Registry No. $[(CH_3)_3Si]_2O$, 107-46-0; F_2POF_2, 13812-07-2; $[(CH_3)_3Si]_2NH$, 999-97-3; OPF_2H, 14939-34-5; $(CF_3)_2PF$, 1426-40-0; $(CF_3)_2PCl$, 650-52-2; $[(CH_3)_3Si]_2S$, 3385-94-2; $[(CF_3)_2P]_2S$, 1486-20-0; $(CF_3)_2P(S)Cl$, 18799-82-1; $Hg[Si(CH_3)_3]_2$, 4656-04-6; HCl, 7647-01-0; $(CH_3)_2NH$, 124-40-3; $(CF_3)_2P(O)Cl$, 646-71-9; $(CH_3)_2NH{\cdot}OPF_2H$, 38680-92-1; $(CH_3)_3SiN(CH_3)_2$, 2083-91-2; $F_2POSi(CH_3)_3$, 38680-94-3; $(CF_3)_2POSi(CH_3)_3$, 19738-46-6; $(CF_3)_2PSSi(CH_3)_3$, 38680-96-5; $CF_3P[OSi(CH_3)_3]N(CH_3)_2$, 38822-36-5.

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Synthesis of Nine-Vertex Monocarbon Metallocarboranes by Polyhedral Contraction

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The base degradation of orange $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}6,7\text{-}B_{10}C_2H_{12})$ has been found to effect a polyhedral contraction reaction to give $[(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_8)]^-$. This reaction constitutes the first reported example of a small metallocarborane formed by the removal of a carbon atom and three boron atoms from the polyhedral framework of a larger metallocarborane.

Introduction

The polyhedral contraction reaction developed in this laboratory[1,2] has been used to convert certain metallocarboranes to their next smaller homolog by the removal of one formal BH^{2+} unit by base degradation followed by a two-electron oxidation back to a neutral carborane. We

$$(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}B_nC_2H_{n+2}) \xrightarrow[2.\ -2e^-]{1.\ -BH^{2+}} (\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}B_{n-1}C_2H_{n+1}) \quad (n = 8 \text{ or } 9)$$

have reported in a recent communication[3] that an attempt to effect a polyhedral contraction reaction with the orange[4-6] $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}6,7\text{-}B_{10}C_2H_{12})$ gave an unusual product. A total of three BH units and one CH unit was removed from the 13-vertex parent metallocarborane giving, as the principal product, an anionic complex formulated as $[(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_8)]^-$ which contained a metallocarborane moiety with only nine vertices. We report here further details of this reaction and discuss more fully the unique nature of the products.

Results and Discussion

Preparation and Characterization of the Cyclopentadienylcobalt(III) Complexes of the $B_7CH_8{}^{3-}$ Ion and Its *C*-Methyl Derivative. The reaction of orange π-cyclopentadienyl-π-dodecahydro-6,7-dicarba-*nido*-dodecaboratocobalt(III) with excess potassium hydroxide in an ethanol solution at reflux resulted in the formation of π-cyclopentadienyl-π-octahydro-2-carba-*nido*-octaboratocobaltate(1−), $[(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_8)]^-$, I, in high yield. The ion I could be isolated and recrystallized as either its tetramethylammonium or cesium salt.

The 100-MHz ^1H nmr spectrum of the cesium salt of I, Table I, consisted of a sharp singlet of area 5 and a broad singlet of area 1. These were assigned to the cyclopentadienyl protons and to a single carborane CH unit, respectively. The spectrum was scanned to τ 30 but showed no evidence of BHB bridging protons. The 80.5-MHz ^{11}B nmr spectrum of I (Figure 1 and Table II) contained doublets of area ratios 2:2:2:1 indicating that the carborane framework consisted of one unique boron atom and three pairs of equivalent boron atoms.

The chemical analyses of I (Table III) are consistent with the formulations of $[(CH_3)_4N][(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_8)]$ and $Cs[(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_8)]$. Both salts contain a formal cobalt(III) species. The electronic spectrum and the infrared spectrum of the tetramethylammonium salt of I appear in Tables III and IV, respectively.

Other products isolated from the contraction of $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}6,7\text{-}B_{10}C_2H_{12})$ included trace amounts of the previously reported isomers of $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}B_{10}C_2H_{12})$,[4,5] $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}B_9C_2H_{11})$,[7] and $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}B_8C_2H_{10})$.[8] These complexes were identified by their mass spectra and not characterized further.

