a single isomer of $(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_4C_4B_6H_6$ (the title compound) from $(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_3H_5$. Crystal data for $(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_4C_4B_6H_6$: space group $I\bar{4}2d$, $Z = 8$; $a = 13.838(2)$, $c = 20.635(5)$ Å; $V = 3951(1)$ Å^3; $R = 0.034$ for the 1021 reflections for which $F_o^2 > 3\sigma(F_o^2)$.

Introduction

Structural studies of carboranes and metallocarboranes having four carbon atoms in the same polyhedron are proving to be an effective probe of the relationship between electron population and cage geometry, and have revealed a number of unprecedented molecular shapes.[2] Since the formal replacement of a BH by a CH (or C-alkyl) group in a closed polyhedral (closo) system increases the number of valence electrons in the cage skeleton, one can predict from electron-counting arguments[3] that tetracarbon carboranes will exhibit cage structures that are more open than their dicarbon counterparts; simply put, this is a consequence of the fact that the additional electrons in most cases must occupy antibonding orbitals, thereby producing some sort of cage-opening or distortion. However, this general principle does not tell us what kind of distortion to expect in a particular case, or what the geometry of a particular tetracarbon species will be. This is emphatically the case in 12-vertex, 28-electron cage systems[4], which contain two more skeletal electrons than do 26-electron icosahedral species such as $C_2B_{10}H_{12}$ and $B_{12}H_{12}^{2-}$. All of the structurally characterized 28-electron cages are distorted from icosahedral geometry, but the nature of the distortion varies widely; as we pointed out recently[4], at least four different types of cage geometry have been identified among the 12-vertex, 28-electron species that have been structurally characterized.

Most striking are the cases in which isomers produced in the same reaction adopt markedly different polyhedral shapes.[1,5,6] A recent example[1] is given by the oxidative fusion of the small metallocarborane 1,2,3-$(\eta^5\text{-}C_5H_5)CoC_2B_3H_7$ in ethanolic KOH, which produces $(\eta^5\text{-}C_5H_5)CoC_4B_7H_{11}$ and three isomers of $(\eta^5\text{-}C_5H_5)_2Co_2C_4B_6H_{10}$ (a 12-vertex, 28-electron system). We have previously described the synthetic chemistry together with a crystallographic study of one of the three dicobalt isomers.[1] In this paper we report the structural characterization of a second isomer via its C-tetramethyl derivative, and propose a structure for the third isomer as well as a possible pathway for the formation of all three species.

Experimental Section

Crystals of $(C_5H_5)_2Co_2(CH_3)_4C_4B_6H_6$ were grown by the vapor diffusion of pentane into a methylene chloride solution of the compound. One of these multifaceted crystals, a rough parallelopiped with dimensions of 0.5 x 0.5 x 0.25 mm, was mounted on a glass fiber in an arbitrary orientation and examined by preliminary precession photographs which indicated high crystal quality. Crystal data: $Co_2C_{18}B_6H_{28}$; mol wt 427.16; space group $I\bar{4}2d$ (No. 122); Z = 8; a = 13.838(2), c = 20.635(5) Å; V = 3951(1) Å^3; μ(MoKα) = 17.0 cm^{-1}; ρ_c = 1.405 g/cm^3; F(000) = 1760. For this crystal the Enraf-Nonius program SEARCH was used to obtain 25

accurately centered reflections which were then used in the program INDEX to obtain an orientation matrix for data collection and to provide approximate cell dimensions. Refined cell dimensions and their estimated standard deviations were determined using these same 25 reflections and the Enraf-Nonius program UNICELL. The mosaicity of the crystal was examined by the ω scan technique and found acceptable. Systematic absences of $h + k + \ell = 2n + 1$ for $h\ k\ \ell$, $(k + \ell = 2n + 1)$ on $0\ k\ \ell$ and $2h + \ell \neq 4n$ on $h\ k\ \ell$, indicate that the space group is either $I4_1md$ or $I\bar{4}2d$. The latter was shown to be correct. For $Z = 8$, this is consistent with the molecular formula assuming 19.0 A^{o3} per nonhydrogen atom and twofold symmetry for the molecule.

