Organometallics **1985**, *4*, 721–726 721

Metal Atom Synthesis of Metallaboron Clusters. 6.[1] Synthesis and Structural Characterization of a Coupled Diborane–Metallacarborane Cluster: 5:1′,2′-[1-(η-C_5H_5)Co-2,3-(Me_3Si)$_2$$C_2B_4H_3$][$B_2H_5$]

James J. Briguglio and Larry G. Sneddon*

Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

Received September 24, 1984

The reaction of thermally generated cobalt atoms with hexaborane(10), bis(trimethylsilyl)acetylene, and cyclopentadiene has been found to give as major products the cobaltacarborane clusters 5:1′,2′-[1-(η-C_5H_5)Co-2,3-(Me_3Si)$_2$$C_2B_4H_3$][$B_2H_5$], I, 1-($\eta$-$C_5H_5$)Co-4,6-($Me_3Si$)$_2$$C_2B_6H_6$, II, and 1-($\eta$-$C_5H_5$)Co-4,5-($Me_3Si$)$_2$$C_2B_6H_6$, III, along with smaller amounts of 5-(η-C_5H_5)Co-1,8-(Me_3Si)$_2$$C_2B_5H_5$, IV, and 1-($\eta$-$C_5H_5$)Co-2,3-($Me_3Si$)$_2$$C_2B_4H_4$, V. The spectroscopic data for compounds II, III, IV, and V are consistent with their formulations as closo polyhedral cage systems in which one bis(trimethylsilyl)acetylenic unit has been inserted into the cage framework. A single-crystal X-ray study of I has revealed, however, that it has a unique bridged structure composed of a *closo*-1-(η-C_5H_5)Co-2,3-(Me_3Si)$_2$$C_2B_4H_3$– sandwich complex which has an exopolyhedral –B_2H_5 group bound to the 5-boron cage atom by means of a boron–boron–boron three-center bond. Compound I can thus be considered a bridge-substituted organometallic derivative of diborane. Crystal data for I: space group $C2/c$; $Z = 8$; $a = 29.890$ (9) Å, $b = 9.213$ (2) Å, $c = 15.127$ (6) Å, $\beta = 91.57$ (3)°; $V = 4164.4$ Å^3. The structure was refined by full-matrix least-squares techniques to a final R of 0.033 and R_w of 0.042 for the 4005 unique reflections which had $F_o^2 > 3\sigma(F_o^2)$.

Introduction

We have previously reported that the reaction of metal atoms with boron hydrides, acetylenes, and either cyclopentadiene or arenes can lead to the incorporation of an acetylenic unit into the metallaboron cluster framework to yield (η-C_5H_5)metallacarborane[2] or (η^6-C_6R_6)metallacarborane complexes.[3] In general, the yields of metal-containing products in these reactions were found to be low owing, in part, to competing metal atom promoted alkyne oligomerizations. For example, in reactions employing 2-butyne,[2,3] hexamethylbenzene was found to be the major product. This observation prompted our investigation of the reactions of metal atoms and boron hydrides with alkynes, such as bis(trimethylsilyl)acetylene, which would be more resistant to cyclization, with the aim of increasing the overall yields of metallacarborane products and decreasing the complexity of the reaction.

We report here that the reaction of cobalt atoms with hexaborane(10), cyclopentadiene, and bis(trimethylsilyl)acetylene gives much higher yields of cobaltacarborane clusters than previously could be obtained. In addition, we have also shown, by means of a single-crystal X-ray structural determination, that the major product of this reaction has a unique bridged structure involving the bonding of a *closo*-1-(η-C_5H_5)Co-2,3-(Me_3Si)$_2$$C_2B_4H_3$– sandwich to an exopolyhedral –B_2H_5 group by means of a boron–boron–boron three-center bond. Full details of these studies are reported herein.

Experimental Section

Materials and Procedures. Cobalt metal (Random pieces) was obtained from Alfa Products/Ventron Division. Cyclopentadiene was freshly distilled from dicyclopentadiene (Aldrich). Bis(trimethylsilyl)acetylene was obtained from Strem Chemicals, Inc., and used as received. Hexaborane(10) was prepared by using Shore's method.[4] All other reagents were commercially obtained, as indicated, and used as received.

Preparative thin-layer chromatography was conducted on 0.5 mm (20 × 20 cm) silica gel F-254 plates (Merck). Boron-11 and proton Fourier transform NMR spectra at 32.1 and 100 MHz, respectively, were obtained on a JEOL PS-100 spectrometer equipped with the appropriate decoupling accessories. Proton NMR spectra, at 250 MHz, were obtained on a Bruker WH-250 Fourier transform spectrometer. Boron-11 and proton NMR spectra at 64.2 and 200 MHz, respectively, were obtained on an IBM WP200SY Fourier transform spectrometer. Boron-11 NMR spectra, at 115.5 MHz, were obtained on a Bruker WH-360 Fourier transform spectrometer located in the Mid-Atlantic Regional NMR Facility. All boron-11 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 benzene from the lock solvent (99.5% C_6D_6) and then referenced to Me_4Si (0.00 ppm). High- and low-resolution mass spectra were obtained on a Hitachi Perkin-Elmer RMH-2 mass spectrometer and/or a VG Micromass 7070H mass spectrometer interfaced to a Kratos DS50S data system. Infrared spectra were obtained on a Perkin-Elmer 337 spectrophotometer. The melting points are uncorrected. The metal atom apparatus employed in these studies was based on a design by Klabunde[5] and is described elsewhere.[2,6]