As of this writing, the two isomers of the monomethyl derivative of the parent metallocarborane, $(\pi\text{-}C_5H_5)Co^{III}\{\pi\text{-}6,7\text{-}B_{10}C_2H_{11}(CH_3)\}$, prepared from $1,2\text{-}B_{10}C_2H_{11}(CH_3)$, have not been separated. The 6-methyl and the 7-methyl isomers are present in approximately equimolar amounts as evidenced by their nmr spectra. It was not surprising, then, that the base degradation of $(\pi\text{-}C_5H_5)Co^{III}\{\pi\text{-}6,7\text{-}B_{10}C_2H_{11}(CH_3)\}$ gave two products. One was identified as compound I and the other as compound II, a dark green monoanionic complex indicated by elemental analysis (Table III) to be $[(CH_3)_4N][(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_7(CH_3)]$.

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(6) Pending the results of an X-ray crystal structure determination, we have tentatively assigned the carbon atoms to positions 6 and 7 in the metallocarborane framework and to positions 5 and 7 for the red-orange isomer. These structures will be discussed in a future publication.

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Table I. ^1H Nmr Data for the π-2-$B_7CH_8{}^{3-}$ Derivatives

Compd	Resonance, τ[a] (rel area)	Assignment
I[b]	Sharp singlet, 5.18 (5)	Cyclopentadienyl protons
	Broad singlet, 7.24 (1)	Carborane CH
I[c]	Sharp singlet, 5.65 (5)	Cyclopentadienyl protons
	Sharp singlet, 6.56 (12)	Tetramethylammonium ion protons
		Carborane CH not observed
II[d]	Sharp singlet, 5.21 (5)	Cyclopentadienyl protons
	Sharp singlet, 6.63 (12)	Tetramethylammonium ion protons
	Sharp singlet, 7.37 (3)	Carborane methyl protons

[a] Relative to tetramethylsilane. [b] Cesium salt in pyridine, 100 MHz. [c] Tetramethylammonium salt in acetone-d_6, 60 MHz. [d] In pyridine, 60 MHz.

Table II. 80.5-MHz ^{11}B Nmr Spectra of the π-2-$B_7CH_8{}^{3-}$ Derivatives

Compd[a]	Rel intens	Chem shifts, δ[b] (J_{BH}, Hz)
I	2:2:2:1	−41.1 (138), +2.2 (157), +17.3 (151), +25.2 (147)
II	2:2:2:1	−41.7 (138), −2.8 (131), +12.7 (134), +22.0 (128)

[a] Determined in acetone. [b] Relative to $BF_3 \cdot O(C_2H_5)_2$.

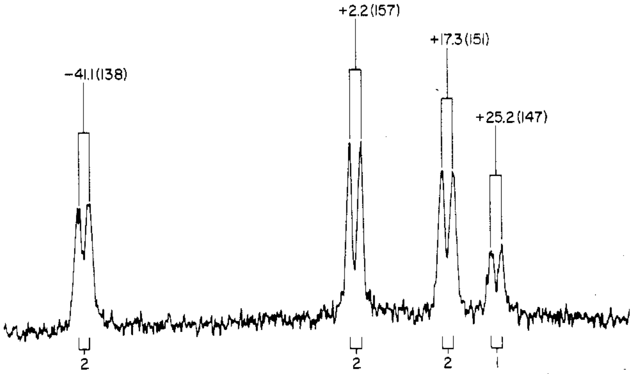

Figure 1. The 80.5-MHz ^{11}B nmr spectrum of $[(CH_3)_4N][(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_8)]$ taken in acetone. Chemical shifts (parts per million relative to $BF_3 \cdot O(C_2H_5)_2$) and coupling constants (hertz) are indicated. Relative areas appear beneath the peaks.

The 60-MHz ^1H nmr spectrum (Table I) of II consisted of sharp singlets of area ratios 5:12:3 which were assigned to the cyclopentadienyl protons, the tetramethylammonium ion protons, and the carborane methyl group protons, respectively. The 80.5-MHz ^{11}B nmr spectrum (Table II) of II showed four doublets of area ratios 2:2:2:1. The nmr data once again suggested that the carborane framework consisted of one carbon atom, one unique boron atom, and three pairs of equivalent boron atoms. The electronic spectrum of II appears in Table III and the infrared spectrum in Table IV.

