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Synthesis and Structural Characterization of a Bis(cyclopentadienyl)methane–Cobaltacarborane Complex: $CH_2[\textit{closo}\text{-}1\text{-}(\eta\text{-}C_5H_4)Co(2,3\text{-}Et_2C_2B_4H_4)]_2$

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Introduction

Ring-bridged (cyclopentadienyl)$_2$E (E = CH_2 or R_2Si) ligands have the ability to either chelate a single metal atom or complex two different metals, and as a result, they have been used to generate a variety of structurally unique organometallic complexes.[2] We hoped to further exploit the bis(cyclopentadienyl)methane ligand to produce a range of multimetal single-cage or multimetal multicage metallaboron clusters. Thus, depending on whether metal–metal-bonded species are formed, the reaction of the bis(η-cyclopentadienyl)methane dianion with a suitable metallaborane or metallacarborane fragment could result in insertion, fusion, or multilayer boron sandwich products containing one or more metal atoms. Recently, there has been considerable interest in the synthesis and properties of, in particular, linked and stacked metallacarboranes containing bridging ligands, since it has been proposed that such complexes may serve as building blocks for electronically conducting solid-state materials.[3]

In this paper, we report the synthesis and structural characterization of an example, $CH_2[\textit{closo}\text{-}1\text{-}(\eta\text{-}C_5H_4)Co(2,3\text{-}Et_2C_2B_4H_4)]_2$, of a new type of linked metallacarborane complex that is derived from the reaction of the *nido*-2,3-$Et_2C_2B_4H_5^-$ anion with cobalt chloride and the bis(η-cyclopentadienyl)methane dianion.

Experimental Section

All experimental manipulations were carried out using standard high-vacuum or inert-atmospheric techniques as described by Shriver.[4] $CoCl_2$ (Aldrich) was dried for 12 h at 100 °C in vacuo and stored under argon until use. Spectrochemical grade THF, Et_2O, and CH_2Cl_2 were purchased from Fischer or EM Science. Degassed THF and Et_2O were stored over sodium benzophenone ketyl until used. CH_2Cl_2 was dried over P_2O_5, transferred onto activated 4-Å molecular sieves, and stored under vacuum until used. The 2,3-$Et_2C_2B_4H_6$[5] and $CH_2(C_5H_5)_2^{2-}$ [2,6] were prepared according to published procedures. All other reagents were commercially obtained and used as received unless noted otherwise.

^{11}B NMR spectra at 64.2 MHz and ^1H NMR spectra at 200 MHz were obtained on a Bruker AF-200 spectrometer equipped with the appropriate decoupling accessories. All ^{11}B chemical shifts were referenced to $BF_3{\cdot}O(C_2H_5)_2$ (0.0 ppm) with a negative sign indicating an upfield shift. All proton chemical shifts were measured relative to internal residual protons from the lock solvent (99.5% C_6D_6 or $CD_3C_6D_5$) and then referenced to $(CH_3)_4Si$ (0.0 ppm).

High- and low-resolution mass spectra were obtained on a VG-ZAB-E high-resolution mass spectrometer. Infrared spectra were obtained on a Perkin-Elmer 1430 spectrophotometer. Preparative thin-layer chromatography was conducted on 0.5 mm (20 × 20 cm) silica gel F-254 plates (Merck-5744). Analytical thin-layer chromatography was performed on 0.25 mm (5 × 10 cm) silica gel F-254 plates (Merck). A 230-400 mesh silica gel (Merck) was used for flash column chromatography.

