boron hydrides and alkynes into metallacarborane clusters at low temperature without the prior synthesis of the carborane cage; that is, the metal atoms or reactive fragments derived from these atoms are being used as sites for cage construction. In only a few previous instances,[9c,22,28] has a carborane or metallacarborane been synthesized by direct reaction of an alkyne and parent borane at a metal site. Second, the low-temperature reaction conditions have led to only adjacent carbon isomers. This is in direct contrast to what is often observed in conventional synthesis of small cage metallacarborane clusters, which, because of the high temperatures employed in either the synthesis of the carboranes themselves or the synthesis of the metal complexes, can readily isomerize to give nonadjacent isomers. Thus many of the adjacent carbon isomers produced in the metal atom reactions are inaccessible by other synthetic technqiues. Third, although some cage fragmentation products were observed, the major products usually contained the same number of boron atoms as the starting boron hydride molecule, again demonstrating the synthetic advantages of the mild conditions employed in the metal atom reaction. Finally, several of the new metallacarboranes produced were shown to be structurally novel. In this regard, the compound which is probably of most interest was the unique four-carbon metallacarborane cluster $4,5,7,8-(C_6H_5)_4-1,4,5,7,8-(\eta-C_5H_5)CoC_4B_3H_3$ (VIII). The isolation of this complex, which contains more carbon than boron cage atoms, indicates that with appropriate conditions metal atom techniques may be used to incorporate an even greater number of carbon or other heteroatoms into these cages to form new hybrid clusters.

In contrast to the results obtained with pentaborane(9) and hexaborane(10), it was found that the metal atom reactions of decaborane(14) were less fruitful. For example, although the reactions of decaborane(14) and cyclopentadiene with cobalt atoms did result in the formation of both $6-(\eta-C_5H_5)CoB_9H_{13}$ and $5-(\eta-C_5H_5)CoB_9H_{13}$[9] in reasonable yields, inclusions of either dimethyl- or diphenylacetylene in the reaction did not result in the formation of metallacarborane products. It is important to note, however, that in the latter reaction diphenyl-*o*-carborane was obtained in small amounts, suggesting that it may be eventually possible to develop metal atom assisted synthesis of carboranes.

It is apparent that the chief disadvantage of the reactions reported herein is their complex nature which often leads to the formation of many products and low individual yields. Thus, while the metal atom technique must be considered a forefront method for the formation of new types of cage systems, further developments will be needed before these techniques can be applied to preparative scale syntheses of the complexes described.

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Registry No. I, 74978-05-5; II, 63179-56-6; III, 75125-07-4; IV, 74978-06-6; V, 67579-06-0; VI, 74978-07-7; VII, 74965-08-5; VIII, 74964-99-1; IX, 74978-08-8; X, 74987-43-2; XI, 74977-73-4; XII, 74965-00-7; $1,2-(C_6H_5)_2-1,2-C_2B_{10}H_{10}$, 17805-19-5; $6-(\eta-C_5H_5)CoB_9H_{13}$, 74978-06-6; $1-(\eta-C_5H_5)CoC_4(C_6H_5)_4$, 1278-02-0; $1,2-(\eta-C_5H_5)_2Co_2B_4H_6$, 50924-50-0; $3-\sigma-C_5H_9-1,2-(\eta-C_5H_5)_2Co_2B_4H_5$, 43062-02-8; $4-\sigma-C_5H_9-1,2-(\eta-C_5H_5)_2Co_2B_4H_5$, 43062-03-9; $1,2,3-(\eta-C_5H_5)_3Co_3B_3H_5$, 59217-07-1; $1,2,4,7-(\eta-C_5H_5)_4Co_4B_4H_4$, 59370-82-0; $1,2,3-(\eta-C_5H_5)_3Co_3B_4H_4$, 59458-52-5; $2-(\eta-C_5H_5)CoB_9H_{13}$, 68457-40-9; $5-(\eta-C_5H_5)CoB_9H_{13}$, 43062-04-0; $2,3-(CH_3)_2-1,7,2,3-(\eta-C_5H_5)_2Co_2C_2B_3H_3$, 51108-06-6; $2,3-(CH_3)_2-1,2,3-(\eta-C_5H_5)CoC_2B_4H_4$, 50932-66-6; $5,6-(CH_3)_2-1,8,5,6-(\eta-C_5H_5)_2Co_2C_2B_5H_5$, 67579-07-1; $2-(\eta-C_5H_5)CoB_4H_8$, 43062-00-6; $1,7-(CH_3)_2-3,1,7-(\eta-C_5H_5)CoC_2B_5H_5$, 74965-09-6; B_5H_9, 19624-22-7; B_6H_{10}, 23777-80-2; $B_{10}H_{14}$, 17702-41-9; 2-butyne, 503-17-3; diphenylacetylene, 501-65-5.

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Crystal and Molecular Structure of $4,5,7,8-(C_6H_5)_4-1,4,5,7,8-(\eta-C_5H_5)CoC_4B_3H_3$: A Four-Carbon Metallacarborane Complex Containing More Carbon Than Boron Cage Atoms

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The crystal and molecular structure of $4,5,7,8-(C_6H_5)_4-1,4,5,7,8-(\eta-C_5H_5)CoC_4B_3H_3$, an unusual four-carbon metallacarborane complex containing more carbon than boron cage atoms, has been determined from single-crystal X-ray diffraction data. The cage framework is best described as a bicapped square antiprism missing two vertices (one cap and one equatorial position). This structure is not predicted by simple electron counting rules but is consistent with the structures observed for certain other eight-atom 20-skeletal-electron systems. Crystal data: space group $P2_1/c$, $Z = 4$, $a = 14.997$ (5) Å, $b = 10.472$ (6) Å, $c = 17.576$ (8) Å, $\beta = 109.83$ (1)°, $V = 2596$ Å^3. The structure was refined by full-matrix least-squares methods to final R of 0.042 and R_w of 0.039 for the 2278 reflections which had $F_o^2 > 3\sigma(F_o^2)$.

