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(6) Tetracarbon Metallacarboranes. 10.[1] On the Thermodynamically Favored Geometry of Large Nido Cages. Structure of the Thermal Rearrangement Product (Isomer III) of $(\eta^5-C_5H_5)Co(CH_3)_4C_4B_7H_7$

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Tetracarbon Metallacarboranes. 10.[1] On the Thermodynamically Favored Geometry of Large Nido Cages. Structure of the Thermal Rearrangement Product (Isomer III) of $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_7$

Richard B. Maynard, Ekk Sinn, and Russell N. Grimes*

Abstract. The preferred structure of 12-vertex, 28-electron (nido) polyhedral cages, which contain two skeletal electrons beyond the 26 required for a regular closo icosahedral system, and which have thus far been found in at least 7 different structural classes, was the focus of this investigation. The crystal and molecular structure of the title compound, which was formed by thermal rearrangement of isomer I at 140°C, were determined by single-crystal X-ray diffraction. Isomer III has an open cage geometry in which all four carbon atoms and two borons reside on a 6-membered open face, with one of the carbons isolated from the other three. The cage is isostructural with the previously eta 5 characterized metallacarboranes $(\eta^5\text{-}C_5H_5)Fe(CH_3)_4C_4B_7H_8$ and $(\eta^5\text{-}C_5H_5)_2Co_2C_4B_6H_{10}$, isomer VII; however, the structures of the three isomers of $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_7$ are grossly different from each other. The observed geometry of isomer III implies a thermodynamic preference of skeletal carbon atoms for low-coordinate vertices on the open rim, even though this requires three of the four carbons to remain adjacent. The adoption of a high-coordinate

→ next page

vertex by cobalt is also significant. The 7 established classes of 12-vertex, 28-electron cage systems are discussed in light of the present study. Crystal data: mol wt 314.9, space group C2/c, Z = 8; a = 25.944(8), b = 8.686(3), c = 15.410(5) Å, β = 108.47(3)°; V = 3294 Å³; R = 0.052 for 1542 independent reflections having $F_o^2 > 3\sigma(F_o)^2$.

deg.

beta

square

sigma

sub 0

Introduction

The four-carbon carboranes $(CH_3)_4C_4B_8H_8$, $(CH_3)_4C_4B_8H_8^{2-}$, $(CH_3)_4C_4B_7H_9$, and metallacarboranes derived from them, form a structurally diverse family of cages having 11 to 14 vertices. As revealed by X-ray investigations,[2] the framework geometries of many of these systems are highly irregular, in that they deviate markedly from ideal closo polyhedra or fragments thereof. In most of the metal-containing species it is apparent that the cage structures are dictated primarily by the mode of metal attack on the carborane framework,[3] and are kinetically rather than thermodynamically stabilized. This has been conclusively established[4] for the 14-vertex $(\eta^5\text{-}C_5H_5)_2Fe_2(CH_3)_4C_4B_8H_8$ isomers I-IV, which form by metal insertion into $(CH_3)_4C_4B_8H_8^{2-}$ under mild conditions and feature asymmetric, open-cage structures; at 300°C these isomers ultimately rearrange to the thermodynamically favored D_{2d} closo polyhedron. For most other C_4 metallacarborane systems, however, the most-stable geometry has not been determined.

An intrinsically important class of cage structures consists of species having 12 framework atoms and 28 skeletal electrons (Figure 1).[5] These molecules are (2n + 4)-electron (nido) systems[6] whose special significance lies in the presence of two "extra" electrons beyond the normal allotment of 26 for a regular 12-vertex icosahedron. Known 26-electron species such as $B_{12}H_{12}^{2-}$ and $C_2B_{10}H_{12}$ are closed-shell electronic systems in which the

13 available bonding molecular orbitals in the cage skeleton are precisely filled;[7] introduction of more electrons must therefore induce distortion from icosahedral symmetry. However, the nature of such distortions depends crucially on the type, number, and location of skeletal heteroatoms[5] and leads to a fascinating variety of cage structures, as can be seen in the Figure.

Earlier papers[1-5] have dealt with a number of 28-electron and 30-electron (nido and arachno) 12-vertex metallacarboranes, most of which were obtained under mild conditions and hence could not be presumed to reflect thermodynamically preferred geometries. In the present article we report the structure of a new isomer (III) of a 28-electron, 12-vertex species, $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_7$, whose isomers I and II have previously been characterized.[1,8] Since isomer III was formed by thermal rearrangement of isomer I at 140°C,[8] its geometry is obviously relevant to the question of thermodynamic stability in MC_4B_7 nido systems, and in 12-vertex nido cages in general.

