protons is lost upon oxidation.

The title complex is further characterized by the reactivity patterns which it displays. For example, both $[(en)_2Co(SC(O)COO)]^+$ and $[(en)_2Co(SC(O)C(O)S)]^+$ undergo rapid base hydrolysis to yield H_2S, cobalt(II), and free oxalate. Both complexes also undergo acid hydrolysis and yield H_2S and oxalic acid on heating in ca. 6 M acid. In addition, $[(en)_2Co(SC(O)COO)]^+$ is much more resistant to oxidation than $[(en)_2Co(SCH_2COO)]^+$, but it can be oxidized under stringent conditions (e.g., by using silver-catalyzed persulfate).

Crystal Structure. Structural parameters observed for $[(en)_2Co(SC(O)COO)]_2(S_2O_6)$ (Tables VI and VII) are in reasonable agreement with those obtained by Gainsford, Jackson, and Sargeson[32] in a study of the analogous chloride salt. In general, the structure of the $[(en)_2Co(SC(O)COO)]^+$ cation is as expected from the known structure of the parent thiolato complex $[(en)_2Co(SCH_2COO)]^+$.[3] However, the structural trans effect (STE) induced by the coordinated sulfur atom is significantly smaller[37] for the thiooxalato complex than for the thiolato complex (0.005 (8) vs. 0.043 (5) Å). This result is in harmony with the hypothesis that charge donation from sulfur to cobalt(III) is the underlying cause of the STE.[34] The electron-withdrawing effect of the adjacent carbonyl in thiooxalate reduces the tendency of the sulfur atom of this ligand to donate electron density (relative to the sulfur atom of the parent thiolato ligand). This result allows us to extend the previously noted[34] STE series for cobalt(III): $SO_3^{2-} > RSO^- > RSO_2^- > RS^- > S_2O_3^{2-} \simeq RSR \simeq RC(O)S^-$.

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Registry No. $[(en)_2Co(SC(O)COO)]_2(S_2O_6)\cdot 2H_2O$, 73612-11-0; $[(en)_2Co(SC(O)COO)]Cl$, 73612-12-1; $[(en)_2Co(SC(O)COO)]ClO_4$, 73612-13-2; $[(en)_2Co(OOCCOO)]^+$, 17835-71-1; $[(en)_2Co(SC(O)COO)]^+$, 73612-09-6; $[(en)_2Co(SC(O)C(O)S)]^+$, 73650-78-9; $[(en)_2Co(SCH_2COO)]Cl$, 54453-35-9; $[(en)_2Co(OOCCOO)]Cl$, 17439-00-8; $[(en)_2Co(SC(O)C(O)S)]Cl$, 14267-12-0; $[(en)_2Co(SCH_2COO)]ClO_4$, 26743-67-9; *cis*-$[(en)_2CoCl_2]Cl$, 14040-32-5.

Supplementary Material Available: Tables A–C giving $|F_o|$ and F_c, anisotropic thermal parameters, and positional parameters of hydrogen atoms (9 pages). Ordering information is given on any current masthead page.

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[37] Sargeson[32] also finds the shortest Co–N bond to be that trans to O. The sulfur STE computed from his data for the chloride salt is 0.018 (3) Å.

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Tetracarbon Metallacarboranes. 9.[1] New Types of Nido Cage Geometry. Crystal and Molecular Structures of $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$ (Isomer 1) and $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_7$ (Isomer 2)

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The structures of the title compounds have been determined by single-crystal X-ray diffraction and consist, respectively, of a 13-vertex nido NiC_4B_8 and a 12-vertex nido CoC_4B_7 cage framework. The NiC_4B_8 cluster resembles a 14-vertex closo polyhedron (bicapped hexagonal antiprism) from which one vertex has been removed and is the first example of a 13-vertex nido cage. The CoC_4B_7 geometry is also unprecedented and consists of an irregular basket-shaped framework with one carbon atom bridging three framework atoms across the open top of the basket. The two compounds are structurally related, since one can formally convert a CoC_4B_8 cage (analogous to the NiC_4B_8) to the observed CoC_4B_7 species by removal of one BH unit and linkage of two carbon atoms. Such a mechanism is proposed to account for the structure of the CoC_4B_7 cage. Both species are $(2n + 4)$-electron frameworks and are formally nido, in agreement with their gross geometries. Crystal data for $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$: mol wt 659.9, space group *Pbca*, $Z = 8$; $a = 16.666$ (2), $b = 17.666$ (1), $c = 24.00$ (2) Å; $V = 7066$ Å^3; $R = 0.042$ for 3144 independent reflections having $F_o^2 > 3\sigma(F_o^2)$. Crystal data for $(\eta^5\text{-}C_5H_5)Co(NH_3)_4C_4B_7H_7$: mol wt 314.9, space group $P2_1/b$ (unique axis *a*), $Z = 4$; $a = 7.930$ (3), $b = 14.151$ (6), $c = 14.809$ (5) Å; $\alpha = 101.2°$; $V = 1631$ Å^3; $R = 0.047$ for 1542 independent reflections having $F_o^2 > 3\sigma(F_o^2)$.

Introduction

Previous papers in this series have demonstrated that large carboranes and metallacarboranes containing four carbon atoms rather than the usual two in the polyhedral framework tend to adopt irregular, unorthodox open-cage structures.[1-8] That such species are of the open type is not surprising, since the presence of four carbons usually produces an electron-rich condition (relative to the requirement[9-11] of $2n + 2$ skeletal electrons for n-vertex closo, or fully triangulated, clusters); this in turn normally leads to cage opening to produce a nido ($2n + 4$) or arachno ($2n + 6$) system. This paradigm, while very useful as a general rule for classifying clusters, has proved

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inadequate for predicting specific cage geometries, particularly in systems of 12 or more vertices. We have structurally characterized a number of large tetracarbon carboranes and metallacarboranes containing from $(2n + 2)$ to $(2n + 6)$ framework electrons, whose geometries are strongly influenced by local steric and/or electronic effects in the vicinity of the framework carbon atoms.[1-8,12] While some of these clusters correspond to "model" closo polyhedra or fragments thereof, others are so irregular as to defy simple description (and virtually preclude systematic naming).

Since quantitative theoretical treatments of large, carbon-rich clusters of low symmetry are generally not feasible, understanding of the relationship between geometry and skeletal electron distribution in these systems must lean heavily on synthetic and structural investigations. In addition, knowledge of the detailed molecular geometry of the tetracarbon metallacarboranes can tell us much about the processes of metal insertion into neutral and anionic carborane substrates (e.g., $(CH_3)_4C_4B_8H_8$ and $(CH_3)_4C_4B_8H_8^{2-}$). In this article we describe the crystal structure analysis of two prototype tetracarbon monometallic clusters which were separately obtained but nevertheless exhibit a significant structural relationship.

Experimental Section

Irregular red crystals of $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$, isomer 1, obtained by treatment of $Na_2(CH_3)_4C_4B_8H_8$ with dichloro(1,2-bis(diphenylphosphino)ethane)nickel(II) in THF as described previously[8] were grown by vapor diffusion of pentane into a methylene chloride solution. A small platelet was selected for data collection and mounted on a glass fiber in an arbitrary orientation. Crystal data: $NiP_2C_{34}B_8H_{44}$, mol wt 659.9, space group *Pbca*, $Z = 8$; $a = 16.666$ (2), $b = 17.666$ (1), $c = 24.00$ (2) Å; $V = 7066$ Å^3; μ(Mo Kα) = 6.6 cm^{-1}; $\rho_{calcd} = 1.242$ g cm^{-3}; crystal dimensions (distances in mm from centroid) (102) 0.06, ($\bar{1}0\bar{2}$) 0.06, ($10\bar{2}$) 0.06, ($\bar{1}02$) 0.06, ($\bar{1}0\bar{1}$) 0.18, (010) 0.23, ($0\bar{1}0$) 0.23, (001) 0.065, ($00\bar{1}$) 0.065. 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. The choice of the orthorhombic space group *Pbca* was based on systematic absences of $k = 2n + 1$ for $0kl$, of $l = 2n + 1$ for $h0l$, and of $h = 2n + 1$ for $hk0$. For $Z = 8$ this is consistent with the molecular formula with the assumption of 19.6 Å^3 per nonhydrogen atom.

A red-brown rhombohedron of $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_7$ was grown by vapor diffusion of pentane into a methylene chloride solution and mounted on a glass fiber for data collection. Crystal data: $CoC_{13}B_7H_{24}$, mol wt 314.9, space group $P2_1/b$ (unique axis a), $Z = 4$; $a = 7.930$ (3), $b = 14.151$ (6), $c = 14.809$ (5) Å; $\alpha = 101.1$ (2)°; $V = 1631$ Å^3; μ(Mo Kα) = 10.8 cm^{-1}; $\rho = 1.283$ g cm^{-3}; crystal dimensions (distances given as above) (100) 0.12, ($\bar{1}00$) 0.12, (011) 0.14, ($0\bar{1}\bar{1}$) 0.14, ($01\bar{1}$) 0.14, ($0\bar{1}1$) 0.14. The same procedures as described above for the nickel compound were followed to produce an orientation matrix and refined cell constants. The mosaicity of the crystal, examined by the ω-scan technique, was excellent. Systematic absences for $h = 2n + 1$ on $h00$ and $k = 2n + 1$ on $0kl$ uniquely establish the space group as $P2_1/b$ (in this unconventional setting the equivalent positions are as follows: x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $^1/_2 - x, ^1/_2 + y, z$; $^1/_2 + x, ^1/_2 - y, \bar{z}$). For $Z = 4$ this is consistent with the molecular formula with the assumption of 19.4 Å^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 Mo Kα radiation from a highly oriented graphite crystal monochromator. The θ–2θ scan technique was used to record the intensities for all reflections for which $1° \leq 2\theta \leq 46°$. 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 Kα_1–Kα_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. Reflection data were considered insignificant for intensities registering less than 10 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, and their standard deviations were calculated in the usual manner from counting statistics ($p = 0.03$).[13] This results in 4852 reflections for $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$ of which 3144 had $F_o^2 > 3\sigma(F_o^2)$ and in 3820 reflections for $(C_5H_5)Co(CH_3)_4C_4B_7H_7$ of which 1542 had $F_o^2 > 3\sigma(F_o^2)$, after averaging of equivalent reflections. Only those reflections for which $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement of structural parameters.

