Inorg. Chem. **1989**, *28*, 961–964 **961**

Notes

Contribution from the Department of Chemistry
and Laboratory for Research on the Structure
of Matter, University of Pennsylvania,
Philadelphia, Pennsylvania 19104-6323

Metal Atom Synthesis of Metallaboron Clusters. 11.[1] Synthesis and Characterization of (η-C_5R_5)cobaltathiaborane Clusters (R = H, Me)

Sang Ook Kang, Patrick J. Carroll, and Larry G. Sneddon*

Received August 30, 1988

We recently demonstrated[1] that metal vapor techniques can be employed to generate (η^6-arene)ferrathiaborane complexes in good yields. For example, reaction of *nido*-6-$SB_{10}H_{12}$ with iron atoms and toluene resulted in the formation of 2-(η^6-MeC_6H_5)-Fe-1-$SB_{10}H_{10}$ in 59% yield, while the analogous reaction with *nido*-6-SB_9H_{11} gave 8-(η^6-MeC_6H_5)Fe-7-SB_9H_{11} in 65% yield. These results suggested that metal vapor reactions might provide a useful approach to the synthesis of a wide range of new metallathiaborane clusters. In this note we explore the extension of this technique to the preparation of (η-C_5H_5)Co-substituted complexes derived from the thiaboranes *nido*-7-$SB_{10}H_{12}$, *nido*-6-SB_9H_{11}, and *arachno*-4-SB_8H_{12}.

Experimental Section

Materials. Cobalt metal (99.9%, 100 mesh) was obtained from Alfa Ventron Corp. Cyclopentadiene was freshly distilled from dicyclopentadiene (Aldrich). Pentamethylcyclopentadiene was prepared by using a standard method.[2] Toluene was dried over calcium chloride. The thiaboranes *nido*-7-$SB_{10}H_{12}$,[3] *nido*-6-SB_9H_{11},[4] and *arachno*-4-SB_8H_{12}[3] were prepared as described previously. All other reagents were commercially obtained and used as received.

Preparative thin-layer chromatography was conducted on 0.5-mm (20 × 20 cm) silica-gel F-254 plates (Merck). Analytical thin-layer chromatography was conducted on 0.25-mm (5 × 10 cm) silica-gel F-254 plates (Merck). Flash column chromatography was performed with silica gel (230–400 mesh, EM Science). The Chromatotron (7924T) was purchased from Harrison Research, Palo Alto, CA.

Physical Measurements and Instrumentation. Boron-11 NMR spectra at 160.5 MHz were obtained on a Bruker AP-500 spectrometer equipped with the appropriate decoupling accessories. Proton NMR spectra at 250 and 200 MHz were obtained on Bruker WM-250 and AP-200 Fourier transform spectrometers, respectively. All boron-11 chemical shifts are referenced to $BF_3 \cdot O(C_2H_5)_2$ (0.0 ppm), with a negative sign indicating an upfield shift.

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. Infrared spectra were obtained on a Perkin-Elmer 1310 spectrophotometer.

The metal atom apparatus employed in these studies was based on a published design[5] and is described elsewhere.[6]

Reaction of Cobalt Vapor with *nido*-7-$SB_{10}H_{12}$ and C_5H_6. A 1.5-g (9.9-mmol) sample of *nido*-7-$SB_{10}H_{12}$ was placed in the bottom of the metal vapor reactor before assembly. The reactor was evacuated, and cobalt vapor (0.3 g) was cocondensed into the reactor at −196 °C over a 1–2-h period with 20 mL of cyclopentadiene. Upon completion of metal vaporization and ligand cocondensation, the reactor was warmed to room temperature and the condensate allowed to melt and flow to the bottom of the reactor, where it mixed with the *nido*-7-$SB_{10}H_{12}$. This mixture was then stirred for 1 h at room temperature. Removal of the excess ligands in vacuo left a residue, from which 0.5 g (3.3 mmol) of unreacted *nido*-7-$SB_{10}H_{12}$ was sublimed. The remaining yellow solid was then dissolved in the methylene chloride, and the solution was filtered. Separation of the filtrate by TLC on silica-gel plates using a 1:1 hexane/benzene solution as the eluant gave the known complex *closo*-2-(η-C_5H_5)Co-1-$SB_{10}H_{10}$ (I): $R_f = 0.62$; orange; 70 mg (4%); mp 267 °C (lit.[7] mp 267.5–268.5 °C); ^1H NMR (δ, C_6D_6, 250 MHz) 4.4 (C_5H_5); mass measurement calcd for $^{12}C_5{}^1H_{15}{}^{32}S^{11}B_{10}{}^{59}Co$ 276.116, found 276.112.

