Organometallics **1985**, *4*, 1619–1623

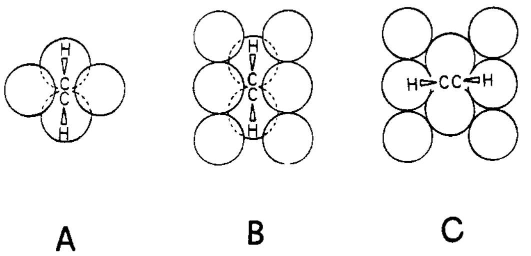

Figure 8. Schematic structures of the title complex and acetylene adsorbed on metal surfaces: A, $Co_4(CO)_{12}C_2H_2$; B, acetylene on Pd(110);[27] C, acetylene on Ni(111).

frequencies of the species belonging to the other group fall in the range 1200–1300 cm^{-1}, values which suggest that the adsorbed molecule is coordinated to more than three metal atoms. Complex I can be a good model for these species, as the butterfly arrangement of four metal atoms can be recognized in the (110) fcc crystal plane involving metal atoms in the first and second layer (Figure 8): an example can be the loss peak at 1240 cm^{-1}, assigned to ν(C–C) of the acetylene adsorbed on Pd(110) at room temperature.[27] On the other hand, the four-atom framework in the (111) fcc crystal plane can be regarded as a "flat" butterfly. The proposed structure of the acetylene adsorbed on it resembles that of complex I (Figure 8), and, actually, the loss peaks corresponding to ν(C–C) have been found at 1215 cm^{-1} for Ni(111) faces[28] and at 1307 cm^{-1} for Cu(111) faces.[25]

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Registry No. I, 12282-40-5; Ia, 96532-36-4; Ib, 96532-37-5; Ic, 96503-22-9; $Co_2(CO)_8$, 10210-68-1; $Co_4(CO)_{12}$, 17786-31-1; DCCD, 1070-74-2; HCCH, 74-86-2; $H^{13}C^{13}CH$, 35121-31-4; CaC_2, 75-20-7; D_2O, 7789-20-0.

Supplementary Material Available: Listing of observed and calculated structure factors, thermal anisotropic parameters, and data of Figure 3 (formula of the complexes, structural values, and full bibliographic references) (21 pages). Ordering information is given on any current masthead page.

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Metal Atom Synthesis of Metallaboron Clusters. 7.[1] Synthesis and Structural Characterization of an Open-Cage Metallathiaborane Cluster Having a Triple-Decker Structure: $4,6\text{-}(\eta\text{-}C_5H_5)_2Co_2\text{-}3,5\text{-}S_2B_2H_2$

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The reaction of thermally generated cobalt atoms with cyclopentadiene, pentaborane(9), and either carbonyl sulfide or hydrogen sulfide was found to give a number of sulfur-containing clusters including the new small cage dicobaltadithiaborane cluster $4,6\text{-}(\eta\text{-}C_5H_5)_2Co_2\text{-}3,5\text{-}S_2B_2H_2$ and the previously reported compounds $\mu_3\text{-}CO\text{-}(\eta\text{-}C_5H_5)_3Co_3S$, $2,3\text{-}(\eta\text{-}C_5H_5)_2Co_2\text{-}6\text{-}SB_5H_7$, and $6,8\text{-}(\eta\text{-}C_5H_5)_2Co_2\text{-}7,9\text{-}S_2B_5H_5$. The results of an X-ray crystallographic study of $4,6\text{-}(\eta\text{-}C_5H_5)_2Co_2\text{-}3,5\text{-}S_2B_2H_2$ demonstrated that the compound has a triple-decker structure based on a pentagonal bipyramid missing one equatorial vertex, with the cobalt atoms occupying apical and the sulfur atoms equatorial positions on the open face. Such a cage geometry is consistent with the cluster's $2n + 4$ skeletal electron count but is not the pentagonal-pyramidal nido structure normally adopted by isoelectronic boron hydride and carborane cage compounds. Crystal data for $4,6\text{-}(\eta\text{-}C_5H_5)_2Co_2\text{-}3,5\text{-}S_2B_2H_2$: space group $P2_1/c$; $Z = 4$; $a = 9.847$ (7) Å, $b = 9.939$ (6) Å, $c = 12.565$ (5) Å, $\beta = 94.01$ (5)°; $V = 1227$ Å^3. The structure was refined by full-matrix least squares to a final R of 0.059 and R_w of 0.062 for the 1418 reflections which had $F_o^2 > 3\sigma(F_o^2)$.