Experimental Section

Orange plates of $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_7$, isomer III, obtained by pyrolysis of isomer I as described elsewhere,[8] were grown over 14 days by vapor diffusion of hexane into a tetrahydrofuran (THF) solution at 0°C. A crystal was selected for data collection and mounted on a glass fiber in an arbitrary orientation. Crystal data: $CoC_{13}B_7H_{24}$, mol wt 314.9, space group C2/c, Z = 8; a = 25.944(8), b = 8.686(3), c = 15.410(5) Å; β = 108.47(3)°;

$V = 3294\ \mathring{A}^3$; $\mu(MoK\alpha) = 10.7\ cm^{-1}$; $\rho_{calcd} = 1.27\ g\ cm^{-3}$; crystal dimensions (mm from centroid): (100) 0.125, ($\bar{1}00$) 0.125, (010) 0.21, ($0\bar{1}0$) 0.21, (001) 0.02, ($00\bar{1}$) 0.02. The Enraf-Nonius program SEARCH was used to obtain 25 accurately centered reflections which were then employed in the program INDEX to obtain an orientation matrix for data collection and also to provide approximate cell constants. Refined cell dimensions and their estimated standard deviations were obtained from least squares refinement of 25 accurately centered reflections. The mosaicity of the crystal was examined by the ω-scan technique and found to be satisfactory. Systematic absences of $h + k = 2n + 1$ for $hk\ell$, $l = 2n + 1$ for $h0\ell$, and $k = 2n + 1$ for $0k0$ indicated possible space groups C2/c or Cc; since the centric space group C2/c was found to provide a satisfactory model, the noncentric group Cc was not considered further. For Z = 8 this is consistent with the molecular formula assuming $19.6\ \mathring{A}^3$ per nonhydrogen atom.

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 $MoK\alpha$ radiation from a highly oriented graphite crystal monochrometer. The θ-2θ scan technique was used to record the intensities for all reflections for which $1^\circ \leq 2\theta \leq 46^\circ$. 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 $K\alpha_1 - K\alpha_2$ splitting. The values of A and B respectively were 0.60 and 0.35° for both compounds. 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. 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 and their standard deviations were calculated in the usual manner from counting statistics ($\rho = 0.03$).[9] This resulted in 2437 reflections of which 1542 had $F_o^2 > 3\sigma(F_o^2)$ after averaging of equivalent reflections. Only those data for which $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement of structural parameters.

Solution and Refinement of the Structure. A three-dimensional Patterson synthesis was used to locate the metal atom, whose position permitted the location of all other nonhydrogen atoms and B-H hydrogen atoms from difference Fourier maps. Some methyl hydrogens were located from the Fourier maps; the remaining methyl hydrogens, and all cyclopentadienyl hydrogens, were introduced into calculated positions. All hydrogens were included in the refinement for several cycles and thereafter held fixed. Following absorption corrections (maximum and minimum absorption coefficients were 0.95 and 0.91), refinement was continued to convergence with final values of $R = 0.052$ and $R_w = 0.055$, where $R = \Sigma||F_o|| - |F_c||/\Sigma|F_o|$ and $R_w = (\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2)^{1/2}$.

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[10] and those for hydrogen from Stewart.[11] The effects of anomalous dispersion were included in F_c using Cromer and Ibers'[12] values of $\Delta f'$ and $\Delta f''$. The computing system and programs are described elsewhere.[13] Tables of observed and calculated structure factors are available (see paragraph at end of paper regarding supplementary material).

The error in an observation of unit weight was 2.0, and the largest parameter shift in the last cycle of refinement was 0.05 times the estimated standard deviation. There are no close intermolecular contacts, the shortest (nonhydrogen) distance being 3.448(7) Å between C(2P) and C(3P).

Results and Discussion

Final positional and thermal parameters are given in Table I, while Tables II and III list interatomic distances and angles; Figures 2 and 3 present stereoviews of the molecular structure and unit cell packing, respectively. The cage framework is an open basket with a well-defined open face on which all four framework carbons are located. This structure is entirely consistent with the previously reported[8] ^{1}H and ^{11}B spectra, which indicated a CoC_4B_7 cage of low symmetry in which all boron and framework carbons are non-equivalent.

Comparison with Isostructural Complexes. The molecule clearly belongs in the structural class designated as Type 5 in Figure 1; it is isostructural (and also cage-isoelectronic) with the previously characterized Type 5 species $(\eta^5\text{-}C_5H_5)Fe(CH_3)_4C_4B_7H_8$[14] and $(\eta^5\text{-}C_5H_5)_2Co_2C_4B_6H_{10}$, isomer VII,[15] both of which are also depicted in Figure 1. The Type 5 geometry can be described as a 13-vertex closo polyhedron[16] from which a high-coordinate vertex has been removed. As such, it is the only one of the six structural classes in Figure 1 that readily fits the standard definition[6d] of a nido cage as a closo polyhedron minus one vertex.