Reaction of Cobalt Vapor with C_5H_6, B_6H_{10}, and $[Me_3SiC]_2$. Approximately 1.5 g of cobalt was placed in an integral tungsten alumina crucible (Sylvania Emissive Products, CS-1008) and cobalt vapor (~0.75 g) was generated by electrical heating (~8.0 V, ~60 A). In the bottom of the reactor flask was placed 6 mL of bis(trimethylsilyl)acetylene along with 10 mL of cyclopentadiene. The flask was evacuated and metal vapor condensed with 15 mL of cyclopentadiene and 8 mL of hexaborane(10) over a 1.5-h period onto the walls of the reactor, which was maintained at –196 °C. After metal deposition was completed, the matrix was allowed to warm to room temperature and stirred for 1 h. Excess ligands were removed in vacuo, and the reactor was flushed

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Table I. ^{11}B NMR Data

compound	δ (J, Hz)	rel areas
5:1′,2′-[1-(η-C_5H_5)Co-2,3-$(Me_3Si)_2C_2B_4H_3$][B_2H_5] (I)[b]	13.8 (186)	2
	4.5 (164)	1
	−7.0[c]	3
1-(η-C_5H_5)Co-4,6-$(Me_3Si)_2C_2B_6H_6$ (II)[d]	27.4 (154)	1
	10.6 (138)	2
	−2.2 (154)	2
	−10.3 (154)	1
1-(η-C_5H_5)Co-4,5-$(Me_3Si)_2C_2B_6H_6$ (III)[d]	72.0 (144)	1
	7.1 (173)	1
	−1.6 (183)	1
	−4.7 (183)	1
	−13.4 (164)	1
	−18.0 (161)	1

[a] All complexes were run in CH_2Cl_2 with internal C_6D_6 lock material. [b] ^{11}B NMR spectrum at 115.5 MHz. [c] Unresolved multiplet. [d] ^{11}B NMR spectrum at 64.2 MHz.

Table II. ^{1}H NMR Data

compd	δ (rel area)	assignt
I[a,b]	4.15 (5)	C_5H_5
	0.24 (18)	CH_3
	5.11[d]	BH
	3.51[d]	BH
	3.47[d]	BH
	0.88[d]	BH
	−0.55[d]	BHB
II[a,c]	4.54 (5)	C_5H_5
	0.35 (18)	CH_3
	3.17[d]	BH
	2.51[d]	BH
	1.13[d]	BH
	1.21[d]	BH
III[a,c]	4.46 (5)	C_5H_5
	0.37 (9)	CH_3
	0.34 (9)	CH_3
	9.58[d]	BH
	3.76[d]	BH
	2.92[d]	BH
	2.46[d]	BH
	1.59[d]	BH
	0.14[d]	BH

[a] Complex run in C_6D_6. [b] ^{1}H NMR spectrum at 250 MHz. [c] ^{1}H NMR spectrum at 200.1 MHz. [d] ^{11}B spin-decoupled ^{1}H NMR spectrum at 200.1 MHz.

Table III. Infrared Data

compd[a,b]	IR absorptions, cm^{-1}
I	3101 (w), 2970 (sh), 2960 (m), 2901 (w), 2625 (sh), 2601 (s), 2575 (s), 2571 (sh), 2502 (s), 2499 (sh), 2460 (s), 2440 (s), 2300 (w), 2080 (w), 1975 (sh), 1925 (m), 1650 (m), 1440 (m), 1240 (s), 1200 (m), 1183 (m), 1160 (m), 1140 (s), 1110 (w), 1090 (m), 1010 (sh), 972 (s), 928 (m), 870 (sh), 840 (s, br), 772 (m), 750 (sh), 700 (w), 640 (sh), 630 (m), 618 (sh), 580 (w), 500 (m)
II	3120 (vw), 2950 (m), 2900 (sh), 2575 (s), 2570 (sh), 2550 (s), 2525 (sh), 1440 (w), 1240 (s), 1120 (br, w), 1020 (w), 1010 (sh), 905 (w), 870 (m), 840 (sh), 830 (s), 755 (w), 675 (w), 630 (m)
III	2950 (s), 2900 (m), 2580 (sh), 2550 (s), 1400 (w), 1250 (sh), 1240 (s), 1170 (s), 1115 (sh), 1095 (s), 1010 (s), 970 (m), 930 (m), 890 (sh), 830 (s, br), 780 (m), 755 (m), 700 (m), 630 (s), 595 (w), 555 (w), 475 (w)

[a] KBr pellet. [b] Perkin-Elmer 337.