Introduction

We have previously reported[2] the use of metal atom vaporization techniques to produce small cage metallathiaborane, $2,3\text{-}(\eta\text{-}C_5H_5)_2Co_2\text{-}6\text{-}SB_5H_7$, and metalladithiaborane, $6,8\text{-}(\eta\text{-}C_5H_5)_2Co_2\text{-}7,9\text{-}S_2B_5H_5$ and $7\text{-}(\eta\text{-}C_5H_5)Co\text{-}6,8\text{-}S_2B_6H_8$, clusters. These compounds were obtained by the cocondensation of thermally generated cobalt atoms with either pentaborane(9) or hexaborane(10) and cyclopentadiene, followed by reaction with a sulfur source such as cyclohexene sulfide. These results led us to investigate the use other potential sulfur sources in metal atom–boron hydride reactions which might result in either higher yields or the generation of new types of cluster systems. We have now found that if metal vapors are reacted with small boron hydrides and either carbonyl sulfide or hydrogen sulfide, cage fragmentation reactions occur to generate smaller cage metallathiaboron clusters. As an example, we report here the isolation and structural characterization of a unique hybrid cluster, $4,6\text{-}(\eta\text{-}C_5H_5)_2Co_2\text{-}3,5\text{-}S_2B_2H_2$, containing equal numbers of cobalt, sulfur, and boron cage framework atoms.

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Experimental Section

Materials. Cobalt metal (99.9%, 50 mesh) was obtained from Alfa Products/Ventron Division. Cyclopentadiene was freshly distilled from dicyclopentadiene (Aldrich). Pentaborane(9) was obtained from laboratory stock. Carbonyl sulfide (technical grade) and hydrogen sulfide (technical grade) were obtained from Union Carbide. All other reagents were commercially obtained, as indicated, and used as received, except where noted otherwise.

Preparative thin-layer chromatography was performed on 0.5 mm (20 × 20 cm) silica gel F-254 plates (Merck). Silica gel (60–200 mesh) used in silica gel slurries was obtained from VWR Scientific Inc.

Physical Measurements. 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. 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 interfaced to a Kratos DS50S data system. Infrared spectra were obtained on a Perkin-Elmer 337 spectrophotometer.

The metal atom apparatus employed in these studies was based on a design published by Klabunde[3] and is described elsewhere.[4,5]

Reaction of Cobalt Vapor with B_5H_9, C_5H_6, and SCO. Cobalt vapor (~0.9 g) was cocondensed with 15 mL of pentaborane(9), 25 mL of cyclopentadiene, and carbonyl sulfide at −196 °C. Upon completion of metal evaporation and ligand condensation, the reactor was warmed gradually to room temperature and the dark slurry was stirred for an additional 45 min. The reactor was vented to the pump periodically during warm-up to prevent a pressure buildup greater than approximately 460–660 mm of Hg above the reaction mixture. Excess substrates were then removed in vacuo, and the remaining dark residue was immediately extracted with methylene chloride. The extract was filtered through a coarse frit, stirred with silica gel, and filtered again. The resulting filtrate was separated by TLC on silica gel using a 40% benzene in carbon tetrachloride solution. This separation gave as the major product the known complex $(\eta\text{-}C_5H_5)_3Co_3SCO$[6] (30.5 mg), which was identified by direct comparison with a known sample. Also isolated were a number of known metallaborane and metallathiaborane clusters, which were identified by comparison of their mass spectral and ^{11}B NMR data with literature values: 2,3-$(\eta\text{-}C_5H_5)_2Co_2$-6-$SB_5H_7$[2] (5.0 mg), 6,8-$(\eta\text{-}C_5H_5)_2Co_2$-7,9-$S_2B_5H_5$[2] (0.55 mg), 1,2-$(\eta\text{-}C_5H_5)_2Co_2B_4H_6$[7,8] (0.4 mg), 1,2,3-$(\eta\text{-}C_5H_5)_3Co_3B_3H_5$[8] (0.3 mg), and $(\eta\text{-}C_5H_5)_3Co_3B_4H_4$[8] (0.55 mg).