Although the three Type 5 cages are of similar gross shape, the arrangement of skeletal carbon atoms is different. In the dicobalt species, all four carbons occupy contiguous vertices on the open face; in the iron complex, only three carbons are on the open face, the fourth being as far from it as possible;[17] and in the present (monocobalt) species, all four carbons are on the open face but one is separated from the others. Moreover, a comparison of the analogous framework C-C and Co-C bond distances in the three species (Table IV) reveals a striking difference between the dicobalt compound and the other two: the central carbon-carbon interaction [C(11)-C(12)] in $(C_5H_5)_2Co_2C_4B_6H_{10}$ is much shorter (by 0.14 Å) than the corresponding C-C distances in the FeC_4B_7 and CoC_4B_7 complexes. On the other hand, the C(7)-C(12) bond lengths in the three molecules are similar and relatively short (1.42 - 1.45 Å) suggesting that there is significant localized bonding between the low-coordinate carbon C(7) and its neighboring carbon atom in each system; in the CoC_4B_7 and FeC_4B_7 cages, this localized C(7)-C(12) bonding is evidently at the expense of the C(11)-C(12) interaction which is depleted in electron density and hence relatively weak. In the dicobalt complex, it would appear that the presence of a second metal atom at the other end of the cage induces a more even distribution of bonding electron density through the three-carbon chain on the open rim, with more nearly equal C-C distances [the C(11)-C(10) length, which has no counterpart in the CoC_4B_7 and FeC_4B_7 cages, is 1.530(8) Å].[15] If this interpretation is valid, one should of course expect to see corresponding effects in other Type 5 metallacarboranes as their X-ray structures become available.

Comparison with $(\eta^5\text{-}C_5H_5Co(CH_3)_4C_4B_7H_7$, Isomers I and II. The structures of isomers I and II (Figure 4) have previously been established via X-ray studies of the parent compounds[1,18] and a B-ethoxy derivative[5] of isomer I. Although the cage geometries of isomers I, II and, III are of Types 4, 6, and 5 respectively (Figure 1), this is not the first example of metallacarborane isomers involving three different structural classes; it was shown in earlier work[15,19] that the dicobalt system $(\eta^5\text{-}C_5H_5)_2Co_2C_4B_6H_{10}$ forms isomers of Types 2, 4, and 5 (only the latter two have been crystallographically confirmed). Similarly, the 14-vertex $(\eta^5\text{-}C_5H_5)_2Fe_2(CH_3)_4C_4B_8H_8$ isomers also exhibit at least three different types of cage structure.[4] In contrast, gross structural variation among isomers is extremely rare in dicarbon metallacarboranes,[20] where isomerism usually is restricted to interchange of heteroatoms among different vertices of a common polyhedral framework.

The synthetic origins of isomers I and II of $(\eta^5-C_5H_5)Co(CH_3)_4C_4B_7H_7$ have been described earlier.[8] Isomer I was produced, together with two isomers of $(\eta^5-C_5H_5)Co(CH_3)_4C_4B_6H_6$, by reaction of $(\eta^5-C_5H_5)Co(CO)_2$ with $(CH_3)_4C_4B_7H_7$ in THF under UV light; it has also been obtained by oxidation of the sandwich compound closo, nido-$[(CH_3)_2C_2B_4H_4]CoH[(CH_3)_2C_2B_3H_5]$ in the presence of $CoCl_2$ and $C_5H_5^-$. Isomer II was a minor product of the treatment of $(CH_3)_4C_4B_8H_8^{2-}$ ion with $CoCl_2$, $C_5H_5^-$, and HCl in THF. All of these syntheses were conducted at room temperature.

The thermolysis of isomer I at 140°C for 18 hr in n-nonane solution under a nitrogen atmosphere formed isomer III in 50% yield, with no other products detected.[8] Thus, the cage structure of isomer III is thermodynamically favored relative to that of I; moreover, we believe it to be the most stable arrangement for this system (see below) although this has not been conclusively proved. We will not discuss here the cage rearrangement mechanism, but will note that a possible pathway for interconversion of $(C_5H_5)_2Co_2C_4B_6H_{10}$ isomers of Type 4 and Type 5 geometry has been presented elsewhere (see ref. 19, Figure 3); an analogous scheme would apply equally to the present isomerization of CoC_4B_7 species.