Reaction of Cobalt Vapor with *nido*-7-$SB_{10}H_{12}$, $C_5(CH_3)_5H$, and Toluene. In a similar manner as described above, 0.3 g of cobalt vapor was reacted with 10 mL of pentamethylcyclopentadiene, 20 mL of toluene, and 1.5 g (9.9 mmol) of *nido*-7-$SB_{10}H_{12}$. Following the reaction, excess ligands were removed in vacuo and unreacted *nido*-7-$SB_{10}H_{12}$ (0.4 g, 2.6 mmol) was sublimed from the products, leaving a yellow residue, which was extracted in methylene chloride. This solution was filtered, and the products were separated on silica-gel TLC plates with a 1:4 hexane/benzene solution as the eluant solvent. This separation gave *closo*-2-(η-$C_5(CH_3)_5$)Co-1-$SB_{10}H_{10}$ (II): $R_f = 0.62$; yellow; 120 mg (5%); mp 240 °C; ^1H NMR (δ, $CDCl_3$, 200 MHz) 1.86 ($C_5(CH_3)_5$); mass measurement calcd for $^{12}C_{10}{}^1H_{25}{}^{32}S^{11}B_{10}{}^{59}Co$ 346.194, found 346.198.

Reaction of Cobalt Vapor with *nido*-6-SB_9H_{11} and C_5H_6. In a manner similar to that described above, 0.3 g of cobalt metal was cocondensed with 20 mL of cyclopentadiene. After metal vaporization was complete, the reactor was allowed to warm to −78 °C, whereupon the matrix melted, flowed to the bottom of the reactor, and mixed with 1.5 g (10.7 mmol) of *nido*-6-SB_9H_{11}. The resulting dark viscous solution was stirred at −78 °C for 40 min and then slowly warmed to room temperature. After an additional 30-min stirring at room temperature, the volatile materials were removed in vacuo. The residue was extracted with methylene chloride, and the mixture was filtered and evaporated to dryness. Extraction with hexane gave a yellow oily product that was identified by its mass spectrum and ^{11}B NMR data as the known hydroboration product,[8] *nido*-9-C_5H_7-6-SB_9H_{10} (0.7 g). The remaining solid materials, which were insoluble in hexane, were redissolved in methylene chloride and separated by use of the Chromatotron. Elution with carbon tetrachloride gave the red-violet compound *arachno*-7-(η-C_5H_5)Co-6,8-$S_2B_6H_8$ (2 mg), which was identified by comparison of its NMR data with reported values.[9] Elution with 3:2 carbon tetrachloride/chloroform gave the following compounds. *closo*-7-I-2,3-(η-C_5H_5)$_2$Co$_2$-1-SB_9H_8 (IV): $R_f = 0.56$ (in chloroform); dark red; 22 mg (0.4%); mp 303 °C dec; ^1H NMR (δ, $CDCl_3$, 250 MHz) 5.52 (C_5H_5); mass measurement calcd for $^{12}C_{10}{}^1H_{18}{}^{32}S^{11}B_9{}^{59}Co_2{}^{127}I$ 513.9673, found 513.9677. *closo*-2,3-(η-C_5H_5)$_2$Co$_2$-1-SB_9H_9 (III): $R_f = 0.49$ (in chloroform); dark red; 86 mg (2%); mp 304 °C dec; ^1H NMR (δ, $CDCl_3$, 250 MHz) 5.2 (C_5H_5); mass measurement calcd for $^{12}C_{10}{}^1H_{19}{}^{32}S^{11}B_9{}^{59}Co_2$ 388.071, found 388.081. *closo*-7-C_5H_7-2,3-(η-C_5H_5)$_2$Co$_2$-1-SB_9H_8: $R_f = 0.60$ (in chloroform); red; 1 mg; mass measurement calcd for $^{12}C_{15}{}^1H_{25}{}^{32}S^{11}B_9{}^{59}Co_2$ 454.1178, found 454.1166. Chloroform as the eluant gave *arachno*-9-[(η-C_5H_5)Co(η-C_5H_4)$^+$][6-$SB_9H_{11}{}^-$] (V): $R_f =$ 0.44 (in 1:1 benzene/methylene chloride); bright yellow; 64 mg (2%); mp > 340 °C; ^1H NMR (δ, CD_2Cl_2, 200 MHz) 5.52 (m, 2, C_5H_4), 5.43 (5, C_5H_5), 5.37 (m, 2, C_5H_4); mass measurement calcd for $^{12}C_{10}{}^1H_{20}{}^{32}S^{11}B_9{}^{59}Co$ 330.146, found 330.153. Extraction of the remaining reaction residue with acetonitrile followed by addition of methylene chloride resulted in precipitation of [(η-C_5H_5)$_2$Co]$^+$[$B_{18}H_{21}$]$^-$: $R_f = 0.48$ (in 1:1 acetonitrile/methylene chloride); yellow; 92 mg (4%); identified by comparison of its NMR data with reported values.[10]

Reaction of Cobalt Vapor with *nido*-6-SB_9H_{11}, $C_5(CH_3)_5H$, and Toluene. Cobalt vapor (0.3 g) was cocondensed with a mixture of 10 mL of pentamethylcyclopentadiene and 20 mL of toluene at −196 °C. The

---

[1] For Part 10, see: Kang, S. O.; Carroll, P. J.; Sneddon, L. G. *Organometallics* **1988**, *7*, 772–776.

[2] Manriquez, J. M.; Fagan, P. J.; Schertz, L. D.; Marks, T. J. *Inorg. Synth.* **1982**, *21*, 181–185.

[3] Kang, S. O.; Sneddon, L. G. *Inorg. Chem.* **1988**, *27*, 3298–3300.