In the previous paper[2] it was demonstrated that metal atom techniques can be used to produce several types of structurally novel metalloboron clusters. One complex of particular interest, which was isolated from the reaction of pentaborane(9), cyclopentadiene, and diphenylacetylene with cobalt atoms, was the compound $4,5,7,8-(C_6H_5)_4-1,4,5,7,8-(\eta-C_5H_5)CoC_4B_3H_5$. This complex is an unusual example of a four-carbon metallacarborane containing more carbon than boron cage atoms. Furthermore, it is an eight-atom $2n + 4$ cluster system (eight cage atoms, 20 skeletal electrons) and is thus of additional interest since such cluster systems have previously been proposed to deviate from the structures expected on the basis of

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[2] G. J. Zimmerman, L. W. Hall, and L. G. Sneddon, *Inorg. Chem.*, preceding paper in this issue.

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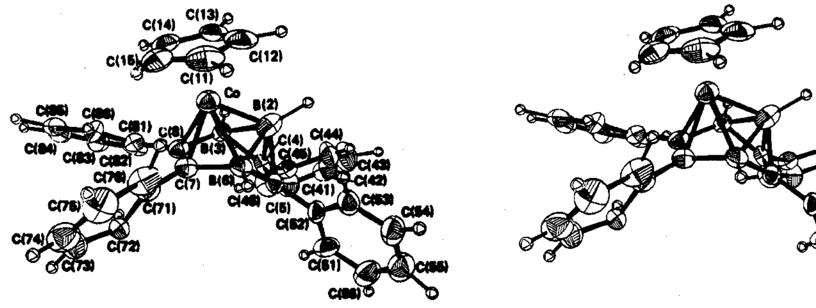

Figure 1. Stereo ORTEP drawing of $4,5,7,8\text{-}(C_6H_5)_4\text{-}1,4,5,7,8\text{-}(\eta\text{-}C_5H_5)CoC_4B_3H_3$ (full molecule). Nonhydrogen atoms are shown as 50% thermal ellipsoids.

simple electron counting rules. Unfortunately the compound could be produced in only small amounts, and reliable structural conclusions based upon the spectroscopic data were not possible. An X-ray crystallographic investigation was therefore undertaken to establish the detailed structure of this complex, and the results of this study are reported here.

Experimental Section

Several cube-shaped red crystals of $4,5,7,8\text{-}(C_6H_5)_4\text{-}1,4,5,7,8\text{-}(\eta\text{-}C_5H_5)CoC_4B_3H_3$, isolated from the reaction of cobalt vapor with pentaborane(9), cyclopentadiene, and diphenylacetylene, were grown over an 18-h period by vapor diffusion of heptane into a dilute carbon disulfide solution of the compound. A well-formed parallelepiped-shaped crystal (0.15 × 0.125 × 0.1 mm) was selected for data collection, mounted on a glass fiber, and then transferred to the diffractometer. The Enraf-Nonius program SEARCH was used to obtain eight accurately centered reflections which were then used in the program INDEX to obtain an orientation matrix for data collection and also to provide approximate cell dimensions. This orientation matrix was improved by the addition of 17 new reflections. Refined cell dimensions and their standard deviations were obtained from the least-squares refinement of these 25 accurately centered reflections. Crystal data: $CoC_{33}B_3H_{28}$, mol wt 515.96, space group $P2_1/c$, $Z = 4$, $a = 14.997$ (5) Å, $b = 10.472$ (6) Å, $c = 17.576$ (8) Å, $\beta = 109.83$ (1)°, $V = 2596$ (4) Å^3, ρ(calcd) = 1.320 g cm^{-3}. The mosaicity of the crystal was judged acceptable on the basis of several θ scans. Systematic absences for $k = 2n + 1$ on $0k0$ and $l = 2n + 1$ on $h0l$ uniquely establish the space group as $P2_1/c$.

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 PDP 8/A computer, using Mo Kα radiation from a highly oriented graphite-crystal monochromator. A combined θ–2θ, ω scan technique was used to record the intensities for all reflections for which $1.0° < 2\theta < 50°$; scan widths (SW) were calculated from the formula $SW = A + B \tan\theta$, where A is estimated from the mosaicity of the crystal and B allows for the increase in peak width due to Kα_1 and Kα_2 splitting. The values for A and B were 0.68 and 0.35. This calculated scan angle was extended at each side by 25% for background determination (BG1 + 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 if intensities registered less than 30 counts above background on a rapid prescan, such reflections being rejected automatically by the computer. The intensities of three standard reflections measured at intervals of 100 reflections showed no systematic change during data collection. The raw intensities were then corrected for Lorentz and polarization effects by using the Enraf-Nonius program DATARED. Of the 4752 measured intensities 2278 had $F_o^2 > 3\sigma(F_o^2)$ and were used in the analysis.

Solution and Refinement of the Structure. All calculations were performed on a PDP 11/60 computer using the Enraf-Nonius structure package.[3]

Normalized structure factors were calculated by using a K curve, and the intensity distribution statistics support a centrosymmetric space group. The coordinates of the cobalt atom were located from a three-dimensional Patterson synthesis. The Patterson map yielded two significant peaks, (0.0, 0.9160, 0.4941) and (0.4902, 0.500, 0.2461). The corresponding Harker sections for $P2_1/c$, $(0, {}^1/_2 - 2y, {}^1/_2)$ and $(2x, {}^1/_2, {}^1/_2 - 2z)$, gave the respective x, y, and z coordinates of the cobalt atom. Full-matrix least-squares refinement of these cobalt coordinates, using preliminary scale and thermal parameters from the Wilson plot, showed minimal shifting. A Fourier map phased on these refined positions led to the location of the five cyclopentadienyl carbon atoms, 12 phenyl ring carbon atoms, and two carbon atoms in the cage framework. Several cycles of isotropic least-squares refinement on these new atom positions and a Fourier map phased on all of these refined positions led to the location of the remaining 12 phenyl carbon atoms and the two additional carbon atoms in the cage. Additional isotopic refinements on these new positions followed by another Fourier synthesis gave the positions of the three boron cage atoms. Several cycles of anisotropic least-squares refinement on all of these parameters followed by a difference Fourier synthesis located all 28 hydrogen atoms in the molecule. Final refinement with an absorption correction (transmission coefficient: maximum, 95.37; minimum, 91.21) including anisotropic thermal parameters for nonhydrogen atoms and fixed isotropic thermal parameters for the hydrogen atoms led to the final residual factors $R = 0.042$ and $R_w = 0.039$.