Collection and Reduction of the Data. Diffraction data were collected at 295°K on an Enraf-Nonius four circle CAD-4 diffractometer controlled by a PDP8/M computer, using MoKα radiation from a highly oriented graphite crystal monochrometer. The θ-2θ scan technique was used to record the intensities for all reflections for which $1^\circ \leq 2\theta \leq 52^\circ$. Scan widths were calculated from the formula $SW = A + B\tan\theta$ where A is estimated from the mosaicity of the crystal and B compensates for the increase in the width of the peak due to $K\alpha_1$ and $K\alpha_2$ splitting. The values of A and B were 0.60 and 0.35° respectively. This calculated scan angle was extended at each side by 25% for background determination (BG1 and BG2). The net count (NC) was then calculated as NC = TOT - 2(BG1 + BG2) where TOT is the estimated peak intensity.

Reflection data were considered insignificant for intensities registering less than ten counts above background on a rapid prescan, and these reflections were rejected automatically by the computer. The intensities of three standard reflections were monitored at intervals of 100 reflections and showed no systematic trends. Raw intensity data were corrected for Lorentz-polarization effects which resulted in a total of 1264 intensities of which 1021 had $F_o^2 \geq 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics using an ignorance factor[7] of 0.03. These latter reflections were used in the final refinement of the structural parameters.

Solution and Refinement of the Structure. Initial efforts at solution and refinement were performed assuming $I4_1md$ as the space group. With this choice, solution of the Patterson map for the possible coordinates of the unique cobalt was achieved but many strong peaks in the map were not accounted for. This set of coordinates failed to refine. Various reasonable estimates of the cobalt position consistent with minor symmetry for the molecule (with Z = 8) and spectroscopic information (NMR) likewise failed to refine in $I4_1md$. Therefore this initial choice was abandoned in favor of $I\bar{4}2d$. With some difficulty, the Patterson was solved unambiguously for the position of the unique cobalt. The second cobalt in the molecule is related to the first by the crystallographic fourfold roto-inversion operation in $I\bar{4}2d$ carried out twice. Least squares refinement

of the cobalt atom coordinates and thermal parameters reduced the conventional residual R to 0.255. An electron density difference map phased on this refined cobalt yielded ten of the twelve unique remaining nonhydrogen atoms; subsequent maps were used to locate the last two. Isotropic followed by anistropic refinement lowered R to 0.045 and R_w to 0.069, where R and R_w are defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $(\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$ respectively.

Several more electron density difference maps were then used to locate the positions of the terminal hydrogens bonded to the boron atoms as well as possible locations for the methyl hydrogens. The former successfully refined with isotropic thermal parameters. The latter did not, and were replaced by hydrogen atoms held fixed at calculated positions 0.95 Å from their respective carbons. Further refinement reduced the residuals to their final values of R = 0.034 and R_w = 0.043. The estimated standard deviation of an observation of unit weight is 2.301 and the ratio of data to parameters is 7.9. During the last cycle of refinement the largest parameter shift was 0.01 times its estimated error. A structure factor calculation including those data for which $F_o^2 < 3\sigma(F_o^2)$ gave R = 0.050. No absorption correction was attempted because of the very irregular multifaceted nature of the crystal. Given the crystal's boxlike shape and its relatively

small absorption coefficient, the error from this source was judged insignificant. A final electron density difference map was featureless.

Full matrix least squares refinement was based on F, and the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The weights w were taken as $[2F_o/\sigma(F_o^2)]^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber[8] and those for hydrogen from Stewart.[9] The effects of anomalous dispersion were included in F_c using Cromer and Ibers'[10] values of $\Delta f'$ and $\Delta f''$. The computing system and programs are described elsewhere.[11] A table of observed and calculated structure factors is available (see paragraph at end of paper regarding supplementary material).

Results and Discussion

Final positional and thermal parameters are given in Table I while Tables II and III contain intramolecular distances and angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figure quoted and were derived from the inverse matrix in the course of least squares refinement calculations. Tables IV and V list selected mean planes and intermolecular contacts, respectively. Figure 1 is a stereoscopic view of the molecule.