Solution and Refinement of the Structures. For both compounds three-dimensional Patterson syntheses were used to locate the metal atom, whose positions phased the data sufficiently well to locate the other nonhydrogen atoms from difference Fourier maps. In each case, anisotropic refinement of these atomic positions with subsequent difference Fourier maps disclosed the location of most of the hydrogen atoms, and the remaining hydrogen positions were calculated. Following absorption corrections (maximum and minimum transmission coefficients were respectively 0.95 and 0.93 for the nickel complex and 0.94 and 0.92 for the cobalt species), refinement was continued to convergence to final values of $R = 0.042$ and $R_w = 0.050$ for $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$ and $R = 0.047$ and $R_w = 0.057$ for $(C_5H_5)Co(CH_3)_4C_4B_7H_7$.

Full-matrix least-squares refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. 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[14] and those for hydrogen from Stewart.[15] The effects of anomalous dispersion were included in F_c by using Cromer and Ibers'[16] values of $\Delta f'$ and $\Delta f''$. The computing system and programs are described elsewhere.[17] 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 2.02 for the nickel and 1.93 for the cobalt species, and the largest parameter shifts in the last cycle of refinement were 0.27 and 0.10 times the estimated standard deviation, for the nickel and cobalt compounds, respectively.

Results and Discussion

Final positional and thermal parameters are given in Tables I and II for $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$ and $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_7$, respectively. Tables III and IV list bond lengths for both compounds, while Tables V and VI contain selected bond 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 VII and VIII list selected mean planes and the dihedral angles between them. The closest nonhydrogen intermolecular contacts in the nickel species are 3.565 Å between C(D4) and C(M9) and 3.580 Å between C(D5) and C(M9); in both cases the symmetry operation is $\bar{x}, y - ^1/_2, ^1/_2 - z$. For the cobalt complex, the closest intermolecular contacts are 3.629 Å for C(4M)–C(P1), 3.717 Å for C(4M)–C(P5) (symmetry operation $x - ^1/_2, -^1/_2 - y, 1 - z$), and 3.689 Å for C(P4)–C(P4) (symmetry operation $1 - x, \bar{y}, 1 - z$).

Figures 1 and 2 depict the molecular structure and unit cell

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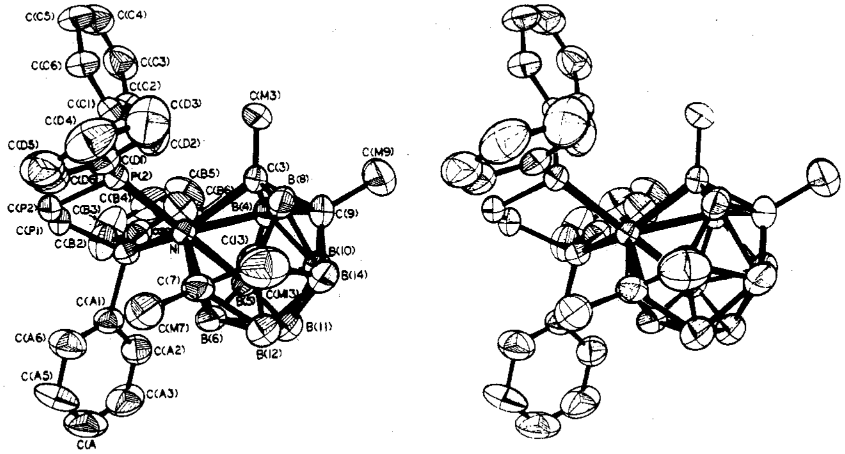

Figure 1. Molecular structure of $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$, with hydrogen atoms omitted.

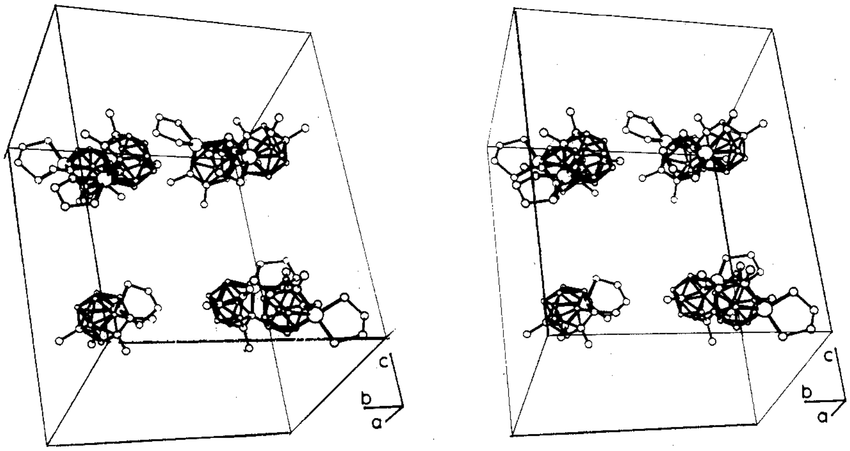

Figure 2. Unit cell contents for $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$, with phenyl groups omitted for clarity.

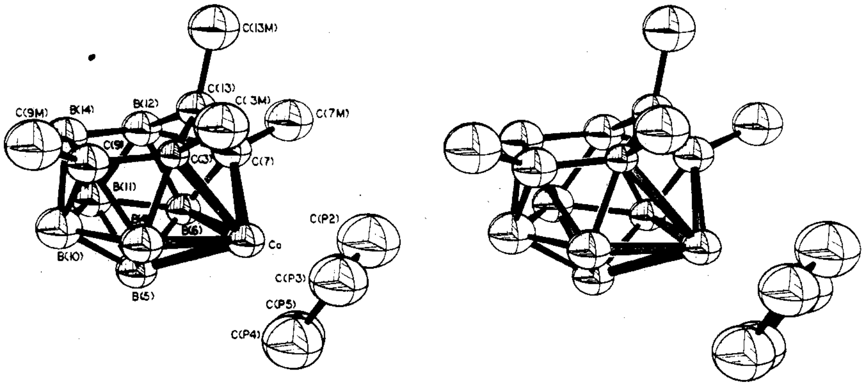

Figure 3. Molecular structure of $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_7$, with hydrogen atoms omitted.

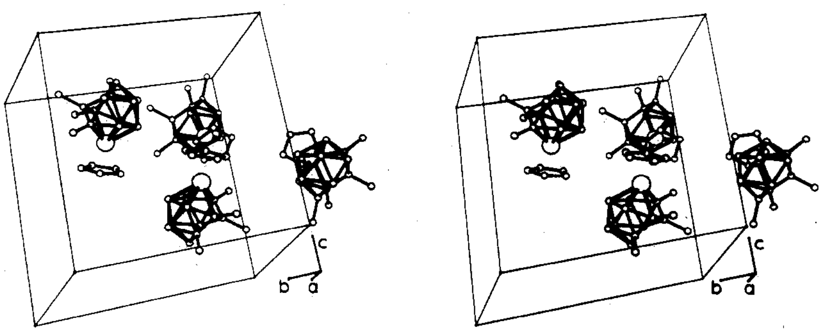

Figure 4. Unit cell contents for $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_7$.

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$[a,b]

atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0.14381 (3)	0.18727 (3)	0.11688 (2)	2.93 (2)	2.34 (2)	3.84 (2)	−0.21 (2)	0.56 (2)	0.15 (2)
P(1)	0.15014 (8)	0.13269 (7)	0.03490 (6)	3.16 (5)	3.13 (6)	3.82 (6)	−0.16 (6)	0.53 (6)	0.06 (5)
P(2)	0.07305 (8)	0.08977 (7)	0.14507 (6)	3.10 (5)	2.46 (5)	4.37 (6)	−0.21 (5)	0.74 (5)	0.17 (6)
C(P1)	0.1036 (3)	0.0367 (3)	0.0414 (2)	4.1 (2)	2.5 (2)	5.1 (3)	−0.3 (2)	0.4 (2)	−0.7 (2)
C(P2)	0.1050 (3)	0.0104 (3)	0.1008 (2)	3.7 (2)	2.4 (2)	5.8 (3)	−0.1 (2)	1.3 (2)	−0.3 (2)
C(A1)	0.2498 (3)	0.1111 (3)	0.0068 (2)	3.5 (2)	4.7 (3)	3.7 (2)	−0.2 (2)	0.4 (2)	−0.4 (2)
C(A2)	0.2885 (3)	0.1605 (3)	−0.0283 (2)	5.3 (3)	4.8 (3)	6.0 (3)	−0.5 (3)	2.0 (3)	−0.1 (3)
C(A3)	0.3658 (4)	0.1455 (4)	−0.0464 (3)	6.3 (3)	8.6 (4)	7.6 (4)	−2.3 (3)	3.7 (3)	−1.6 (3)
C(A4)	0.4043 (3)	0.0818 (4)	−0.0291 (3)	3.9 (3)	10.6 (5)	8.1 (4)	−0.0 (3)	2.1 (3)	−2.9 (4)
C(A5)	0.3675 (4)	0.0331 (4)	0.0057 (3)	4.1 (3)	9.5 (4)	8.9 (4)	2.5 (3)	1.6 (3)	−0.5 (4)
C(A6)	0.2899 (3)	0.0472 (4)	0.0233 (3)	4.8 (3)	6.5 (3)	6.1 (3)	0.7 (3)	1.5 (3)	0.8 (3)
C(B1)	0.0988 (3)	0.1703 (3)	−0.0260 (2)	4.3 (2)	4.3 (3)	3.9 (2)	−0.9 (2)	0.4 (2)	−0.1 (2)
C(B2)	0.0984 (4)	0.1308 (3)	−0.0760 (3)	8.1 (4)	5.1 (3)	5.2 (3)	−0.5 (3)	−1.0 (3)	0.3 (3)
C(B3)	0.0567 (5)	0.1556 (4)	−0.1207 (2)	11.5 (5)	7.4 (4)	3.9 (3)	−3.0 (4)	−2.1 (3)	0.5 (3)
C(B4)	0.0144 (4)	0.2219 (4)	−0.1178 (3)	6.9 (4)	9.0 (4)	5.9 (3)	−0.8 (3)	−2.1 (3)	2.7 (3)
C(B5)	0.0135 (4)	0.2619 (4)	−0.0698 (3)	8.7 (4)	8.7 (4)	6.3 (4)	3.0 (3)	−0.3 (3)	1.6 (3)
C(B6)	0.0568 (4)	0.2368 (4)	−0.0237 (2)	6.3 (3)	6.4 (3)	4.6 (3)	1.3 (3)	−0.6 (3)	−0.0 (3)
C(C1)	−0.0358 (3)	0.0907 (3)	0.1305 (2)	3.1 (2)	2.9 (2)	5.2 (3)	0.1 (2)	0.8 (2)	−0.7 (2)
C(C2)	−0.0638 (3)	0.1305 (3)	0.0853 (2)	3.9 (2)	4.3 (3)	5.9 (3)	0.3 (2)	0.2 (2)	−0.6 (3)
C(C3)	−0.1439 (4)	0.1269 (4)	0.0695 (3)	5.0 (3)	6.5 (3)	6.8 (3)	1.0 (3)	−0.9 (3)	−1.4 (3)
C(C4)	−0.1958 (4)	0.0834 (4)	0.0998 (3)	3.5 (3)	8.0 (4)	9.7 (4)	−0.3 (3)	−0.0 (3)	−2.6 (4)
C(C5)	−0.1696 (3)	0.0453 (4)	0.1458 (3)	4.0 (3)	6.9 (3)	9.9 (4)	−1.8 (3)	2.6 (3)	−1.9 (3)
C(C6)	−0.0891 (3)	0.0474 (3)	0.1612 (2)	3.4 (2)	4.9 (3)	6.6 (3)	−0.6 (2)	1.4 (2)	−0.4 (3)
C(D1)	0.0797 (3)	0.0554 (3)	0.2161 (2)	3.2 (2)	3.3 (2)	4.9 (3)	−0.7 (2)	1.0 (2)	0.6 (2)
C(D2)	0.0595 (4)	0.1026 (3)	0.2595 (2)	8.2 (4)	3.9 (3)	5.1 (3)	−0.4 (3)	1.5 (3)	0.6 (3)
C(D3)	0.0692 (4)	0.0797 (4)	0.3144 (2)	10.5 (4)	6.3 (3)	4.6 (3)	−1.4 (4)	2.0 (3)	0.0 (3)
C(D4)	0.1007 (4)	0.0098 (4)	0.3256 (3)	6.2 (3)	7.4 (4)	6.1 (3)	−1.5 (3)	−0.3 (3)	2.7 (3)
C(D5)	0.1200 (3)	−0.0370 (3)	0.2833 (3)	5.4 (3)	5.4 (3)	7.7 (4)	0.1 (3)	1.4 (3)	2.3 (3)
C(D6)	0.1099 (3)	−0.0159 (3)	0.2287 (2)	4.2 (2)	4.5 (3)	5.4 (3)	−0.1 (2)	1.0 (2)	1.5 (2)
C(3)	0.0827 (3)	0.2674 (2)	0.1699 (2)	3.3 (2)	2.0 (2)	5.0 (3)	−0.2 (2)	0.7 (2)	−0.2 (2)
C(7)	0.2435 (3)	0.1778 (3)	0.1798 (2)	2.8 (2)	3.6 (2)	4.9 (2)	0.1 (2)	−0.2 (2)	0.5 (2)
C(9)	0.1318 (3)	0.3494 (3)	0.1770 (2)	4.6 (3)	2.6 (2)	6.2 (3)	−0.3 (2)	0.5 (3)	−0.9 (2)
C(13)	0.2219 (3)	0.2325 (3)	0.2262 (2)	5.1 (3)	4.7 (3)	3.7 (2)	−0.5 (2)	−0.0 (2)	−0.4 (2)
C(M3)	−0.0074 (3)	0.2715 (3)	0.1802 (2)	3.4 (2)	3.5 (2)	6.7 (3)	0.4 (2)	1.2 (2)	−0.5 (2)
C(M7)	0.2798 (3)	0.1021 (3)	0.1962 (2)	4.5 (3)	4.7 (3)	6.3 (3)	0.2 (2)	−1.1 (2)	1.6 (3)
C(M9)	0.0881 (4)	0.4203 (3)	0.1976 (3)	6.6 (3)	4.2 (3)	7.9 (4)	0.4 (3)	1.6 (3)	−1.0 (3)
C(M13)	0.2460 (4)	0.2158 (4)	0.2859 (3)	5.5 (3)	9.0 (4)	5.7 (3)	−0.5 (3)	−1.0 (3)	−0.4 (3)
B(4)	0.1115 (4)	0.3060 (3)	0.1123 (3)	4.2 (3)	2.7 (2)	4.5 (3)	0.1 (2)	0.4 (3)	−0.1 (3)
B(5)	0.2094 (4)	0.2808 (3)	0.0854 (3)	3.8 (3)	2.8 (2)	5.0 (3)	−0.7 (2)	0.9 (3)	0.7 (3)
B(6)	0.2729 (3)	0.2140 (3)	0.1235 (3)	2.7 (2)	3.6 (3)	4.6 (3)	−0.3 (2)	0.3 (2)	0.2 (3)
B(8)	0.1365 (4)	0.2747 (3)	0.2223 (3)	4.3 (3)	3.3 (2)	4.0 (3)	−0.9 (3)	0.6 (3)	−0.7 (2)
B(10)	0.1968 (4)	0.3631 (3)	0.1266 (3)	4.5 (3)	2.8 (3)	6.3 (4)	−0.5 (2)	0.9 (3)	−0.1 (3)
B(11)	0.2855 (4)	0.3133 (4)	0.1315 (3)	4.0 (3)	3.7 (3)	5.6 (4)	−0.8 (3)	0.7 (3)	−0.3 (3)
B(12)	0.3035 (4)	0.2546 (4)	0.1875 (3)	4.1 (3)	4.2 (3)	5.3 (3)	−0.6 (3)	0.6 (3)	−0.1 (3)
B(14)	0.2319 (4)	0.3329 (4)	0.1976 (3)	4.2 (3)	4.5 (3)	6.1 (4)	−1.4 (3)	0.5 (3)	−1.5 (3)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
H(A2)	0.259 (2)	0.207 (2)	−0.042 (2)	5.0 (11)	H(P21)	0.160 (2)	−0.003 (2)	0.109 (2)	4.7 (10)
H(A3)	0.392 (3)	0.181 (2)	−0.071 (2)	6.7 (12)	H(P22)	0.075 (2)	−0.033 (2)	0.108 (2)	4.2 (10)
H(A4)	0.460 (3)	0.074 (3)	−0.038 (2)	7.1 (12)	H(4)	0.068 (2)	0.336 (2)	0.076 (2)	4.4 (10)
H(A5)	0.396 (3)	−0.017 (2)	0.015 (2)	6.3 (12)	H(5)	0.216 (2)	0.288 (2)	0.036 (2)	3.9 (10)
H(A6)	0.263 (2)	0.012 (2)	0.048 (2)	5.0 (11)	H(6)	0.318 (2)	0.184 (2)	0.097 (2)	4.1 (10)
H(B2)	0.127 (2)	0.086 (2)	−0.077 (2)	5.8 (11)	H(8)	0.103 (2)	0.299 (2)	0.262 (1)	3.0 (9)
H(B3)	0.057 (3)	0.129 (2)	−0.154 (2)	6.2 (12)	H(10)	0.184 (2)	0.420 (2)	0.109 (2)	5.6 (11)
H(B4)	−0.015 (2)	0.240 (2)	−0.149 (2)	5.8 (11)	H(11)	0.338 (2)	0.352 (2)	0.111 (2)	4.7 (10)
H(B5)	−0.019 (3)	0.306 (3)	−0.066 (2)	6.5 (12)	H(12)	0.370 (2)	0.251 (2)	0.210 (1)	3.2 (9)
H(B6)	0.060 (2)	0.267 (2)	0.011 (2)	5.0 (11)	H(14)	0.251 (2)	0.371 (2)	0.232 (1)	3.8 (9)
H(C2)	−0.031 (2)	0.163 (2)	0.063 (2)	4.2 (10)	H(M31)	0.400 (2)	0.302 (2)	0.284 (2)	4.9 (10)
H(C3)	−0.167 (2)	0.152 (2)	0.038 (2)	5.1 (11)	H(M32)	0.465 (2)	0.221 (2)	0.320 (2)	5.4 (11)
H(C4)	−0.251 (2)	0.078 (2)	0.090 (2)	5.4 (11)	H(M33)	0.465 (2)	0.303 (2)	0.343 (2)	5.0 (10)
H(C5)	−0.203 (3)	0.015 (2)	0.166 (2)	6.4 (12)	H(M71)	0.321 (2)	0.103 (2)	0.221 (2)	4.4 (10)
H(C6)	−0.069 (2)	0.022 (2)	0.196 (2)	4.9 (11)	H(M72)	0.285 (2)	0.067 (2)	0.162 (2)	5.6 (11)
H(D2)	0.034 (2)	0.150 (2)	0.252 (2)	5.3 (11)	H(M73)	0.249 (2)	0.069 (2)	0.221 (2)	4.9 (10)
H(D3)	0.056 (3)	0.116 (2)	0.344 (2)	5.9 (11)	H(M91)	0.054 (2)	0.441 (2)	0.162 (2)	5.2 (11)
H(D4)	0.110 (2)	−0.006 (2)	0.364 (2)	5.0 (11)	H(M92)	0.051 (2)	0.407 (2)	0.233 (2)	5.5 (11)
H(D5)	0.138 (2)	−0.086 (2)	0.292 (2)	5.0 (11)	H(M93)	0.138 (2)	0.457 (2)	0.210 (2)	5.7 (11)
H(D6)	0.124 (2)	−0.050 (2)	0.200 (2)	5.1 (11)	H(M131)	0.303 (2)	0.201 (2)	0.294 (2)	5.6 (11)
H(P11)	0.046 (2)	0.043 (2)	0.030 (2)	5.5 (11)	H(M132)	0.198 (3)	0.170 (2)	0.297 (2)	6.4 (12)
H(P12)	0.127 (2)	0.002 (2)	0.016 (2)	4.7 (11)	H(M133)	0.244 (3)	0.260 (2)	0.311 (2)	6.3 (12)

