

of the C_7H_6 ring (as in **1b**) has been reduced by electron donation from Fe.

It is well-established that the values of the carbonyl IR stretching frequencies for related complexes are a reliable measure of changes in metal-carbonyl back-bonding. The absorptions of **1**, **7**, and **8** occur at slightly lower values than those of other reported carbonyl-containing carbene complexes⁵² (see Table VI), implying that in these aromatic carbene species more π -electron density is available at Fe for back-bonding to the CO ligands; i.e., CHT ligands are poorer acceptors of electron density than other carbene ligands. Table VII lists selected bond lengths and CO stretching frequencies for cationic complexes of the type $[(\eta^5-C_5H_5)(L)_nFe(CO)_{3-n}]^+$, in which $n = 0-2$. Comparison of the Fe-C(carbonyl) bond lengths and the CO absorptions suggests that the CHT ligand(s) is a better σ donor (similar to PPh_3 ?) than π acceptor. However, as shown by the IR data of Table VI, the virtual equivalence of the CO stretching frequencies of **1**, **7**, and **8** precludes an ordering of the relative back-bonding capabilities of these CHT complexes from these IR data alone.

It appears, therefore, that CHT carbene ligands are principally donor ligands, which upon complexation with a transition-metal atom depend not upon the back-donation of

electron density from the metal for stability but rather primarily upon the aromaticity of the CHT ring. Nonetheless, from both crystallographic and spectroscopic data, there is sufficient evidence to indicate that $d\pi \rightarrow p\pi$ back-bonding is not altogether absent and, in fact, may be significant in **1** and perhaps in **8** but is far less so in **7**. Finally, comparison of the chemical and thermal reactivity of $(C_7H_6)W(CO)_5$ (**2**) with the closely related complexes (2,3-diphenylpropenylidene)pentacarbonyltungsten and (2,3-di-*tert*-butylcyclopropenylidene)pentacarbonyltungsten⁵⁷ has shown that **2** is more reactive. Since spectral data suggest more $W \rightarrow CHT$ back-bonding in **2** than in the other two $W(CO)_5$ complexes, this greater reactivity may be a consequence of easier loss of CO from **2** in reactions in which CO loss is important.

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Supplementary Material Available: Tabulations of observed and calculated structure amplitudes, anisotropic thermal parameters, and hydrogen positional and isotropic thermal parameters (54 pages). Ordering information is given on any current masthead page.

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Structural Characterization of

6:4',5'-[1-(η - C_5H_5)Co-2,3-(CH_3)₂C₂B₄H₃][2',3'-(CH_3)₂C₂B₄H₃]: A Coupled-Cage Cobaltacarborane Complex Containing a Three-Center Boron Linkage

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The molecular structure of 6:4',5'-[1-(η - C_5H_5)Co-2,3-(CH_3)₂C₂B₄H₃][2',3'-(CH_3)₂C₂B₄H₃] has been determined from single-crystal X-ray diffraction data. The compound was shown to be a coupled-cage cobaltacarborane consisting of a [(CH_3)₂C₂B₄H₃]Co(η - C_5H_5) sandwich complex linked to a (CH_3)₂C₂B₄H₃ carborane fragment by means of a three-center boron-boron-boron bond. Crystal data: space group $P2_1/n$, $Z = 4$, $a = 14.092$ (4) Å, $b = 13.270$ (1) Å, $c = 9.988$ (2) Å, $\beta = 103.06$ (2)°, $V = 1819$ (2) Å³. The structure was refined by full-matrix least-squares methods to a final R of 0.042 and R_w of 0.048 for the 2282 reflections that had $F_o^2 > 3\sigma(F_o^2)$.