The new metallathiaborane complex 4,6-$(\eta\text{-}C_5H_5)_2Co_2$-3,5-$S_2B_2H_2$ was also isolated in small amounts [R_f 0.60, 3.2 mg] and was purified by TLC by successive developments in a 30% benzene in hexanes solution: purple, mp dec; mass measurement calcd for $^{12}C_{10}{}^{1}H_{12}{}^{32}S_2{}^{11}B_2{}^{59}Co_2$ 335.9228, found 335.9262 (major fragments at m/e 290, $(C_5H_5)(C_5H_4)Co_2SB^+$, m/e 189, $(C_5H_5)_2Co^+$, and m/e 124, $(C_5H_5)Co^+$; ^{11}B NMR (ppm, C_6D_6, 32.1 MHz) 17.6 (J_{BH} = 169 Hz); ^1H NMR (δ, C_6D_6, 100 MHz, ^{11}B spin decoupled) 4.05 (s, $\eta\text{-}C_5H_5$), 5.94 (s, B–H); IR (CS_2 solution, cm^{-1}) 2936 (w), 2908, (m), 2836 (w), 2511 (s), 1956 (w), 1906 (vw), 1804 (vw), 1721 (vw), 1396 (m), 1336 (vw), 1249 (m), 1205 (m), 1106 (w), 1009 (m), 998 (sh, w), 905 (m), 824 (sh, w), 817 (s), 761 (s), 754 (s), 633 (vw), 455 (vw).

Table I. Data Collection and Structure Refinement Information for 4,6-$(\eta\text{-}C_5H_5)_2Co_2$-3,5-$S_2B_2H_2$

space group	$P2_1/c$
a, Å	9.847 (7)
b, Å	9.939 (6)
c, Å	12.565 (5)
β, deg	94.01 (5)
V, Å^3	1227 (2)
Z	4
ρ(calcd), g cm^{-3}	1.818
cryst dimens, mm	0.274 × 0.126 × 0.074
mol formula	$Co_2S_2C_{10}B_2H_{12}$
mol wt	335.82
λ(Mo Kα), Å	0.71073
scanning range, deg	$0 < 2\theta < 55$
h,k,l collected	−12, +12, ±16
no. of measd intensities	2810
unique reflctns, $F_0^2 > 3\sigma(F_0^2)$	1418
no. of variables	145
abs coeff μ, cm^{-1}	29.94
transmissn coeff, %	
maximum	80.51
minimum	69.36
R	0.059
R_w	0.062

Reaction of Cobalt Vapor with B_5H_9, C_5H_6, and H_2S. Cobalt vapor (~0.9 g) was cocondensed with 15 mL of pentaborane(9), 25 mL of cyclopentadiene, and hydrogen sulfide. Upon completion of metal and ligand cocondensation, the resulting matrix was warmed to room temperature and stirred for 45 min. Excess substrates were then removed in vacuo, and the reactor was flushed with nitrogen and opened to the air. The dark residue was immediately extracted in methylene chloride, filtered through a coarse frit funnel, and then stirred with silica gel. The mixture was filtered and separated by TLC on silica gel using a 40% benzene in hexanes solution. The resultant separation yielded 4,6-$(\eta\text{-}C_5H_5)_2Co_2$-3,5-$S_2B_2H_2$ [R_f 0.38, 7.0 mg], along with the complexes 2,3-$(\eta\text{-}C_5H_5)_2Co_2$-6-$SB_5H_7$[2] (5.6 mg), 6,8-$(\eta\text{-}C_5H_5)_2Co_2$-7,9-$S_2B_5H_5$[2] (1.4 mg), 1,2,3-$(\eta\text{-}C_5H_5)_3Co_3B_3H_5$[8] (0.8 mg), and $(\eta\text{-}C_5H_5)_3Co_3SCO$ (2.0 mg) which were identified by comparison of their mass spectral and NMR data with known samples.