The 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 $(4F_o/\sigma(F_o^2))^2$, 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[4a] and those for hydrogen from Stewart.[4b] The effects of anomalous dispersion were included in F_c by using Cromer and Ibers' values[5] for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

The final positional and thermal parameters for $4,5,7,8\text{-}(C_6H_5)_4\text{-}1,4,5,7,8\text{-}(\eta\text{-}C_5H_5)CoC_4B_3H_3$ are given in Table I. Intramolecular bond distances, selected bond angles, and molecular planes are presented in Tables II–IV, respectively. Figure 1 shows a stereoscopic view of the complete molecule, while Figure 2 shows only the cage framework. A unit cell packing diagram is given in Figure 3. A listing of observed and calculated structure factors is available as supplementary material.

Results and Discussion

The recognition[6] of relationships between skeletal electron count and molecular geometry in polyhedral cluster systems has allowed amazingly accurate structural predictions in such diverse areas as boron hydride and transition-metal cluster chemistry. There is still, however, much confusion concerning factors affecting the geometries of eight-vertex systems. This is especially true of eight-vertex $2n + 4$ (20 skeletal electrons) systems, of which $4,5,7,8\text{-}(C_6H_5)_4\text{-}1,4,5,7,8\text{-}(\eta\text{-}C_5H_5)CoC_4B_3H_3$ is an example. For instance, there have been only seven previously reported cases of eight-vertex $2n + 4$ systems: B_8H_{12},[7] $C_2B_6H_{10}$,[8] $(CH_3)_4C_4B_4H_4$,[9] $(C_2H_5)_4C_4B_4(CH_3)_4$,[10]