Description of the Structure. The molecule consists of two pyramidal CoC_2B_3 units whose pentagonal faces are partially fused along their respective B(4)-B(5)-B(6)-C(2) and B(4')-B(5')-B(6')-C(2') edges (primed and unprimed atoms are related by a crystallographic twofold axis through the molecule). The distances between the pair of framework carbons atoms C(2), C(3) and their counterparts C(2'), C(3') are clearly nonbonding (2.7 Å or greater), so that the cage has a large opening on the side facing the viewer in Figure 1. This geometry is very similar to that of 1,2,3,7,8-$(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_6\text{-}OC_2H_5$[4] (Figure 2a), an analogue of the present structure in which one $Co(C_5H_5)$ unit has been replaced by $B\text{-}OC_2H_5$; for comparison, the dihedral angle between the C_2B_3 ring planes is 26.3° in the present structure and 28.5° in the monocobalt species.[4] Similarly, the C(3)-C(3') distance across the open face in the dicobalt species is 2.791(5) Å, while the corresponding vector in the monocobalt structure [C(3)-C(7)] is 2.854(6) Å. These data indicate that the $Co_2C_4B_6$ framework is slightly less open than the CoC_4B_7 cage. On the other hand, both the $Co_2C_4B_6$ and CoC_4B_7 systems are significantly different from $(CH_3)_4C_4B_8H_8$[12] (Figure 2b), in which the central C-C interaction is bonding [1.53(1) Å]. Since these three species form an

isoelectronic series with 28 skeletal electrons, one can say that formal replacement of one apex BH unit in $(CH_3)_4C_4B_8H_8$- with a $Co(\eta^5\text{-}C_5H_5)$ group produces a major structural change, but replacement of the second apex BH has little effect. These findings are important in light of the severe differences that have been observed between $Co_2C_4B_6$ isomers, to be discussed below.

Relationship to the Structures of $(\eta^5\text{-}C_5H_5)_2Co_2C_4B_6H_{10}$- Isomers. As described elsewhere[1], the nido complex 1,2,3-$(\eta^5\text{-}C_5H_5)CoC_2B_3H_7$ can be deprotonated by treatment with KOH/ethanol or sodium hydride in tetrahydrofuran. The resulting anion, when exposed to air in 10% ethanolic KOH solution, undergoes oxidative fusion[2] to generate a series of tetracarbon metallocarboranes as well as other products,[1] in yields of a few percent each.

$$(C_5H_5)CoC_2B_3H_7 \xrightarrow{C_2H_5O^-} (C_5H_5)CoC_2B_3H_6^- \xrightarrow{C_2H_5O^-}$$

$(C_5H_5)_2Co_2C_4B_6H_{10}$ Isomers V, VI, and VII
$+(C_5H_5)CoC_4B_7H_{11}$
$+1,7,2,3\text{-}(C_5H_5)_2Co_2C_2B_3H_5$

When the C,C'-dimethyl species 1,2,3-$(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_3H_5$ is treated in identical fashion, the only tetracarbon metallocarborane obtained is a single isomer of $(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_4C_4B_6H_6$, the compound whose structure we report in this paper. From the 32.1-MHz ^{11}B and 100-MHz ^1H pulse Fourier transform

NMR spectra[1], it is clear that this complex is a C-tetramethyl derivative of $(\eta^5\text{-}C_5H_5)_2Co_2C_4B_6H_{10}$, isomer V; hence, the gross cage geometry of the tetramethyl species (Figure 1) is assumed to be that of the parent isomer V.

The structures of the two crystallographically characterized isomers, V and VII[1], are clearly different (Figure 3), and in fact constitute different types of nido cages. The geometry of V can be described as a severely distorted icosahedron, while VII resembles a 13-vertex closo polyhedron from which the unique high-coordinate vertex has been removed (this type of cage is also found in $(\eta^5\text{-}C_5H_5)Fe(CH_3)_4C_4B_7H_8$,[5] an isoelectronic analogue of VII). From NMR data, to be discussed below, it is highly probable that the remaining isomer, VI, falls into yet another structural class.

The formation of three structurally dissimilar cobaltocarborane isomers at room temperature in the same reaction can only be interpreted in terms of kinetic factors which are dependent on reaction conditions. Whatever the thermodynamically preferred geometry of the $Co_2C_4B_6$ system may be (and it could well be different from any of the three observed isomers V, VI, or VII), the structures of the isolated products no doubt reflect specific pathways by which they are generated from the CoC_2B_3 precursor. In Figure 3 we suggest a scheme for the formation of all three isomers. The initial step probably involves formation of a "quadruple-decker" complex (I) in which two $(\eta^5\text{-}C_5H_5)CoC_2B_3H_3^{2-}$ ligands are

sandwiched around a central CoH^{4+} group; this process would be precisely analogous to the known synthesis[13] of $[(CH_3)_2C_2B_4H_4]_2CoH$ from the $(CH_3)_2C_2B_4H_5^-$ ion and $CoCl_2$ in THF. In the present case, the source of the central cobalt ion is doubtless the degradation of the original monocobalt complex in basic media, which is extensive and produces a variety of products.[1] Complex I has not been isolated due to its rapid conversion to other species, but NMR evidence for the existence of its C-tetramethyl derivative has been obtained.[14]