Crystallographic Data for 4,6-$(\eta\text{-}C_5H_5)_2Co_2$-3,5-$S_2B_2H_2$. Several opaque, purple crystals of the compound were grown overnight by slow evaporation in air of a benzene solution of the compound. An irregularly shaped crystal of suitable size was selected, and preliminary precession photographs were obtained. Analysis of these photographs clearly showed the existence of two interpenetrating reciprocal lattices, indicating that the crystal was twinned. The twinning was found to arise by a rotation of 180° about the c axis, resulting in the a^* axis of twin one coinciding with the $-a^*$ axis of twin two and the b^* axis of twin one coinciding with the $-b^*$ axis of twin two. This interpenetration of the two reciprocal lattices was readily observable on a zero level precession photograph of the a^*c^* plane. According to this twinning model, reflections hkl of twin one will overlap with reflections $h'k'l'$ of twin two only when $h' = -(h + {}^1/_9)$, $k' = k$, and $l' = l$. This leads to three occurrences of overlapping reflections: $hk0$, $hk9$, and $hk{-9}$ of twin one with $h'k'0$, $h'k'9$, and $h'k'{-9}$ of twin two, respectively. Since it was observed that the intensities of the reflections due to one twin were weaker by a factor of approximately 2, only data on the larger twin were collected and nothing was done to analytically separate the intensities of those relatively few reflections that did overlap. The crystal was then transferred to the diffractometer and an orientation matrix obtained based on only one lattice. Refined cell dimensions and their standard deviations were obtained from the least-squares refinement of 25 accurately centered reflections. See Table I 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 DATARD.

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

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Table II. Final Positional Parameters and Their Estimated Standard Deviations for 4,6-$(\eta\text{-}C_5H_5)_2Co_2$-3,5-$S_2B_2H_2$

atom	x	y	z	B_{eqv}, Å^2	atom	x	y	z	B_{eqv}, Å^2
Co4	0.2551 (1)	0.2326 (1)	0.36848 (9)	3.57 (2)	C43	0.2720 (11)	0.0653 (10)	0.4596 (7)	6.2 (3)
Co6	0.2597 (1)	0.5410 (1)	0.37686 (10)	4.37 (3)	C44	0.1480 (9)	0.0668 (10)	0.4021 (8)	6.3 (3)
S3	0.2342 (3)	0.3814 (3)	0.5001 (2)	5.80 (7)	C45	0.1748 (10)	0.0659 (9)	0.2936 (8)	5.6 (3)
S5	0.3682 (3)	0.3896 (3)	0.2827 (2)	6.29 (7)	C61	0.1481 (10)	0.7085 (10)	0.4062 (9)	6.5 (3)
B1	0.1086 (9)	0.3886 (9)	0.3901 (8)	3.8 (2)	C62	0.1942 (11)	0.7158 (10)	0.3060 (9)	6.9 (3)
B2	0.1741 (11)	0.3925 (9)	0.2633 (7)	3.9 (2)	C63	0.3347 (10)	0.7110 (10)	0.3150 (10)	8.4 (3)
C41	0.3127 (9)	0.0664 (9)	0.2879 (7)	4.9 (2)	C64	0.3781 (11)	0.7049 (11)	0.4193 (11)	9.7 (4)
C42	0.3734 (9)	0.0634 (9)	0.3910 (7)	4.8 (2)	C65	0.2578 (13)	0.7014 (11)	0.4777 (9)	8.0 (3)

Table III. Selected Intramolecular Bond Distances (Å) for 4,6-$(\eta\text{-}C_5H_5)_2Co_2$-3,5-$S_2B_2H_2$

Co4–S3	2.239 (2)	S3–B1	1.791 (7)
Co4–S5	2.237 (2)	S5–B2	1.909 (7)
Co4–B1	2.148 (6)	B1–B2	1.760 (9)
Co4–B2	2.181 (6)	C41–C42	1.389 (8)
Co4–C41	2.039 (6)	C41–C45	1.365 (8)
Co4–C42	2.054 (6)	C42–C43	1.365 (9)
Co4–C43	2.020 (7)	C43–C44	1.375 (10)
Co4–C44	2.018 (7)	C44–C45	1.407 (9)
Co4–C45	2.038 (7)	C61–C62	1.371 (10)
Co6–S3	2.244 (2)	C61–C65	1.357 (11)
Co6–S5	2.232 (2)	C62–C63	1.381 (11)
Co6–B1	2.138 (6)	C63–C64	1.352 (12)
Co6–B2	2.181 (7)	C64–C65	1.437 (12)
Co6–C61	2.043 (7)	Co4–Co6	3.067 (1)
Co6–C62	2.036 (7)	S3–S5	3.117 (3)
Co6–C63	2.021 (8)		
Co6–C64	2.051 (8)		
Co6–C65	2.037 (8)		