Several trends are evident in the I → III rearrangement: (1) adoption of a true nido (Type 5) geometry; (2) retention of low-coordinate vertices on the open face by the carbon atoms; (3) movement of one carbon to an isolated position with respect to the other carbons; and (4) adoption of a 6-coordinate vertex by the cobalt atom. The first trend is not surprising, since the

Type 5 arrangement is more compact and probably permits more efficient framework electron delocalization, and hence a lower-energy system, than does Type 4 (isomer I). Trend (2) is probably not a major driving force in the isomerization, since all cage carbons are low-coordinate in both isomers. Trend (3) reflects the well-known tendency of framework carbon atoms to separate from each other; it is noteworthy, however, that <u>none of the carbons chooses to leave the open face in order to achieve carbon-carbon separation</u>. Thus, clearly the preference of carbon atoms to achieve (or retain) low coordination[6d] outweighs their mutual repulsion, and the observed structure represents the maximum possible C-C separation for a Type 5 cage in which all carbons are on the open rim.

Finally, the increase in coordination of cobalt from five to six with respect to the cage may be a factor in the rearrangement since there is a general (but by no means invariable) tendency for iron and cobalt atoms to adopt high-coordinate vertices when given a choice; one can argue that the higher coordination sites permit slightly better overlap between metal and cage orbitals (with electron-rich metals such as nickel, however, the situation is often reversed so that low-coordinate vertices are favored[21]).

All of the evidence to date leads us to believe that Type 5 geometry is the preferred arrangement for 12-vertex, 28-electron metallacarboranes. This does not, however, hold true for 12-vertex, 28-electron carboranes lacking metal atoms, in which the tendency to retain a near-icosahedral arrangement is clearly evident

(Figure 1). As earlier work has shown, $(CH_3)_4C_4B_8H_8$ exists in solution[22] as an equilibrium mixture of two forms (evidently Types 2 and 3, Figure 1), and in the solid[23] as Type 3 only; the compound does not rearrange up to its decomposition temperature. Thus, the presence of one or more metal atoms in the cage can have a profound influence on the cage geometry even when the formal skeletal electron count is held constant.

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Supplementary Material Available: Listings of observed and calculated structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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TABLE I. POSITIONAL AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS[a,b]

ATOM	X	Y	Z	B11	B22	B33	B12	B13	B23
CO	0.16769(3)	-0.0231(1)	0.06401(6)	2.53(3)	2.84(3)	4.93(3)	0.04(4)	1.28(2)	-0.32(4)
C(7)	0.0849(2)	0.0050(7)	0.0340(4)	2.0(2)	3.1(3)	4.2(2)	0.4(2)	1.2(2)	-0.0(2)
C(9)	0.0855(2)	-0.2813(7)	-0.0399(4)	3.5(3)	2.9(3)	4.1(3)	-0.2(2)	0.9(2)	-0.8(3)
C(11)	0.0950(2)	-0.2293(8)	0.1434(4)	3.8(3)	5.5(4)	3.5(3)	-0.3(3)	1.4(2)	0.9(3)
C(12)	0.1029(2)	-0.0492(8)	0.1265(4)	3.2(2)	5.2(4)	4.5(3)	0.3(3)	2.0(2)	-0.9(3)
C(7M)	0.0585(3)	0.1646(9)	0.0144(5)	3.8(3)	5.0(4)	7.0(4)	1.3(3)	1.3(3)	-0.1(3)
C(9M)	0.0512(3)	-0.3528(10)	-0.1298(5)	5.5(4)	5.8(4)	5.7(4)	-1.1(3)	1.3(3)	-1.1(3)
C(11M)	0.0699(3)	-0.2615(11)	0.2185(5)	7.2(4)	9.5(6)	5.0(3)	-1.2(4)	2.9(3)	1.2(4)
C(12M)	0.0981(3)	0.0572(10)	0.2017(5)	7.1(4)	7.6(5)	6.2(3)	0.5(4)	3.5(3)	-1.6(4)
C(1P)	0.1914(3)	0.2043(8)	0.0922(5)	5.2(3)	3.1(3)	8.8(4)	-1.3(3)	2.6(3)	-1.6(3)
C(2P)	0.1839(3)	0.1708(9)	0.0017(5)	5.1(3)	5.3(4)	7.9(4)	-1.9(3)	1.6(3)	1.0(4)
C(3P)	0.2189(3)	0.0583(9)	-0.0022(6)	8.9(3)	5.4(4)	14.0(4)	-4.1(3)	8.9(2)	-3.7(4)
C(4P)	0.2487(3)	0.0141(9)	0.0854(8)	3.1(3)	3.5(4)	19.9(8)	-0.4(3)	3.5(4)	0.6(5)
C(5P)	0.2316(3)	0.1089(10)	0.1450(6)	5.7(4)	7.8(5)	7.3(5)	-4.3(3)	-1.4(4)	1.0(4)
B(1)	0.1860(3)	-0.2612(9)	0.0884(6)	2.9(3)	3.3(4)	6.1(4)	0.5(3)	1.4(3)	0.2(3)
B(3)	0.1491(3)	-0.2238(9)	-0.0251(5)	3.6(3)	3.0(4)	4.9(4)	0.2(3)	1.6(3)	-0.6(3)
B(4)	0.1355(3)	-0.3891(9)	0.0248(6)	4.2(3)	2.4(4)	7.1(4)	0.4(3)	2.1(3)	-0.0(4)
B(5)	0.1424(3)	-0.3577(10)	0.1382(6)	4.1(4)	3.6(4)	5.9(4)	0.1(3)	0.3(3)	1.7(4)
B(6)	0.1625(3)	-0.1717(11)	0.1692(6)	4.1(4)	4.9(5)	4.7(4)	0.2(4)	0.5(3)	0.4(4)
B(8)	0.0877(3)	-0.0892(9)	-0.0428(5)	2.4(3)	3.6(3)	3.8(3)	0.5(3)	0.9(2)	0.9(3)
B(10)	0.0752(3)	-0.3331(9)	0.0529(5)	3.0(3)	3.5(4)	5.1(4)	-0.2(3)	1.2(3)	0.6(3)
H(1)	0.233(2)	-0.294(7)	0.114(4)	4.(1)					
H(3)	0.160(2)	-0.215(6)	-0.094(3)	4.(1)					
H(4)	0.144(2)	-0.499(6)	0.002(3)	4.(1)					
H(5)	0.156(2)	-0.460(7)	0.192(3)	5.(1)					