Introduction

We have previously reported² that the mercury-sensitized photolysis of various small boranes and carboranes leads in certain cases to the corresponding coupled-cage borane or carborane in high yields. Furthermore, we also demonstrated³ the insertion of metals into these multicage systems to produce a range of novel linked-cage metal complexes. In particular, the reaction of [2,3-(CH_3)₂C₂B₄H₃]₂ with sodium hydride followed by reaction with sodium cyclopentadienide and cobaltous chloride was found to yield a variety of such complexes, including compounds that contain metals in either or both of the cages. The spectroscopic data obtained for the major products of this reaction suggested that the two cages in each

compound were linked by a single boron-boron bond. We report here, however, that a structural investigation of one of these compounds⁴ has revealed that it does not contain such a simple boron-boron cage linkage, but instead the two cages are joined by a single boron-boron-boron three-center bond. Full details of this structural determination are reported.

Experimental Section

Several crystals of the compound were grown over an 18-h period by evaporation of a dilute heptane solution. A very thin rectangular-shaped crystal, 0.19 × 0.58 × 0.029 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 25 reflections, which were then used in the program INDEX to obtain an orientation matrix for data collection. This orientation matrix was improved by the substitution of new reflections, and refined cell dimensions and their standard deviations were obtained from the

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Table I. Final Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	atom	x	y	z
Co	0.20576 (3)	0.09949 (4)	0.21300 (4)	C10H	0.048 (2)	0.079 (2)	0.309 (3)
C10	0.0675 (2)	0.0696 (3)	0.2290 (4)	C11H	0.054 (2)	0.214 (2)	0.149 (3)
C11	0.0684 (3)	0.1478 (3)	0.1380 (4)	C12H	0.118 (2)	0.156 (3)	-0.026 (3)
C12	0.1079 (3)	0.1088 (4)	0.0307 (4)	C13H	0.155 (2)	-0.026 (3)	0.007 (3)
C13	0.1302 (3)	0.0098 (4)	0.0592 (4)	C14H	0.112 (2)	-0.068 (2)	0.216 (3)
C14	0.1055 (3)	-0.0149 (3)	0.1801 (5)	C3CH1	0.410 (2)	0.067 (2)	0.051 (3)
C3	0.3471 (2)	0.0841 (3)	0.2067 (3)	C3CH2	0.460 (2)	-0.002 (3)	0.168 (3)
C3C	0.3986 (3)	0.0206 (4)	0.1203 (4)	C3CH3	0.366 (2)	-0.038 (3)	0.090 (3)
C2	0.3307 (2)	0.0471 (3)	0.3381 (3)	C2CH1	0.376 (2)	-0.104 (2)	0.330 (3)
C2C	0.3665 (3)	-0.0530 (3)	0.3954 (4)	C2CH2	0.429 (2)	-0.060 (3)	0.419 (3)
C3'	0.1563 (2)	0.1817 (3)	0.5955 (3)	C2CH3	0.326 (2)	-0.088 (2)	0.419 (3)
C2'	0.2107 (3)	0.2609 (3)	0.6701 (4)	C3'CH1	0.023 (2)	0.109 (2)	0.550 (3)
C2'C	0.1663 (4)	0.3401 (5)	0.7487 (5)	C3'CH2	0.033 (2)	0.195 (3)	0.664 (3)
C3'C	0.0506 (3)	0.1686 (5)	0.5924 (4)	C3'CH3	0.015 (2)	0.202 (2)	0.524 (3)
B7	0.3832 (3)	0.1699 (3)	0.3422 (4)	C2'CH1	0.115 (2)	0.341 (3)	0.700 (3)
B6	0.2853 (3)	0.1298 (3)	0.4163 (4)	C2'CH2	0.116 (2)	0.301 (3)	0.793 (3)
B5	0.2718 (3)	0.2303 (3)	0.3131 (4)	C2'CH3	0.214 (2)	0.356 (3)	0.810 (3)
B4	0.3139 (3)	0.1957 (4)	0.1758 (4)	B7H	0.458 (2)	0.188 (3)	0.391 (3)
B4'	0.2168 (3)	0.0987 (4)	0.5476 (4)	B5H	0.248 (2)	0.300 (3)	0.337 (3)
B5'	0.3370 (3)	0.1320 (4)	0.6176 (4)	B4H	0.323 (2)	0.235 (3)	0.088 (3)
B6'	0.3190 (4)	0.2490 (5)	0.6988 (5)	B4'H	0.185 (2)	0.027 (3)	0.515 (3)
B1'	0.2561 (3)	0.1409 (4)	0.7196 (4)	B5'H	0.402 (2)	0.086 (2)	0.639 (3)
				B6'H	0.370 (2)	0.294 (2)	0.767 (3)
				B1'H	0.248 (2)	0.101 (3)	0.794 (3)
				HB5'-6'	0.348 (2)	0.231 (2)	0.613 (3)