Table IV. Selected Bond Angles (deg) for 4,6-$(\eta\text{-}C_5H_5)_2Co_2$-3,5-$S_2B_2H_2$

S3–Co4–S5	88.27 (7)	Co4–B1–B2	67.0 (3)
S3–Co4–B1	48.1 (2)	Co6–B1–S3	69.0 (2)
S3–Co4–B2	85.3 (2)	Co6–B1–B2	67.2 (3)
S5–Co4–B1	85.3 (2)	S3–B1–B2	115.0 (4)
S5–Co4–B2	51.2 (2)	Co4–B2–Co6	89.4 (2)
B1–Co4–B2	48.0 (2)	Co4–B2–S5	65.9 (2)
S3–Co6–S5	88.28 (7)	Co4–B2–B1	65.0 (3)
S3–Co6–B1	48.2 (2)	Co6–B2–S5	65.7 (2)
S3–Co6–B2	85.2 (2)	Co6–B2–B1	64.7 (3)
S5–Co6–B1	85.7 (2)	S5–B2–B1	108.1 (4)
S5–Co6–B2	51.3 (2)	C42–C41–C45	108.4 (6)
B1–Co6–B2	48.1 (2)	C41–C42–C43	107.6 (6)
Co4–S3–Co6	86.35 (6)	C42–C43–C44	109.3 (7)
Co4–S3–B1	63.3 (2)	C43–C44–C45	106.8 (7)
Co6–S3–B1	62.8 (2)	C41–C45–C44	107.9 (6)
Co4–S5–Co6	86.69 (7)	C62–C61–C65	108.1 (8)
Co4–S5–B2	62.9 (2)	C61–C62–C63	108.5 (8)
Co6–S5–B2	63.0 (2)	C62–C63–C64	109.1 (9)
Co4–B1–Co6	91.4 (2)	C63–C64–C65	106.3 (9)
Co4–B1–S3	68.6 (2)	C61–C65–C64	107.9 (9)

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 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 both cobalt atoms. Subsequent Fourier maps phased on these coordinates led to the location of the remaining heavy atoms of the complex. The positions of all hydrogen atoms were calculated and included (but not refined) in the structure factor calculations. Final refinement included an absorption correction along with anisotropic thermal parameters for non-hydrogen atoms and fixed isotropic thermal parameters (5.00) for the hydrogen atoms. The final difference Fourier map displayed an unusually large peak (1.24 e/Å^3) between the sulfur atoms in the B1,B2,S3,S4 plane.

Final positional parameters are given in Table II. Selected intramolecular bond distances and angles are given in Tables III and IV. Listings of final thermal parameters, calculated hydrogen positions, molecular planes, and observed and calculated structure factors are available as supplementary material.

Results and Discussion

Previous work by Zimmerman[2] had demonstrated that metal atom techniques could be used to prepare small cage metallathiaborane clusters directly from boron hydrides, such as pentaborane(9) and hexaborane(10). These reactions utilized cyclohexane sulfide as a sulfur source, and it is significant that in each reaction the metallathiaborane complexes produced retained the same number of boron framework atoms as the starting borane. Thus, reactions with pentaborane(9) gave 6,8-$(\eta\text{-}C_5H_5)_2Co_2$-7,9-$S_2B_5H_5$ and 2,3-$(\eta\text{-}C_5H_5)_2Co_2$-6-$SB_5H_7$ while reactions with hexaborane(10) gave exclusively 7,6,8-$(\eta\text{-}C_5H_5)CoS_2B_6H_8$.

In the present study, the reaction of cobalt atoms with cyclopentadiene, pentaborane(9), and either carbonyl sulfide or hydrogen sulfide were examined, and it was found that these compounds can function as sulfur sources for the formation of metallathiaboranes. However, in contrast to the results obtained with cyclohexene sulfide, it was found that cage fragmentation reactions occur and smaller cage metallathiaborane clusters are produced. Thus, in both reactions with pentaborane(9) the new small cage metallathiaborane cluster 4,6-$(\eta\text{-}C_5H_5)_2Co_2$-3,5-$S_2B_2H_2$ is produced along with the five-boron clusters, 2,3-$(\eta\text{-}C_5H_5)_2Co_2$-6-$SB_5H_7$ and 6,8-$(\eta\text{-}C_5H_5)_2Co_2$-7,9-$S_2B_5H_5$.