with nitrogen gas. The residue was extracted with methylene chloride, filtered through a coarse frit, and then stirred with silica gel. The mixture was then filtered through a coarse frit and separated by TLC on silica gel by using a 50% hexanes in benzene solution. The separation gave as the major product I, 5:1′,2′-[1-(η-C_5H_5)Co-2,3-$(Me_3Si)_2C_2B_4H_3$][B_2H_5] [R_f 0.7; yellow; 118.5 mg; mp 173 °C; mass measurement calcd for $^{12}C_{13}{}^{1}H_{31}{}^{11}B_6{}^{28}Si_2{}^{59}Co$ 368.1874, found 368.1785 [major fragment at m/e 124, (η-C_5H_5)Co]], along with another band which was subsequently separated by using hexanes as an eluent to give II, 1-(η-C_5H_5)-Co-4,6-$(Me_3Si)_2C_2B_6H_6$ [R_f 0.63; orange; 45.8 mg; mass measurement calcd for $^{12}C_{13}{}^{1}H_{29}{}^{11}B_6{}^{28}Si_2{}^{59}Co$ 366.1717, found 366.1729 [major fragment at m/e 124, (η-C_5H_5)Co]], and III, 1-(η-C_5H_5)Co-4,5-$(Me_3Si)_2C_2B_6H_6$ [R_f 0.15; pink; 22.3 mg; mp 110–112 °C; mass measurement calcd for $^{12}C_{13}{}^{1}H_{29}{}^{11}B_6{}^{28}Si_2{}^{59}Co$ 366.1717, found 366.1719 [major fragment at m/e 124, (η-C_5H_5)Co]]. Also isolated in much smaller amounts (~1 mg) were IV, 5-(η-C_5H_5)Co-1,8-$(Me_3Si)_2C_2B_5H_5$ [R_f 0.43, green; mass measurement calcd for $^{12}C_{13}{}^{1}H_{28}{}^{11}B_5{}^{28}Si_2{}^{59}Co$ 354.1543, found 354.1532 [major fragment at m/e 124, (η-C_5H_5)Co]; ^{11}B NMR (C_6D_6, 64.2 MHz) δ (J_{BH}) 59.2 (185 Hz), 19.5 (156 Hz), −0.02 (156 Hz), −9.2 (173 Hz), −16.5 (146 Hz) in a ratio of 1:1:1:1:1, ^{1}H NMR (C_6D_6, 250 MHz) δ 4.44 (η-C_5H_5), 0.27, 0.25 (CH_3)], V, 1-(η-C_5H_5)Co-2,3-$(Me_3Si)_2C_2B_4H_4$ [R_f 0.15; orange; mass measurement calcd for $^{12}C_{13}{}^{1}H_{27}{}^{11}B_4{}^{28}Si_2{}^{59}Co$ 342.1368, found 342.1351 [major fragment at m/e 124, (η-C_5H_5)Co]; ^{11}B NMR (C_6D_6, 64.2 MHz) δ (J_{BH}) 9.4 (149 Hz), 4.7 (156 Hz) in a ratio of 3:1; ^{1}H NMR (C_6D_6, 250 MHz) δ 4.21 (η-C_5H_5), 0.36 (CH_3)], and VI, 5-(η-C_5H_5)CoB_9H_{13}.[7] An additional compound, VII, was isolated in insufficient amounts (< 1 mg) to allow complete characterization; however, high-resolution mass spectral data suggest the formula (η-C_5H_5)Co-$(Me_3Si)_2C_2B_7H_7$ [mass measurement calcd for $^{12}C_{13}{}^{1}H_{30}{}^{11}B_7{}^{28}Si_2{}^{59}Co$ 378.1893, found 378.1884, [major fragment at m/e 124, (η-C_5H_5)Co]].

Thermolysis of 5:1′,2′-[1-(η-C_5H_5)Co-2,3-$(Me_3Si)_2C_2B_4H_3$][B_2H_5], I. A 2.0-mg sample of I (yellow) was heated at 150 °C in an evacuated Pyrex tube for 12 h. The brown residue which resulted was separated by TLC on silica gel using hexanes as an eluent to give 0.8 mg of IV and 0.6 mg of V.

Thermal Isomerization of 1-(η-C_5H_5)Co-4,6-$(Me_3Si)_2C_2B_6H_6$.[8] A 10 mg sample of II (orange) was heated at 150 °C in an evacuated Pyrex tube for 12 h. The resulting pink material (8.5 mg) was shown to be the isomer III, 1-(η-C_5H_5)-Co-4,5-$(Me_3Si)_2C_2B_6H_6$.

Crystallographic Data for 5:1′,2′-[1-(η-C_5H_5)Co-2,3-$(Me_3Si)_2C_2B_4H_3$][B_2H_5]. Single crystals were grown in one day by slow evaporation in air of a methylene chloride/heptane solution. A crystal of suitable size was mounted and 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. Refined cell dimensions and their standard deviations were obtained from the least-squares refinement of these 25 accurately centered reflections. On the basis of several theta scans the mosaicity of the crystal was judged acceptable. See Table IV for crystal data.

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, employing Mo Kα radiation from a highly oriented graphite crystal monochromator. The raw intensities were corrected for Lorentz and polarization effects by using the Enraf-Nonius program START.

Solution and Refinement of the Structure. All calculations were performed on a PDP 11/60 computer using the Enraf-Nonius structure package.[9] 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 non-hydrogen atoms were taken from

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[9] Enraf-Nonius Inc., Garden City Park, NY.

Table IV. Data Collection and Structure Refinement Information

space group	$C2/c$
a, Å	29.890 (9)
b, Å	9.213 (2)
c, Å	15.127 (6)
β, deg	91.57 (3)
V, Å^3	4164.4
Z	8
ρ(calcd), g cm^{-3}	1.172
cryst dimens, mm	0.30 × 0.35 × 0.50
mol formula	$B_6C_{13}H_{31}Si_2Co$
mol wt	368.18
λ(Mo Kα), Å	0.71073
scanning range, deg	$0° < 2\theta < 55°$
scan mode	$\omega - 2\theta$
$\pm h, \pm k, \pm l$ collected	$+38, +11, \pm 19$
no. of measd intensities	5298
unique reflections $F_o^2 > 3\sigma(F_o^2)$	4005
no. of variables	323
abs coeff (μ), cm^{-1}	9.26
transmissn coeff	
max	80.16%
min	73.99%
R	0.0327
R_w	0.0421

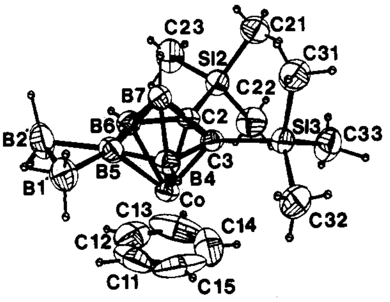

Figure 1. ORTEP Drawing of 5:1′,2′-[1-(η-C_5H_5)Co-2,3-$(Me_3Si)_2C_2B_4H_3$][B_2H_5]. Non-hydrogen atoms are shown as 50% thermal ellipsoids.