[4] (a) Rudolph, R. W.; Pretzer, W. R. *Inorg. Synth.* **1983**, *22*, 226–231. (b) Pretzer, W. R.; Rudolph, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 1441–1447.

[5] Klabunde, K. J.; Timms, P.; Skell, P. S.; Ittel, S. D. *Inorg. Synth.* **1979**, *19*, 59–86.

[6] Zimmerman, G. J.; Hall, L. J.; Sneddon, L. G. *Inorg. Chem.* **1980**, *19*, 3642–3650.

[7] Hertler, W. R.; Klanberg, F.; Muetterties, E. L. *Inorg. Chem.* **1967**, *6*, 1696–1706.

[8] (a) Meneghelli, B. J.; Rudolph, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 4626–4627. (b) Meneghelli, B. J.; Bower, M.; Canter, N.; Rudolph, R. W. *J. Am. Chem. Soc.* **1980**, *102*, 4355–4360.

[9] Zimmerman, G. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **1981**, *103*, 1102–1111.

[10] Swicker, F. A. Ph.D. Thesis, University of Pittsburgh, 1971.

0020-1669/89/1328-0961$01.50/0

Table I. ^{11}B NMR Data[a]

compd	δ, ppm (J, Hz)	rel intens
closo-2-(η-C_5H_5)Co-1-$SB_{10}H_{10}$[b] (I)	15.3 (160), 13.9 (145), 11.2 (150), 2.5 (160), −4.4 (145), −14.1 (165)	1:2:1:2:2:2
closo-2-(η-$C_5(CH_3)_5$)Co-1-$SB_{10}H_{10}$[b] (II)	16.4 (130), 14.0 (145), 6.2 (145), 3.9 (145), −6.5 (130), −15.4 (160)	2:1:1:2:2:2
closo-2,3-(η-C_5H_5)$_2$$Co_2$-1-$SB_9H_9$[b] (III)	39.5 (130), 10.7 (∼100),[c] 10.1 (∼130),[c] 7.6 (145), −5.8 (160), −21.7 (180)	1:2:2:1:2:1
closo-7-I-2,3-(η-C_5H_5)$_2$$Co_2$-1-$SB_9H_8$[b] (IV)	24.8 (s), 12.3 (130), 10.0 (∼145),[c] −6.8 (160), −22.8 (175)	1:2:3:2:1
arachno-9-[(η-C_5H_5)Co(η-C_5H_4)$^+$][6-$SB_9H_{11}^-$][d] (V)	5.9 (120), −6.8 (∼165),[c] −9.5 (∼200),[c] −12.2 (∼120),[c] −29.5 (135), −35.6 (150)	1:2:1:1:2:2
nido-8-(η-$C_5(CH_3)_5$)Co-7-SB_9H_{11}[b] (VI)	13.5 (145), 6.8 (160), 0.6 (145), −9.5 (∼175),[c] −10.8 (∼175),[c] −15.4 (∼160),[c] −16.7 (∼200),[c] −18.0 (∼175)[c]	1:1:2:1:1:1:1:1
closo-6-(η-C_5H_5)Co-1-SB_8H_8[b] (VII)	77.2 (160), 7.1 (145), 1.5 (160), −9.6 (160), −20.9 (150)	1:2:1:2:2

[a] CD_2Cl_2 solutions. [b] 160.5 MHz [c] Coupling constants could not be reliably measured due to overlapping peaks. [d] 64.2 MHz.

reactor was then warmed to room temperature, which resulted in the condensate melting and flowing to the bottom of the reactor where it mixed with 1.2 g (8.5 mmol) of *nido*-6-SB_9H_{11}. After the reaction mixture was stirred at room temperature for 90 min, the volatile reactants were removed in vacuo. Sublimation at 40 °C under high vacuum gave 0.3 g (2.1 mmol) of unreacted *nido*-6-SB_9H_{11}. The residue was extracted with methylene chloride and the filtrate separated by TLC on silica gel using a 1:1 hexane/benzene eluant to give one major product *nido*-8-(η-$C_5(CH_3)_5$)Co-7-SB_9H_{11} (VI): $R_f = 0.65$ (in benzene); orange-yellow; 86 mg (4%); mp 220 °C; ^{1}H NMR (δ, $CDCl_3$, 250 MHz) 1.84 (15, $C_5(CH_3)_5$), −4.6 (1, BHB), −13.1 (1, qt, J = 35 Hz, BHCo); mass measurement calcd for $^{12}C_{10}{}^1H_{26}{}^{32}S^{11}B_9{}^{59}Co$ 336.193, found 336.189. Only trace amounts (<1 mg) of other products were found, including *nido*-4,6-(η-$C_5(CH_3)_5$)$_2$-3,5-$Co_2S_2B_2H_2$[11] and *closo*-2-(η-$C_5(CH_3)_5$)Co-1-$SB_{10}H_{10}$.