Subsequent air-oxidation of I results in oxidative fusion of the two $(\eta^5\text{-}C_5H_5)CoC_2B_3H_5^{2-}$ ligands to produce the neutral $(\eta^5\text{-}C_5H_5)_2Co_2C_4B_6H_{10}$ complexes.[1] In our proposed scheme this occurs through the partially linked intermediate II, which with minor adjustment becomes the observed isomer V; again, this is a process directly analogous to the known conversion,[13,15] of $[(CH_3)_2C_2B_4H_4]_2CoH$ or $[(CH_3)_2C_2B_4H_4]_2FeH_2$ to $(CH_3)_4C_4B_8H_8$. Indeed, as was pointed out earlier, isomer V is a structural counterpart of $(CH_3)_4C_4B_8H_8$ in which the central C-C interaction is stretched to nonbonding distance.

Intermediate II is also proposed to undergo an alternative type of rearrangement to produce the symmetric intermediate III from which isomers VI and VII are formed as shown. The suggested structure of VI is based on its ^{11}B and ^1H NMR spectra[1], which indicate C_{2v} symmetry with two boron environments in a 2:4 ratio

and equivalent $(C_5H_5)Co$ groups. The area-2 ^{11}B signal appears at very low field (δ 69.1 ppm relative to BF_3 etherate), strongly suggesting the presence of two four-coordinate BH units [B(5), B(5')] located adjacent to both cobalt nuclei.[16,17] These data are highly restrictive, and while alternative structures cannot be ruled out, a pseudo-icosahedral type cage seems strongly indicated for isomer VI. Mild distortion of the idealized C_{2v} geometry in Figure 3 (perhaps lowering the symmetry to C_2) would not be surprising, but a highly opened framework (such as VII, for example) would be difficult to recondile with the NMR observations.

The scheme shown in Figure 3 also provides a rationale for the fact that only isomer V of $(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_4C_4B_6H_6$ is obtained when the starting material is $(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_3H_5$, as opposed to the three isomers (V, VI, VII) that are formed from the parent (non-methylated) complex. In isomers VI and VII, the framework carbon atoms are in close proximity, requiring the two HC-CH pairs in intermediate III to move toward each other. In isomer V, on the other hand, no such close approach is involved and the two pairs of carbon atoms are in fact well separated. One might then expect that in the C- tetramethylated system, the cage geometry of V would be strongly favored and those of VI and VII hindered, as a consequence of methyl-methyl repulsions.

Conclusions

The structure reported in this paper, taken together with previously established structures,[1,2,4,12,13] extends our understanding of tetracarbon cobaltacarborane stereochemistry in a significant way: it allows us to consider in some detail the mechanisms of formation and interconversion of the $Co_2C_4B_6$ cage isomers. In general, we appear to have reached a point at which the available structural information in this area can support at least some mechanistic ideas. In other publications we shall attempt to deal with the observed[15] reversible rearrangement of $(CH_3)_4C_4B_8H_8$ isomers, the formation and stereochemistry of $(CH_3)_4C_4B_8H_8^{2-}$ and $(CH_3)_4C_4B_8H_9^-$ ions,[5] the insertion of transition metals into these species to give tetracarbon metallocarboranes of various types,[2] and related problems.

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Supplementary Material Available: Listing of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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(17) Support for this assignment is the fact that (1) no other known tetracarbon metallocarborane has an ^{11}B resonance lower than $\delta \sim 35$ ppm, and (2) no previously characterized tetracarbon metallocarborane has a low-coordinate boron adjacent to more than one metal. Thus, the strikingly different ^{11}B spectrum of VI implies a structural type not previously seen in this class of compounds.