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Co	−0.24866 (5)	−0.20964 (7)	0.12632 (4)	0.00425 (3)	0.00635 (6)	0.00335 (2)	−0.0010 (1)	0.00276 (4)	−0.0002 (1)
C8	−0.1413 (3)	−0.0798 (5)	0.1593 (3)	0.0039 (3)	0.0042 (5)	0.0032 (2)	−0.0012 (7)	0.0026 (4)	−0.0007 (5)
C81	−0.0406 (3)	−0.1107 (5)	0.1695 (3)	0.0039 (3)	0.0059 (5)	0.0026 (2)	0.0005 (7)	0.0024 (3)	−0.0013 (6)
C82	0.0053 (3)	−0.0402 (5)	0.1266 (3)	0.0042 (3)	0.0085 (6)	0.0031 (2)	−0.0009 (8)	0.0028 (4)	−0.0005 (6)
C83	0.0980 (3)	−0.0681 (6)	0.1331 (3)	0.0045 (3)	0.0111 (7)	0.0045 (2)	−0.0039 (8)	0.0049 (4)	−0.0021 (7)
C84	0.1470 (3)	−0.1638 (6)	0.1823 (3)	0.0033 (3)	0.0121 (8)	0.0046 (2)	0.0003 (8)	0.0026 (4)	−0.0028 (7)
C85	0.1033 (4)	−0.2351 (5)	0.2237 (3)	0.0047 (3)	0.0074 (6)	0.0045 (2)	0.0031 (8)	0.0010 (5)	−0.0014 (7)
C86	0.0100 (3)	−0.2104 (6)	0.2174 (3)	0.0045 (3)	0.0078 (5)	0.0037 (2)	0.0011 (8)	0.0030 (4)	0.0011 (7)
C7	−0.1836 (3)	−0.0928 (5)	0.2199 (3)	0.0040 (2)	0.0053 (5)	0.0032 (2)	−0.0016 (7)	0.0039 (3)	−0.0010 (5)
C71	−0.1321 (3)	−0.1246 (5)	0.3056 (3)	0.0043 (3)	0.0064 (5)	0.0025 (2)	0.0009 (7)	0.0023 (4)	0.0005 (6)
C72	−0.0466 (3)	−0.0659 (5)	0.3479 (3)	0.0046 (3)	0.0080 (6)	0.0023 (2)	0.0012 (8)	0.0019 (4)	0.0013 (6)
C73	0.0029 (4)	−0.0975 (6)	0.4274 (3)	0.0057 (3)	0.0098 (7)	0.0031 (2)	0.0006 (9)	0.0010 (4)	−0.0002 (7)
C74	−0.0301 (4)	−0.1874 (6)	0.4672 (3)	0.0087 (4)	0.0097 (7)	0.0027 (2)	0.0022 (10)	0.0031 (5)	0.0021 (7)
C75	−0.1162 (4)	−0.2423 (5)	0.4275 (3)	0.0097 (4)	0.0079 (7)	0.0039 (2)	0.0004 (8)	0.0076 (4)	0.0034 (6)
C76	−0.1672 (4)	−0.2121 (6)	0.3476 (3)	0.0068 (3)	0.0082 (6)	0.0033 (2)	−0.0022 (9)	0.0045 (4)	0.0011 (7)
C51	−0.3895 (3)	0.2809 (5)	0.1494 (3)	0.0045 (3)	0.0080 (6)	0.0051 (2)	−0.0005 (9)	0.0045 (4)	−0.0019 (7)
C52	−0.3974 (3)	0.1495 (5)	0.1486 (3)	0.0028 (2)	0.0092 (6)	0.0022 (2)	0.0010 (7)	0.0014 (3)	−0.0003 (6)
C53	−0.4777 (3)	0.0975 (5)	0.1584 (3)	0.0038 (3)	0.0091 (6)	0.0035 (2)	0.0003 (8)	0.0028 (4)	−0.0003 (6)
C54	−0.5486 (3)	0.1735 (6)	0.1674 (3)	0.0037 (3)	0.0149 (8)	0.0043 (2)	0.0014 (8)	0.0044 (4)	0.0011 (7)
C55	−0.5394 (4)	0.3032 (6)	0.1669 (3)	0.0056 (3)	0.0139 (7)	0.0050 (2)	0.0078 (9)	0.0054 (4)	−0.0012 (8)
C56	−0.4602 (4)	0.3555 (6)	0.1591 (4)	0.0076 (4)	0.0102 (7)	0.0071 (3)	−0.0003 (9)	0.0080 (5)	−0.0012 (8)
C11	−0.3009 (4)	−0.3773 (5)	0.1547 (4)	0.0077 (4)	0.0079 (6)	0.0069 (3)	−0.0053 (9)	0.0084 (5)	−0.0006 (7)
C12	−0.1892 (4)	−0.3710 (5)	0.0954 (3)	0.0068 (4)	0.0070 (6)	0.0046 (2)	−0.0002 (9)	0.0049 (5)	−0.0021 (6)
C13	−0.3459 (4)	−0.3475 (5)	0.0725 (4)	0.0053 (4)	0.0077 (6)	0.0058 (3)	−0.0044 (8)	−0.0002 (5)	−0.0031 (7)
C14	−0.2765 (4)	−0.3425 (5)	0.0357 (3)	0.0072 (4)	0.0077 (5)	0.0034 (2)	−0.0027 (8)	0.0026 (5)	−0.0035 (6)
C15	−0.2064 (4)	−0.3944 (5)	0.1665 (3)	0.0089 (4)	0.0056 (5)	0.0049 (3)	−0.0041 (9)	0.0009 (5)	−0.0017 (7)
C41	−0.2555 (4)	0.3431 (6)	−0.0571 (3)	0.0063 (3)	0.0118 (7)	0.0050 (2)	−0.0016 (9)	0.0035 (5)	0.0063 (7)
C42	−0.3435 (4)	0.3502 (6)	−0.1127 (3)	0.0089 (4)	0.0094 (6)	0.0034 (2)	0.0047 (9)	0.0036 (5)	0.0036 (7)
C43	−0.4124 (4)	0.2761 (7)	−0.1043 (4)	0.0049 (4)	0.0183 (9)	0.0048 (3)	0.0006 (11)	−0.0017 (6)	0.0084 (9)
C44	−0.3943 (4)	0.1901 (6)	−0.0417 (3)	0.0046 (3)	0.0120 (7)	0.0045 (2)	−0.0024 (9)	0.0012 (4)	0.0041 (8)
C45	−0.3044 (3)	0.1777 (5)	0.0144 (3)	0.0034 (2)	0.0061 (6)	0.0026 (2)	0.0001 (6)	0.0022 (3)	0.0001 (5)
C46	−0.2352 (4)	0.2551 (5)	0.0050 (3)	0.0048 (3)	0.0121 (8)	0.0037 (2)	−0.0009 (8)	−0.0000 (5)	0.0051 (7)
C4	−0.2809 (3)	0.0788 (5)	0.0790 (3)	0.0028 (2)	0.0066 (5)	0.0023 (2)	−0.0010 (7)	0.0017 (3)	0.0006 (5)
C5	−0.3233 (3)	0.0665 (5)	0.1371 (3)	0.0028 (2)	0.0068 (5)	0.0026 (2)	−0.0006 (7)	0.0016 (3)	0.0002 (6)
B3	−0.2128 (4)	−0.0372 (6)	0.0750 (3)	0.0041 (3)	0.0061 (6)	0.0024 (2)	0.0005 (8)	0.0021 (4)	−0.0000 (6)
B6	−0.2927 (4)	−0.0631 (6)	0.1904 (3)	0.0042 (3)	0.0079 (7)	0.0030 (2)	−0.0011 (9)	0.0034 (4)	0.0000 (7)
B2	−0.3368 (4)	−0.0663 (6)	0.0774 (4)	0.0041 (3)	0.0079 (7)	0.0036 (2)	−0.0014 (9)	0.0041 (4)	−0.0000 (7)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
HC82	−0.026 (3)	0.031 (4)	0.093 (2)	3.6000 (0)	HC56	−0.451 (3)	0.429 (4)	0.154 (2)	3.6000 (0)
HC83	0.125 (3)	−0.018 (4)	0.104 (2)	3.6000 (0)	HC41	−0.206 (3)	0.390 (4)	−0.065 (2)	3.6000 (0)
HC84	0.215 (3)	−0.175 (4)	0.186 (2)	3.6000 (0)	HC42	−0.355 (3)	0.411 (4)	−0.154 (2)	3.6000 (0)
HC85	0.130 (3)	−0.299 (4)	0.259 (2)	3.6000 (0)	HC43	−0.473 (3)	0.284 (4)	−0.139 (2)	3.6000 (0)
HC86	−0.021 (3)	−0.259 (4)	0.245 (2)	3.6000 (0)	HC44	−0.436 (3)	0.136 (4)	−0.031 (2)	3.6000 (0)
HC72	−0.021 (3)	0.002 (4)	0.318 (2)	3.6000 (0)	HC46	−0.178 (3)	0.251 (4)	0.045 (2)	3.6000 (0)
HC73	0.060 (3)	−0.065 (4)	0.456 (2)	3.6000 (0)	HC11	−0.343 (3)	−0.379 (4)	0.190 (2)	3.6000 (0)
HC74	0.006 (3)	−0.219 (4)	0.525 (2)	3.6000 (0)	HC12	−0.121 (3)	−0.360 (4)	0.085 (2)	3.6000 (0)
HC75	−0.133 (3)	−0.308 (4)	0.451 (2)	3.6000 (0)	HC13	−0.411 (3)	−0.328 (4)	0.041 (2)	3.6000 (0)
HC76	−0.226 (3)	−0.248 (4)	0.318 (2)	3.6000 (0)	HC14	−0.284 (3)	−0.325 (4)	−0.022 (2)	3.6000 (0)
HC51	−0.333 (3)	0.320 (4)	0.143 (2)	3.6000 (0)	HC15	−0.168 (3)	−0.392 (4)	0.208 (2)	3.6000 (0)
HC53	−0.480 (3)	0.008 (4)	0.161 (2)	3.6000 (0)	HB3	−0.197 (3)	−0.047 (4)	0.017 (2)	3.6000 (0)
HC54	−0.598 (3)	0.131 (4)	0.173 (2)	3.6000 (0)	HB6	−0.332 (3)	0.090 (4)	0.230 (2)	3.6000 (0)
HC55	−0.585 (3)	0.354 (4)	0.175 (2)	3.6000 (0)	HB2	−0.413 (3)	−0.086 (4)	0.028 (2)	3.6000 (0)