Reaction of Cobalt Vapor with *arachno*-4-SB_8H_{12} and C_5H_6. Approximately 0.6 g (4.6 mmol) of *arachno*-4-SB_8H_{12} was dissolved in hexane and quickly transferred to the metal vapor reactor. The hexane was then vacuum-evaporated and *arachno*-4-SB_8H_{12} sublimed onto the walls of the reactor. Cobalt vapor and 20 mL of cyclopentadiene were then condensed onto the walls at −196 °C. After metal deposition was complete, the reactor was allowed to warm to −78 °C whereupon the matrix melted and flowed to the bottom of the reactor. This mixture was stirred for 40 min at −78 °C and then warmed to room temperature and stirred for an additional 90 min. The volatile components were removed in vacuo, the reaction residue was extracted with methylene chloride, and the mixture was filtered and concentrated. Separation by flash column chromatography with hexane gave a small amount (∼50 mg) of unreacted *arachno*-4-SB_8H_{12}. Further separation with chloroform gave a reddish orange solution, which was then separated by TLC on silica-gel plates with chloroform eluant to give the following compounds. *closo*-6-(η-C_5H_5)Co-1-SB_8H_8 (VII): $R_f = 0.72$ (in chloroform); reddish orange; 2 mg; mp 173 °C; ^{1}H NMR (δ, C_6D_6, 250 MHz) 4.1 (C_5H_5); mass measurement calcd for $^{12}C_5{}^1H_{13}{}^{32}S^{11}B_8{}^{59}Co$ 252.082, found 252.081. *closo*-2-(η-C_5H_5)Co-1-$SB_{10}H_{10}$ (I): 3 mg.

Iodination of *closo*-2,3-(η-C_5H_5)$_2$$Co_2$-1-$SB_9H_9$ (III). A 20-mg (0.051-mmol) sample of III was mixed with ∼20 mg (excess) of I_2 in a reaction tube. The tube was evacuated, sealed, and heated at 250 °C for 1 day. The purple I_2 color faded, and a reddish black solid was formed. The tube was opened, and the contents were extracted with methylene chloride. The compound *closo*-7-I-2,3-(η-C_5H_5)$_2$$Co_2$-1-$SB_9H_8$ (IV) (∼1 mg) was identified by comparison of its R_f value and color with those of an authentic sample.

Crystallographic Studies of *closo*-7-I-2,3-(η-C_5H_5)$_2$$Co_2$-1-$SB_9H_8$ (IV) and *arachno*-9-[(η-C_5H_5)Co(η-C_5H_4)$^+$][6-$SB_9H_{11}^-$] (V). Single crystals were grown over several days by slow diffusion of heptane into a dichloroethane solution of IV and by slow evaporation in air of an acetonitrile/methylene chloride solution of V. Diffraction data were collected at 295 K on an Enraf-Nonius four-circle CAD-4 diffractometer employing Mo Kα radiation from a graphite-crystal monochromator. Procedures for data collection and refinement are reported elsewhere.[1] Details concerning IV and V are given in Table II.

Three-dimensional Patterson syntheses gave the coordinate of the metal atoms, and subsequent Fourier maps led to the location of the remaining heavy atoms. Anisotropic refinements followed by difference Fourier syntheses resulted in the location of all cage hydrogens in IV. Hydrogen positions on the cyclopentadiene ring of compound IV were calculated by using the HYDRO program. All hydrogens of IV were included (but not refined) in the structure factor calculations. All hydrogens of V were located by difference Fourier syntheses and refined. Final refinements included numerical absorption corrections along with anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms. The largest residual peaks not in the areas of the heavy atoms in the final difference Fourier maps for IV and V were 0.49 and 0.32 e/Å^3, respectively.

Table II. Data Collection and Structure Refinement Information

	IV	V
space group	$P2_1/n$	$P2_1/n$
a, Å	9.039 (1)	11.409 (2)
b, Å	14.183 (1)	13.491 (2)
c, Å	13.622 (2)	10.761 (1)
β, deg	96.01 (1)	103.58 (1)
V, Å^3	1736.9	1610.0
Z	4	4
ρ(calcd), g cm^{-3}	1.959	1.355
cryst dimens, mm	0.15 × 0.28 × 0.23	0.20 × 0.50 × 0.25
mol formula	$C_{10}H_{15}B_9Co_2IS$	$C_{10}H_{20}B_9CoS$
mol wt	512.39	328.57
λ(Mo Kα), Å	0.71703	0.71703
scanning range, deg	$4 \leq 2\theta \leq 55$	$4 \leq 2\theta \leq 55$
scan mode	ω–2θ	ω–2θ
$\pm h,\pm k,\pm l$ collected	±11,18,17	±14,17,14
no. of measd I's	4314	4050
no. of $F_o^2 > 3\sigma(F_o^2)$	3447	2885
no. of variables	208	270
abs coeff (μ), cm^{-1}	37.695	20.940
trans coeff, %	52.4	60.6
max, min trans, %	59.1, 38.8	68.3, 38.1
R	0.049	0.045
R_w	0.070	0.054

Results and Discussion

The reaction of cobalt atoms with either cyclopentadiene or pentamethylcyclopentadiene and *nido*-7-$SB_{10}H_{12}$ resulted in hydrogen loss and cobalt insertion into the open face of the thiaborane to form the known sandwich complex *closo*-2-(η-C_5H_5)Co-1-$SB_{10}H_{10}$ (I)[7] and its Cp* analogue *closo*-2-(η-C_5Me_5)Co-1-$SB_{10}H_{10}$ (II), respectively.