H(6)	0.181(2)	-0.129(7)	0.246(4)	4.(1)
H(8)	0.070(2)	-0.040(6)	-0.116(3)	3.(1)
H(10)	0.043(2)	-0.421(7)	0.043(3)	4.(1)
H(1P)	0.172(2)	0.277(8)	0.118(4)	6.(2)
H(2P)	0.158(2)	0.221(7)	-0.047(4)	5.(1)
H(3P)	0.220(2)	0.016(8)	-0.062(4)	7.(2)
H(4P)	0.274(2)	-0.065(8)	0.102(4)	7.(2)
H(5P)	0.244(2)	0.100(8)	0.208(4)	6.(2)
H(71M)	0.022(2)	0.168(7)	-0.000(3)	4.(1)
H(72M)	0.062(2)	0.194(7)	-0.040(4)	5.(2)
H(73M)	0.077(2)	0.213(7)	0.071(4)	6.(2)
H(91M)	0.011(2)	-0.340(7)	-0.153(4)	6.(2)
H(92M)	0.059(3)	-0.457(8)	-0.127(4)	8.(2)
H(93M)	0.065(2)	-0.316(8)	-0.174(4)	7.(2)
H(111M)	0.039(2)	-0.195(7)	0.274(4)	6.(2)
H(112M)	0.075(2)	-0.365(8)	0.237(4)	7.(2)
H(113M)	0.034(2)	-0.239(7)	0.201(4)	5.(2)
H(121M)	0.125(2)	0.007(7)	0.268(4)	6.(2)
H(122M)	0.062(2)	0.061(8)	0.202(4)	6.(2)
H(123M)	0.110(3)	0.160(8)	0.194(4)	7.(2)

---

[a] THE FORM OF THE ANISOTROPIC THERMAL PARAMETER IS: $\exp\left[-(B_{11}h^2(a^*)^2 + B_{22}k^2(b^*)^2 + B_{33}\ell^2(c^*)^2)/4 + (B_{12}hka^*b^* + B_{13}h\ell a^*c^* + B_{23}k\ell b^*c^*)/2\right]$. [b] For all hydrogen atoms, standard isotropic B values are reported.