The compound 4,6-$(\eta\text{-}C_5H_5)_2Co_2$-3,5-$S_2B_2H_2$ was isolated as a purple, relatively air-stable solid (decomposes slowly over several months). Exact mass measurements on the parent envelope are consistent with the proposed molecular formula. The mass spectrum also shows fragmentation corresponding to the loss of a SBH_3 group (P − 46 m/e) along with peaks characteristic of $CoCp_2^+$ (m/e 189) and $CoCp^+$ (m/e 124).

The ^{11}B NMR spectrum at 32.1 MHz shows a single doublet resonance. The boron-decoupled ^1H NMR spectrum at 100 MHz displays a single B–H resonance along with a single cyclopentadienyl resonance in a 1:5 ratio. Thus, the NMR data indicate that both boron atoms and both cobalt atoms must be in equivalent cage positions, requiring at least local C_s symmetry for the cobaltathiaborane cage.

The compound is an example of a $2n + 4$ skeletal electron cage system (6 cage atoms, 16 skeletal electrons), and with use of simple electron-counting rules[13] its structure would be predicted to be based on an open-cage six-vertex (nido) configuration. As shown in Figure 2, there are two different nido cage geometries possible for the compound which are consistent with the NMR data. The pentago-

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Table V. **Metal-Metal and Metal-Ring Distances (Å) in Triple-Decker Complexes**

compd[a]	M1-M2[b]	M1-OR[c]	M2-OR[c]	M1-IR[d]	M2-IR[d]	ref
4,6-(η-C_5H_5)$_2$$Co_2$-3,5-$S_2B_2H_2$	3.067	1.660	1.666	1.535	1.532	this work
2-CH_3-1,7,2,4-(η-C_5H_5)$_2$$Co_2C_2B_3H_4$ (I)	3.137	1.655		1.570		28
μ-(2,3)-C_3H_4-1,7,2,3-(η-C_5H_5)$_2$$Co_2C_2B_3H_3$ (II)	3.135	1.662	1.657	1.571	1.564	29
4,5-(C_2H_5)$_2$-3,6-(CH_3)$_2$-1-(η-C_5H_5)Fe-7-(η-C_5H_5)Co-2,4,5-C_3B_2H (III)	3.204	1.659	1.659	1.624	1.580	30
4,5-(C_2H_5)$_2$-3,6-(CH_3)$_2$-1,7-(η-C_5H_5)$_2$$Fe_2$-2-$SC_2B_2$ (IV)	3.236					31
2-C_6H_5-3-C_2H_5-1,7-(η-C_5H_5)$_2$$Fe_2$-2-$BC_4H_3$ (V)	3.268					32
4,5-(C_2H_5)$_2$-3,6-(CH_3)$_2$-1-(η-C_5H_5)Ni-7-(η-C_5H_5)Co-2,4,5-C_3B_2H (VI)	3.337	1.775	1.665	1.725	1.609	30
4,5-(C_2H_5)$_2$-3,6-(CH_3)$_2$-1,7-(η-C_5H_5)$_2$$Ni_2$-2,4,5-$C_3B_2H$ (VII)	3.416	1.775	1.747	1.720	1.698	30
[1,7-(η-C_5H_5)$_2$$Ni_2C_5H_5$]$^+$ (VIII)	3.576	1.745	1.711	1.771	1.805	33
(η-C_5H_5)$_2$$V_2$($\eta^6$-$C_6H_6$) (IX)	3.403	1.922		1.702		34

[a] The complexes in this table have been numbered by using the recently proposed nomenclature system for polyhedral cage compounds. See: Casey, J. B.; Evans, W. J.; Powell, W. H. *Inorg. Chem.* **1983**, *22*, 2228-2235, 2236-2245. [b] Metal-Metal distance. [c] Metal to outer-ring centroid distance. [d] Metal to inner-ring centroid distance.

nal-pyramidal structure in Figure 2a is based on a pentagonal bipyramid missing an apical position, while the structure shown in Figure 2b is obtained by removing an equatorial position.