[a] The form of the anisotropic thermal parameter is $\exp[-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl]$.

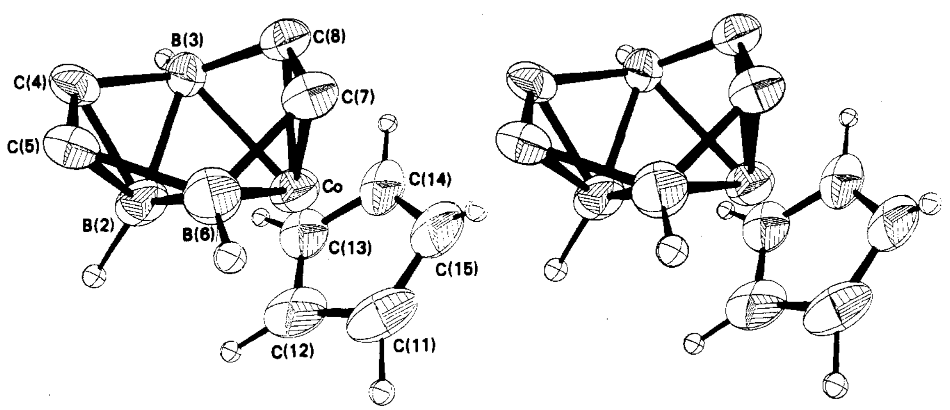

Figure 2. Stereo ORTEP drawing of the cage framework (phenyl rings attached to carbon cage atoms omitted).

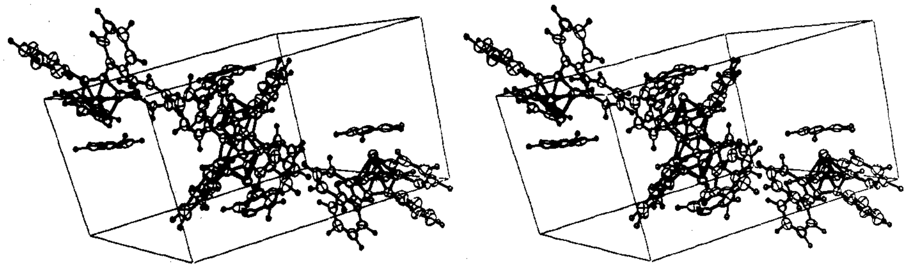

Figure 3. Molecular packing diagram. The contents of one unit cell are shown as viewed down the *b* axis, the *c* axis being horizontal.

Table II. Intramolecular Bond Distances (Å) for 4,5,7,8-$(C_6H_5)_4$-1,4,5,7,8-$(\eta\text{-}C_5H_5)CoC_4B_3H_3$

Co–C8	2.035 (4)	B3–B2	1.896 (7)
Co–C7	2.016 (4)	B6–B2	1.869 (7)
Co–B3	2.116 (5)	C11–C15	1.372 (7)
Co–B6	2.137 (5)	C15–C12	1.382 (6)
Co–B2	1.991 (5)	C12–C14	1.404 (6)
Co–C11	2.052 (5)	C14–C13	1.400 (6)
Co–C12	2.067 (4)	C13–C11	1.406 (7)
Co–C13	2.041 (5)	C81–C82	1.393 (5)
Co–C14	2.049 (4)	C82–C83	1.386 (6)
Co–C15	2.083 (4)	C83–C84	1.364 (6)
C8–C7	1.419 (5)	C84–C85	1.356 (6)
C8–C81	1.495 (5)	C85–C86	1.390 (6)
C8–B3	1.570 (6)	C86–C81	1.393 (5)
C7–B6	1.570 (6)	C71–C72	1.388 (5)
C7–C71	1.479 (5)	C72–C73	1.382 (5)
C5–B6	1.625 (6)	C73–C74	1.361 (6)
C5–B2	1.712 (6)	C74–C75	1.369 (6)
C5–C4	1.379 (5)	C75–C76	1.389 (6)
C5–C52	1.478 (5)	C76–C71	1.387 (5)
C4–B3	1.604 (6)	C51–C52	1.381 (5)
C4–B2	1.729 (6)	C52–C53	1.385 (5)
C4–C45	1.489 (5)	C53–C54	1.380 (6)
C54–C55	1.366 (7)	C75–HC75	0.89 (3)
C55–C56	1.356 (7)	C76–HC76	0.93 (3)
C56–C51	1.374 (7)	C51–HC51	0.99 (3)
C41–C42	1.351 (6)	C53–HC53	0.94 (4)
C42–C43	1.340 (7)	C54–HC54	0.89 (3)
C43–C44	1.376 (6)	C55–HC55	0.91 (4)
C44–C45	1.380 (5)	C56–HC56	0.79 (4)
C45–C46	1.370 (5)	C41–HC41	0.91 (3)
C46–C41	1.381 (6)	C42–HC42	0.94 (4)
C11–HC11	1.02 (3)	C43–HC43	0.92 (3)
C12–HC12	1.10 (3)	C44–HC44	0.91 (3)
C13–HC13	0.96 (3)	C46–HC46	0.90 (4)
C14–HC14	1.00 (3)	B3–HB3	1.03 (4)
C15–HC15	0.77 (3)	B6–HB6	1.09 (5)
C82–HC82	0.96 (3)	B2–HB2	1.19 (5)
C83–HC83	0.91 (4)	C84–HC84	1.01 (3)
C85–HC85	0.91 (3)	C86–HC86	0.93 (3)
C72–HC72	1.02 (3)	C73–HC73	0.89 (3)
C74–HC74	1.04 (3)		