Synthesis of $CH_2[\textbf{closo}\text{-}1\text{-}(\eta\text{-}C_5H_4)Co(2,3\text{-}Et_2C_2B_4H_4)]_2$ (1). Separate solutions of $CH_2(C_5H_4)_2^{2-}$ and 2,3-$Et_2C_2B_4H_5^-$ were prepared as follows: A 3.56-g (54-mmol) sample of freshly distilled cyclopentadiene was condensed over 1.24 g (50 mmol) of 97% NaH in ~30 mL of THF in a 100-mL flask equipped with a vacuum stopcock and Teflon stirbar. The solution was allowed to warm to 0 °C and then stirred with periodic degassing until bubbling ceased. The faint pink solution was warmed to 25 °C for 10 min, and then 2.12 g (25 mmol) of CH_2Cl_2 was vacuum transferred into the flask. The flask was then placed into a 50 °C oil bath and stirred for 2 h. The off-pink solution produced a white precipitate upon cooling to 0 °C. Ice water (2 mL) was added to the reaction and the mixture extracted with ether. The resulting pale yellow solution was dried over $MgSO_4$, filtered, and stripped of solvent under vacuum without heating to a volume of 20 mL. The $(C_5H_6)_2CH_2$ solution was then added dropwise to a stirred mixture of 8.2 mL of *n*-butyllithium (1.4 M solution in hexanes) and 15 mL of THF at −78 °C over 30 min. The initial white precipitate dissolved, and the solution darkened to a bright orange during the course of the addition.

The 2,3-$Et_2C_2B_4H_5^-$ solution was prepared by adding a 677 mg (5.1 mmol) sample of 2,3-$Et_2C_2B_4H_6$ to 127 mg (5.1 mmol) of NaH in ~30 mL of THF in a 100-mL flask equipped with a vacuum stopcock and Teflon stirbar. The solution was allowed to warm to 25 °C and stirred with periodic degassing until bubbling ceased.

With the aid of two 25-mL pressure-equalizing dropping funnels, the $CH_2(C_5H_5)_2^{2-}$ and 2,3-$Et_2C_2B_4H_5^-$ solutions were slowly added under a N_2(g) atmosphere to a 714 mg (5.5 mmol) sample of anhydrous $CoCl_2$ dissolved in 30 mL of THF in a 250-mL three-neck round-bottom flask equipped with a Teflon stirbar. The $CH_2(C_5H_5)_2^{2-}$ solution was maintained at −78 °C over the 30-min addition. The green-black reaction mixture was then allowed to stir for 16 h. Following the addition of 100 mL of 1 M HCl and 10 mL of acetone, oxygen was bubbled into the stirred suspension for 2 h. The resulting orange layer was separated and then extracted with CH_2Cl_2 and the extract filtered through a short silica gel column. Separation by thin-layer chromatography (2:3 CH_2Cl_2:hexane) gave 12 products. Two bands were found to be 2,3-$Et_2C_2B_4H_5CoH$-2,3-$Et_2C_2B_4H_5$[7] (62 mg) and $Et_4C_4B_8H_8$[8] (280 mg), as evidenced by their ^{11}B and ^1H NMR and mass spectra. The remaining bands were found to contain mixtures of products. Further separations gave a orange band at R_f = 0.4 that was found to contain 110 mg (8.3% yield based on starting 2,3-$Et_2C_2B_4H_6$) of $CH_2[\textit{closo}\text{-}1\text{-}(\eta\text{-}C_5H_4)Co(2,3\text{-}Et_2C_2B_4H_4)]_2$. The product could then be further purified by vacuum sublimation at 80 °C onto a dry ice cold finger. The remaining bands from the chromatographic separations were isolated in quantities insufficient for complete characterization; however, the ^{11}B and ^1H NMR data and the mass spectra of several of these bands were consistent with the formulas $CH_2[(\eta\text{-}C_5H_4)_2Co_2(Et_2C_2B_4H_4)(Et_2C_2B_3H_5)]$ or $CH_2[(\eta\text{-}C_5H_4)_2Co_2(Et_2C_2B_3H_5)]_2$.