[a] The form of the anisotropic thermal parameter is $\exp[-(B_{11}h^2(a^*)^2 + B_{22}k^2(b^*)^2 + B_{33}l^2(c^*)^2)/4 + (B_{12}hka^*b^* + B_{13}hla^*c^* + B_{23}klb^*c^*)/2]$. [b] For all hydrogen atoms, standard isotropic *B* values are reported.

contents for $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$, and Figures 3 and 4 give the corresponding views for $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_7$.

Synthesis. Both complexes were prepared by the reaction of the $(CH_3)_4C_4B_8H_8^{2-}$ dianion with transition-metal reagents at room temperature in tetrahydrofuran solution, as described

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $(C_5H_5)Co(CH_3)_4C_4B_7H_7$[a, b]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	0.18308 (7)	−0.15056 (5)	0.33459 (4)	2.56 (2)	4.43 (3)	3.31 (2)	−0.05 (3)	0.03 (2)	1.08 (2)
C(3)	0.1776 (5)	−0.1790 (3)	0.1767 (3)	1.2 (1)	2.9 (2)	2.2 (2)	0.1 (2)	0.7 (1)	0.1 (1)
C(9)	0.1062 (6)	−0.1035 (4)	0.1313 (4)	3.7 (2)	5.6 (3)	4.0 (2)	−0.4 (2)	−0.1 (2)	1.7 (2)
C(13)	0.0375 (5)	−0.2524 (3)	0.1922 (3)	2.8 (2)	3.1 (2)	3.8 (2)	0.4 (2)	−0.6 (2)	0.5 (2)
C(7)	−0.0044 (6)	−0.2432 (4)	0.2869 (3)	2.8 (2)	3.7 (2)	4.8 (2)	0.2 (2)	0.2 (2)	1.5 (3)
C(3M)	0.3474 (6)	−0.2280 (5)	0.1385 (4)	3.3 (2)	7.7 (3)	4.0 (2)	1.1 (2)	0.6 (2)	0.8 (2)
C(9M)	0.1890 (8)	−0.0807 (5)	0.0450 (4)	7.0 (3)	7.9 (3)	4.9 (3)	−0.1 (3)	0.9 (2)	3.3 (2)
C(13M)	0.0400 (7)	−0.3469 (5)	0.1259 (5)	5.6 (3)	6.1 (3)	5.4 (3)	0.7 (3)	−0.8 (2)	0.2 (3)
C(7M)	−0.0589 (8)	−0.3323 (4)	0.3257 (4)	6.3 (3)	5.3 (3)	6.6 (3)	−1.2 (2)	0.6 (3)	2.4 (2)
C(P1)	0.2205 (8)	−0.1904 (6)	0.4565 (5)	6.4 (3)	13.4 (5)	6.5 (3)	−3.0 (3)	−2.3 (3)	5.9 (3)
C(P2)	0.3346 (8)	−0.2391 (5)	0.3932 (5)	9.4 (4)	6.2 (3)	10.1 (4)	1.8 (3)	−6.1 (3)	1.3 (3)
C(P3)	0.4290 (7)	−0.1736 (7)	0.3647 (4)	3.0 (2)	15.7 (6)	4.6 (3)	1.4 (3)	−0.5 (2)	1.0 (3)
C(P4)	0.3817 (8)	−0.0833 (6)	0.4107 (5)	7.4 (3)	11.9 (4)	7.9 (3)	−5.7 (3)	−5.3 (2)	5.1 (3)
C(P5)	0.2557 (9)	−0.0939 (6)	0.4680 (4)	6.1 (3)	11.8 (5)	4.1 (3)	2.0 (3)	−1.0 (3)	−0.6 (3)
B(6)	−0.0848 (7)	−0.1402 (5)	0.3346 (4)	2.6 (2)	4.9 (3)	4.5 (3)	0.4 (2)	1.0 (2)	1.5 (2)
B(4)	0.1941 (7)	−0.0631 (5)	0.2368 (4)	3.8 (3)	4.0 (3)	4.6 (3)	−1.2 (2)	0.4 (2)	0.8 (2)
B(12)	−0.1509 (7)	−0.1972 (5)	0.2186 (5)	2.5 (2)	4.9 (3)	5.5 (3)	0.3 (2)	−0.2 (2)	0.7 (3)
B(11)	−0.1598 (7)	−0.0729 (5)	0.2516 (5)	3.5 (3)	4.6 (3)	6.3 (3)	1.5 (2)	0.3 (2)	0.9 (3)
B(14)	−0.0959 (8)	−0.1210 (5)	0.1391 (5)	3.9 (3)	5.5 (3)	6.1 (3)	0.6 (3)	−1.0 (3)	2.0 (3)
B(5)	0.0275 (8)	−0.0340 (4)	0.3175 (5)	4.5 (3)	3.6 (3)	4.5 (3)	0.2 (2)	0.8 (2)	0.5 (2)
B(10)	0.0066 (8)	−0.0170 (5)	0.2028 (5)	5.4 (3)	4.6 (3)	5.0 (3)	0.5 (3)	−0.0 (3)	1.8 (2)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H(6)	−0.149 (5)	−0.144 (4)	0.392 (3)	4 (1)	H(9M3)	0.146 (6)	−0.032 (4)	0.027 (4)	6 (1)
H(4)	0.311 (6)	−0.022 (4)	0.227 (4)	5 (1)	H(13M1)	−0.055 (6)	−0.378 (4)	0.135 (4)	5 (1)
H(12)	−0.262 (7)	−0.255 (4)	0.211 (4)	5 (1)	H(13M2)	0.050 (7)	−0.349 (4)	0.064 (4)	7 (2)
H(11)	−0.271 (8)	−0.031 (5)	0.293 (5)	9 (2)	H(13M3)	0.140 (7)	−0.392 (5)	0.131 (5)	8 (2)
H(14)	−0.189 (6)	−0.128 (4)	0.073 (4)	5 (1)	H(7M1)	0.056 (7)	−0.369 (4)	0.331 (4)	8 (2)
H(5)	0.018 (6)	0.030 (4)	0.370 (4)	5 (1)	H(7M2)	−0.085 (7)	−0.311 (4)	0.398 (4)	6 (1)
H(10)	−0.003 (7)	0.054 (5)	0.187 (4)	7 (2)	H(7M3)	−0.149 (7)	−0.375 (5)	0.275 (5)	8 (2)
H(3M1)	0.318 (5)	−0.267 (4)	0.078 (3)	4 (1)	H(CP1)	0.169 (7)	−0.233 (4)	0.490 (4)	7 (2)
H(3M2)	0.387 (5)	−0.277 (3)	0.176 (3)	3 (1)	H(CP2)	0.346 (6)	−0.307 (4)	0.371 (4)	6 (1)
H(3M3)	0.417 (6)	−0.174 (4)	0.122 (4)	5 (1)	H(CP3)	0.516 (6)	−0.177 (4)	0.332 (4)	6 (1)
H(9M1)	0.173 (6)	−0.146 (4)	−0.001 (4)	6 (1)	H(CP4)	0.427 (6)	−0.022 (4)	0.404 (4)	6 (1)
H(9M2)	0.316 (6)	−0.081 (4)	0.056 (4)	5 (1)	H(CP5)	0.194 (7)	−0.052 (5)	0.498 (4)	7 (2)

[a] The form of the anisotropic thermal parameter is $\exp[-(B_{11}h^2(a^*)^2 + B_{22}k^2(b^*)^2 + B_{33}l^2(c^*)^2)/4 + (B_{12}hka^*b^* + B_{13}hla^*c^* + B_{23}klb^*c^*)/2]$. [b] For all hydrogen atoms, standard isotropic B values are reported.

elsewhere.[2,8] In each case, mixtures of isomers were obtained and were separated by thin-layer chromatography in air.

$$(CH_3)_4C_4B_8H_8{}^{2-} + [(C_6H_5)_2PCH_2]_2NiCl_2 \rightarrow [(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_7H_7 + [(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$$
$$\text{2 isomers} \qquad \text{3 isomers}$$

$$(CH_3)_4C_4B_8H_8{}^{2-} \xrightarrow[\text{(2) HCl}]{\text{(1) CoCl}_2,\ C_5H_5^-} (\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_7 + (\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_8H_8 + \sigma\text{-}[(\eta^5\text{-}C_5H_5)Co(\eta^5\text{-}C_5H_4)]^+[(CH_3)_4C_4B_8H_8]^-$$

Of the products indicated in these equations, the only one for which full structural characterization has previously been reported[1] is the zwitterionic cobalt species. This paper reports the structure determinations of one of the NiC_4B_8 isomers and of the CoC_4B_7 system.