Table III. Selected Bond Angles (Deg) for 4,5,7,8-$(C_6H_5)_4$-1,4,5,7,8-$(\eta\text{-}C_5H_5)CoC_4B_3H_3$

C11–Co–C13	40.2 (2)	B6–C5–B2	68.1 (3)
C13–Co–C14	40.0 (2)	B2–C5–C4	67.0 (3)
C14–Co–C12	39.9 (2)	B6–C5–C4	113.2 (3)
C12–Co–C15	38.9 (2)	B6–C5–C52	119.4 (3)
C15–Co–C15	38.7 (2)	B2–C5–C52	128.7 (3)
C8–Co–C7	41.0 (1)	C4–B2–C52	127.1 (4)
C7–Co–B6	44.3 (2)	C5–C4–B2	65.7 (3)
B6–Co–B2	53.7 (2)	B2–C4–B3	69.2 (2)
B2–Co–B3	54.1 (2)	B3–C4–C5	115.0 (3)
B3–Co–C8	43.7 (2)	B3–C4–C45	118.9 (3)
B3–C8–Co	72.6 (2)	B2–C4–C45	127.6 (3)
Co–C8–C7	68.8 (2)	C5–C4–C45	125.5 (3)
C7–C8–C81	125.5 (4)	C8–B3–Co	63.7 (2)
B3–C8–C81	120.9 (3)	Co–B3–B2	58.2 (2)
Co–C8–C81	124.0 (3)	B2–B3–C4	58.5 (2)
B3–C8–C7	113.5 (4)	C4–B3–C8	114.5 (3)
C8–C7–Co	70.2 (2)	C7–B6–Co	63.8 (2)
Co–C7–B6	71.9 (2)	Co–B6–B2	59.1 (2)
C8–C7–B6	114.5 (4)	B2–B6–C5	58.2 (2)
C8–C7–C71	125.0 (4)	C7–B6–C5	114.5 (3)
Co–C7–C71	129.5 (3)	Co–B2–B3	67.7 (2)
B6–C7–C71	114.5 (4)	B3–B2–C4	52.3 (2)
C4–B2–C5	47.3 (2)	C72–C71–C7	121.0 (4)
C5–B2–B6	53.7 (2)	C76–C71–C7	121.9 (4)
B6–B2–Co	67.1 (2)	C52–C51–C56	120.0 (5)
C13–C11–C15	107.2 (5)	C51–C56–C55	121.5 (5)
C11–C15–C12	109.9 (5)	C56–C55–C54	119.8 (5)
C15–C12–C14	107.5 (5)	C55–C54–C53	119.3 (5)
C12–C14–C13	107.3 (5)	C54–C53–C52	121.6 (5)
C14–C13–C11	108.1 (5)	C53–C52–C51	117.8 (4)
C81–C82–C83	120.6 (4)	C53–C52–C5	120.8 (4)
C81–C82–C83	121.1 (5)	C51–C52–C5	121.4 (4)
C82–C83–C84	119.3 (5)	C45–C44–C43	120.8 (5)
C84–C85–C86	120.8 (5)	C44–C43–C42	121.1 (5)
C85–C86–C81	121.0 (4)	C43–C42–C41	119.3 (5)
C86–C81–C82	117.2 (4)	C42–C41–C46	120.5 (5)
C82–C81–C8	119.0 (4)	C41–C46–C45	121.1 (5)
C86–C81–C8	123.8 (4)	C46–C45–C44	117.0 (4)
C71–C72–C73	121.1 (4)	C46–C45–C4	120.7 (4)
C72–C73–C74	121.4 (5)	C44–C45–C4	122.1 (4)
C73–C74–C75	118.2 (5)	C74–C75–C76	121.3 (4)
C75–C76–C71	120.7 (4)	C76–C71–C72	117.2 (4)

$(\eta\text{-}C_5H_5)_4Ni_4B_4H_4$,[11] $(\eta\text{-}C_5H_5)_2Ni_2(CH_3)_2B_4H_4$,[11] and $(\eta\text{-}C_5H_5)_2Co_2SB_5H_7$.[12] Electron counting rules[6] predict that such cluster systems should adopt a nido structure consisting of a tricapped trigonal prism missing one equatorial vertex; however, this structure has been confirmed for only one of these compounds, $(\eta\text{-}C_5H_5)_2Co_2SB_5H_7$.[12] An X-ray investigation[7] of B_8H_{12} revealed that, instead of the predicted structure, the compound has a molecular geometry based on a bicapped square antiprism missing two vertices (one cap and one equatorial position). Such a structure would be expected for a $2n + 6$ skeletal electron (arachno) system rather than a $2n + 4$ system. Definitive structural data has not yet been obtained for either $C_2B_6H_{10}$[8] or $(CH_3)_4C_4B_4H_4$,[9] but the NMR data favors an arachno structure such as observed for B_8H_{12}, although a nido structure can be proposed in each case if the molecules are assumed to be fluxional in solution. In this regard, the compound $(C_2H_5)_4C_4B_4(CH_3)_4$,[10] which has the same cage skeleton as $(CH_3)_4C_4B_4H_4$, gives NMR data suggesting that it has a nonfluxional nido structure.