$CH_2[\textit{closo}\text{-}1\text{-}(\eta\text{-}C_5H_4)Co(2,3\text{-}Et_2C_2B_4H_4)]_2$ (1): orange; $^{11}B\{^1H\}$ NMR (C_6D_6) 12.9 (1 B), 9.8 (1 B), 4.7 ppm (2 B); ^1H NMR (C_6D_6) 4.33 (t, *J* = 2.0 Hz, Cp), 4.04 (t, *J* = 2.0 Hz, Cp), 3.36 (s, CH_2 bridge),

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(2) See, for example: (a) Bitterwolf, T. E.; Rheingold, A. L. *Organometallics* **1987**, *6*, 2138–2140. (b) Bitterwolf, T. E. *J. Organomet. Chem.* **1986**, *312*, 197–206. (c) Bitterwolf, T. E. *J. Organomet. Chem.* **1987**, *320*, 121–127. (d) Davis, R.; Khazal, N. M. S.; Bitterwolf, T. E. *J. Organomet. Chem.* **1990**, *397*, 51–58. (e) Bryndza, H. E.; Bergman R. G. *J. Am. Chem. Soc.* **1979**, *101*, 4766–4768. (f) Katz, T. J.; Acton, N.; Martin, G. *J. Am. Chem. Soc.* **1969**, *91*, 2804–2805. (g) Katz, T. J.; Acton, N.; Martin, G. *J. Am. Chem. Soc.* **1973**, *95*, 2934–2939. (h) Nelson, G. O.; Wright M. E. *J. Organomet. Chem.* **1982**, *239*, 353–364. (i) Fendrick, C. M.; Mintz, E. A.; Schertz, L. D.; Marks, T. J.; Day, V. W. *Organometallics* **1984**, *3*, 819–821. (j) Fendrick, C. M.; Schertz, L. D.; Day, V. W.; Marks, T. J. *Organometallics* **1988**, *7*, 1828–1838. (k) Werner, H.; Scholz, H. J.; Zolk, R. *Chem. Ber.* **1985**, *118*, 4531–4542. (l) Werner, H.; Lippert, F.; Bohley, T. *J. Organomet. Chem.* **1989**, *369*, C27–C32. (m) Schneider, D.; Werner, H. *J. Organomet. Chem.* **1990**, *384*, C33–C37. (n) Knox, S. A. R.; Macpherson, K. A.; Orpen, A. G.; Rendle, M. C. *J. Chem. Soc., Dalton Trans.* **1989**, 1807–1813. (o) Smith, J. A., Seyerl, J. V.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1979**, *173*, 175–185. (p) Lippard, S. J.; Dauplaise H.; Kvick, A.; Kerber, R. C. *Organometallics* **1984**, *3*, 1427–1434. (q) Wang, Y.-P.; Lin, T.-S.; Shyu, R.-G. Hwu, J.-M.; Wang, Y.; Cheng, M.-C. *J. Organomet. Chem.* **1989**, *357*, 57–69. (r) Petersen, J. L.; Reddy, K. P. *Organometallics* **1989**, *8*, 2107–2113. (s) Cordes, A. W.; Durham, B.; Askew, E. *Acta Crystallogr.* **1989**, C45, 1229–1231. (t) Cordes, A. W.; Durham, B.; Askew, E. *Acta Crystallogr.* **1989**, C45, 1231–1232. (u) Cordes, A. W.; Durham, B.; Askew, E. *Acta Crystallogr.* **1989**, C45, 1994–1996. (v) Härter, P.; Boguth, G.; Herdtweck, E.; Riede, J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1008–1009.

(3) See: (a) Grimes, R. N. *Pure App. Chem.* **1991**, *63*, 369–372. (b) Grimes, R. N. In *Electron-Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; Wiley: New York, 1990. (c) Grimes, R. N. In *Advances in Boron and the Boranes*; Liebman, J. F., Greenberg, A., Williams, R. E., Eds.; VCH: New York, 1988, and references therein.