The most common structure for six-vertex nido cage systems is the pentagonal pyramid, and, in fact, there is a complete series of nido borane–carborane–hydrocarbon clusters which adopt this configuration: B_6H_{10},[14] CB_5H_9,[15] $C_2B_4H_8$,[16] $C_3B_3H_7$,[17] $C_4B_2H_6$,[18] [C_5Me_5BI]$^+$,[19] and $Me_6C_6{}^{2+}$.[20] There are also numerous examples of metallaborane, -carborane, and -hydrocarbon complexes, including compounds such as $(CO)_3FeB_5H_{10}$,[21] $(CO)_3FeC_2B_3H_7$,[22] $(CO)_3Mn(\eta\text{-}C_5H_5)$,[23] and $R_4C_4Fe_2(CO)_6$[24] having the pentagonal-pyramidal structure.

The alternate structure which has a missing equatorial, rather than apical, position appears to be relatively rare. Although two metal clusters $(\eta\text{-}C_5H_5)_2Ni_2Fe_2(CO)_6(C_2Et_2)$[25] and $S_2Os_4(CO)_{12}$[26] have been shown to adopt this structure, there have been no previous reports of a boron or metallaboron cluster with this cage geometry. However, as can be seen in the ORTEP drawing in Figure 1, an X-ray crystallographic determination of 4,6-$(\eta\text{-}C_5H_5)_2Co_2$-3,5-$S_2B_2H_2$, carried out on a twinned crystal, has established that the compound has such a structure.

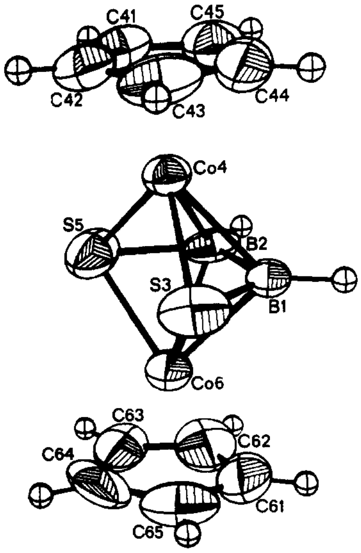

Figure 1. ORTEP Drawing of 4,6-$(\eta\text{-}C_5H_5)_2Co_2$-3,5-$S_2B_2H_2$.

The cage has C_{2v} symmetry with the cobalt atoms located in the apical positions and the boron and sulfur atoms in equatoral positions of the parent pentagonal-bipyramidal polyhedron. The two cobalt atoms and the two sulfur atoms are situated on the open face of the cluster. The nonbonded S3–S5 distance of 3.117 (3) Å is similar to the analogous S–S distance observed in the isostructural cluster $S_2Os_4(CO)_{12}$ (3.191 Å).[26] The boron and sulfur atoms are planar, and this plane is parallel to the planes of the two cyclopentadienyl rings. The compound can thus be considered a "triple-decker" complex in which each cobalt atom is sandwiched between one cyclopentadienyl ring and the open $S_2B_2H_2$ ligand in the bridging position.

The first triple-decker complex $(\eta\text{-}C_5H_5)_3Ni_2{}^+$ was reported by Werner and Salzer in 1972.[27] Since that time a number of such complexes have been reported in which

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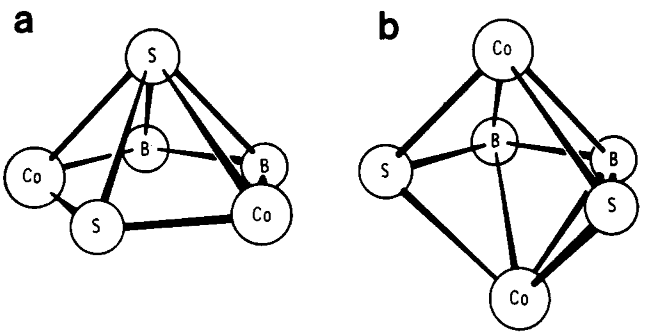

Figure 2. Possible nido cage structures for (η-C_5H_5)$_2Co_2S_2B_2H_2$.

two metals are sandwiched between three planar rings or "decks" with the central deck usually consisting of a five-membered ring. The two metals and the central ring can thus be considered to form a closo pentagonal-bipyramidal polyhedron. Complexes with bridging arene ligands have also recently been characterized.[34] Examples of structurally characterized triple-decker complexes along with the observed metal–metal and metal–ring distances are presented in Table V for comparison with 4,6-(η-C_5H_5)$_2Co_2$-3,5-$S_2B_2H_2$.