The above data indicate that both I and II contain a nine-vertex metallocarborane moiety incorporating a cobalt atom, a single carbon atom, and seven boron atoms. A degradation reaction which produces, in high yield, a metallocarborane which is smaller than the parent metallocarborane by four vertices is unprecedented. Furthermore, the removal of a carbon atom from a polyhedral carborane environment has been reported in only one previous instance[9,10] and has never before been observed with metallocarboranes.

The $B_7CH_8{}^{3-}$ ion and its *C*-methyl derivative are members of a newly established series of anionic, monocarbon *nido*-carborane ligands whose general formula is $B_nCH_{n+1}{}^{3-}$. The only other known member of this series is the $B_{10}CH_{11}{}^{3-}$ carbollide ion.[11-13] Work is in progress in this laboratory to establish the existence of the intermediate homologs of this series.

The structure that we propose for I appears in Figure 2 and consists of a nine-vertex, tricapped trigonal prism isostructural with the known compounds $B_9H_9{}^{2-}$,[14] $B_7C_2H_9$,[15] $[(\pi\text{-}B_6C_2H_8)Mn(CO)_3]^-$,[16] and $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}B_6C_2H_8)$.[17,18] The structure is compatible with the nmr data in that it contains a plane of symmetry passing through the cobalt atom, the carbon atom at vertex no. 2, and the unique boron atom at vertex no. 8. The three pairs of equivalent boron atoms appear at vertices 1 and 6, 4 and 7, and 5 and 9.

It has been observed in this laboratory[18,19] that low-coordinate boron atoms, when adjacent to a cobalt atom, appear at extremely low field in the ^{11}B nmr spectra. The proposed structure of I is consistent with this generalization in that the apical boron atoms at vertices 1 and 6 have a lower coordination number than boron atoms 4, 5, 7, and 9. The low-field resonance of area 2 at approximately −41 ppm in the spectra of I and II might then be assigned to boron atoms 1 and 6.

An equally probable structure that is consistent with the nmr data would have the carbon atom at the low-coordinate, apical position 8 and a boron atom at vertex 2. The argument in favor of this structure is that a unique boron atom appears at high field in the ^{11}B nmr spectrum and this might indicate that boron atom occupies a nonapical position. However, there is no conclusive evidence in the ^{11}B nmr spectra of metallocarboranes that low-coordinate boron atoms not adjacent to a metal necessarily appear at low field. Furthermore, there is no known synthetic route to metallocarboranes where the resulting complex does not have at least one carbon atom in the open π-bonding face of the ligand. The products of the thermal rearrangement of derivatives of $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}B_9C_2H_{11})$ constitute the only exception to this rule and temperatures in excess of 500° are necessary to effect this rearrangement.[20,21] With little information available with regard to the mechanism of the degradation reaction, it is difficult to assign, with certainty, the position of the carbon atom. An X-ray structure determination of the cesium salt of I is currently in progress.

It is interesting to note that the red-orange $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}5,7\text{-}B_{10}C_2H_{12})$[6] did not degrade under the above conditions to give a seven boron atom metallocarborane. This suggests that the contraction mechanism involves a CH unit at a specific vertex in the parent metallocarborane. Furthermore, the orange $(\pi\text{-}C_5H_5)Co^{III}\{\pi\text{-}6,7\text{-}B_{10}C_2H_{10}(CH_3)_2\}$

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Table III. Analytical Data, $E_{1/2}$ Values, and Electronic Spectra of the π-2-$B_7CH_8{}^{3-}$ Derivatives

	Elemental analyses, %											
	C		H		B		Co		N or Cs			
Compd	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	$E_{1/2}$,[a] V	Electronic spectra,[b] λ_{max}, mμ (ϵ)
I[c]	40.88	40.77	8.51	8.54	25.75	25.98	20.03	20.35	4.77	4.90	+0.08	568 (169), 381 (839), 320 (4350), 258 (7230)
I[d]	20.42	20.02	3.72	3.82	21.46	21.36	16.71	16.40	37.69	38.41		
II	42.87	43.15	8.86	8.85	24.58	24.33	19.14	18.82	4.55	4.45	0.00	580 (145), 376 (795), 316 (4710), 251 (3180)

[a] $Co^{III} - e^- \rightarrow Co^{IV}$, determined in acetonitrile with 0.1 *F* tetraethylammonium perchlorate as supporting electrolyte; platinum button electrode. [b] In spectroquality acetonitrile. [c] Tetramethylammonium salt. [d] Cesium salt.