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Table I. Crystallographic Data

formula	$Co_2C_{23}B_8H_{38}$
fw	518.91
cryst class	triclinic
space group	$P1$ (No. 1)
Z	1
cell const:	
a, Å	7.446 (2)
b, Å	8.717 (2)
c, Å	10.334 (2)
α, deg	94.65 (2)
β, deg	91.03 (2)
γ, deg	97.53 (2)
V, Å^3	662.5 (5)
μ, cm^{-1}	12.60
transm (min, max, av)	87.7, 94.1, 92.1
D_{calc}, g/cm^3	1.301
$F(000)$	270
radiation	Mo Kα (λ = 0.71073 Å)
θ range, deg	2.0–27.5
scan mode	ω–2θ
h, k, l collcd	+9, ±11, ±13
no. of reflcns measd	3274
no. of unique reflcns	3036
no. of reflcns used in the refinement	2600 ($F^2 > 3.0\sigma$)
no. of params	295
data/param ratio	8.8
R	0.037
R_w	0.046
GOF	1.268

Table II. Refined Positional Parameters[a]

atom	x	y	z	B_{eq}, Å^2
Co1	0.7266	0.6551	0.3118	2.65 (1)
C2	0.7204 (7)	0.7515 (6)	0.1400 (5)	3.3 (1)
C3	0.6364 (7)	0.8415 (6)	0.2456 (5)	2.94 (9)
B4	0.4838 (8)	0.7407 (7)	0.3112 (6)	3.3 (1)
B5	0.4699 (8)	0.5617 (8)	0.2347 (6)	3.5 (1)
B6	0.6322 (9)	0.5779 (8)	0.1236 (6)	3.6 (1)
B7	0.4788 (9)	0.7198 (8)	0.1410 (6)	3.8 (1)
C21	0.8619 (9)	0.8320 (8)	0.0562 (6)	4.7 (1)
C22	0.952 (1)	0.727 (1)	−0.0334 (9)	7.5 (2)
C31	0.6834 (9)	1.0144 (7)	0.2703 (6)	4.2 (1)
C32	0.560 (1)	1.0997 (7)	0.1945 (8)	5.6 (2)
Cp1	0.7580 (7)	0.5156 (6)	0.4586 (5)	3.3 (1)
Cp2	0.8031 (7)	0.6720 (7)	0.5032 (5)	3.5 (1)
Cp3	0.9510 (7)	0.7383 (8)	0.4329 (6)	4.3 (1)
Cp4	0.9967 (7)	0.6236 (7)	0.3416 (6)	4.1 (1)
Cp5	0.8786 (7)	0.4841 (7)	0.3541 (6)	3.6 (1)
Co1′	0.27340 (9)	0.34490 (9)	0.68824 (7)	2.99 (1)
C2′	0.1779 (7)	0.2020 (7)	0.8209 (5)	3.5 (1)
C3′	0.3068 (7)	0.1289 (7)	0.7385 (6)	3.6 (1)
B4′	0.260 (1)	0.1234 (8)	0.5911 (7)	4.1 (1)
B5′	0.066 (1)	0.2011 (9)	0.5844 (7)	4.5 (1)
B6′	0.0214 (9)	0.2489 (9)	0.7382 (8)	4.2 (1)
B7′	0.082 (1)	0.0625 (9)	0.6944 (7)	4.5 (2)
C21′	0.196 (1)	0.2041 (8)	0.9674 (6)	4.9 (1)
C22′	0.054 (1)	0.279 (1)	1.0405 (6)	6.5 (2)
C31′	0.4583 (9)	0.0547 (8)	0.7999 (7)	5.4 (2)
C32′	0.569 (1)	−0.0305 (9)	0.7110 (9)	6.5 (2)
Cp1′	0.4927 (7)	0.4623 (6)	0.5991 (5)	3.2 (1)
Cp2′	0.3256 (8)	0.5161 (6)	0.5675 (6)	3.7 (1)
Cp3′	0.2499 (9)	0.5726 (7)	0.6839 (7)	4.6 (1)
Cp4′	0.368 (1)	0.5543 (7)	0.7868 (6)	4.8 (1)
Cp5′	0.5162 (8)	0.4884 (8)	0.7372 (6)	4.4 (1)
Cc	0.6191 (7)	0.3941 (7)	0.5094 (6)	3.7 (1)

[a] $B_{eq} = {}^4/_3[\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab\cos\gamma + \beta_{13}ac\cos\beta + \beta_{23}bc\cos\alpha]$.