$[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$, Isomer 1. The molecule has a well-defined 13-vertex nido cage structure (Figures 1 and 5), the first confirmed example of this geometry, and can be regarded as derived from a 14-vertex closo polyhedron (bicapped hexagonal antiprism) by removal of one equatorial vertex; in the parent 14-vertex cage, the nickel atom and B(14) would occupy the six-coordinate (apex) vertices.[18] This geometry is in agreement with our earlier proposal[2] based on electron-counting considerations,[9-11] in that the framework has 30 skeletal valence electrons (two from each BH and $[(C_6H_5)_2PCH_2]_2Ni$ unit and three from each C–CH$_3$), and hence is a $(2n + 4)$-electron system. Although nido structures are normally adopted by $(2n + 4)$-electron cages, the skeletal electron-count theory has been little tested in polyhedra of more than 12 vertices, and quantitative treatments of large boron cages have only recently appeared.[19]

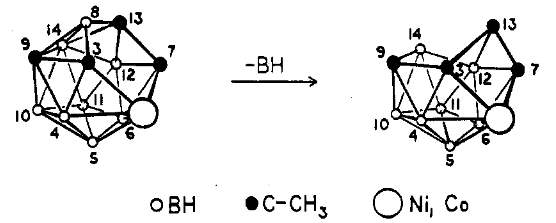

Figure 5. Comparison of cage frameworks in the 14-vertex complex $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$ and its proposed[2] analogue, $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_8H_8$ (left), with the 13-vertex system $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_7$, isomer 2 (right).

While the gross structure does obey the electron-counting formalism, the locations of nickel and carbon atoms in the framework strongly suggest that the structure is not the thermodynamically most stable arrangement. There are several indications of this: (1) The placements of atoms C(9) and B(8) are reversed relative to the normal tendencies of carbon and boron to adopt low- and high-coordinate vertices, respectively. (2) Nickel occupies a vertex on the open face where its orbital overlap with neighboring atoms must be less than optimal. (3) One boron atom [B(14)] occupies an un-

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[18] The previously reported[1] zwitterionic complex $(\eta^5\text{-}C_5H_5)Co(\eta^5\text{-}C_5H_4)^+(CH_3)_4C_4B_8H_8^-$ contains a C_4B_8 cage which is also a fragment (in this case, one of 12 vertices) of a bicapped hexagonal antiprism.

[19] (a) Bicerano, J.; Marynick, D. S.; Lipscomb, W. N. *Inorg. Chem.* **1978**, *17*, 2041, 3443. (b) Lipscomb, W. N. *Ibid.* **1979**, *18*, 901.

Table III

Bond Distances (Å) in $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$

Ni–P(1)	2.193 (1)	C(13)–C(M13)	1.515 (5)
Ni–P(2)	2.194 (1)	P(1)–C(P1)	1.871 (3)
Ni–C(3)	2.159 (3)	P(1)–C(A1)	1.834 (4)
Ni–B(4)	2.168 (4)	P(1)–C(B1)	1.819 (4)
Ni–B(5)	2.121 (4)	P(2)–C(P2)	1.838 (3)
Ni–B(6)	2.208 (4)	P(2)–C(C1)	1.847 (4)
Ni–C(7)	2.250 (3)	P(2)–C(D1)	1.813 (4)
C(3)–B(4)	1.613 (5)	C(P1)–C(P2)	1.500 (5)
C(3)–B(8)	1.550 (5)	C(A1)–C(A2)	1.373 (5)
C(3)–C(9)	1.672 (4)	C(A2)–C(A3)	1.385 (6)
C(3)–C(M3)	1.524 (5)	C(A3)–C(A4)	1.360 (7)
B(4)–B(5)	1.810 (6)	C(A4)–C(A5)	1.346 (7)
B(4)–C(9)	1.766 (6)	C(A5)–C(A6)	1.383 (6)
B(4)–B(10)	1.778 (6)	C(A6)–C(A1)	1.369 (5)
B(5)–B(6)	1.829 (6)	C(B1)–C(B2)	1.386 (5)
B(5)–B(10)	1.770 (6)	C(B2)–C(B3)	1.351 (6)
B(5)–B(11)	1.777 (6)	C(B3)–C(B4)	1.368 (7)
B(6)–C(7)	1.573 (5)	C(B4)–C(B5)	1.352 (7)
B(6)–B(11)	1.777 (6)	C(B5)–C(B6)	1.393 (6)
B(6)–B(12)	1.769 (6)	C(B6)–C(B1)	1.368 (5)
C(7)–B(12)	1.697 (6)	C(C1)–C(C2)	1.374 (5)
C(7)–C(13)	1.517 (5)	C(C2)–C(C3)	1.390 (6)
C(7)–C(M7)	1.521 (5)	C(C3)–C(C4)	1.366 (6)
B(8)–C(9)	1.711 (6)	C(C4)–C(C5)	1.364 (7)
B(8)–C(13)	1.611 (6)	C(C5)–C(C6)	1.392 (6)
B(8)–B(14)	1.985 (6)	C(C6)–C(C1)	1.385 (5)
C(9)–B(10)	1.641 (6)	C(D1)–C(D2)	1.377 (5)
C(9)–B(14)	1.764 (6)	C(D2)–C(D3)	1.387 (6)
C(9)–C(M9)	1.530 (5)	C(D3)–C(D4)	1.368 (6)
B(10)–B(11)	1.724 (6)	C(D4)–C(D5)	1.349 (6)
B(10)–B(14)	1.877 (7)	C(D5)–C(D6)	1.371 (6)
B(11)–B(12)	1.724 (7)	C(D6)–C(D1)	1.389 (5)
B(11)–B(14)	1.853 (6)	⟨C–H⟩ (nonmethyl)	0.965
B(12)–C(13)	1.693 (6)	⟨C–H⟩ (all H atoms)	0.986
B(12)–B(14)	1.843 (7)	⟨B–H⟩	1.17
C(13)–B(14)	1.910 (6)	⟨B–C⟩	1.684
		⟨B–B⟩	1.809

Nonbonded Distances (Å) on Open Face

Ni–C(13)	3.04	C(3)–C(13)	2.76
Ni–B(8)	2.97	C(7)–B(8)	2.67
C(3)–C(7)	3.12		

Table IV

Bond Distances (Å) in $(C_5H_5)Co(CH_3)_4C_4B_7H_7$

Co–C(3)	2.296 (3)	C(9)–B(14)	1.629 (5)
Co–B(4)	2.080 (4)	C(9)–C(9M)	1.526 (5)
Co–B(5)	2.113 (4)	B(10)–B(11)	1.763 (6)
Co–B(6)	2.129 (3)	B(10)–B(14)	1.784 (7)
Co–C(7)	2.018 (3)	B(11)–B(12)	1.733 (6)
C(3)–B(4)	1.713 (5)	B(11)–B(14)	1.750 (7)
C(3)–C(9)	1.480 (4)	B(12)–C(13)	1.697 (5)
C(3)–C(13)	1.567 (4)	B(12)–B(14)	1.796 (5)
C(3)–C(3M)	1.499 (5)	C(13)–C(13M)	1.499 (5)
B(4)–B(5)	1.776 (5)	Co–C(P1)	2.015 (5)
B(4)–C(9)	1.706 (5)	Co–C(P2)	2.046 (4)
B(4)–B(10)	1.736 (6)	Co–C(P3)	2.040 (4)
B(5)–B(6)	1.805 (6)	Co–C(P4)	2.060 (4)
B(5)–B(10)	1.768 (6)	Co–C(P5)	2.066 (4)
B(5)–B(11)	1.804 (6)	C(P1)–C(P2)	1.386 (8)
B(6)–C(7)	1.622 (5)	C(P2)–C(P3)	1.322 (8)
B(6)–B(12)	1.827 (6)	C(P3)–C(P4)	1.379 (8)
B(6)–B(11)	1.794 (6)	C(P4)–C(P5)	1.338 (8)
C(7)–B(12)	1.747 (5)	C(P5)–C(P1)	1.372 (8)
C(7)–C(13)	1.424 (4)	⟨C–H⟩ (C_5H_5)	0.907
C(7)–C(7M)	1.543 (5)	⟨C–H⟩ (CH_3)	1.002
C(9)–B(10)	1.657 (6)	⟨B–H⟩	1.121