The reaction of cobalt atoms with cyclopentadiene and *nido*-6-SB_9H_{11} resulted in the low-yield formation of several new thiametallaboranes; however, the major product of the reaction was the hydroboration product, 9-C_5H_7-6-SB_9H_{11}. Rudolph[8] has previously demonstrated that *nido*-6-SB_9H_{11} is unique among the polyhedral boranes in that it readily hydroborates olefins, including cyclopentadiene. Thus, this competing reaction inhibits cobaltathiaborane formation.

Three metal complexes were isolated in sufficient amounts to allow characterization. On the basis of exact mass measurements, complex III had the composition (C_5H_5)$_2$$Co_2SB_9H_9$. A compound of this formula would be a 12-vertex $2n + 2$ skeletal electron system and should have a structure based on icosahedral geometry. The ^{11}B NMR spectrum of III showed six doublets of relative intensities 1:2:2:1:2:1, and the ^{1}H NMR spectrum showed only one cyclopentadienyl singlet, indicating that the complex must have mirror symmetry. A structure that is in agreement with these data and with the structural study, discussed below, of compound IV is an icosahedron in which the two cobalt atoms and the sulfur atom are located on one triangular face. An isomer of III, 2,4-(η-C_5H_5)$_2$$Co_2$-1-$SB_9H_9$, has been cited[12] previously; however, details of its synthesis and characterization have not been published. Likewise, a selenium analogue, (η-C_5H_5)$_2$$Co_2SeB_9H_9$, in which the relative heteroatom positions were not assigned, has also been prepared.[13]

---

(11) Kang, S. O.; Sneddon, L. G. *Inorg. Chem.* **1988**, *27*, 3769–3772.

(12) Plzák, Z.; Plešek, J.; Štíbr, B. *J. Chromatogr.* **1979**, *168*, 280–283.

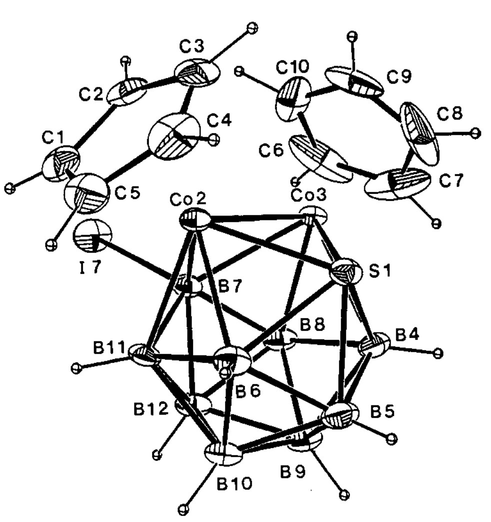

Figure 1. ORTEP drawing of the molecular structure of *closo*-7-I-2,3-$(\eta\text{-}C_5H_5)_2Co_2$-1-$SB_9H_8$ (IV).

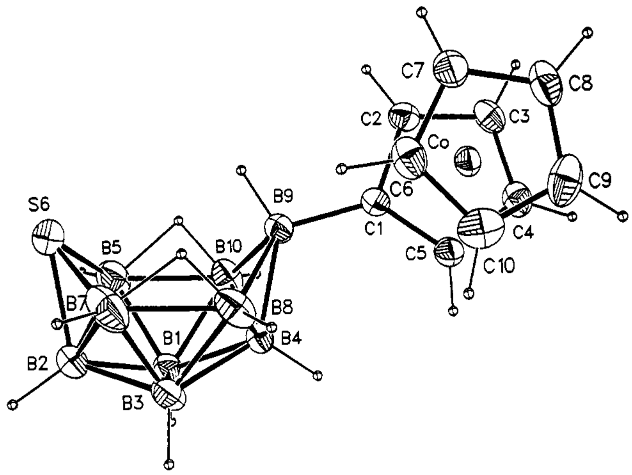

Figure 2. ORTEP drawing of the molecular structure of *arachno*-9-$[(\eta\text{-}C_5H_5)Co(\eta\text{-}C_5H_4)^+][6\text{-}SB_9H_{11}^-]$ (V).

Surprisingly, compound IV, *closo*-7-I-2,3-$(\eta\text{-}C_5H_5)_2Co_2$-1-$SB_9H_8$, which was found to be an iodo derivative of III, was also isolated from the reaction. The synthesis[4] of *nido*-SB_9H_{11} involves the iodine oxidation of *arachno*-$SB_9H_{12}^-$; thus, the iodine substituent in IV must have come from reaction of trace iodine impurities remaining in the starting *nido*-SB_9H_{11}. Indeed, a separate experiment demonstrated that IV can be formed by the direct reaction of III with iodine.

A crystallographic investigation of IV established the cage geometry shown in Figure 1 and supports the structure proposed above for III. The compound adopts a closed icosahedral geometry where the sulfur and cobalt atoms are located in adjacent positions. The iodine atom is bound to the 7-boron atom, which is also adjacent to the two cobalt atoms. The structure is essentially identical with that observed for the isoelectronic cluster *closo*-7-Cl-2,3-$(\eta\text{-}C_5(CH_3)_5)_2Rh_2$-1-$SB_9H_8$.[14] The two cobalt atoms in IV are separated by 2.4953 (8) Å, and the remaining bond angles and distances are within the normal ranges observed for thiaborane and metallathiaborane clusters.