Cromer and Waber[10] and those for hydrogen from Stewart.[11] The effects of anomalous dispersion were included in F_c by using Cromer and Iber's values[12] for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

A three-dimensional Patterson synthesis gave the coordinates of the cobalt atom. Subsequent Fourier maps led to the location of the remaining heavy atoms. Anisotropic refinement followed by a difference Fourier synthesis resulted in the location of all 31 hydrogen atoms. Final refinement included a numerical absorption correction along with anisotropic thermal parameters for non-hydrogen atoms and fixed isotropic thermal parameters for the hydrogen atoms.

Final positional parameters are given in Table V. Intramolecular bond distances and selected bond angles are presented in Tables VI and VII, respectively. Figure 1 gives an ORTEP view of I.

Listing of final thermal parameters, selected molecular planes, and observed and calculated structure factors are available as supplementary material.

Results

The reaction of cobalt vapor with cyclopentadiene, hexaborane(10), and bis(trimethylsilyl)acetylene was found to give as the major product I, a yellow crystalline material which was both air and water stable. An exact mass determination established the composition of the compound as (η-C_5H_5)Co$(Me_3Si)_2C_2B_6H_8$. A metallacarborane cluster of this formula would normally be expected to adopt a nine-vertex nido cage geometry similar to the structures observed for compounds such as, 1,2-$C_2B_7H_{11}$[13] or 1,6,7,8-(η-C_5H_5)$_3$Ni$_3$CB$_5$H$_6$.[14] A single-crystal X-ray structural determination demonstrated, however, that the compound does not have a single-cage structure but instead adopts the linked cage configuration 5:1′,2′-[1-(η-C_5H_5)Co-2,3-$(Me_3Si)_2C_2B_4H_3$][B_2H_5], shown in Figure 1.[15]

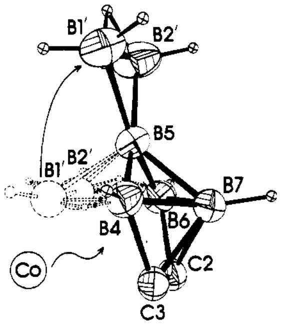

Figure 2. Possible scheme for the formation of 5:1′,2′-[1-(η-C_5H_5)Co-2,3-$(Me_3Si)_2C_2B_4H_3$][B_2H_5] from hexaborane(10).

The structure of I is thus seen to be composed of a 1-(η-C_5H_5)Co-2,3-$(Me_3Si)_2C_2B_4H_3$–cobaltacarborane sandwich complex which is linked at the 5-boron cage position to a bridging position in an exopolyhedral –B_2H_5 unit. The compound can therefore be considered a bridge-substituted organometallic derivative of diborane.

There are a number of examples of bridge-substituted diborane molecules which have been reported, including compounds such as μ-$(CH_3)_2NB_2H_5$,[16] μ-$CH_3SB_2H_5$,[17] μ-$CH_3SeB_2H_5$,[18] $K^+[(\eta^2\text{-}B_2H_5)Fe(CO)_4]^-$,[19] and ($\eta$-$C_5H_5$)$(CO)_2Fe(\mu\text{-}B_2H_5)$.[20] Triborane compounds such as B_3H_7CO[21] and $B_3H_7NH_3$[22] can also be considered as bridge-substituted diborane derivatives [i.e., $(\mu\text{-}BH_2CO)B_2H_5$ and $(\mu\text{-}BH_2NH_3)B_2H_5$]. The structure of the B_2H_5 unit in I was found to be remarkably similar to those which have been reported for B_3H_7CO,[21] $B_3H_7NH_3$,[22] and (η-C_5H_5)$(CO)_2Fe(\eta^2\text{-}B_2H_5)$,[20] indicating that the bonding in the B_2H_5 unit is relatively insensitive to the nature of the bridging substituent. For example, the B1′–B2′ distance 1.753 (3) Å is similar to that which was found for analogous boron–boron distances in B_3H_7CO (1.77 (1) Å), $B_3H_7NH_3$ (1.744 (5) Å) and (η-C_5H_5)$(CO)_2Fe(\eta^2\text{-}B_2H_5)$ (1.80 Å) and is, in fact, close to the boron–boron bond distance observed in diborane 1.77 Å.[23] The four terminal hydrogens of the