Table IV. Infrared Spectra and Melting Point Data for the $B_7CH_8{}^{3-}$ Derivatives

Compd	Mp,[a] °C	Infrared spectra,[b] cm^{-1}
I[c]	>300	2500 (s), 1480 (s), 1410 (m), 1280 (w), 1115 (m), 1108 (m), 1090 (w), 1065 (w), 1050 (w), 1010 (w), 997 (w), 948 (s), 920 (w), 831 (w), 809 (m), 682 (w)
II	>300	2495 (s), 1480 (s), 1405 (m), 1280 (m), 1110 (w), 1015 (m), 992 (m), 948 (s), 922 (w), 969 (w), 840 (w), 831 (w), 818 (s), 697 (w)
III	79–81	2530 (s), 1415 (w), 1260 (w), 1110 (m), 1080 (m), 1060 (m), 1015 (m), 932 (w), 882 (w), 824 (s), 806 (m), 786 (w), 743 (w), 685 (w)
IV	72–74	3100 (m), 2570 (s), 1855 (w), 1790 (w), 1685 (w), 1420 (m), 1265 (w), 1120 (w), 1095 (w), 1060 (w), 1025 (m), 972 (s), 944 (m), 929 (m), 904 (m), 889 (w), 852 (m), 829 (s), 772 (m), 680 (m)

[a] Sealed capillary. [b] Nujol mull. [c] Tetramethylammonium salt.

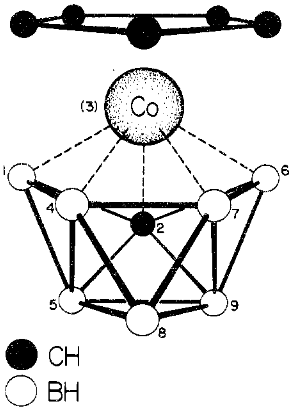

Figure 2. The proposed structure of π-cyclopentadienyl-π-octahydro-2-carba-*nido*-octaboratocobaltate(1−), $[(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_8)]^-$.

did not degrade. The reason for this may be either steric or electronic in nature. The results are consistent with the observation that it is far more difficult to degrade 1,2-$B_{10}C_2H_{10}(CH_3)_2$ with ethanolic potassium hydroxide to 7,8-$B_9C_2H_{10}(CH_3)_2{}^-$ than it is to degrade 1,2-$B_{10}C_2H_{12}$ to 7,8-$B_9C_2H_{12}{}^-$.[22]

Preparation and Characterization of the Cyclopentadienyl Cobalt(IV) Complexes of the $B_7CH_8{}^{3-}$ Ion and Its *C*-methyl Derivative. Cyclic voltammetry and controlled-potential coulometry measurements (Table III) indicated that both I and II would undergo a reversible one-electron oxidation to neutral formal cobalt(IV) species. A cobalt(IV) complex is not without precedent since Knoth has observed[12,13] that the homologous carbollide ion tends to stabilize high formal metal oxidation states, and he has prepared bis-carbollyl complexes which contain manganese, nickel, and cobalt in the formal oxidation state of IV.

The reaction of I with an equimolar amount of ferric chloride in dichloromethane resulted in the formation of π-cyclopentadienyl-π-octahydro-2-carba-*nido*-octaboratocobalt(IV), compound III, according to

$$[(CH_3)_4N][(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_8)] + Fe^{III}Cl_3 \xrightarrow{CH_2Cl_2} (\pi\text{-}C_5H_5)Co^{IV}(\pi\text{-}2\text{-}B_7CH_8) + Fe^{II}Cl_2 + [(CH_3)_4N]^+Cl^-$$

Both III and its *C*-methyl derivative, compound IV, form intensely green solutions in dichloromethane and both may be sublimed at room temperature under high vacuum to a −80° cold finger. They react rapidly with donor solvents and decompose at room temperature even if stored *in vacuo*, under nitrogen, or in the absence of light. They may be stored for several days at 0° as a solid or in a dichloromethane solution without noticeable decomposition.