As shown in Figure 2, an X-ray structure study of V, *arachno*-9-$[(\eta\text{-}C_5H_5)Co(\eta\text{-}C_5H_4)^+][6\text{-}SB_9H_{11}^-]$, revealed a zwitterionic structure in which a cobaltocenium group is bound to the thiaborane cage via a carbon–boron bond (1.586 (4) Å) between one of the cyclopentadienyl ring carbons and B9, with substitution occurring at the exo position on the boron. The starting *nido*-6-SB_9H_{11} cage has thus been reduced and is a derivative of the *arachno*-$SB_9H_{12}^-$ anion. The cage geometry and location of the bridging hydrogens for V are consistent with structures previously observed for *arachno*-$SB_9H_{12}^-$[15] and its derivatives, such as *arachno*-9-NEt_3-6-SB_9H_{11}.[16] The structure of the cobaltocenium unit is similar to that found in other cobaltocenium–carborane zwitterions, such as $[(\eta\text{-}C_5H_5)Co(C_5H_4)^+][C_2B_9H_{11}^-]$[17] and $[(\eta\text{-}C_5H_5)Co(C_5H_4)^+][Me_4C_4B_8H_8^-]$,[18] with the boron-linked cyclopentadienyl carbon having a somewhat longer bonding distance to the cobalt (2.077 (3) Å) than the other ring carbons (2.028 Å average).

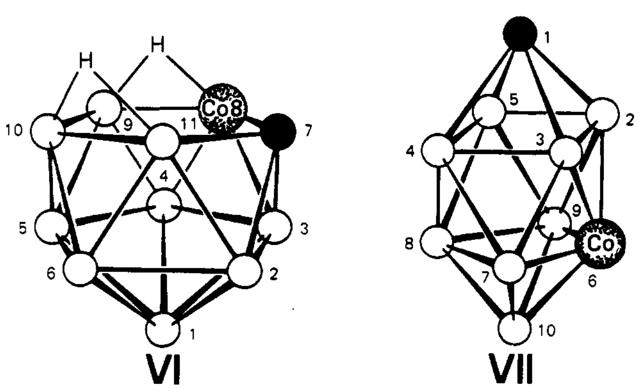

Figure 3. Proposed structures for *nido*-8-$(\eta\text{-}C_5(CH_3)_5)Co$-7-$SB_9H_{11}$ (VI) and *closo*-6-$(\eta\text{-}C_5H_5)Co$-1-SB_8H_8 (VII). (The cyclopentadienyl rings are not shown for clarity.)

It should also be noted that the salt, $[(\eta\text{-}C_5H_5)_2Co]^+[B_{18}H_{21}]^-$, was isolated in small amounts from the above reaction with *nido*-SB_9H_{11}. The formation of this compound is especially interesting, since it may have been formed by a metal-induced desulfurization/borane-coupling reaction of *nido*-6-SB_9H_{11}, suggesting that other metal reagents could perhaps induce such coupling reactions in higher yields. We are presently exploring these possibilities.

To suppress the hydroboration reactions of *nido*-6-SB_9H_{11}, reactions with pentamethylcyclopentadiene were examined and found to result in the formation of only one thiametallaborane cluster, *nido*-8-$(\eta\text{-}C_5(CH_3)_5)Co$-7-$SB_9H_{11}$ (VI). The ^{11}B NMR spectrum of VI is similar to that observed for the isoelectronic complex *nido*-8-$[\eta^6\text{-}C_6H_5CH_3]$-8,7-$FeSB_9H_{11}$;[1] therefore, an analogous structure (Figure 3) based on an icosahedron missing one vertex is proposed. The ^1H NMR spectrum is also consistent with this structure, since it exhibits two different bridging-hydrogen resonances, −4.6 and −13.1 ppm, with the upfield peak showing quartet coupling (J_{H-B} = 35 Hz) characteristic of a B–H–Co interaction.

The reaction of cobalt atoms with *arachno*-4-SB_8H_{12} and cyclopentadiene resulted in the low-yield formation of both I and an eight-boron cluster (VII) that, according to exact mass measurements, had the composition $(C_5H_5)CoSB_8H_8$. Electron counting rules predict that VII would adopt a closed-cage 10-vertex bicapped square-antiprism structure similar to those that have been proposed for *closo*-1-SB_9H_9[4b] and the isoelectronic carborane clusters *closo*-$(\eta\text{-}C_5H_5)Ni\text{-}CB_8H_9$ (two isomers).[19] The ^{11}B NMR spectrum of VII is in fact quite similar to that obtained for *closo*-6-$(\eta\text{-}C_5H_5)Ni$-1-CB_8H_9,[19] and a *closo*-6-$(\eta\text{-}C_5H_5)Co$-1-SB_8H_8 structure is therefore proposed for VII, as shown in Figure 3.