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atom	X	Y	Z	U11	U22	U33	U12	U13	U23
Co	0.33176(4)	0.05600(4)	0.03268(3)	0.0341(2)	0.0315(2)	0.0407(2)	0.0008(2)	-0.0058(2)	0.0047(2)
C(2)	0.3941(3)	-0.0445(3)	0.0899(2)	0.033(2)	0.027(2)	0.036(2)	0.001(2)	-0.001(2)	0.005(2)
C(3)	0.4135(3)	0.0519(3)	0.1105(2)	0.034(2)	0.028(2)	0.033(2)	0.004(2)	-0.003(1)	-0.002(2)
CM(2)	0.3393(3)	-0.1166(3)	0.1304(3)	0.045(2)	0.035(2)	0.069(3)	-0.005(2)	-0.001(3)	0.012(2)
CM(3)	0.3851(3)	0.0884(3)	0.1775(2)	0.047(2)	0.048(2)	0.047(2)	0.005(2)	0.004(2)	-0.010(2)
CP(1)	0.2417(4)	0.1725(4)	0.0310(4)	0.052(2)	0.043(2)	0.201(6)	0.021(2)	-0.065(3)	-0.022(4)
CP(2)	0.2542(4)	0.1319(4)	-0.0358(3)	0.048(2)	0.085(3)	0.102(4)	0.003(3)	-0.019(3)	0.051(3)
CP(3)	0.2190(4)	0.0387(5)	-0.0337(3)	0.049(2)	0.085(4)	0.064(3)	0.001(3)	-0.024(2)	-0.001(3)
CP(4)	0.1861(4)	0.0183(4)	0.0287(3)	0.042(2)	0.061(3)	0.092(4)	-0.001(2)	-0.015(3)	0.016(3)
CP(5)	0.1979(4)	0.0974(5)	0.0690(3)	0.049(2)	0.088(4)	0.067(3)	0.023(3)	-0.007(3)	-0.003(3)
B(4)	0.4746(3)	0.1117(3)	0.0616(3)	0.035(2)	0.029(2)	0.050(2)	0.001(2)	-0.000(2)	0.002(2)
B(5)	0.4613(4)	0.0512(4)	-0.0178(2)	0.041(2)	0.049(3)	0.038(2)	-0.001(2)	0.002(2)	0.007(2)
B(6)	0.4181(4)	-0.0665(4)	0.0132(2)	0.038(2)	0.038(2)	0.040(2)	-0.005(2)	-0.006(2)	-0.010(2)
H(4)	0.490(3)	0.192(3)	0.063(2)	2.1(7) [b]					
H(5)	0.452(4)	0.084(4)	-0.069(2)	5.9(14)					
H(6)	0.377(3)	-0.122(3)	-0.012(2)	2.4(8)					
H(21)	0.334	-0.176	0.107	6.0					
H(22)	0.372	-0.127	0.170	6.0					
H(23)	0.276	-0.092	0.139	6.0					
H(31)	0.404	0.154	0.182	6.0					
H(32)	0.317	0.084	0.182	6.0					
H(33)	0.416	0.051	0.210	6.0					

THE FORM OF THE ANISOTROPIC THERMAL PARAMETER IS $\exp\left[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}h\ell a^*c^* + 2U_{23}k\ell b^*c^*)\right]$. [b]For hydrogen atoms, standard isotropic B values are given.

Table II. Interatomic Distances (Å)[a]

Bonded Distances

Co-C(2)	2.017(3)	C(3)-CM(3)	1.524(4)
Co-C(3)	1.965(3)	B(4)-B(5)	1.849(5)
Co-B(4)	2.205(4)	B(4)-B(6')	1.895(5)
Co-B(5)	2.074(3)	B(4)-H(4)	1.14(3)
Co-B(6)	2.112(4)	B(5)-B(5')	1.776(8)
Co-CP(1)	2.039(3)	B(5)-B(6)	1.848(5)
Co-CP(2)	2.062(4)	B(5)-B(6')	1.800(5)
Co-CP(3)	2.090(4)	B(5)-H(5)	1.17(4)
Co-CP(4)	2.084(4)	B(6)-H(6)	1.09(3)
Co-CP(5)	2.079(4)	CP(1)-CP(2)	1.500(7)
C(2)-C(3)	1.425(4)	CP(2)-CP(3)	1.379(6)
C(2)-B(4')	2.122(4)	CP(3)-CP(4)	1.394(6)
C(2)-B(6)	1.645(4)	CP(4)-CP(5)	1.385(6)
C(2)-CM(2)	1.507(4)	CP(5)-CP(1)	1.436(7)
C(3)-B(4)	1.555(4)		

Nonbonded Distances

Co-Co'	4.907(1)	C(2)-C(3')	2.698(4)
C(2)-C(2')	3.178(6)	C(3)-C(3')	2.791(5)

[a]Atoms marked with a prime are related to their unmarked counterparts by an inversion axis which bisects the B(5)-B(5') and C(3)-C(3') vectors.