2.41 (m, CH_2), 2.19 (m, CH_2), 1.25 ppm (t, CH_3); exact mass calcd for $^{12}C_{23}{}^{11}B_8{}^{59}Co_2{}^{1}H_{38}$ 520.2382, found 520.2318; IR (KBr, cm^{-1}) 2930 s, 2935 m, 2880 w, 2550 vs, 1455 m, 1430 m, 1405 m, 1390 s, 1360 w, 1300 w, 1265 m, 1100 m, 1065 w, 1050 w, 1030 m, 930 w, 925 w, 895 w, 875 m, 845 s, 810 m, 720 w, 700 w, 670 w.

Collection and Reduction of the Crystallographic Data. Crystals of **1** suitable for X-ray analysis were grown at −5 °C by slow evaporation of a CH_2Cl_2 solution. Refined cell dimensions and their standard deviations were obtained from least-squares refinement of 25 accurately centered reflections. Diffraction data were collected at 295 K on an Enraf-Nonius four-circle CAD-4 diffractometer employing Mo Kα radiation from a highly oriented graphite-crystal monochromator. The intensities of three standard reflections measured at intervals of 3500 s showed no systematic change during data collection. The raw intensities were corrected for Lorentz and polarization effects by using the Enraf-Nonius program BEGIN.

Table III. Bond Distances (Å)

Co1–C2	2.027 (6)	B5–B7	1.743 (10)	C2′–C3′	1.467 (8)
Co1–C3	2.003 (5)	B6–B7	1.791 (10)	C2′–B6′	1.550 (9)
Co1–B4	2.045 (6)	C21–C22	1.485 (11)	C2′–B7′	1.784 (9)
Co1–B5	2.094 (6)	C31–C32	1.501 (10)	C2′–C21′	1.516 (8)
Co1–B6	2.084 (6)	Cp1–Cp2	1.399 (8)	C3′–B4′	1.552 (9)
Co1–Cp1	2.048 (6)	Cp1–Cp5	1.449 (8)	C3′–B7′	1.739 (9)
Co1–Cp2	2.037 (5)	Cp1–Cc	1.513 (7)	C3′–C31′	1.525 (9)
Co1–Cp3	2.084 (6)	Cp2–Cp3	1.416 (8)	B4′–B5′	1.680 (11)
Co1–Cp4	2.086 (5)	Cp3–Cp4	1.397 (9)	B4′–B7′	1.772 (11)
Co1–Cp5	2.055 (6)	Cp4–Cp5	1.421 (8)	B5′–B6′	1.659 (11)
C2–C3	1.487 (7)	Co1′–C2′	2.004 (6)	B5′–B7′	1.738 (11)
C2–B6	1.563 (8)	Co1′–C3′	2.038 (6)	B6′–B7′	1.769 (11)
C2–B7	1.784 (8)	Co1′–B4′	2.092 (7)	C21′–C22′	1.496 (11)
C2–C21	1.513 (8)	Co1′–B5′	2.081 (7)	C31′–C32′	1.469 (11)
C3–B4	1.545 (8)	Co1′–B6′	2.044 (7)	Cp1′–Cp2′	1.427 (8)
C3–B7	1.764 (8)	Co1′–Cp1′	2.081 (5)	Cp1′–Cp5′	1.431 (8)
C3–C31	1.502 (7)	Co1′–Cp2′	2.026 (6)	Cp1′–Cc	1.479 (8)
B4–B5	1.681 (9)	Co1′–Cp3′	2.019 (6)	Cp2′–Cp3′	1.418 (9)
B4–B7	1.753 (9)	Co1′–Cp4′	2.049 (6)	Cp3′–Cp4′	1.398 (10)
B5–B6	1.683 (9)	Co1′–Cp5′	2.088 (6)	Cp4′–Cp5′	1.399 (10)