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Table V. Positional Parameters and Their Estimated Standard Deviation for 5:1′,2′-[1-(η-C_5H_5)Co-2,3-$(Me_3Si)_2C_2B_4H_3$][B_2H_5]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Co	0.41851 (1)	0.29171 (3)	0.41102 (2)	HB4	0.4237 (7)	0.514 (2)	0.544 (1)
Si2	0.30152 (2)	0.25143 (7)	0.34491 (4)	HB6	0.3634 (7)	0.065 (2)	0.479 (1)
Si3	0.35694 (2)	0.62764 (6)	0.40550 (4)	HB7	0.3272 (7)	0.361 (2)	0.576 (1)
C11	0.48303 (9)	0.2369 (5)	0.4042 (2)	HC11	0.4992 (7)	0.214 (2)	0.459 (1)
C12	0.4592 (1)	0.1419 (3)	0.3600 (3)	HC12	0.4606 (7)	0.062 (2)	0.374 (1)
C13	0.4375 (1)	0.2098 (5)	0.2939 (2)	HC13	0.4261 (7)	0.190 (2)	0.269 (1)
C14	0.4490 (1)	0.3532 (4)	0.3000 (2)	HC14	0.4416 (7)	0.405 (2)	0.272 (1)
C15	0.4769 (1)	0.3643 (4)	0.3676 (3)	HC15	0.4884 (7)	0.410 (2)	0.385 (1)
C2	0.35133 (6)	0.2946 (2)	0.4199 (1)	H21A	0.2603 (7)	0.468 (2)	0.367 (1)
C3	0.37163 (6)	0.4375 (2)	0.4419 (1)	H21C	0.2479 (7)	0.355 (2)	0.431 (1)
C21	0.25419 (8)	0.3696 (3)	0.3736 (2)	H21B	0.2291 (7)	0.343 (2)	0.342 (1)
C22	0.3156 (1)	0.2680 (3)	0.2269 (2)	H22A	0.3358 (7)	0.195 (2)	0.208 (1)
C23	0.28423 (9)	0.0603 (3)	0.3639 (2)	H22B	0.2874 (7)	0.262 (2)	0.192 (1)
C31	0.3131 (1)	0.6939 (3)	0.4796 (2)	H22C	0.3304 (7)	0.342 (2)	0.211 (1)
C32	0.4077 (1)	0.7427 (3)	0.4155 (2)	H23C	0.3104 (7)	−0.001 (2)	0.341 (1)
C33	0.33687 (9)	0.6391 (3)	0.2883 (2)	H23B	0.2804 (7)	0.051 (2)	0.420 (1)
B1′	0.4489 (1)	0.2585 (4)	0.6392 (2)	H23A	0.2619 (7)	0.048 (2)	0.332 (1)
B2′	0.4211 (1)	0.0939 (4)	0.6185 (2)	H31B	0.3060 (7)	0.798 (2)	0.478 (1)
B4	0.40789 (8)	0.4226 (3)	0.5208 (2)	H31C	0.3261 (7)	0.715 (2)	0.518 (1)
B5	0.40874 (8)	0.2486 (3)	0.5495 (2)	H31A	0.2908 (7)	0.632 (2)	0.498 (1)
B6	0.37256 (8)	0.1679 (3)	0.4802 (2)	H32C	0.3993 (8)	0.814 (2)	0.390 (1)
B7	0.35510 (8)	0.3343 (3)	0.5310 (2)	H32A	0.4323 (7)	0.712 (2)	0.378 (1)
HBB′	0.4519 (7)	0.143 (2)	0.664 (1)	H32B	0.4117 (7)	0.757 (2)	0.479 (1)
HB1′B	0.4792 (7)	0.277 (2)	0.614 (1)	H33C	0.3096 (7)	0.586 (2)	0.276 (1)
HB1′A	0.4371 (7)	0.323 (2)	0.695 (1)	H33B	0.3317 (7)	0.741 (2)	0.270 (1)
HB2′B	0.3915 (7)	0.073 (2)	0.659 (1)	H33A	0.3585 (7)	0.615 (2)	0.245 (1)
HB2′A	0.4368 (7)	0.007 (2)	0.584 (1)				

Table VI. Bond Distances (Å) for 5:1′,2′-[1-(η-C_5H_5)Co-2,3-$(Me_3Si)_2C_2B_4H_3$][B_2H_5]

Co–C11	1.999 (2)	C2–C3	1.483 (2)
Co–C12	2.008 (2)	C2–B6	1.602 (2)
Co–C13	2.022 (2)	C2–B7	1.721 (2)
Co–C14	2.015 (2)	C3–B4	1.596 (2)
Co–C15	1.996 (2)	C3–B7	1.732 (2)
Co–C2	2.016 (1)	B1′–B2′	1.753 (3)
Co–C3	2.006 (1)	B1′–B5	1.789 (2)
Co–B4	2.083 (2)	B1′–HBB′	1.129 (15)
Co–B5	2.160 (2)	B1′–HB1′B	1.01 (2)
Co–B6	2.088 (2)	B1′–HB1′A	1.093 (15)
Si2–C2	1.889 (1)	B2′–B5	1.799 (3)
Si2–C21	1.846 (2)	B2′–HBB′	1.226 (15)
Si2–C22	1.851 (2)	B2′–HB2′B	1.112 (14)
Si2–C23	1.860 (2)	B2′–HB2′A	1.068 (15)
Si3–C3	1.885 (1)	B4–B5	1.661 (2)
Si3–C31	1.852 (2)	B4–B7	1.786 (2)
Si3–C32	1.854 (2)	B4–HB4	1.025 (15)
Si3–C33	1.859 (2)	B5–B6	1.661 (2)
C11–C12	1.301 (4)	B5–B7	1.802 (2)
C11–C15	1.308 (5)	B6–B7	1.799 (2)
C12–C13	1.333 (5)	B6–HB6	0.987 (15)
C13–C14	1.368 (6)	B7–HB7	1.123 (14)
C14–C15	1.306 (5)		

B_2H_5 unit are coplanar with B1′ and B2′, with the dihedral angle between this plane and the B1′,B2′,HBB′,B5 plane being 89.4°. The B1′–HBB′ and B2′–HBB′ distances of 1.129 (15) Å and 1.226 (15) Å and the B1′–HBB′–B2′ angle of 93.4° are normal and in the range observed in the compounds cited above.