Table III. Selected Bond Angles (deg)

C(2)-Co-C(3)	41.9(1)	C(2')-B(4)-C(3)	93.1(2)
C(2)-Co-B(6)	46.9(1)	C(2')-B(4)-B(6')	47.9(2)
C(3)-Co-B(4)	43.3(1)	B(5)-B(4)-B(6')	57.4(2)
B(4)-Co-B(5)	51.1(1)	C(3)-B(4)-B(5)	106.2(2)
B(5)-Co-B(6)	52.4(2)	Co-B(5)-B(4)	68.1(2)
Co-C(2)-C(3)	67.1(1)	Co-B(5)-B(6)	64.9(2)
Co-C(2)-B(6)	69.6(2)	B(4)-B(5)-B(6')	62.6(2)
C(3)-C(2)-B(4')	109.3(2)	B(5')-B(5)-B(6')	62.3(2)
C(3)-C(2)-B(6)	115.0(3)	B(5')-B(5)-B(6)	59.5(2)
B(4')-C(2)-B(6)	58.8(2)	B(4)-B(5)-B(6)	97.2(2)
Co-C(2)-CM(2)	124.5(2)	Co-B(6)-C(2)	63.5(2)
C(3)-C(2)-CM(2)	123.3(3)	Co-B(6)-B(5)	62.8(2)
B(4')-C(2)-CM(2)	107.0(2)	C(2)-B(6)-B(4')	73.3(2)
B(6)-C(2)-CM(2)	120.8(3)	B(4')-B(6)-B(5')	60.0(2)
Co-C(3)-C(2)	71.0(2)	B(5)-B(6)-B(5')	58.2(2)
Co-C(3)-B(4)	76.6(2)	C(2)-B(6)-B(5)	103.6(2)
C(2)-C(3)-B(4)	114.0(3)	CP(2)-CP(1)-CP(5)	106.2(3)
Co-C(3)-CM(3)	125.7(2)	CP(1)-CP(2)-CP(3)	106.3(4)
C(2)-C(3)-CM(3)	122.2(3)	CP(2)-CP(3)-CP(4)	109.5(4)
B(4)-C(3)-CM(3)	123.5(3)	CP(3)-CP(4)-CP(5)	110.8(4)
Co-B(4)-C(3)	60.1(2)	CP(1)-CP(5)-CP(4)	107.1(4)
Co-B(4)-B(5)	60.8(2)		

Table IV. Selected Intramolecular Planes

Atom	Deviation	Atom	Deviation
	Plane 1: C(2), C(3), B(4), B(5), B(6) 0.9081x - 0.3516y + 0.2274z = 5.5732		
C(2)	-0.017	B(6)	-0.066
C(3)	0.111	Co	1.524
B(4)	-0.137	CM(2)	0.131
B(5)	0.109	CM(3)	0.332
	Plane 2: C(2'), C(3'), B(4'), B(5'), B(6') 0.9081x - 0.3516y - 0.2274z = 6.9927		
	Plane 3: CP(1), CP(2), CP(3), CP(4), CP(5) 0.9083x - 0.3337y + 0.2521z = 2.3999		
CP(1)	-0.002	CP(4)	-0.003
CP(2)	0.000	CP(5)	0.003
CP(3)	0.002	Co	-1.682
	Plane 4: CP(1'), CP(2'), CP(3'), CP(4'), CP(5') 0.9083x - 0.3337y - 0.2521z = 10.169		

Planes	Angle, deg	Planes	Angle, deg
1,2	26.3	2,3	27.8
1,3	1.8	2,4	1.8
1,4	27.8	3,4	29.2

Table V. Intermolecular Non-Hydrogen Contacts (<3.8 Å)