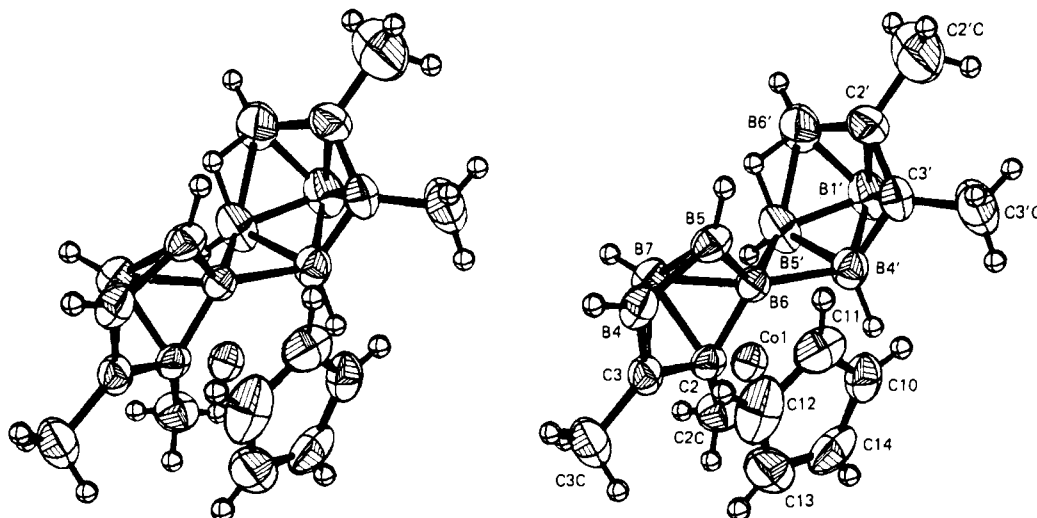


Figure 1. ORTEP stereodrawing of 6:4',5'-[1-(η -C₅H₅)Co-2,3-(CH₃)₂C₂B₄H₃][2',3'-(CH₃)₂C₂B₄H₃]. Nonhydrogen atoms are shown as 50% thermal ellipsoids.

least-squares refinement of these 25 accurately centered reflections. Systematic absences for $k = 2n + 1$ on $0k0$ and $h + l = 2n + 1$ on $h0l$ establish the space group as $P2_1/n$. Crystal data: CoC₁₃B₈H₂₅, mol wt 326.77, space group $P2_1/n$, $Z = 4$, $a = 14.092$ (4) Å, $b = 13.270$ (1) Å, $c = 9.988$ (2) Å, $\beta = 103.06$ (2)°, $V = 1819$ (2) Å³, $\rho(\text{calcd}) = 1.193$ g cm⁻³. The mosaicity of the crystal was judged acceptable on the basis of several θ scans.

Collection and Reduction of Data. The diffraction data were collected at 295 K on an Enraf-Nonius four-circle CAD-4 diffractometer interfaced with a PDP 8/A computer, employing Mo $K\alpha$ radiation from a highly oriented graphite crystal monochromator. A combined θ - 2θ , ω -scan technique was used to record the intensities of all reflections for which $1.0 < 2\theta < 50^\circ$. The raw intensities were corrected for Lorentz and polarization effects by using the Enraf-Nonius program DATARED. Of the 3202 measured intensities, 2282 had $F_o^2 > 3\sigma(F_o^2)$ and were used in the analysis.