Table II. Bond Distances (Å) for (η^5-C_5H_5)Co$(CH_3)_4C_4B_7H_7$, Isomer III

Co-B(1)	2.128(6)	C(7)-C(12)	1.431(6)
Co-B(3)	2.176(5)	C(7)-C(7M)	1.534(6)
Co-B(6)	2.109(6)	B(8)-C(9)	1.670(7)
Co-C(7)	2.063(4)	C(9)-B(10)	1.600(7)
Co-B(8)	2.276(5)	C(9)-C(9M)	1.520(6)
Co-C(12)	2.198(4)	B(10)-C(11)	1.602(7)
B(1)-B(3)	1.738(8)	C(11)-C(12)	1.609(7)
B(1)-B(4)	1.759(8)	C(11)-C(11M)	1.524(7)
B(1)-B(5)	1.768(8)	C(12)-C(12M)	1.518(7)
B(1)-B(6)	1.736(9)	Co-C(1P)	2.074(5)
B(3)-B(4)	1.718(8)	Co-C(2P)	2.048(6)
B(3)-B(8)	1.925(7)	Co-C(3P)	2.040(6)
B(3)-C(9)	1.671(7)	Co-C(4P)	2.047(6)
B(4)-B(5)	1.721(9)	Co-C(5P)	2.076(5)
B (4)-C(9)	1.655(7)	C(1P)-C(2P)	1.377(8)
B (4)-B(10)	1.817(7)	C(2P)-C(3P)	1.348(9)
B(5)-B(6)	1.719(9)	C(3P)-C(4P)	1.38(1)
B(5)-B(10)	1.832(7)	C(4P)-C(5P)	1.40(1)
B(5)-C(11)	1.680(8)	C(5P)-C(1P)	1.378(9)
B(6)-C(11)	1.741(7)	< B-H >	1.16
B(6)-C(12)	1.820(7)	< C-H >(CH_3)	0.96
C(7)-B(8)	1.459(6)	< C-H >(C_5H_5)	0.95

Nonbonded Distances (Å) on Open Face

C(7)-C(9)	2.737(6)	B(8)-C(12)	2.535(7)
C(7)-B(10)	2.969(7)	C(9)-C(11)	2.793(6)
C(7)-C(11)	2.602(6)	C(9)-C(12)	3.179(6)
B(8)-B(10)	2.658(7)	B(10)-C(12)	2.713(7)
B(8)-C(11)	3.066(7)		

Table III. Selected Bond Angles (Deg)

B(1)-Co-B(3)	47.6(2)	Co-C(7)-C(7M)	121.4(3)
B(1)-Co-B(6)	48.4(2)	B(8)-C(7)-C(12)	122.6(4)
B(1)-Co-C(7)	108.2(2)	C(7M)-C(7)-C(12)	118.6(4)
B(1)-Co-B(8)	89.1(2)	C(7M)-C(7)-B(8)	118.7(4)
B(1)-Co-C(12)	89.0(2)	C(7)-B(8)-C(9)	121.8(4)
B(3)-Co-B(6)	86.6(2)	B(8)-C(9)-B(10)	108.8(4)
B(3)-Co-C(7)	87.0(2)	C(9M)-C(9)-B(8)	113.5(4)
B(3)-Co-B(8)	51.2(2)	C(9M)-C(9)-B(3)	120.9(4)
B(3)-Co-C(12)	98.4(2)	C(9M)-C(9)-B(4)	116.0(4)
B(6)-Co-C(7)	85.9(2)	C(9M)-C(9)-B(10)	119.0(4)
B(6)-Co-B(8)	97.8(2)	C(9)-B(10)-C(11)	121.4(4)
B(6)-Co-C(12)	49.9(2)	B(10)-C(11)-C(12)	115.3(4)
C(7)-Co-B(8)	38.9(2)	C(11M)-C(11)-B(5)	114.2(4)
C(7)-Co-C(12)	39.1(2)	C(11M)-C(11)-B(6)	121.4(4)
B(8)-Co-C(12)	69.0(2)	C(11M)-C(11)-B(10)	117.5(4)
Co-B(1)-B(4)	115.5(3)	C(11M)-C(11)-C(12)	114.1(4)
Co-B(1)-B(5)	113.5(3)	C(11)-C(12)-C(7)	117.6(4)
B(3)-B(1)-B(5)	107.5(4)	C(12M)-C(12)-Co	122.1(4)
B(3)-B(1)-B(6)	115.6(4)	C(12M)-C(12)-B(6)	110.2(4)
B(4)-B(1)-B(6)	108.2(4)	C(12M)-C(12)-C(7)	118.7(4)
Co-B(3)-B(4)	115.0(3)	C(12M)-C(12)-C(11)	115.0(4)
B(3)-B(4)-B(5)	110.7(4)	C(2P)-C(1P)-C(5P)	108.0(6)
B(4)-B(5)-B(6)	110.8(4)	C(1P)-C(2P)-C(3P)	108.5(6)
Co-B(6)-B(5)	116.7(4)	C(2P)-C(3P)-C(4P)	109.5(7)
Co-C(7)-B(8)	78.5(2)	C(3P)-C(4P)-C(5P)	106.3(6)
Co-C(7)-C(12)	75.6(2)	C(4P)-C(5P)-C(1P)	107.6(6)