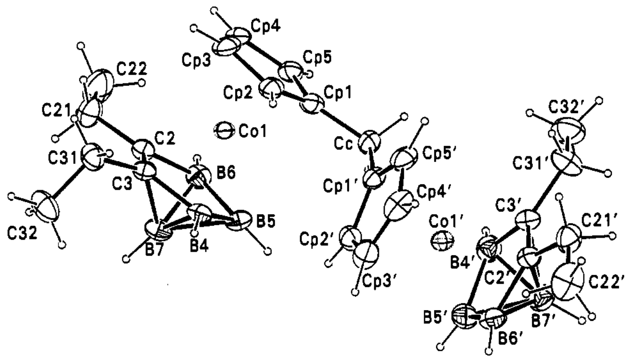

Figure 1. ORTEP drawing of the molecular structure of CH_2[*closo*-1-(η-C_5H_4)Co(2,3-$Et_2C_2B_4H_4$)]$_2$.

Solution and Refinement of the Structure. All calculations were performed on a VAX 11/750 computer using the Enraf-Nonius structure package. The full-matrix least-square refinement was phased on F, and the function minimized was $\Sigma w(|F_0| - |F_c|)^2$. The weights ($w$) were taken as $w = 1/\sigma^2(F)$ where $|F_0|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The neutral-atom scattering factors and complex anomalous dispersion corrections are those stored in the SDP package. Agreement factors are defined as $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$ and $R_w = (\Sigma(|F_0| - |F_c|)^2/\Sigma|F_0|^2)^{1/2}$.

Initially, the Co atoms were found by the interpretation of the Patterson map in the centrosymmetric space group $P\bar{1}$. Failure of further Fourier syntheses to find other heavy atoms necessitated the change to $P1$. Subsequent Fourier maps then led to the locations of all other non-hydrogen atoms. Anisotropic refinements followed by difference Fourier syntheses resulted in the location of all hydrogens. The final refinement included an empirical absorption correction (ψ-scan method) along with anisotropic thermal parameters for non-hydrogen atoms and fixed positional and isotropic thermal parameters for the hydrogen atoms (6 Å^2). A final difference Fourier map was featureless. Data collection and refinement data, final positional paramenters, and selected intramolecular bond distances are presented in Tables I–III, respectively.

Results and Discussion

The reaction of the *nido*-2,3-$Et_2C_2B_4H_5^-$ anion with cobalt chloride and $CH_2(C_5H_5)_2^{2-}$, followed by an oxidative workup yielded as the major product CH_2[*closo*-1-(η-C_5H_4)Co(2,3-$Et_2C_2B_4H_4$)]$_2$ (**1**), along with a number of other metallacarborane products in trace amounts. **1** was initially isolated in crude form by thin-layer chromatography; however, significant decomposition was observed during each separation. Mass spectral analyses of these crude mixtures indicated the formation of compounds of formulas CH_2[(η-C_5H_4)Co($Et_2C_2B_3H_5$)]$_2$ and CH_2[(η-C_5H_4)Co($Et_2C_2B_4H_4$)][(η-C_5H_4)Co($Et_2C_2B_3H_5$)], suggesting that the