Nonbonded Distances (Å) on Open Face

Co–C(13)	2.585 (3)	C(9)–B(12)	2.872 (5)
C(3)–C(7)	2.480 (4)	C(13)–B(14)	2.399 (5)
C(3)–B(12)	2.702 (4)	C(9)–C(13)	2.506 (5)
C(3)–B(14)	2.421 (5)		

Table V. Selected Bond Angles (Deg) in $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$

P(1)–Ni–P(2)	87.55 (4)	B(8)–C(9)–B(14)	69.6 (3)
P(1)–Ni–C(3)	147.1 (1)	B(14)–C(9)–B(10)	66.8 (3)
P(1)–Ni–B(4)	113.0 (1)	B(10)–C(9)–B(4)	62.8 (3)
P(1)–Ni–B(5)	89.9 (1)	B(4)–C(9)–C(3)	55.9 (2)
P(1)–Ni–B(6)	96.4 (1)	C(M9)–C(9)–C(3)	120.6 (3)
P(1)–Ni–C(7)	122.2 (1)	C(M9)–C(9)–B(4)	123.3 (3)
P(2)–Ni–C(3)	94.6 (9)	C(M9)–C(9)–B(10)	115.5 (3)
P(2)–Ni–B(4)	129.9 (1)	C(M9)–C(9)–B(14)	119.7 (3)
P(2)–Ni–B(5)	177.0 (1)	C(M9)–C(9)–B(8)	116.7 (3)
P(2)–Ni–B(6)	132.0 (1)	B(4)–B(10)–B(5)	61.4 (2)
P(2)–Ni–C(7)	97.6 (9)	B(5)–B(10)–B(11)	61.1 (3)
C(3)–Ni–C(7)	90.1 (1)	B(11)–B(10)–B(14)	61.8 (3)
C(3)–Ni–B(4)	43.8 (1)	B(14)–B(10)–C(9)	59.8 (3)
B(4)–Ni–B(5)	49.9 (2)	C(9)–B(10)–B(4)	62.0 (2)
B(5)–Ni–B(6)	49.9 (2)	B(5)–B(11)–B(6)	62.0 (2)
B(6)–Ni–C(7)	41.3 (1)	B(6)–B(11)–B(12)	60.7 (3)
Ni–C(3)–B(8)	105.0 (2)	B(12)–B(11)–B(14)	61.9 (3)
Ni–C(3)–B(4)	68.4 (2)	B(14)–B(11)–B(10)	63.2 (3)
B(4)–C(3)–C(9)	65.0 (2)	B(10)–B(11)–B(5)	60.7 (3)
B(8)–C(3)–C(9)	64.0 (2)	B(6)–B(12)–B(11)	61.1 (3)
C(M3)–C(3)–Ni	126.3 (2)	B(11)–B(12)–B(14)	62.5 (3)
C(M3)–C(3)–B(4)	144.4 (3)	B(14)–B(12)–C(13)	62.3 (3)
C(M3)–C(3)–C(9)	115.1 (3)	C(13)–B(12)–C(7)	53.2 (2)
C(M3)–C(3)–B(8)	115.7 (3)	C(7)–B(12)–B(6)	53.9 (2)
Ni–B(4)–B(5)	63.7 (2)	C(7)–C(13)–B(8)	117.5 (3)
Ni–B(4)–C(3)	67.8 (2)	C(7)–C(13)–B(12)	63.5 (3)
C(3)–B(4)–C(9)	59.1 (2)	B(12)–C(13)–B(14)	61.2 (3)
C(9)–B(4)–B(10)	55.2 (2)	B(14)–C(13)–B(8)	68.0 (3)
B(10)–B(4)–B(5)	59.1 (3)	C(M13)–C(13)–C(7)	120.5 (4)
Ni–B(5)–B(4)	66.4 (2)	C(M13)–C(13)–B(12)	110.5 (3)
Ni–B(5)–B(6)	67.5 (2)	C(M13)–C(13)–B(14)	119.8 (3)
B(4)–B(5)–B(10)	59.5 (2)	C(M13)–C(13)–B(8)	112.3 (3)
B(10)–B(5)–B(11)	58.2 (3)	B(8)–B(14)–C(9)	53.9 (2)
B(11)–B(5)–B(6)	59.0 (2)	C(9)–B(14)–B(10)	53.5 (2)
Ni–B(6)–B(5)	62.6 (2)	B(10)–B(14)–B(11)	55.1 (2)
Ni–B(6)–C(7)	70.8 (2)	B(11)–B(14)–B(12)	55.6 (2)
B(5)–B(6)–B(11)	59.0 (2)	B(12)–B(14)–C(13)	53.6 (2)
B(11)–B(6)–B(12)	58.2 (3)	C(13)–B(14)–B(8)	48.8 (2)
B(12)–B(6)–C(7)	60.7 (3)	Ni–P(1)–C(P1)	107.7 (1)
Ni–C(7)–C(13)	105.7 (3)	Ni–P(1)–C(B1)	122.5 (1)
Ni–C(7)–B(6)	67.9 (3)	Ni–P(1)–C(A1)	117.7 (1)
B(6)–C(7)–B(12)	65.4 (3)	C(A1)–P(1)–C(B1)	101.9 (2)
B(12)–C(7)–C(13)	63.3 (3)	C(A1)–P(1)–C(P1)	102.6 (2)
C(M7)–C(7)–Ni	122.3 (3)	C(B1)–P(1)–C(P1)	101.7 (2)
C(M7)–C(7)–B(6)	117.2 (3)	Ni–P(2)–C(P2)	105.4 (1)
C(M7)–C(7)–B(12)	116.1 (3)	Ni–P(2)–C(C1)	117.5 (1)
C(M7)–C(7)–C(13)	117.6 (3)	Ni–P(2)–C(D1)	121.3 (1)
C(3)–B(8)–C(13)	121.4 (3)	C(C1)–P(2)–C(D1)	104.0 (2)
C(3)–B(8)–C(9)	61.5 (2)	C(C1)–P(2)–C(P2)	100.5 (2)
C(9)–B(8)–B(14)	56.5 (2)	C(D1)–P(2)–C(P2)	105.6 (2)
B(14)–B(8)–C(13)	63.2 (2)	P(1)–C(P1)–C(P2)	110.8 (3)
C(3)–C(9)–B(8)	54.5 (2)	C(P1)–C(P2)–P(2)	107.9 (2)

desirable six-coordinate location in the framework. (4) The cage structure contains no element of symmetry. Thus, the observed geometry appears to be kinetically stabilized, reflecting to a large degree the mechanism of metal insertion into the $(CH_3)_4C_4B_8H_8^{2-}$ substrate (possible pathways for transition-metal insertion have been discussed in detail elsewhere[1,2]).

Bond distances and angles within the cage framework are within normal ranges. As expected, the skeletal C–C distances are short compared to the B–B lengths, but there is a notable difference between the values for C(7)–C(13) [1.517 (5) Å] and C(3)–C(9) [1.672 (4) Å]. This reflects the fact that C(9) occupies a high-coordinate vertex off the open face and must distribute its electron density among five bonds in the polyhedral surface; the other three carbon atoms occupy four-coordinate vertices on the open rim, and the interactions between these latter carbons and their neighbors (especially on the open face) will have relatively high bond order. Similarly, the bonds between the unique boron B(14) and its six neighbors are all long (average B–B 1.890 Å, average B–C 1.837 Å) in comparison to other B–B and B–C interactions in this molecule (average values are 1.773 and 1.650 Å, respectively).

The five-membered open face, defined by Ni, C(3), B(8), C(13), and C(7), is remarkably planar (Table VII, plane 7),