Table IV. Comparison of Corresponding Bond Distances (Å) and Angles (Deg) in Type 5 12-Vertex Nido Cages

Compound	C(7)-C(12	C(11)-C(12)	M[a]-C(7)	Angle(deg) C(12)-C(7)-B(8)	Ref.
$(C_5H_5)Co(CH_3)_4C_4B_7H_7$, Isomer III	1.431(6)	1.609(7)	2.063(4)	122.6(4)	This work
$(C_5H_5)_2Co_2C_4B_6H_{10}$, Isomer VII	1.423(8)	1.473(8)	2.025(5)	123.0(5)	15
$(C_5H_5)Fe(CH_3)_4C_4B_7H_8$	1.454(3)[b]	1.616(3)[b]	2.051(2)	122.6(2)[b]	14

[a] M = Co or Fe. [b] Framework carbon atoms C(11) and C(12) were numbered C(8) and C(9), respectively, in ref. 14.

Figure Captions

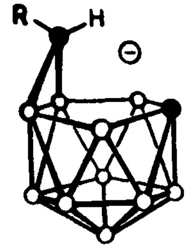
Figure 1. Structural types of 12-vertex, 28-electron (nido) cages. All cage structures depicted have been crystallographically characterized except that shown in Type 2. Type 1: $R_2C_2B_{10}H_{11}^-$ (R = CH_3, C_6H_5) (ref. 24). Type 2: proposed structure of $(CH_3)_4C_4B_8H_8$, isomer B (ref. 3), and of $(C_5H_5)_2Co_2C_4B_6H_{10}$, isomer VI (ref. 19). Type 3: $(CH_3)_4C_4B_8H_8$, isomer A (ref. 23). Type 4: left, $(C_5H_5)_2Co_2(CH_3)_4C_4B_6H_6$, isomer V (ref. 19); right, $(C_5H_5)Co(CH_3)_4C_4B_7H_7$, isomer I (ref. 5, 18). Type 5: left, $(C_5H_5)Fe(CH_3)_4C_4B_7H_8$ (ref. 14); right, $(C_5H_5)_2Co_2C_4B_6H_{10}$, isomer VII (ref. 15); bottom, $(C_5H_5)Co(CH_3)_4C_4B_7H_7$, isomer III (this work). Type 6: $(C_5H_5)Co(CH_3)_4C_4B_7H_7$, isomer II (ref. 1). Type 7: $(C_5H_5)CoSe_2B_9H_9$ (ref. 25).

Figure 2. Stereoview of molecular structure of $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_7$, isomer III (hydrogen atoms omitted).

Figure 3. Stereoview of unit cell packing.

Figure 4. Structures of the structurally characterized isomers of $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_7$.

○B-H ●C-H OR C-CH_3



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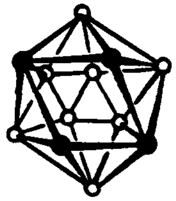

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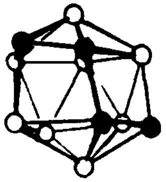

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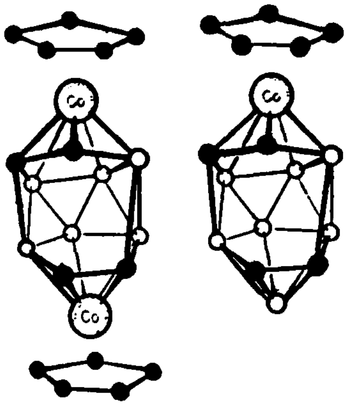

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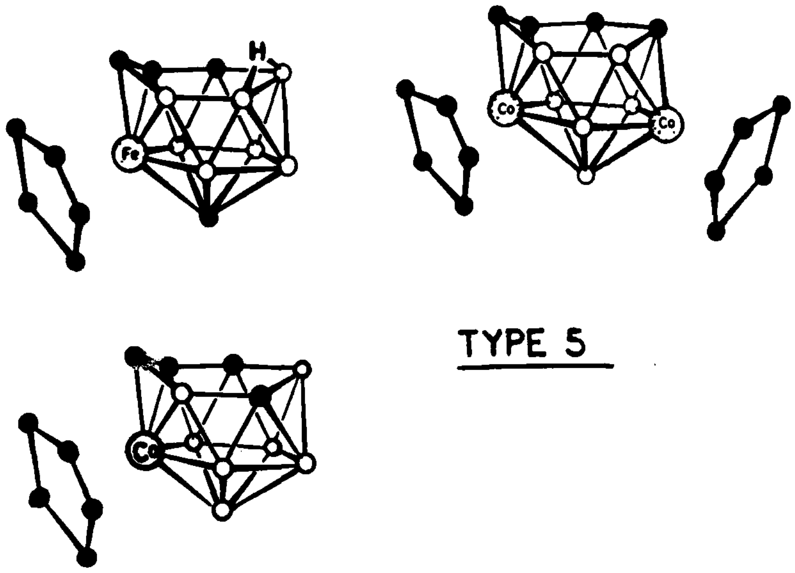