In contrast to the above observations, Grimes has confirmed,[11] through crystallographic studies, a closo dodecahedral structure, which would normally be expected for a $2n + 2$ system, for the compound $(\eta\text{-}C_5H_5)_4Ni_4B_4H_4$, and, on the basis of the NMR data, proposed a similar closo configuration for $(\eta\text{-}C_5H_5)_2Ni_2(CH_3)_2C_2B_4H_4$. Furthermore, he notes[11,13] that

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Table IV. Selected Molecular Planes and Selected Angles between Planes for 4,5,7,8-$(C_6H_5)_4$-1,4,5,7,8-$(\eta$-$C_5H_5)CoC_4B_3H_3$

atom	dev, Å	atom	dev, Å
Plane 1. Cyclopentadienyl Ring $-0.0763x - 0.9707y - 0.2279z = 3.6802$			
Atoms in Plane			
C11	−0.031 (6)	C14	0.000 (5)
C12	−0.008 (5)	C15	0.014 (5)
C13	0.008 (5)		
Other Atoms			
HC11	−0.064 (40)	HC14	0.017 (40)
HC12	−0.167 (41)	HC15	−0.193 (40)
HC13	−0.008 (40)	Co	−1.683 (1)
Plane 2. Phenyl Ring Attached to C8 $-0.0694x - 0.6350y - 0.7694z = -1.2970$			
Atoms in Plane			
C81	−0.010 (5)	C84	−0.010 (5)
C82	0.001 (5)	C85	0.000 (5)
C83	0.009 (5)	C86	0.010 (5)
Other Atoms			
C8	0.015 (5)	HC84	−0.049 (39)
HC82	−0.025 (39)	HC85	−0.035 (38)
HC83	0.003 (39)	HC86	0.027 (39)
Plane 3. Phenyl Ring Attached to C7 $0.6155x - 0.7253y - 0.3084z = -2.9713$			
Atoms in Plane			
C71	0.018 (5)	C74	0.019 (6)
C72	−0.009 (5)	C75	−0.010 (6)
C73	−0.010 (6)	C76	−0.008 (6)
Other Atoms			
C7	0.053 (5)	HC74	0.082 (42)
HC72	−0.030 (42)	HC75	0.123 (41)
HC73	0.023 (41)	HC76	−0.026 (40)
Plane 4. Phenyl Ring Attached to C5 $-0.1243x + 0.0153y - 0.9921z = -1.5697$			
Atoms in Plane			
C51	−0.000 (5)	C54	−0.003 (5)
C52	0.007 (4)	C55	0.010 (5)
C53	−0.005 (5)	C56	−0.008 (6)
Other Atoms			
C5	0.036 (4)	HC54	−0.001 (36)
HC51	0.005 (36)	HC55	−0.019 (36)
HC53	−0.058 (38)	HC56	0.071 (37)
Plane 5. Phenyl Ring Attached to C4 $0.4412x - 0.6954y - 0.5672z = -3.4845$			
Atoms in Plane			
C41	−0.019 (6)	C44	−0.008 (6)
C42	0.015 (6)	C45	0.004 (5)
C43	−0.002 (7)	C46	0.010 (6)
Other Atoms			
C4	0.103 (5)	HC43	−0.042 (41)
HC41	0.041 (40)	HC44	−0.021 (40)
HC42	−0.005 (40)	HC46	−0.063 (39)
Plane 6. Plane through the Four Cage Carbon Atoms $-0.3881x - 0.7766y - 0.4962z = 0.5310$			
Atoms in Plane			
C8	0.002 (5)	C5	0.003 (5)
C7	−0.002 (5)	C4	−0.003 (5)

planes	dihedral angle, deg	planes	dihedral angle, deg
1,2	37.2	2,6	25.6
1,3	43.3	3,4	77.4
1,4	77.2	3,5	18.0
1,5	39.6	3,6	61.5
1,6	26.3	4,5	60.2
2,3	49.1	4,6	58.1
2,4	40.3	5,6	49.4
2,5	32.1		

there have been five structurally characterized eight-vertex boron cages which do not contain bridge hydrogens and in each case the geometry is dodecahedral regardless of the number of skeletal electrons, suggesting that the dodecahedral geometry is especially favored for eight-vertex species.

Thus, on the basis of previous work it appears that at least three different geometries are possible for eight-vertex $2n + 4$ clusters, including structures usually expected for closo, nido, or arachno electron counts. Clearly other factors besides skeletal electron count are important in the determination of cage geometry in these systems. For these reasons an X-ray crystallographic structural determination of 4,5,7,8-$(C_6H_5)_4$-1,4,5,7,8-$(\eta$-$C_5H_5)CoC_4B_3H_3$ was undertaken.

The results of this determination illustrated in Figures 1 and 2 show quite clearly that the compound adopts an arachno type of structure with a similar framework as observed for B_8H_{12}. The cobalt atom occupies a five-coordinate position bound to borons B2, B3, and B6 and to carbons C7 and C8. The cobalt to boron and carbon distances, as well as the carbon–carbon, boron–carbon, and boron–boron distances of atoms bound to the cobalt, are consistent with those previously observed in metallacarboranes. One unusal feature of the compound is the short distance between the nonmetal-bonded carbons C4 and C5 of 1.379 (5) Å, especially when compared with the C7–C8 distance of 1.419 (5) Å. Such phenomena have also been observed[14] in another four-carbon metallacarborane $(\eta$-$C_5H_5)Co(CH_3)_4C_4B_7H_6OC_2H_5$. In this compound the two carbons bound to the metal have a normal bond distance of 1.448 (5) Å, whereas the carbons not bound to the metal are found to have a shortened distance, 1.374 (6) Å, as observed in the present study. These results apparently indicate an increased bond order between these carbons, and it is tempting to ascribe this behavior to more localized bonding brought on by the increased number of carbon atoms in the cage system; however, this conclusion will have to await further X-ray studies on related compounds. The remaining boron–boron and carbon–boron distances are similar to those in other such systems.