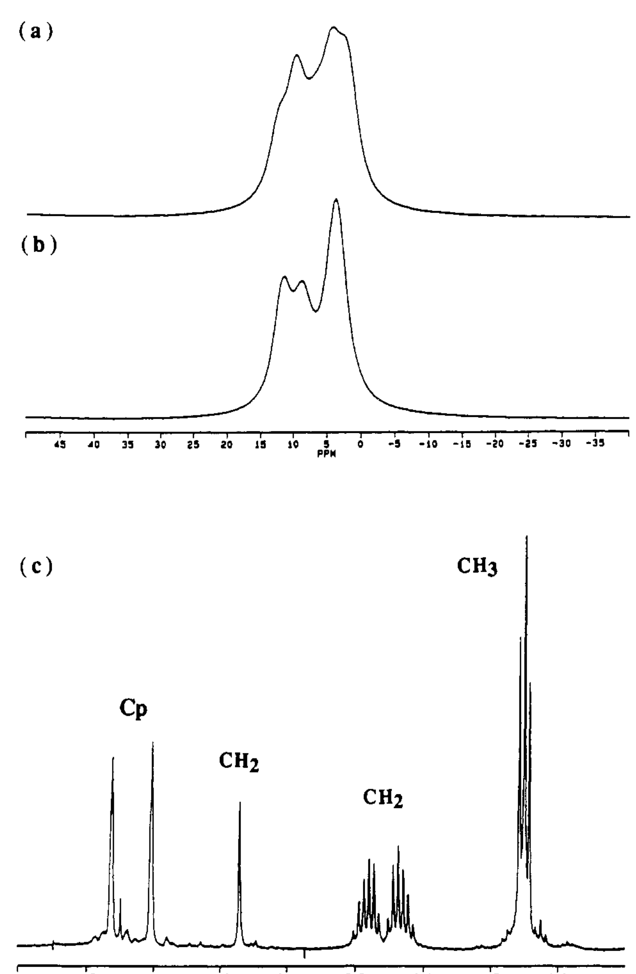

Figure 2. (a) 64.1-MHz ^{11}B NMR spectrum, (b) proton-decoupled ^{11}B NMR spectrum, and (c) 200-MHz ^{1}H NMR spectrum of $CH_2[$*closo*-1-$(\eta$-$C_5H_4)Co(2,3$-$Et_2C_2B_4H_4)]_2$.

removal of either one or two of the apical boron atoms of the carborane cages occurred during the TLC separation. Such decapitation reactions are well-known[3] for metal–2,3-$Et_2C_2B_4H_4$ complexes. Likewise, several of the minor products of the reaction gave mass spectra consistent with these formulas, but they were isolated in amounts insufficient to allow complete characterization.

Pure samples of **1** were obtained by vacuum sublimation of the crude material isolated by TLC. A single crystal X-ray determination of **1** established the structure shown in the ORTEP diagram in Figure 1. The compound is seen to be composed of two *closo*-1-(η-C_5H_4)Co(2,3-$Et_2C_2B_4H_4$) metallacarborane fragments joined by a cyclopentadienyl-bridging methylene group. The bond distances and angles within each cobaltacarborane fragment are normal and within the ranges observed in *closo*-1-(η-C_5H_5)Co(2,3-$Me_2C_2B_4H_4$).[9] The cobalt to cyclopentadienyl ring bonding appears normal, but with slightly longer cobalt to ring carbon distances being observed to the carbons atoms located on the same side of the complex as the carborane ethyl groups (i.e. Co1–Cp3, Co1–Cp4 and Co1′–Cp1′, Co1′–Cp5′). The carborane and cyclopentadienyl rings in both fragments adopt approximately eclipsed configurations with respect to each other.

In many organometallic complexes containing the dicyclopentadienylmethane group, the metal bonding faces of the two rings are located cis to each other, such that metal–metal bonded complexes are observed. Owing to the coordinative saturation of the cobalt atoms in $CH_2[$*closo*-1-$(\eta$-$C_5H_4)Co(2,3$-$Et_2C_2B_4H_4)]_2$, cobalt–cobalt bonding is not possible, and the complex adopts a configuration that minimizes the steric interactions in the molecule. Thus, the two cobaltacarborane fragments are oriented at nearly a right angle, as evidenced by the 83.6 (2)° dihedral angle between the planes of the two cyclopentadienyl rings and the 89.1 (2)° dihedral angle between the planes of the two carborane faces. The closest interaction between the two fragments occurs at B5–Cp2′ (3.65 Å) and HB5–HCp2′ (2.75 Å). Similar types of *transoid* configurations have been observed in $CH_2[(\eta$-$C_5H_4)Cr(CO)_2(NO)][(\eta$-$C_5H_4)Fe(\eta$-$C_5H_4C_2H_3)]$,[2q] $C(Me)R[(\eta$-$C_5H_4)Mn(CO)_3]_2$ (R = $OSiMe_3$, OH or H),[2s–u] and $SiMe_2[(\eta$-$C_5H_4)ZrCl_2(\eta$-$C_5Me_5)]_2$.[2r]