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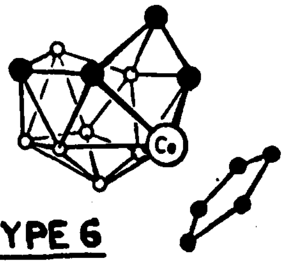

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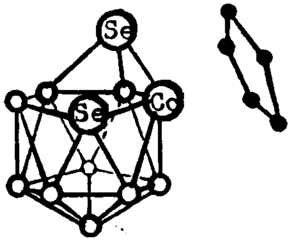

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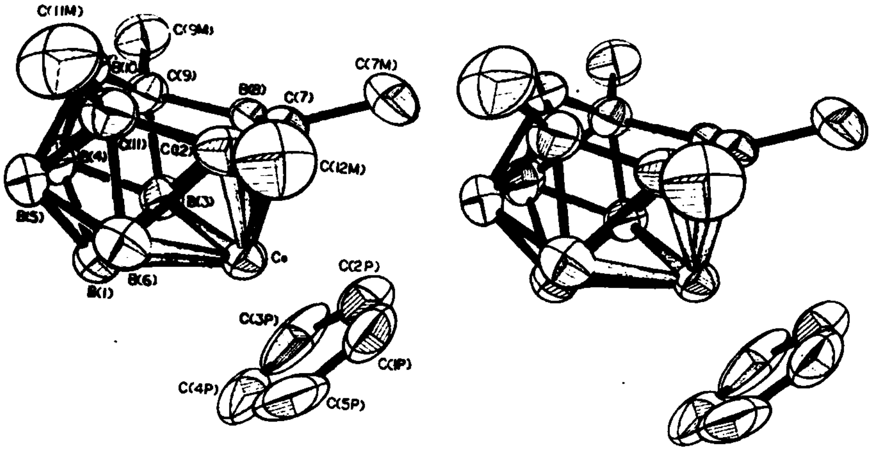
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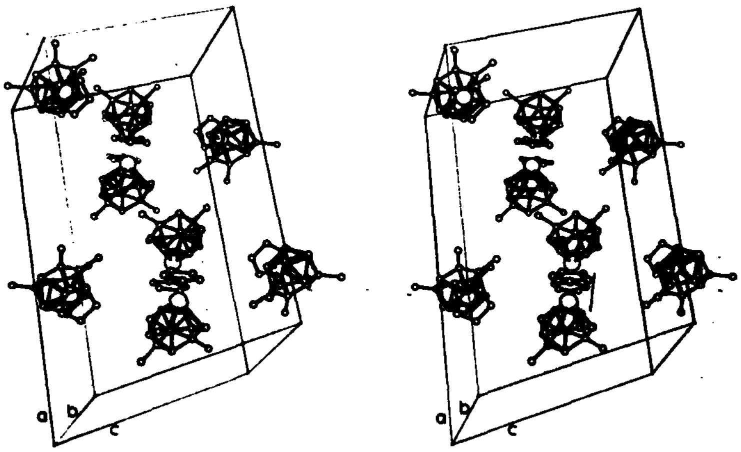
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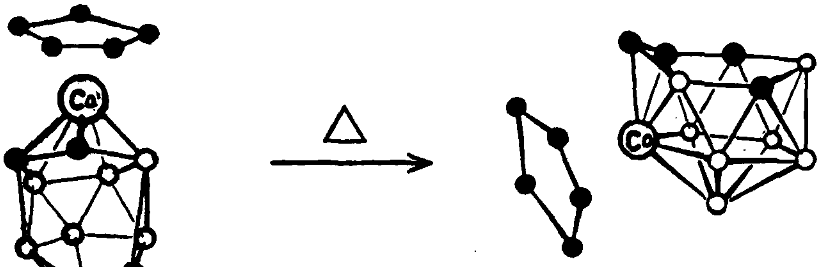
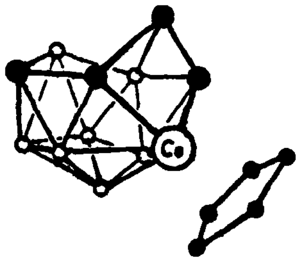


I III

●C-CH$_3$ ○BH



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