The distances and angles found in the [1-(η-C_5H_5)Co-2,3-$(Me_3Si)_2C_2B_4H_3$]–complex are similar to those which have been reported for the parent compound 1-(η-C_5H_5)-Co-2,3-$(CH_3)_2C_2B_4H_4$,[24] suggesting that the bonding of B5 to the B_2H_5 unit has not significantly altered its bonding interactions in the cage.

The participation of a boron atom in a cobaltacarborane cage in an exopolyhedral three center bond is unusual but is not unprecedented. This type of bonding was in fact previously found[25] in the linked cobaltacarborane–carborane complex 6:4′,5′-[1-(η-C_5H_5)Co-2,3-$(CH_3)_2C_2B_4H_3$]-[2′,3′-$(CH_3)_2C_2B_4H_5$], in which a [1-(η-C_5H_5)Co-2,3-$(CH_3)_2C_2B_4H_3$] cobaltacarborane complex is linked to a 2′,3′-$(CH_3)_2C_2B_4H_5$- carborane cage by means of a single three-center boron–boron–boron bond. Thus, in both this compound and in I, one of the ring borons (B6 and B5, respectively) which is directly bonded to a cobalt atom is also involved in an exopolyhedral three-center bond.

The B1′–B5 (1.789 (2) Å) and B2′–B5 (1.799 (3) Å) distances observed in I are typical of boron–boron distances observed for borons atoms in three-center bonds (e.g., 1.820 (6) and 1.803 (6) Å for the corresponding boron–boron bonds in $B_3H_7NH_3$[22]), but are shorter than those observed in 6:4′,5′-[1-(η-C_5H_5)Co-2,3-$(CH_3)_2C_2B_4H_3$]-[2′,3′-$(CH_3)_2C_2B_4H_5$]: B6–B4′, 1.842 (4) Å, and B6–B5′, 1.978 (4) Å. This difference is probably attributable to the greater steric repulsion of the [2′,3′-$(CH_3)_2C_2B_4H_5$]– cage, compared to the smaller B_2H_5 unit, when bound to the cobaltacarborane complex.

It should also be noted that in the complex 6:4′,5′-[1-(η-C_5H_5)Co-2,3-$(CH_3)_2C_2B_4H_3$][2′,3′-$(CH_3)_2C_2B_4H_5$], the plane of the linkage atoms (B6,B4′,B5′) is rotated 85.9° relative to the plane of the basal atoms of the cobaltacarborane cage (C2,C3,B4,B5,B6); whereas in I the linkage atoms (B5,B1′,B2′) are coplanar with the basal ring atoms (C2,C3,B4,B5,B6). These differences suggest that the conformation of the exopolyhedral cage is determined primarily by steric interactions rather than bonding requirements.

The spectroscopic data obtained for I are also characteristic of its unusual structure. Of particular interest is the IR spectrum which shows eight different absorptions between 2620 and 2440 cm^{-1} (B-H terminal stretching region) consistent with the different types of terminal BH

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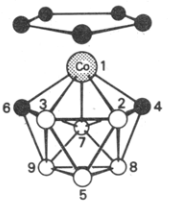
Table VII. Selected Bond Angles (deg) for 5:1′,2′-[1-(η-C_5H_5)Co-2,3-$(Me_3Si)_2B_4H_3$][B_2H_5]

C12–C11–C15	108.5 (3)	B2′–B1′–HB1′B	120.2 (9)	B5–B2′–HB2′A	113.3 (8)
C11–C12–C13	108.5 (3)	B2′–B1′–HB1′A	116.5 (8)	HB2′B–B2′–HB2′A	121 (1)
C12–C13–C14	106.7 (3)	B5–B1′–HBB′	104.7 (8)	C3–B4–B5	106.5 (1)
C13–C14–C15	106.4 (3)	B5–B1′–HB1′B	108.4 (9)	B1′–B5–B2′	58.5 (1)
C11–C15–C14	109.9 (3)	B5–B1′–HB1′A	112.7 (8)	B2′–B5–B4	98.9 (1)
Si2–C2–C3	129.22 (9)	HB1′B–B1′–HB1′A	121 (1)	B2′–B5–B6	97.6 (1)
Si2–C2–B6	118.82 (9)	B1′–HBB′–B2′	93.44 (8)	B4–B5–B6	105.2 (1)
C3–C2–B6	111.4 (1)	B1′–B2′–B5	60.5 (1)	C2–B6–B5	105.9 (1)
Si3–C3–C2	131.97 (9)	B1′–B2′–HBB′	39.8 (7)	C2–B7–C3	50.88 (7)
Si3–C3–C4	116.52 (9)	B1′–B2′–HB2′B	115.3 (8)	C2–B7–B6	54.10 (8)
C2–C3–C4	110.9 (1)	B1′–B2′–HB2′A	121.5 (8)	C3–B7–B4	53.92 (7)
B2′–B1′–B5	61.0 (1)	B5–B2′–HBB′	100.0 (8)	B4–B7–B5	55.15 (8)
B2′–B1′–HBB′	44.0 (8)	B5–B2′–HB2′B	107.6 (7)	B5–B7–B6	54.94 (9)