Due to the complex nature of metal vapor reactions, it is impossible to assign an exact mechanism for the formation of these

---

(13) Friesen, G. D.; Barriola, A.; Daluga, P.; Ragatz, P.; Huffman, J. C.; Todd, L. J. *Inorg. Chem.* **1980**, *19*, 458–462.

(14) Ferguson, G.; Hawthorne, M. F.; Kaitner, B.; Lalor, F. J. *Acta Crystallogr.* **1984**, *C40*, 1707–1709.

(15) Guggenberger, L. J. *J. Organomet. Chem.* **1974**, *81*, 271–280.

(16) Hilty, T. K.; Rudolph, W. R. *Inorg. Chem.* **1979**, *18*, 1106–1108.

(17) Churchill, M. R.; DeBoer, B. G. *J. Am. Chem. Soc.* **1974**, *96*, 6310–6318.

(18) Grimes, R. N.; Pipal, J. R.; Sinn, E. *J. Am. Chem. Soc.* **1979**, *101*, 4172–4180.

(19) (a) Štibr, B.; Janoušek, Z.; Baše, K.; Dolanský, J.; Heřmánek, S.; Solntsev, K. A.; Butman, L. A.; Kuznetsov, I. I.; Kuznetsov, N. T. *Polyhedron* **1982**, *1*, 833–834. (b) Štibr, B.; Janoušek, Z.; Baše, K.; Plešek, J.; Solntsev, K. A.; Butman, L. A.; Kuznetsov, I. I.; Kuznetsov, N. T. *Collect. Czech. Chem. Commun.* **1984**, *49*, 1660–1664.

compounds; however, previous studies[6] suggest that cobalt atoms react initially with cyclopentadiene at low temperatures to give the reactive cobalt hydride species (η^1-C_5H_5)Co-H or (η^5-C_5H_5)Co-H, which can then undergo insertion or dehydroinsertion reactions with polyhedral borane fragments. For more stable cage systems, simple metal insertion is generally observed; however, as the reactivity of the cage increases, more extensive decomposition can occur. Owing principally to the highly reactive nature of the CpCo–H hydrogen fragments, the selectivity and yields of metal complexes obtained in the reactions reported herein are quite low, especially when compared to the corresponding reactions[1] involving metal atom generated (η^6-arene)iron fragments. Furthermore, the distribution and type of products obtained are probably mainly determined by their relative stabilities with respect to further reaction. Thus, while this work has resulted in the production of several new cobaltathiaborane complexes, alternative syntheses or improvements in the metal vapor technique will be required before these complexes can be produced selectively on reasonable scales.

Acknowledgment. We thank the National Science Foundation for support of this research.

Supplementary Material Available: A table of infrared data for compounds I–VII and tables of atomic positional parameters, general temperature factors, intramolecular distances and angles, molecular planes, and dihedral angles for IV and V (21 pages); listings of observed and calculated structure factors for IV and V (20 pages). Ordering information is given on any current masthead page.

Contribution from The Institute of Physical
and Chemical Research (RIKEN), Wako-shi,
Saitama 351-01, Japan, and Institute for Protein Research,
Osaka University, Suita-shi, Osaka 565, Japan

Synthesis and X-ray Structure Analysis of the Tetracapped Octahedral Ruthenium Carbido Cluster $[N(PPh_3)_2]_2[Ru_{10}C(CO)_{24}]$

Teiji Chihara,[*,†] Ryuhei Komoto,[†] Kimiko Kobayashi,[†]
Hiroshi Yamazaki,[*,†] and Yoshiki Matsuura[‡]

Received July 22, 1988

It has been reported[1] that treatment of $Ru_3(CO)_{12}$ with sodium in refluxing bis(2-methoxyethyl) ether (162 °C) gives $[Ru_6C(CO)_{16}]^{2-}$ (**1**) quantitatively. Similar treatment of $Os_3(CO)_{12}$, however, gives only the non-carbido cluster $[Os_6(CO)_{18}]^{2-}$. Thermolysis of this osmium cluster in 2,5,8,11,14-pentaoxapentadecane (230 °C) gives a carbido dianion, $[Os_{10}C(CO)_{24}]^{2-}$ (**2**), having a tetracapped octahedral metal framework. Thermolysis of the same compound in bis(2-methoxyethyl) ether (162 °C) followed by oxidation under a CO atmosphere gives $Os_6C(CO)_{17}$ in a small yield (2%); hence, $[Os_6C(CO)_{16}]^{2-}$ is believed to be an intermediate in the formation of the decanuclear cluster **2**. On the other hand, thermolysis of **1** in 2,5,8,11,14-pentaoxapentadecane (210–230 °C) failed to give the dianionic carbido ruthenium cluster $[Ru_{10}C(CO)_{24}]^{2-}$ (**3**) but gave the dianionic dicarbido cluster $[Ru_{10}C_2(CO)_{24}]^{2-}$,[2] whose metallic structure has been shown to consist of two edge-sharing octahedra. There seems to be no reason for the absence of the tetracapped octahedral ruthenium cluster **3**, which is analogous to the known osmium cluster **2**.[3] We have examined a "redox condensation" reaction[4] of **1** with the neutral ruthenium compound $Ru_3(CO)_{12}$ for the direct synthesis of **3**. Here we report the successful preparation of this compound and the X-ray structure analysis.