Solution and Refinement of Structure. All calculations were performed on a PDP 11/60 computer using the Enraf-Nonius structure determination package.⁵

Normalized structure factors were calculated by using a K curve, and the intensity distribution statistics support a centrosymmetric space group. A three-dimensional Patterson synthesis gave the coordinates

of the cobalt atom. Full-matrix least-squares refinement of these coordinates, with use of preliminary scale and thermal parameters from the Wilson plot, followed by a Fourier map phased on these refined coordinates led to the location of the five cyclopentadienyl carbon atoms and the four carbons of the two carborane rings. Subsequent Fourier maps revealed the positions of the remaining heavy atoms of the complex. Anisotropic least-squares refinements of these atoms followed by a difference Fourier synthesis resulted in the location of the 25 hydrogen atoms. Final refinement with an absorption correction (transmission coefficient: maximum 97.33%, minimum 75.82%) including anisotropic thermal parameters for nonhydrogen atoms and fixed isotropic thermal parameters (3.89) for the hydrogen atoms yielded the final residual factors $R = 0.042$ and $R_w = 0.048$.

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^{6a} and those for hydrogen^{6b} from Stewart. The effects of anomalous dispersion were

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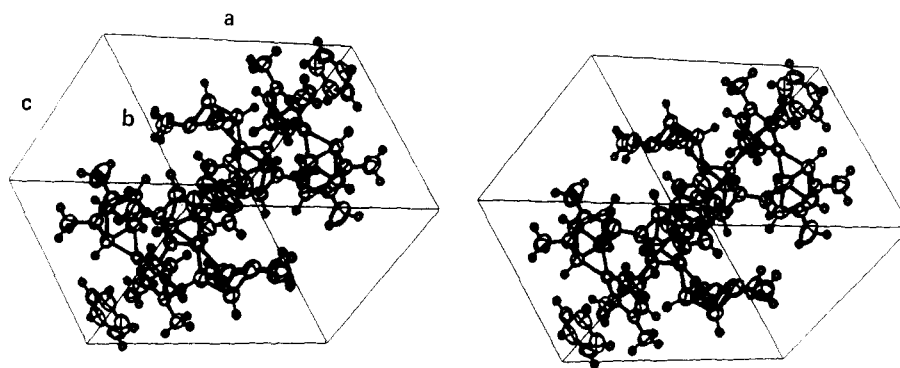


Figure 2. Molecular packing diagram.

Table II. Intramolecular Bond Distances (Å)

C10-C11	1.380 (4)	B1'-B4'	1.772 (4)
C11-C12	1.413 (5)	B1'-B5'	1.697 (4)
C12-C13	1.366 (5)	B1'-B6'	1.724 (4)
C13-C14	1.371 (5)	B1'-C2'	1.745 (5)
C14-C10	1.378 (4)	B1'-C3'	1.737 (4)
C10-C10H	0.91 (2)	B4'-B5'	1.737 (4)
C11-C11H	0.92 (3)	B5'-B6'	1.797 (6)
C12-C12H	0.87 (3)	B5'-(HB5'-6')	1.32 (3)
C13-C13H	0.84 (3)	B1'-B1'H	0.94 (2)
C14-C14H	0.79 (3)	B6'-(HB5'-6')	1.06 (2)
B7-B6	1.787 (4)	B6'-C2'	1.496 (5)
B7-B5	1.728 (4)	C2'-C3'	1.410 (4)
B7-B4	1.761 (4)	C3'-B4'	1.535 (4)
B7-C3	1.753 (4)	B4'-B4'H	1.07 (3)
B7-C2	1.786 (4)	B5'-B5'H	1.08 (2)
B6-B5	1.670 (4)	B6'-B6'H	1.06 (2)
B5-B4	1.676 (4)	C2'-C2'C	1.528 (5)
B4-C3	1.564 (4)	C2'C-C2'CH1	0.78 (2)
C3-C2	1.467 (3)	C2'C-C2'CH2	1.06 (2)
C2-B6	1.564 (4)	C2'C-C2'CH3	0.82 (2)
B7-B7H	1.09 (2)	C3'-C3'C	1.493 (4)
B6-B4'	1.842 (4)	C3'C-C3'CH1	0.94 (2)
B6-B5'	1.978 (4)	C3'C-C3'CH2	0.89 (2)
B5-B5H	1.04 (3)	C3'C-C3'CH3	0.87 (2)
B4-B4H	1.06 (2)	Co-C10	2.029 (3)
C3-C3C	1.505 (4)	Co-C11	2.016 (3)
C3C-C3CH1	0.96 (3)	Co-C12	2.024 (3)
C3C-C3CH2	0.94 (3)	Co-C13	2.042 (3)
C3C-C3CH3	0.92 (3)	Co-C14	2.049 (3)
C2-C2C	1.489 (4)	Co-C3	2.017 (2)
C2C-C2CH1	0.97 (3)	Co-C2	2.037 (2)
C2C-C2CH2	0.87 (3)	Co-B6	2.124 (3)
C2C-C2CH3	0.81 (3)	Co-B5	2.111 (3)
		Co-B4	2.084 (3)