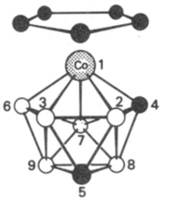
groups in the compound. In addition, two distinct B–H–B bridge stretching vibrations are observed at 1940 cm^{-1} and 1660 cm^{-1}. Similar bridge hydrogen vibrations have been observed in other μ-substituted diborane derivatives.[18-20] The ^{11}B NMR spectrum at 115.5 MHz shows a doublet of intensity 2 and a doublet of intensity 1 which may be assigned to the cobaltacarborane borons B4,6 and B7, respectively. Also present in the spectrum is a broad poorly defined resonance of intensity 3 at −7.0 ppm which must arise from the overlap of the triplet expected for borons B1′ and B2′ and the singlet from B5. Neither proton decoupling nor artifical line narrowing aided in the further resolution of this resonance. The proton NMR spectrum (Table II) showed the expected $Si(CH_3)_3$, η-C_5H_5, terminal BH, and BHB bridging resonances.

In addition to compound I, two other complexes, II and III, were produced in good amounts in the reaction. On the basis of comparisons with published spectral data, these compounds are proposed to be the carbon-substituted, trimethylsilyl derivatives of the known closo cobaltacarborane complexes[26] 1-(η-C_5H_5)Co-4,6-$C_2B_6H_8$[27] and 1-(η-C_5H_5)Co-4,5-$C_2B_6H_8$.[28]



1-(η-C_5H_5)Co-4,6-$(Me_3Si)_2C_2B_6H_6$

II

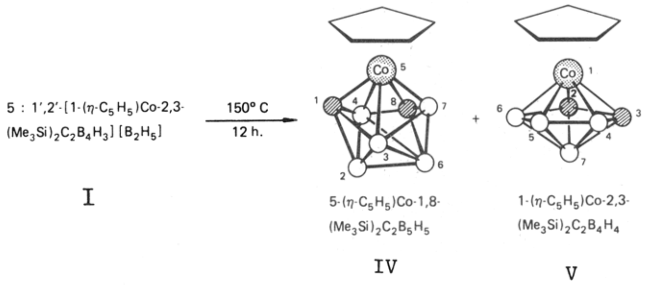


1-(η-C_5H_5)Co-4,5-$(Me_3Si)_2C_2B_6H_6$

III

These compounds have closo skeletal electron counts and, as a result, have structures based on tricapped trigonal prisms with the carbon atoms occupying two of the four-coordinate capping positions and with the cobalt atom in each complex situated in a five-coordinate position. Further conformation of the structures of these two compounds was obtained when it was observed, in agreement with the earlier studies on the parent compounds,[8] that II readily isomerized to III upon moderate heating.

Although the major products I, II, and III, each retained a six-boron framework, two other smaller cage complexes, which were identified as 5-(η-C_5H_5)Co-1,8-$(Me_3Si)_2C_2B_5H_5$, IV, and 1-(η-C_5H_5)Co-2,3-$(Me_3Si)_2C_2B_4H_4$, V, were isolated from the reaction in small amounts, indicating that some cage fragmentation reactions occur during the course of the metal atom reaction. It was subsequently shown that the thermolysis of I under mild conditions led to the high-yield formation of these two compounds.



This result suggests that the decomposition of I (perhaps, metal promoted) during the course of the metal atom reaction may have been the source of compounds IV and V in the original reaction.

Discussion

The previously reported[2] reaction of cobalt atoms with cyclopentadiene, hexaborane(10), and 2-butyne was found to give seven different metallaboron cluster complexes in low (~20 mg) to trace amounts (<1 mg) along with large quantities of hexamethylbenzene. The major metallacarborane products observed were either contracted cage systems, such as 1,2-$(CH_3)_2$-3,1,2-(η-C_5H_5)Co$C_2B_5H_5$, or dimetal hexaboron clusters, such as 6,7-$(CH_3)_2$-2,5,6,7-(η-C_5H_5)$_2$$Co_2C_2B_6H_8$ and 6,7-$(CH_3)_2$-2,4,6,7-(η-C_5H_5)$_2$$Co_2C_2B_6H_6$. In the present study it was found that the use of bis(trimethylsilyl)acetylene, instead of 2-butyne, in these reactions has a profound effect on both the yields and types of metallcarborane clusters produced, as well as eliminating the competing alkyne trimerization reaction. Thus, only three main products, I, II and III, were observed, and each of these were composed of a monometal six-boron cage unit.

In light of our earlier studies[2,3] of the use of metal vapor reactions for the synthesis of metallacarborane clusters, the synthesis of complexes, such as II and III, which have resulted from the incorporation of an acetylenic unit and metal atom into the polyhedral borane framework to yield a closo cobaltacarborane complex, was not unexpected. These complexes may be envisioned as forming via the attack of a (η-C_5H_5)Co unit, formed initially in the reaction, on a hexaborane(10) molecule

$$(\eta\text{-}C_5H_5)Co + B_6H_{10} \rightarrow (\eta\text{-}C_5H_5)Co(\eta^2\text{-}B_6H_{10})$$

As indicated above, this reaction could involve the bonding of the metal atom in a η^2 fashion to the boron–boron single bond in hexaborane(10). Several examples of this type of metal–hexaborane(10) have previously been characterized.[29] The resulting intermediate would be a

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(26) Compounds II and III were originally numbered as 1-(η-C_5H_5)-Co-4,5-$C_2B_6H_8$, II, and 1-(η-C_5H_5)Co-4,6-$C_2B_6H_8$, III (ref 27 and 28); however, using the new nomenclature system (ref 15) the numbering is reversed and II corresponds to the 1-(η-C_5H_5)Co-4,6-$C_2B_6H_8$ isomer while III becomes the 1-(η-C_5H_5)Co-4,5-$C_2B_6H_8$ isomer.