The majority of triple-decker complexes contain 30 valence electrons[35] (or in a cluster terminology 16 skeletal cage electrons) and therefore are in agreement with cluster electron-counting rules. However, complexes having 29 and 31–34 valence electrons (15, 17-20 central cage electrons) are also known.[28-34] The extra electrons in these complexes do not result in cage opening but instead result in a lengthening of the metal to ring distances.[35] Thus, the 30-valence-electron clusters I–V all have metal–metal distances in the range of 3.1–3.27 Å, while the 32-electron compound VI has 3.337 Å, the 33-electron VII has 3.416 Å, and the 34-electron VIII has 3.576 Å metal–metal distances.

The compound 4,6-(η-C_5H_5)$_2Co_2$-3,5-$S_2B_2H_2$ is, in fact, an example of a 30-electron triple-decker [three six-electron-donating decks (assuming a formal $S_2B_2H_2^{4-}$ ligand) and 12 d electrons on the two metals]. As can be seen in the table, the compound has shortened cobalt–cobalt and cobalt–central plane distances consistent with this interpretation. In fact, these distances are shorter than those observed in any of the 30-electron closo triple-decker complexes, I–V. Thus, the open S_2B_2 deck apparently allows a closer interaction between the two metals than is possible in the isoelectronic closo systems. These results suggest that there may be a variety of open cage triple-decker complexes yet to be discovered which will allow a variable range of metal interactions resulting in new electronic properties for these types of complexes.

The fact that 4,6-(η-C_5H_5)$_2Co_2$-3,5-$S_2B_2H_2$ has a structure similar to that shown in Figure 2b rather than the more common pentagonal-byramidal structure, such as the one in Figure 2a, is probably related to the preferred bonding arrangements of the cobalt and sulfur atoms. Indeed, it is not unusual for metallathiaborane clusters to adopt structures somewhat different than their corresponding metallaborane and metallacarborane analogues. For example, we have previously demonstrated[2] that the cluster 2,3-(η-C_5H_5)$_2Co_2$-6-SB_5H_7 is the first example of an eight-vertex $2n + 4$ skeletal electron cluster to adopt a nido geometry, based on a tricapped trigonal prism missing one vertex, while the corresponding metallaborane or metallacarborane complexes adopt either closo or arachno structures.

The structure found for 4,6-(η-C_5H_5)$_2Co_2$·3,5-$S_2B_2H_2$ allows both cobalt atoms to adopt higher coordinate and both sulfur atoms to adopt lower coordinate positions in the polyhedron. Likewise, this structure allows the maximum separation between the two cobalt atoms and between the two sulfur atoms. Such arrangements are, in fact, in agreement with the previously observed bonding tendencies of metals and sulfur atoms in polyhedral boron clusters.

Finally, it should also be noted that the major product of the reaction employing carbonyl sulfide as a reactant was the cobalt–sulfur cluster μ_3-CO-(η-C_5H_5)$_3Co_3S$. This observation suggests that metal atom reactions may be of use in the future not only for the synthesis of new types of metallaboron clusters but may also be useful for the preparation of other transition-metal main-group heteronuclear clusters.

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Registry No. (η-C_5H_5)$_3Co_3SCO$, 37328-31-7; 2,3-(η-C_5H_5)$_2Co_2$-6-SB_5H_7, 78005-20-6; 6,8-(η-C_5H_5)$_2$-7,9-$S_2B_5H_5$, 76705-73-2; 1,2-(η-C_5H_5)$_2Co_2B_4H_6$, 43062-01-7; 1,2,3-(η-C_5H_5)$_3Co_3B_3H_5$, 59217-07-1; (η-C_5H_5)$_3Co_3B_4H_4$, 59458-52-5; 4,6-(η-C_5H_5)$_2Co_2$-3,5-$S_2B_2H_2$, 97391-50-9; Co, 7440-48-4; B_5H_9, 19624-22-7; C_5H_6, 542-92-7; SCO, 463-58-1; H_2S, 7783-06-4.

Supplementary Material Available: Tables of temperature factors, calculated positional parameters, molecular planes and angles, and structure factors (18 pages). Ordering information is given on any current masthead page.

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