included in F_c by using Cromer and Ibers' values⁷ for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|)^{1/2}$.

The final positional parameters are given in Table I. Intramolecular bond distances and selected bond angles are presented in Tables II and III. Figure 1 shows a stereoscopic view of the complete molecule, while Figure 2 shows a unit cell packing diagram. Listings of final thermal parameters, selected molecular planes, and observed and calculated structure factors are available as supplementary material.

Results and Discussion

Multicage boranes and carboranes, although becoming increasingly more common, are compounds which have still not been thoroughly structurally characterized. Because of boron's ability to engage in multicenter bonding, the structural diversity possible in these compounds is great, and in fact, Lipscomb has recently pointed out⁸ that at least ten different modes of cage connection are known for these multicage compounds.

Table III. Selected Bond Angles (Deg)

C10-C11-C12	106.8 (3)	B4-C3-C3C	125.3 (3)
C11-C12-C13	107.8 (3)	C3-C3C-C3CH1	103 (2)
C12-C13-C14	108.8 (3)	C3-C3C-C3CH2	113 (2)
C13-C14-C10	108.3 (3)	C3-C3C-C3CH3	113 (2)
C14-C10-C11	108.4 (3)	C3C-C3-C2	121.3 (3)
C3'-B4'-B5'	104.6 (3)	C3-C2-C2C	122.3 (2)
B4'-B5'-B6'	100.2 (2)	C2-C2C-C2CH1	116 (1)
B5'-B6'-C2'	104.3 (3)	C2-C2C-C2CH2	116 (2)
B6'-C2'-C3'	115.6 (3)	C2-C2C-C2CH3	115 (2)
C2'-C3'-B4'	115.2 (2)	C2C-C2-B6	125.1 (2)
B4'H-B4'-B5'	130 (1)	C2-B6-B5'	114.8 (2)
B4'-B5'-B5'H	130 (1)	B5'-B6-B4'	54.0 (2)
B5'H-B5'-B6'	127 (1)	B4'-B6-B5	127.9 (2)
B5'-B6'-B6'H	129 (1)	B6-B5-B5H	125 (1)
B6'H-B6'-C2'	125 (1)	B5H-B5-B4	129 (1)
B6'-C2'-C2'C	119.6 (3)	B5-B4-B4H	133 (1)
C2'-C2'C-C2'CH1	97 (2)	B7H-B7-B4	131 (1)
C2'-C2'C-C2'CH2	105 (1)	B7H-B7-C3	125 (1)
C2'-C2'C-C2'CH3	102 (2)	B7H-B7-C2	125 (1)
C2'C-C2'-C3'	123.1 (3)	B7H-B7-B6	130 (1)
C2'-C3'-C3'C	121.2 (3)	B7H-B7-B5	137 (1)
C3'-C3'C-C3'CH1	115 (2)	B4'-B5'-B6	59.0 (2)
C3'-C3'C-C3'CH2	114 (2)	B5'-B4'-B6	67.0 (2)
C3'-C3'C-C3'CH3	111 (2)	C3-Co-C2	42.4 (1)
C3'C-C3'-B4'	122.2 (3)	C3-Co-B4	44.8 (1)
C3'-B4'-B4'H	121 (1)	B4-Co-B5	47.1 (1)
B5'-(HB5'-6')-B6'	98 (2)	B5-Co-B6	46.4 (1)
B1'H-B1'-B4'	121 (2)	B6-Co-C2	44.1 (1)
B1'H-B1'-B5'	131 (2)	Co-B4-C3	65.3 (1)
B1'H-B1'-B6'	136 (2)	Co-B4-B5	67.3 (1)
B1'H-B1'-C2'	129 (2)	Co-B5-B4	65.6 (2)
B1'H-B1'-C3'	121 (1)	Co-B5-B6	67.2 (1)
B5-B4-C3	104.1 (2)	Co-B6-B5	66.4 (1)
B4-C3-C2	113.1 (2)	Co-B6-C2	65.0 (1)
C3-C2-B6	112.1 (2)	Co-C2-B6	70.9 (1)
C2-B6-B5	104.7 (2)	Co-C2-C3	68.1 (1)
B6-B5-B4	105.9 (2)	Co-C3-C2	69.5 (1)
B4H-B4-C3	123 (1)	Co-C3-B4	69.9 (1)