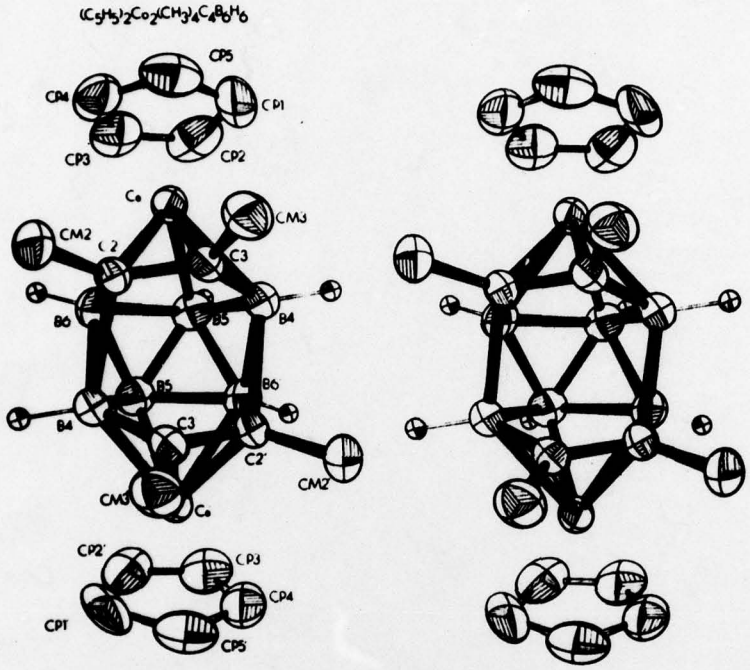
Atom 1	Atom 2	Distance, Å	Relationship
CM(2)	CM(2)	3.699(6)	x, -1/2-y, 1/4-z
CM(2)	CP(2)	3.797(5)	y, -1/2+x, 1/4+z
CP(2)	CP(2)	3.68(1)	1/2-x, y, -1/4-z
CP(3)	CP(5)	3.753(6)	-y, x, -z

Figure Captions

Figure 1. Molecular structure of $(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_4C_4B_6H_6$. Primed atoms are related to the corresponding unprimed atoms by a crystallographic twofold axis bisecting the B(5)-B(5') bond.

Figure 2. Comparison of the structures of $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_6\text{-}OC_2H_5$ (a)[4] and $(CH_3)_4C_4B_8H_8$ (b).[12]

Figure 3. Proposed mechanism of formation of $(\eta^5\text{-}C_5H_5)_2Co_2C_4B_6H_{10}$ isomers. The structures of isomers V and VII are established; that of VI is proposed from NMR evidence. Species I, II, and III are suggested reaction intermediates. The conversion of II to III can occur via insertion of B(5') between B(5) and B(4) and insertion of B(5) between B(5') and B(4'), with subsequent linkage of B(5') to Co(1) and of B(5) to Co(1'); the other rearrangements depicted are obvious.


(C5H5)2Co2(CH3)4C4B6H6
CP5
CP4
CP1
CP3
CP2
C
CM2
C2
CM3
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B6
B5
B4
B5
B6
B4
C3
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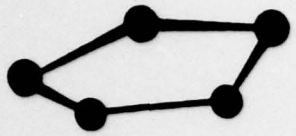
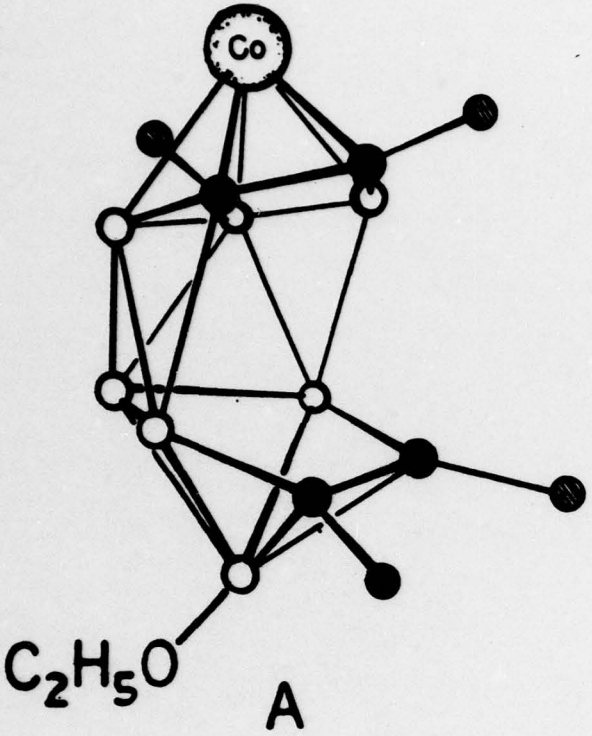
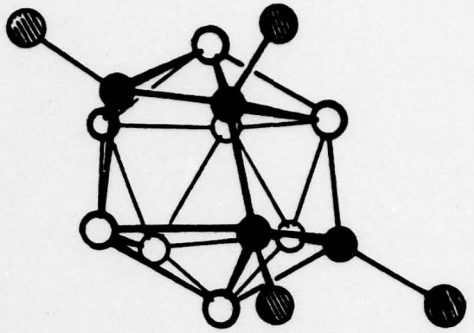
CM3
C
CP2
CP3
CP4
CP1
CP5