Table VI. Selected Bond Angles (Deg) in $(C_5H_5)Co(CH_3)_4C_4B_7H_7$

C(3)-Co-B(4)	45.8 (1)	C(3)-C(9)-B(14)	102.2 (3)
B(4)-Co-B(5)	50.1 (2)	C(3)-C(9)-B(4)	64.6 (2)
B(5)-Co-B(6)	50.4 (2)	C(4)-C(9)-B(10)	62.2 (2)
B(6)-Co-C(7)	46.0 (2)	B(10)-C(9)-B(14)	65.8 (3)
C(7)-Co-C(3)	69.8 (1)	C(9M)-C(9)-B(4)	120.3 (2)
Co-C(3)-C(13)	81.7 (2)	C(9M)-C(9)-B(10)	119.4 (2)
Co-C(3)-B(4)	60.4 (2)	C(9M)-C(9)-B(14)	122.9 (2)
B(4)-C(3)-C(9)	64.1 (2)	C(9M)-C(9)-C(3)	120.2 (2)
C(9)-C(3)-C(13)	100.6 (2)	B(4)-B(10)-B(5)	60.9 (2)
C(3M)-C(3)-Co	109.2 (2)	B(5)-B(10)-B(11)	61.4 (3)
C(3M)-C(3)-B(4)	115.7 (2)	B(11)-B(10)-B(14)	59.1 (3)
C(3M)-C(3)-C(9)	118.2 (2)	B(14)-B(10)-C(9)	56.4 (3)
C(3M)-C(3)-C(13)	113.7 (2)	C(9)-B(10)-B(4)	60.3 (2)
C(3)-B(4)-Co	73.8 (2)	B(5)-B(11)-B(6)	60.2 (2)
Co-B(4)-B(5)	65.9 (2)	B(6)-B(11)-B(12)	62.4 (3)
B(5)-B(4)-B(10)	60.5 (2)	B(12)-B(11)-B(14)	62.1 (3)
B(10)-B(4)-C(9)	57.5 (2)	B(14)-B(11)-B(10)	61.1 (3)
C(9)-B(4)-C(3)	51.3 (2)	B(10)-B(11)-B(5)	59.4 (2)
B(4)-B(5)-Co	64.0 (2)	C(13)-B(12)-B(14)	86.7 (3)
Co-B(5)-B(6)	65.3 (2)	C(13)-B(12)-C(7)	48.8 (2)
B(6)-B(5)-B(11)	59.6 (2)	C(7)-B(12)-B(6)	53.9 (2)
B(11)-B(5)-B(10)	59.2 (3)	B(6)-B(12)-B(11)	60.5 (3)
B(10)-B(5)-B(4)	58.7 (2)	B(11)-B(12)-B(14)	59.4 (3)
B(5)-B(6)-Co	64.4 (2)	C(7)-B(12)-B(14)	123.8 (3)
Co-B(6)-C(7)	63.4 (2)	C(3)-C(13)-C(7)	111.9 (3)
C(7)-B(6)-B(12)	60.5 (2)	C(7)-C(13)-B(12)	67.4 (2)
B(12)-B(6)-B(11)	57.2 (2)	B(12)-C(13)-C(3)	111.7 (3)
B(11)-B(6)-B(5)	60.1 (2)	C(13M)-C(13)-C(7)	123.3 (3)
Co-C(7)-C(13)	95.9 (2)	C(13M)-C(13)-C(3)	115.3 (3)
Co-C(7)-B(6)	70.6 (2)	C(13M)-C(13)-B(12)	118.4 (3)
B(6)-C(7)-B(12)	65.5 (2)	C(P2)-C(P1)-C(P5)	107.7 (5)
B(12)-C(7)-C(13)	63.8 (2)	C(P1)-C(P2)-C(P3)	107.3 (5)
C(7M)-C(7)-Co	126.8 (2)	C(P2)-C(P3)-C(P4)	109.1 (5)
C(7M)-C(7)-C(13)	120.4 (2)	C(P3)-C(P4)-C(P5)	108.1 (5)
C(7M)-C(7)-B(6)	117.3 (2)	C(P4)-C(P5)-C(P1)	107.7 (5)
C(7M)-C(7)-B(12)	116.8 (2)		

and the transannular distances within this ring (Table III) are clearly nonbonding inasmuch as the shortest of these, C(7)–B(8), is 2.67 Å.

The molecule can be viewed as a coordination complex of formal $(CH_3)_4C_4B_8H_8^{2-}$, in which the geometry of the ligand differs sharply from that of the $(CH_3)_4C_4B_8H_8^{2-}$ moiety as found[1] in the cobaltocenium-substituted species $[(\eta^5\text{-}C_5H_5)Co(\eta^5\text{-}C_5H_4)](CH_3)_4C_4B_8H_8$. We have suggested previously[1,2] that the $(CH_3)_4C_4B_8H_8^{2-}$ ion exists in solution as an equilibrium mixture of two or more isomers, which would account for the production of metallacarborane isomers when solutions of the ion are treated with transition-metal-inserting groups. In the present nickel complex, the face coordinated to the metal [C(3)–B(4)–B(5)–B(6)–C(7)] is planar, with the nickel situated 1.31 Å from that plane. This distance is much shorter than metal–ligand vectors in complexes where first-row transition metals are coordinated to a *five*-membered carborane face (typically 1.5–1.6 Å[20]) but is comparable to observed values for metal–*six*-membered ring interactions in metallacarboranes, which range from about 1.25 to 1.35 Å.[4,21] The close approach of the metal in the present complex is consistent with its formation as a closo 14-vertex polyhedron with one vacant vertex (vide supra), in which the "missing" atom is part of the 6-membered ligand face coordinated to the metal. Thus, if the vacant site were filled with a BH^{2+} unit, the resulting closo polyhedron would be analogous to 1,14,2,5,9,12-$(\eta^5\text{-}C_5H_5)_2Fe_2(CH_3)_4C_4B_8H_8$, a bicapped hexagonal antiprism in which the two iron atoms occupy the six-coordinate vertices.[21]

Bond distances and angles in the bis(diphenylphosphino)ethane ligand are normal, and the plane defined by the nickel and two phosphorus atoms is nearly perpendicular to the plane of the open face on the polyhedron. The fact that both the P(2)–Ni–P(1) and C(3)–Ni–C(7) angles are close to 90° is consistent with octahedral (d^2sp^3) hybridization of the metal valence orbitals. All four phenyl rings are planar within experimental error, the largest deviation being 0.014 Å.

$(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_7$, Isomer 2. The unique basketlike cage structure (Figures 3 and 5) is not a fragment of a standard closo polyhedron and incorporates a novel triply bridging carbon atom. In terms of its skeletal framework electron count of 28 (based on a contribution of two electrons from each BH and $Co(C_5H_5)$ and three from each $C\text{–}CH_3$ unit), the molecule is of the nido ($2n + 4$) class. Remarkably, this species is the fifth geometrically distinct *type* of 12-vertex nido cage system to be identified; the four previously established structural classes[3-6,8,22,23] are depicted in ref 5.

The unique carbon atom C(13) is linked to only three atoms in the skeletal framework, one of which [C(3)] is not bonded to the other two; thus, C(13) forms a bridge across the open top of the basket. Of the three framework carbon–carbon bonding interactions, two are relatively short [C(3)–C(9), 1.480 (4) Å; C(7)–C(13), 1.424 (4) Å], as is typical of the links between low-coordinate carbon atoms in carborane polyhedra. However, the central C(3)–C(13) bond [1.567 (4) Å] is significantly longer and is typical of alkane C–C distances, suggesting that, although C(13) is firmly attached to atoms C(7) and B(12) in the cage framework, its trans-cage bridging interaction with C(3) is somewhat weaker. The bond angles around C(13) are consistent with this picture. While the B(12)–C(13)–C(7) angle is 67°, all others are much larger (112–123°); thus, C(13) can be described as having partial "cage" character with respect to its interaction with C(7) and B(12) and partial "saturated hydrocarbon" (i.e., localized bond) character toward C(13M) and C(3). This tendency of framework carbon atoms to occupy, where possible, low-coordinate sites and relatively localized bonding interactions with neighboring atoms is very noticeable in the tetracarbon carboranes and metallacarboranes as a group;[1-8] for example, it is particularly conspicuous in the cobaltocenium-substituted derivative of $(CH_3)_4C_4B_8H_9^-$, in which one of the cage carbons has moved out of the framework proper and adopted a methylene-like bridging role.[1]

The remaining distances and angles in the cage skeleton are normal. When the complex is viewed as a cobalt sandwich, the metal atom is coordinated to a ligand bonding face [C(3)–C(7)–B(6)–B(5)–B(4)] which is distinctly nonplanar (Table VIII). Clearly, this molecule is another member of the class of kinetically stabilized unconventional cage structures mentioned in the Introduction. Its observed geometry can, however, be rationalized on a mechanistic basis as we show in the following section.

Structural Relationship between the Two Complexes. Although the clusters described here contain different metals and were obtained in separate reactions, there are important structural similarities that help to explain both the formation of the CoC_4B_7 complex and its peculiar geometry. Since the $[(C_6H_5)_2PCH_2]_2Ni$ and $(\eta^5\text{-}C_5H_5)Co$ moieties are equivalent in terms of electron contributions to skeletal bonding (both being two-electron donors[9-11]), one would anticipate the existence of $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_8H_8$, a structural analogue $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$. As noted above, a cobaltacarborane of that composition has been isolated[2] from the same reaction which produced the isomer of $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_7$ discussed in this paper, and it has been suggested that the CoC_4B_7 species is generated from this CoC_4B_8 cluster by loss of a BH unit.[2] Figure 5 schematically depicts such a conversion, based on the assumption that the