One of the rarer types of cage linkage that has been observed involves the joining of two cages by means of boron-boron-boron three-center bonds. For example, the only compound of this type that has been structurally characterized is the anion $B_{20}H_{18}^{2-}$, which has been shown⁹ to consist of two $B_{10}H_9$ cages joined by means of two three-center B-B-B bonds. More recently, the carborane $C_4B_{18}H_{22}$ has been synthesized and has been proposed,¹⁰ based on its spectral data, to have a structure composed of two *nido*- $C_2B_9H_{11}$ cages, again linked by two three-center boron bonds.

Only one example has been previously reported of a multicage compound linked by a single B-B-B three-center bond, $B_{15}H_{23}$. This compound has been assigned a structure,¹¹ based on the NMR data, in which a B_9H_{13} unit is attached through

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a three-center boron bond to a basal bridge position of a B_6H_{10} cage. Structural data for $B_{15}H_{23}$ have not yet been reported; however, the structure of the closely related compound $[N-(\eta-C_4H_5)_4]^+[Fe(CO)_4B_7H_{12}]^-$ has been determined.¹² This latter compound, although not a two-cage system, has a boron cage structure with a BH_3 group bonded to a $B_6H_5Fe(CO)_4$ fragment (isoelectronic in terms of cage electrons with B_6H_{10}) across a basal boron-boron bond. Thus, this compound provides a model for the single three-center boron linkage observed in $B_{15}H_{23}$.

The completed structure determination of the title compound, as depicted in the ORTEP plot presented in Figure 1, clearly demonstrates that the compound is a coupled-cage cobaltacarborane consisting of a $(CH_3)_2C_2B_4H_3Co(\eta-C_5H_5)$ sandwich complex which is joined to a $(CH_3)_2C_2B_4H_5$ carborane by means of a single three-center boron-boron-boron bond and is thus the first structurally characterized example of this type of linkage in a two-cage system.