Table I. Crystallographic Data for $[N(PPh_3)_2]_2[Ru_{10}C(CO)_{24}]$

chem formula: $C_{97}H_{60}N_2O_{24}P_4Ru_{10}$
a = 17.520 (5) Å
b = 27.102 (9) Å
c = 10.444 (2) Å
α = 100.61 (3)°
β = 96.28 (3)°
γ = 85.74 (6)°
V = 4838 (2) Å^3
Z = 2

fw: 2772.1
space group: $P\bar{1}$ (No. 2)
T = 19 °C
λ = 0.71073 Å
ρ_{calcd} = 1.90 g cm^{-3}
μ = 16.24 cm^{-1}
$R(F_o)$ = 0.050
$R_w(F_o)$ = 0.043

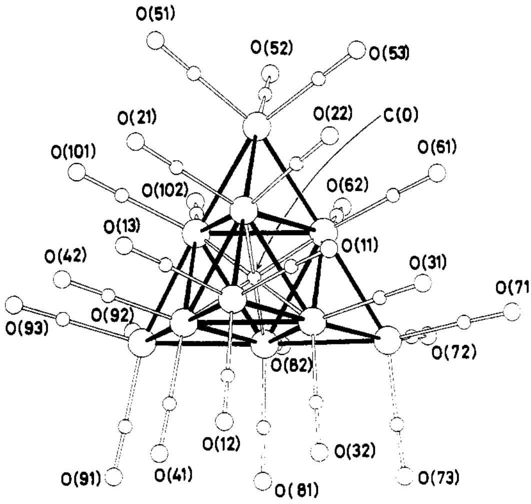

Figure 1. Structure of $[Ru_{10}C(CO)_{24}]^{2-}$ (**3**) with the numbering of the oxygen atoms corresponding to that of the relevant carbonyl carbon atoms. The first digit of each oxygen number is the number of the osmium atom to which the carbonyl is attached.

Experimental Section

Preparation of $[Ru_{10}C(CO)_{24}]^{2-}$ (3). A solution of $[N(PPh_3)_2]_2[Ru_6C(CO)_{16}]$[1] (402 mg, 0.188 mmol) and $Ru_3(CO)_{12}$ (180 mg, 0.282 mmol) in 12 mL of dry bis(2-methoxyethyl) ether was refluxed for 3 h under an argon atmosphere. The color of the solution changed from orange to brown to deep green. Then the solvent was removed under vacuum, and the residue was dissolved in a minimum quantity of CH_2Cl_2 and applied to a 10% water-containing alumina column. Elution with a benzene–CH_2Cl_2 (1:1) solvent mixture separated a deep green band. Crystallization from CH_2Cl_2–MeOH provided deep green crystals of $[N(PPh_3)_2]_2[Ru_{10}C(CO)_{24}]$ (422 mg, 0.152 mmol, 81% yield based on $[N(PPh_3)_2]_2[Ru_6C(CO)_{16}]$): IR ($\nu$(CO) in CH_2Cl_2): 2066 (sh), 2026 (s), 1997 (w), 1984 (s) cm^{-1}. ^{1}H NMR (acetone-d_6): δ 7.5–7.9 (phenyl protons, m). Anal. Calcd for $C_{97}H_{60}N_2O_{24}P_4Ru_{10}$: C, 42.02; H, 2.18; N, 1.01. Found: C, 42.06; H, 2.11; N, 1.01. $[NEt_4]_2[Ru_{10}C(CO)_{24}]$ was also obtained from the $[NEt_4]^+$ salt by the same procedure.

Crystallographic Analysis. A deep green crystal of **3** was mounted in a thin-walled glass capillary. Diffraction measurements were made at 19 °C on a Rigaku AFC4 automatic diffractometer using graphite-monochromatized Mo Kα radiation from a rotating anode generator operated at 40 kV and 200 mA. Unit cell dimensions were derived from the least-squares fit of the angular settings of 25 reflections with $20° < 2\theta < 25°$. Crystal data, data collection parameters, and results of the analyses are listed in Table I. Absorption correction was not made, because deviations of F_0 for axial reflections at χ = 90° were within ±5%. The structure was solved by direct methods by use of the program MULTAN,[5] which located 10 ruthenium atoms. The remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses and refined by the block-diagonal least-squares method[6] with anisotropic

---

[*] To whom correspondence should be addressed.
[†] The Institute of Physical and Chemical Research.
[‡] Institute for Protein Research.

(1) Hayward, C.-M. T.; Shapley, J. R. *Inorg. Chem.* **1982**, *21*, 3816.
(2) Hayward, C.-M. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1982**, *104*, 7347.
(3) Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Nelson, J. H.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1982**, 2099.
(4) Vargas, M. D.; Nicholls, J. N. *Adv. Inorg. Chem. Radiochem.* **1986**, *30*, 123.
(5) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declerq, J.-P.; Woolfson, M. M. "MULTAN 78"; University of York: York, England, 1978.
(6) Sakurai, T.; Kobayashi, K. *Rikagaku Kenkyusho Hokoku* **1979**, *55*, 69.

0020-1669/89/1328-0964$01.50/0 © 1989 American Chemical Society