The 112.6 (9)° Cp1–Cc–Cp2 angle observed at the bridging methylene carbon is similar to comparable angles in both metal–metal-bonded dicyclopentadienylmethane complexes where the metals are by necessity oriented in a cis fashion—$CH_2[C_5H_4Rh(CO)]_2$-μ-CH_2, 112.5 (5)°,[2a] $CH_2[C_5H_4Rh(CO)]_2$-μ-CO, 112.3 (4)°,[2k] $CH_2[C_5H_4Ru(CO)_2]_2$, 114.5 (7)°,[2k] and $CH_2[C_5H_4Ru(CO)(\mu$-$CHMe)]_2$, 115.7 (5)°[2n]—and other non metal–metal-bonded bridged dicyclopentadienylmethane complexes where the metals are oriented in the *transoid* configuration such as $CH_2[(\eta$-$C_5H_4)Cr(CO)_2(NO)][(\eta$-$C_5H_4)Fe(\eta$-$C_5H_4$-$C_2H_3)]$ (114.1 (4)°)[2q] or $C(Me)R[(\eta$-$C_5H_4)Mn(CO)_3]_2$ (R = $OSiMe_3$, 108.7 (6)°, OH, 110.2 (3)°, or H, 111.0 (3)°).[2s–u]

The NMR data for **1** are consistent with the observed structure. As shown in Figure 2, the ^{11}B NMR spectrum consists of three resonances in a 1:1:2 ratio at shifts characteristic of *closo*-1-(η-C_5H_5)Co(2,3-$R_2C_2B_4H_4$) complexes.[3] The ^{1}H NMR spectrum shows, in addition to the resonances from the carborane ethyl groups, two triplet resonances arising from the two sets of cyclopentadienyl ring protons and a singlet resonance of intensity 2 at 3.36 ppm which is assigned to the two bridging methylene protons. The observation of a singlet bridging methylene resonance is consistent with the spectra observed for other non metal–metal-bonded dicyclopentadienylmethane-bridged complexes[2b,q,s] and suggests the free rotation of the cyclopentadienyl rings about the bridging methylene in solution. Equivalent bridging-methylene protons have also been observed[10] in other methylene-bridged metallacarborane complexes derived from the benzyltetramethylcyclopentadienyl ligand.

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Registry No. **1**, 136676-20-5; CH_2Cl_2, 75-09-2; $(C_5H_6)_2CH_2$, 31196-70-0; 2,3-$Et_2C_2B_4H_6$, 80583-48-8; $CoCl_2$, 7646-79-9; 2,3-$Et_2C_2B_4H_4CoH$-2,3-$Et_2C_2B_3H_5$, 80593-36-8; $Et_4C_4B_8H_8$, 115796-00-4; $CH_2[(\eta$-$C_5H_4)Co(Et_2C_2B_3H_5)]_2$, 136676-21-6; $CH_2[(\eta$-$C_5H_4)Co(Et_2C_2B_4H_4)][(\eta$-$C_5H_4)Co(Et_2C_2B_3H_5)]$, 136676-22-7; cyclopentadiene, 542-92-7.

Supplementary Material Available: Tables of thermal parameters, bond angles, hydrogen atom coordinates, and least-squares planes (10 pages); a table of observed and calculated structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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X-ray Crystal Structure of $[Bi(NMe_2)_3]$

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Much of the current interest in the chemistry of bismuth derives from its importance as a constituent in the copper oxide based superconducting materials with high critical temperatures.[1]