The bond distances and angles in the cobaltacarborane cage are essentially identical with those observed in related metallacarboranes such as $[(CH_3)_2C_2B_4H_4]_2FeH_{13}$ and are also similar to those observed in the parent carborane, 2,3- $(CH_3)_2C_2B_4H_6$,¹⁴ with the exception that the basal boron-boron distances are contracted ($B_4-B_5 = 1.676$ (4) Å and $B_5-B_6 = 1.670$ (4) Å vs. 1.778 Å in 2,3- $(CH_3)_2C_2B_4H_6$) due to the absence of bridging groups. The cyclopentadienyl ring distances and angles are normal, and the plane of this ring and that of the basal atoms of the cobaltacarborane fragment (C2, C3, B4, B5, and B6) are nearly parallel (dihedral angle 4.1°) but are slightly farther apart on the side to which the $(C-H)_2C_2B_4H_5$ unit is attached, perhaps reflecting the effects of minor steric interactions of the carborane fragment with both the cobaltacarborane cage and cyclopentadienyl ring.

Although a number of bridge-substituted 2,3- $C_2B_4H_8$ derivatives are known,^{15,16} only one of these, $[nido-(4,5-\mu)\{trans-(Et_3P)_2Pt(H)\}-(5,6-\mu)-H-2,3-C_2B_4H_6]$, has been structurally characterized.¹⁶ The distances and angles found in the 2',3'- $(CH_3)_2C_2B_4H_5$ fragment of the cobaltacarborane are similar to those found in the platinum compound with the exception that the remaining bridge hydrogen, $HB5'-6'$, is in an asymmetrical position. Thus, $HB5'-6'$ is closer to $B6'$ (1.06 (2) Å) than to $B5'$ (1.32 (3) Å), whereas the comparable

distances in the platinum compound are 1.20 and 1.21 Å.

The joining of the two cages is achieved by a single three-center boron bond involving $B4'$ and $B5'$ in the carborane cage and atom $B6$ in the cobaltacarborane cage; therefore, $B6$ occupies a bridging position on the $(CH_3)_2C_2B_4H_5$ carborane cage. The distances between the cages, $B6-B4'$ (1.842 (4) Å) and $B6-B5'$ (1.978 (4) Å), are in the range observed for similar distances in both $[Fe(CO)_4B_7H_{12}]^-$ (1.864 and 1.871 Å)¹¹ and $B_{20}H_{18}^{2-}$ (1.72 (1.65) and 1.92 (1.86) Å).⁸ The plane of the linkage atoms, $B4'$, $B6$, and $B5'$, is rotated 85.9° relative to the plane of the basal atoms of the cobaltacarborane cage (C2, C3, B4, B5, and B6) and 113.2° relative to the basal atoms of the carborane cage (C2', C3', B4', B5', and B6'). The $B4'-B6-B5'$ angle is small (54.0 (2)°) but again similar to the corresponding angles in $[Fe(CO)_4B_7H_{12}]^-$ (55°) and $B_{20}H_{18}^{2-}$ (55 (57)°) and with the B-Si-B angle of 42.6° observed in 1-Br- μ - $(CH_3)_3SiB_5H_7$.¹⁷

The confirmation of this unique bridged structure for multicage compounds is especially significant in light of our earlier observations³ concerning facile migrations between different boron sites in other boron-boron-coupled carboranes such as $(\eta-C_5H_5)_2Co_2C_2B_5H_6-C_2B_5H_6$. It was demonstrated that these migrations do not involve skeletal rearrangements of either the carborane or cobaltacarborane cages but instead must involve a direct shift of the cages. It was proposed that such a shift could occur by means of a three-center intermediate¹⁸ in which one of the cage boron atoms adopts a bridging position on the second cage. The structure of the coupled cobaltacarborane presented here is in fact an example of this type of configuration and provides added support for the involvement of such species in these rearrangements.

Finally, these results indicate that the structures of other multicage metallocarboranes now deserve detailed X-ray investigation since they may also exhibit new and unexpected types of cage linkage. Such studies are now in progress in this laboratory and will be reported in future publications.

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Registry No. 6:4',5'-[1-($\eta-C_5H_5$)Co-2,3-(CH_3)₂C₂B₄H₃][2',3'-(CH_3)₂C₂B₄H₅], 80339-96-4.

Supplementary Material Available: Listings of general temperature factor expressions, selected molecular planes, and observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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