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16-electron complex and would be capable of binding a bis(trimethylsilyl)acetylene.

$$(\eta\text{-}C_5H_5)Co(\eta^2\text{-}B_6H_{10}) + R_2C_2 \rightarrow (\eta\text{-}C_5H_5)Co(\eta^2\text{-}B_6H_{10})(\eta^2\text{-}R_2C_2)$$

Fusion of the coordinated hexaborane(10) and acetylene groups accompanied by the loss of 2 equiv of H_2 could then yield compounds II and III.

It was indeed surprising that the major product of the reaction, compound I, did not have a single cage structure but instead adopted the unique diborane–metallacarborane structure (Figure 1). At first glance it is difficult to understand how such a structure could be derived from hexaborane(10); however, as shown in Figure 2 the reaction can be envisioned as occurring in much the same way as that proposed for the formation of II and III. Thus, the fusion of an acetylene to the open face of the hexaborane cage generates a pentagonal ring, composed of the two carbons and borons 4, 5, and 6, suitable for bonding to a $(\eta\text{-}C_5H_5)$Co atom. If, as the cobalt atom bonds to this ring, the B4–bridging hydrogen and B6–bridging hydrogen bonds are cleaved, then a $-B_2H_5$ unit can be extruded from the cobaltaborane cage as shown in the figure. Thus, the driving force leading to this unique bridged structure may result from the favored formation of the cobaltaborane sandwich, $1\text{-}(\eta\text{-}C_5H_5)Co\text{-}2,3\text{-}(Me_3Si)_2C_2B_4H_3$-complex.

Acknowledgment. We thank the National Science Foundation and the Army Research Office for the support of this work.

Supplementary Material Available: Tables of general temperature factors, molecular planes, and observed and calculated structure factors (32 pages). Ordering formation is given on any current masthead page.

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Spontaneous Rearrangement of Aminochlorocarbene into Chloro Aminocarbyne Complexes. Synthesis of Aminocarbene and Aminocarbyne Complexes and Kinetics and Mechanism of the Rearrangement Reaction[†1]

Helmut Fischer,* Andreas Motsch, Robert Märkl, and Klaus Ackermann

Anorganisch-chemisches Institut der Technischen Universität München, D-8046 Garching, West Germany

Received August 13, 1984

The reaction of $(CO)_5Cr[C(OEt)NR_2]$ (NR_2 = NMe_2, NC_5H_{10}, NEt_2) (**3a–c**) with BCl_3 gives $[(CO)_5Cr{\equiv}CNR_2]^+$ (**4a–c**). The corresponding cationic NPh_2 and N-*i*-Pr_2 compounds (**4d** and **4e**) can be prepared from $(CO)_5Cr[C(NR_2]N{=}C(OMe)Ph]$ (R = Ph, *i*-Pr) and excess BCl_3. **4c** exchanges ^{13}CO for CO at 0 °C with a rate constant of $(2.5 \pm 0.8) \times 10^{-4}\ s^{-1}$. No stereochemical preference for ligand exchange cis or trans to the carbyne ligand could be detected. In solution the cations **4a–d** add Cl^- rapidly to the carbyne carbon to give $(CO)_5Cr[C(Cl)NR_2]$ (**6a–d**). When solutions of **6a–d** are heated, the carbene complexes spontaneously rearrange with extrusion of one CO ligand and neutral carbyne complexes *trans*-$Cl(CO)_4Cr{\equiv}CNR_2$ (**7a–d**) are formed. The reaction of **4e** with Cl^- at −60 °C immediately affords *trans*-$Cl(CO)_4Cr{\equiv}CN$-*i*-Pr_2 instead of $(CO)_5Cr[C(Cl)N$-*i*-$Pr_2]$. The rearrangement of **6a–d** into **7a–d** with elimination of a CO group follows a first-order rate law. The reaction rate is not influenced by the presence of Cl^-, radical initiators, radical inhibitors, PPh_3, or CO (up to a CO pressure of 78 atm) in the solution. The activation entropy is low. The solvent influence is small. Increasing the bulk of the amino substituent, however, strongly enhances the reaction rate. These results suggest that the rearrangement is an intramolecular process involving concerted Cr–CO dissociation and C/Cr migration of Cl. The mechanistic conclusions are discussed with respect to the mechanism for the general synthesis of carbyne complexes by reaction of carbene complexes with halides of group 13 elements.

Introduction

Metal-bound alkylidene (carbene) and alkylidyne (carbyne) groups are believed to play a pivotal role in several catalytic reactions.[2] Complexes in low oxidation states containing a terminally bonded carbene and carbyne ligand, respectively, are closely interrelated: carbene complexes can be transformed into carbyne complexes and vice versa. For instance, the most common method for the preparation of carbyne complexes employs the abstraction of an alkoxy, alkylthio or amino group from a carbene ligand by halides of group 13 elements to give cationic carbyne complexes (eq 1) or, with simultaneous CO/X^-

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[†] The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

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