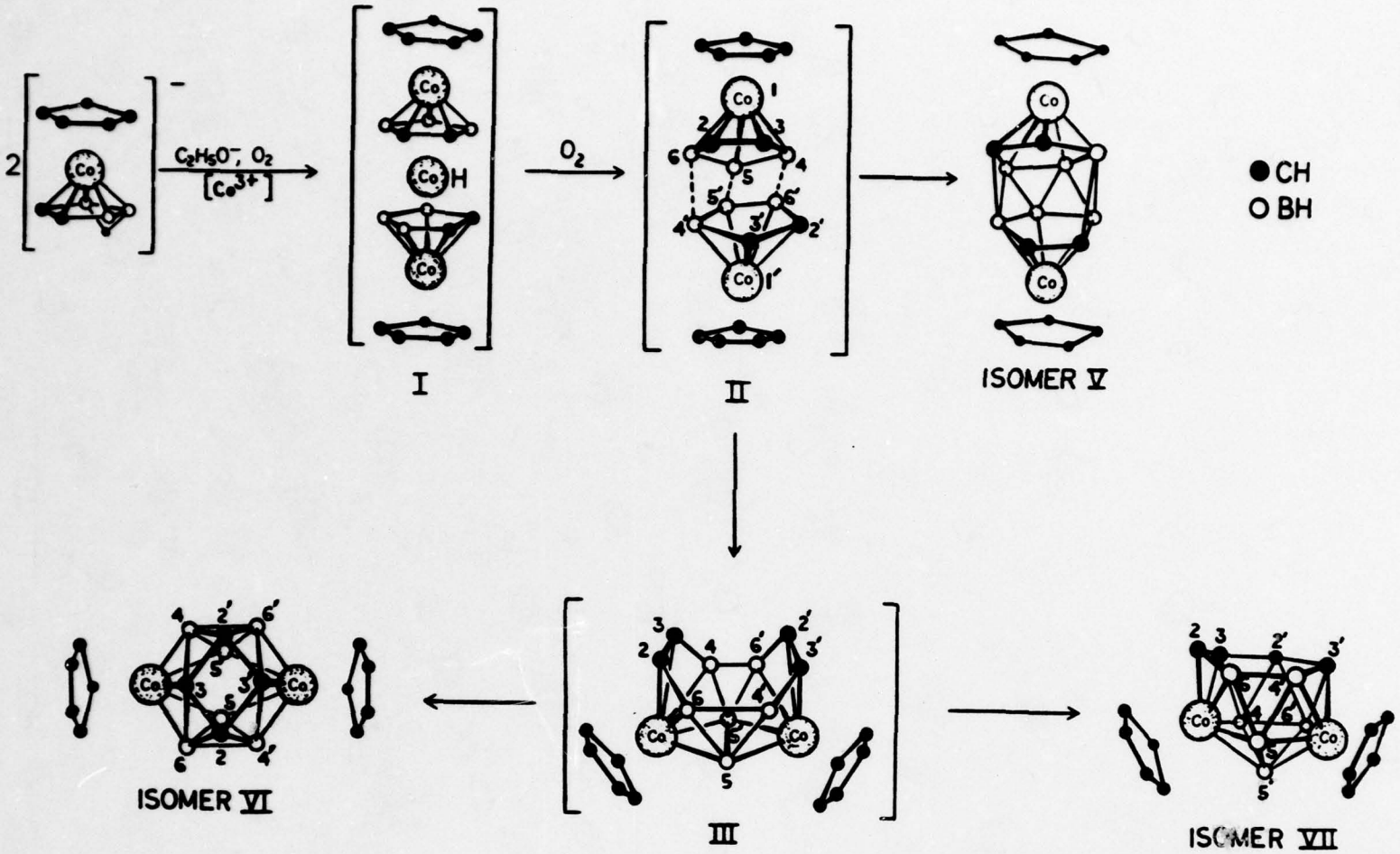


A



B

○B, BH ●C, CH ◉CH_3



FORMATION OF $(C_5H_5)_2Co_2C_4B_6H_{10}$ ISOMERS

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