The fact that three different geometries have previously been observed for electronically analogous cluster systems indicates that these three geometries are energically similar and other factors may dictate the cage geometry. Indeed extended Hückel calculations[15] for $B_8H_8^{2-}$ (a $2n + 2$ system) has shown little energy difference between D_{4d}, D_{2d}, and C_{2v} geometries and it has, in fact, been possible to observe[16] by NMR methods, both the D_{4d} and C_{2v} isomers in solution. Furthermore, it was concluded in this NMR study that the nature of the cation structure and the solvent were the determining factors in cage geometry observed. The present study has confirmed an arachno structure for 4,5,7,8-$(C_6H_5)_4$-1,4,5,7,8-$(\eta C_5H_5)CoC_4B_3H_3$. The adoption of this open type of structure rather than a more compact nido or closo structure would, of course, be favored for steric reasons since the interactions of the four phenyl groups and the cyclopentadienyl group would clearly be more severe in these latter geometries. However, it is also perhaps significant that an arachno structure has been either confirmed or proposed for those $2n + 4$ boron clusters containing either one or no metal atoms, while those that contain more than one metal adopt more closed geometries. This suggests that factors such as metal–metal interactions within the cage system, which would be enhanced in a more closed geometry, dominate in multimetal systems. A final determination of the relative importance of these and other factors in the determination of cage geometries

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in eight-vertex systems will, however, have to await further synthetic and structural studies of related compounds.

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Registry No. 4,5,7,8-$(C_6H_5)_4$-1,4,5,7,8-(η-C_5H_5)$CoC_4B_3H_3$, 74964-99-1.

Supplementary Material Available: A listing of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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Small Molecule Analogues for the Specific Iron-Binding Site of Lactoferrin: A Single-Crystal X-ray Structure of Bis(methanol)bis[2-(5-methylpyrazol-3-yl)phenolato]iron(III) Nitrate–Methanol and Spectroscopic Studies on Iron(III) Phenolate Complexes

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In an attempt to model the specific iron-binding site of the human milk protein, lactoferrin, a range of iron(III) phenolate complexes, embracing the chromophore types FeO_6 to $FeO_2N_2O'_2$ (where O represents a phenolate oxygen, N an aliphatic or aromatic nitrogen, and O′ a carboxylate oxygen or a methanolic oxygen) (see Figure 1 for the ligands used), has been studied to determine which types spectroscopically match diferric lactoferrin. In particular the factors that influence the energy of the oxygen $p_\pi \rightarrow d_\pi^*$ charge-transfer band have been investigated, and it is found that increasing the number of phenolate oxygens and imidazole nitrogens bound to iron(III) results in a hypsochromic shift, whereas increased binding strength results in a bathochromic shift. It has been found that EPR and Mössbauer spectra are insensitive to variations in ligand types and numbers. A single-crystal X-ray structure on one of the complexes, bis(methanol)bis[2-(5-methylpyrazol-3-yl)phenolato]iron(III) nitrate–methanol, $[Fe(IIIa)_2(MeOH)_2]NO_3\cdot MeOH$, has been determined by direct methods and refined by least-squares methods to a conventional R factor of 0.045. A total of 1451 reflections with $I > 3\sigma(I)$ were used. The dark purple needlelike crystals have space group $P2_1/n$, with $Z = 2$, and unit cell dimensions $a = 11.326$ (2) Å, $b = 7.384$ (1) Å, $c = 17.918$ (2) Å, and $\beta = 107.72$ (1)°. The iron atom lies on a center of symmetry and is required to be coplanar with the IIIa ligand donor atoms which are arranged in an all-trans arrangement. The Fe–O(phenolate) bond length is 1.888 (3) Å, and Fe–N is 2.068 (3) Å. The two methanol molecules are axially coordinated with Fe–O bond lengths of 2.094 (3) Å. They are hydrogen bonded to the lattice methanol, which is hydrogen bonded to ionic nitrate, which is further hydrogen bonded to the N–H proton of the pyrazolyl group. Collectively the data support the iron of diferric lactoferrin occupying a site of rhombic symmetry and bound to three tyrosyl and two cis histidyl residues, while the bicarbonate (or carbonate) ion, which is isoelectronic with the nitrate ion, may be hydrogen bonded to a coordinated aquo ligand.

Introduction

Lactoferrin occurs in high concentrations in human milk and also in other bodily secretions and intracellular components.[2-4] Its physiological role has yet to be defined with certainty, but, because of its ability to bind iron(III) tightly, it has been postulated to have a bacteriostatic function in depriving microorganisms of essential iron for their growth,[5] and a nutritional role has also been suggested.[6] Like the related proteins human serum transferrin and ovotransferrin, lactoferrin has a molecular weight of about 80 000 and specifically binds two high-spin iron(III) ions concomitantly with two bicarbonate ions.[2-4]

Recently we reported[7] that lactoferrin (Lf) forms complexes of the type M_2Lf (M = Cr(III), Mn(III), Co(III)) which, along with the known Fe_2Lf and Cu_2Lf, exhibit electronic absorption spectra similar to transferrin (Tf) and ovotransferrin analogues.[8-10] However, the exact nature and number of the groups involved in the binding of these metal ions have not been resolved. Spectrophotometric titrations and UV difference spectra have indicated that for all three iron-binding proteins three tyrosyl residues are involved[11-15] while other evidence suggests only two[10,16] per each iron atom. Binding of each iron to transferrin has been found to protect two histidines from ethoxyformylation, and the protein remains active.[17] One water molecule has also been found to be bound to each iron from NMR studies.[18] The precise involvement of bicarbonate, essential for the binding of iron,[19] is still uncertain. Studies indicate that transferrin has an essential arginine residue for each iron-binding center[20] which in its

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