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Table VII

Selected Mean Planes in $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$

atom	dev, Å	atom	dev, Å
Plane 1 (Cage Atoms Bonded to Ni): C(7), C(3), B(6), B(4), B(5) $-0.4050x - 0.7588y - 0.5101z = -6.2245$			
C(7)	−0.002	Ni	1.313
C(3)	0.003	P(1)	3.005
B(6)	0.002	P(2)	2.753
B(4)	−0.003	C(M7)	0.566
B(5)	0.001	C(M3)	0.430
Plane 2: Ni, P(1), P(2) $-0.8403x + 0.4676y - 0.2743z = -1.2362$			
Ni	0.000	C(P2)	−0.813
P(1)	0.000	C(3)	1.170
P(2)	0.000	C(7)	−1.888
C(P1)	−0.184	B(5)	0.061
Plane 3 (Phenyl Ring A): C(A1), C(A2), C(A3), C(A4), C(A5), C(A6) $-0.3621x - 0.4968y - 0.7887z = -2.6100$			
C(A1)	−0.001	C(A6)	0.006
C(A2)	−0.004	P(1)	−0.121
C(A3)	0.003	P(2)	−1.364
C(A4)	0.003	C(P1)	0.878
C(A5)	−0.007	C(P2)	−0.023
		Ni	−2.113
Plane 4 (Phenyl Ring B): C(B1), C(B2), C(B3), C(B4), C(B5), C(B6) $0.8048x + 0.5069y - 0.3087z = 3.0502$			
C(B1)	−0.007	C(B6)	0.008
C(B2)	0.005	P(1)	−0.106
C(B3)	−0.003	P(2)	−2.341
C(B4)	0.004	C(P1)	−1.638
C(B5)	−0.006	C(P2)	−2.296
		Ni	−0.310
Plane 5 (Phenyl Ring C): C(C1), C(C2), C(3), C(C4), C(C5), C(C6) $0.1969x - 0.7883y - 0.5830z = -3.2119$			
C(C1)	0.005	C(C6)	0.006
C(C2)	−0.008	P(1)	1.369
C(C3)	−0.001	P(2)	0.173
C(C4)	0.012	C(P1)	2.461
C(C5)	−0.014	C(P2)	2.002
		Ni	−0.559
Plane 6 (Phenyl Ring D): C(D1), C(D2), C(D3), C(D4), C(D5), C(D6)			
C(D1)	0.006	C(D6)	−0.007
C(D2)	0.002	P(1)	1.636
C(D3)	−0.009	P(2)	0.143
C(D4)	0.008	C(P1)	0.277
C(D5)	0.001	C(P2)	0.113
		Ni	1.890
Plane 7 (Atoms on Open Rim): C(3), B(8), C(13), C(7), Ni $0.4737x + 0.7555y - 0.4525z = 2.3633$			
C(3)	0.015	P(2)	−2.164
B(8)	−0.033	C(P1)	−1.505
C(13)	0.035	C(P2)	−2.491
C(7)	−0.020	C(M3)	−0.754
Ni	0.003	C(M7)	−0.923
P(1)	0.214	C(M13)	−0.644
Plane 8 (Atoms Bonded to B(14)): C(13), B(8), C(9), B(10), B(11), B(12) $-0.3517x - 0.7024y - 0.6188z = -7.5938$			
C(13)	0.050	B(12)	−0.129
B(8)	0.085	B(14)	−0.830
C(9)	−0.142	Ni	2.692
B(10)	0.055	C(M9)	−1.0713
B(11)	0.081	C(M13)	−0.7704

Dihedral Angles between Planes

planes	angle, deg	planes	angle, deg	planes	angle, deg	planes	angle, deg
1,2	82.79	2,8	82.14	1,8	7.65	4,6	20.17
1,3	22.19	3,4	107.45	2,3	73.24	4,7	25.32
1,4	123.58	3,5	38.73	2,4	110.77	5,6	96.42
1,5	35.34	3,6	121.19	2,5	111.97	5,7	103.80
1,6	131.17	3,7	100.95	2,6	126.84	6,7	43.37
1,7	122.29	4,5	93.51	2,7	85.45	7,8	114.66

complex $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_8H_8$ has a structure corresponding to that of the $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$ complex discussed here. We do not have direct proof of this analogy, since X-ray data on the CoC_4B_8 cluster itself is not available, and its ^{11}B and ^1H NMR spectra[2] convey no useful structural information other than that it is asymmetric; however, the facility of the proposed conversion and the fact that CoC_4B_8 and CoC_4B_7 complexes are generated in the same reaction make this in our view a reasonable hypothesis.

The structural relationship between the cobalt and nickel species can be gauged by a direct comparison of corresponding bond lengths, which is facilitated by choice of a common numbering system. As can be seen in Figure 5, the proposed formation of the CoC_4B_7 species from the cobalt analogue of the NiC_4B_8 cluster involves primarily removal of B(8)–H and formation of a bond between C(13) and C(3). The atoms most directly affected are those to which B(8) is bonded in the NiC_4B_8 complex, namely, C(3), C(9), C(13), and B(14). As expected, bond distances involving these atoms are substantially different in the two molecules; as one moves from the NiC_4B_8 to the CoC_4B_7 system, C(3)–C(13) decreases by 1.19 Å (i.e., from a nonbonding to a bonding distance), C(13)–B(14) *increases* by 0.49 Å (corresponding to bond cleavage), the nonbonded C(3)–C(7) distance shortens by 0.64 Å, and several other B–B, B–C, and C–C distances change by 0.1 Å or more: C(3)–B(4), C(3)–C(9), C(9)–B(14), and B(11)–B(14). Particularly dramatic bond shortening occurs between B(14) and its neighbors owing to the change from a six-coordinate to a four-coordinate vertex. In addition, the metal–carborane distances in the cobalt system are smaller by an average 0.10 Å (excluding C(3) which moves away from the metal in order to bond to the bridging carbon, C(13)); this value corresponds approximately to the estimated difference in radius between Ni(II) and Co(III).[24] Significantly, skeletal bond distances

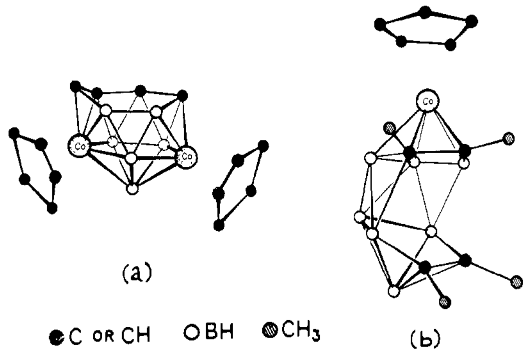

Figure 6. (a) Structure of $(\eta^5\text{-}C_5H_5)_2Co_2C_4B_6H_{10}$.[4] (b) Structure of $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_7$, isomer 1.[5,25]

Table VIII

Selected Mean Planes in $(C_5H_5)Co(CH_3)_4C_4B_7H_7$

atom	dev, Å	atom	dev, Å
Plane 1 (Cage Atoms Bonded to Co): C(3), C(7), B(4), B(5), B(6)			
$-0.7042x + 0.2328y - 0.6707z = -3.5970$			
C(3)	0.176	Co	−1.405
C(7)	−0.167	C(13)	0.555
B(4)	−0.160	C(3M)	−0.537
B(5)	0.026	C(7M)	−0.559
B(6)	0.125	C(13M)	0.920
Plane 2 (Cyclopentadienyl Ring)			
$-0.6550x + 0.2073y - 0.7266z = -6.8102$			
C(P1)	0.016	C(P4)	0.004
C(P2)	−0.014	C(P5)	−0.012
C(P3)	0.007	Co	1.687
Plane 3: C(3), C(7), C(9), B(12), B(14)			
$-0.1413x - 0.6812y - 0.7309z = 0.0291$			
C(3)	0.163	Co	−1.484
C(7)	−0.116	C(13)	0.781
C(9)	−0.147	C(3M)	0.911
B(12)	0.081	C(7M)	0.424
B(14)	0.020	C(9M)	0.355

Dihedral Angles between Planes

planes	angle, deg	planes	angle, deg
1,2	4.51	2,3	65.36
1,3	68.85		

involving boron and carbon atoms *not* adjacent to B(8) (the extracted atom) are nearly the same in the two cages, the average difference between such bonds in the NiC_4B_8 cluster and their counterparts in the CoC_4B_7 system being only 0.032 Å.

Conclusion. The gross cage structures can be understood from simple electron-counting and mechanistic considerations. The NiC_4B_8 cluster is a 13-vertex nido cage, derivable from a 14-vertex closo polyhedron by removal of one vertex, and is consistent with the presence of $(2n + 4)$ skeletal electrons. The CoC_4B_7 complex is a highly irregular framework which probably forms by removal of the B(8)–H vertex from a CoC_4B_8 species analogous to the nickel system; abstraction of B(8) leaves C(13) in a coordinatively unsaturated situation which is rectified by formation of a bond between C(13) and C(3).

Without doubt, neither structure represents the thermodynamically preferred arrangement. The most stable geometry for the NiC_4B_8 system is probably a monocapped hexagonal antiprism with nickel occupying the cap and the four carbons on the open rim. For $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_7$, the preferred geometry is likely to be similar to that of the established structure[4] of $(\eta^5\text{-}C_5H_5)_2Co_2C_4B_6H_{10}$, an open basket derived from a 13-vertex closo polyhedron by removal of one vertex (Figure 6a) with a BH unit replacing one of the $Co(C_5H_5)$ groups; again, the framework carbon atoms are expected to adopt low-coordinate vertices on the rim.

Although a different isomer (isomer 1) of $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_7H_7$ has previously been structurally defined in parent[25] as well as in ethoxy-substituted[5] form, that geometry (Figure 6b) is not thermodynamically stable and rearranges on heating to an as yet unknown structure.[2,26] Nido cage systems such as those described here may not in all cases survive thermal rearrangement, instead undergoing degradation. However, in an earlier study[7] we demonstrated that asymmetric, irregular isomers of a 14-vertex system, $(\eta^5\text{-}C_5H_5)_2Fe_2(CH_3)_4C_4B_8H_8$, do ultimately convert to a highly symmetric (D_{2d}) polyhedral cage. Clearly, further investigations of this kind will be required to elucidate the stereochemistry of large "electron-rich" metallacarboranes.

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Registry No. Isomer 1, 63454-29-5; isomer 2, 70304-26-6.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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(24) Phillips, C. S. G.; Williams, R. J. P. "Inorganic Chemistry"; Oxford University Press: New York, 1966; Vol. II, pp 241, 286.

(25) Welch, A. J., private communication.

(26) The structure of the thermally rearranged[2] isomer (IIII) has now been determined crystallographically and, as predicted above, consists of an open 12-vertex basket like that of $(\eta^5\text{-}C_5H_5)_2Co_2C_4B_6H_{10}$ (Figure 6a)[4] with the cobalt atom in the 2-position but with the carbon atoms in the 7-, 9-, 11-, and 12-vertices on the open face, such that *one carbon is isolated from the others* (for numbering system see ref 4). This structure will be reported in detail later.