The paramagnetic nature of III and IV preclude obtaining any nmr data but we have no reason to believe that the gross structure of the two complexes is significantly different from that of I and II. The infrared spectra appear in Table IV. The mass spectrum of III had a cutoff at *m/e* 221 corresponding to the $^{11}B_7{}^{12}C_6{}^1H_{13}{}^{59}Co^+$ ion. The cutoff of IV was at *m/e* 235 corresponding to the $^{11}B_7{}^{12}C_7{}^1H_{15}{}^{59}Co^+$ ion. In lieu of chemical analyses of III and IV, we obtained high-resolution mass spectra: calculated for $^{11}B_7{}^{12}C_6{}^1H_{13}$-$^{59}Co$, 221.1001; observed, 221.1004 ± 0.0006; calculated for $^{11}B_7{}^{12}C_7{}^1H_{15}{}^{59}Co$, 235.1157; observed, 235.1156 ± 0.0007.

Experimental Section

Physical Measurements. The 80.5-MHz ^{11}B nmr spectra were obtained with an instrument designed by Professor F. A. L. Anet of this department. The electrochemical apparatus for cyclic voltammetry and controlled-potential coulometry was based on the design of Lawless and Hawley.[23] Infrared spectra were determined using a Perkin-Elmer Model 137 sodium chloride spectrophotometer, and mass spectra were obtained with an Associated Electrical Industries Model MS-9 spectrometer. Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Materials. Anhydrous sublimed ferric chloride, tetramethylammonium chloride, and cesium chloride were obtained from Matheson Coleman and Bell. Reagent grade ethanol, benzene, chloroform, acetone, and dichloromethane were used without further purification.

Orange $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}6,7\text{-}B_{10}C_2H_{12})$ was prepared by the method previously described.[5] The monomethyl and dimethyl derivatives were prepared in a similar manner from 1,2-$B_{10}C_2H_{11}(CH_3)$ and 1,2-$B_{10}C_2H_{10}(CH_3)_2$, respectively.

$[(CH_3)_4][(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_8)]$, I. To a 100-ml, three-necked, round-bottom flask fitted with a mechanical stirrer, reflux condenser topped with a nitrogen inlet, and a thermometer were added 0.30 g (1.1 mmol) of orange $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}6,7\text{-}B_{10}C_2H_{12})$ and 75 ml of absolute ethanol. The solution was heated to the reflux temperature and 5.0 g of potassium hydroxide was added directly as a solid. The mixture was allowed to reflux for 48 hr during

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which the color changed from orange to green-brown. The solvent was removed by rotary evaporation and the residual oil was redissolved in 250 ml of distilled water. The aqueous solution was extracted with four 125-ml portions of benzene and then added to a solution of 5 g tetramethylammonium chloride in 25 ml of water. The cloudy solution was clarified by the addition of 50 ml of acetone and then rotary-evaporated to a volume of about 25 ml by which time the formation of black crystals had occurred. The crystals were filtered, washed with ethanol, and weighed; yield 0.21 g (0.71 mmol, 65%).

$Cs[(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_8)]$. A 0.30-g sample of orange $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}6,7\text{-}B_{10}C_2H_{12})$ was degraded by potassium hydroxide in ethanol as described above for I. After the aqueous phase was extracted with benzene, it was added to a solution of 5 g of cesium chloride in 25 ml of water and rotary-evaporated to dryness. The solid was redissolved in 50 ml of water and 50 g of Dry Ice was added in order to convert the excess potassium hydroxide to potassium carbonate. The solution was again evaporated to dryness, redissolved in 25 ml of acetone, and filtered. A water solution of cesium chloride was added to ensure the complete precipitation of the complex and all of the solvent was again removed by rotary evaporation. The residue was redissolved in 25 ml of acetone and filtered. The addition of chloroform to the filtrate followed by cooling to 0° produced 0.20 g (0.57 mmol, 51%) of $Cs[(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_8)]$. The product was recrystallized from acetone and chloroform to give 70 mg of very good crystals which were submitted for an X-ray diffraction study.

$[(CH_3)_4N][(\pi\text{-}C_5H_5)Co^{III}\{\pi\text{-}2\text{-}B_7CH_7(CH_3)\}]$, II. A 0.31-g (1.1-mmol) sample of a mixture of the orange isomers of $(\pi\text{-}C_5H_5)Co^{III}\{\pi\text{-}6,7\text{-}B_{10}C_2H_{11}(CH_3)\}$ was degraded by 5.0 g of potassium hydroxide in ethanol in exactly the same manner as described for I. The crystalline product isolated after the addition of tetramethylammonium chloride was a mixture of $[(CH_3)_4N][(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_8)]$ and $[(CH_3)_4N][(\pi\text{-}C_5H_5)Co^{III}\{\pi\text{-}2\text{-}B_7CH_7(CH_3)\}]$ in a ratio of about 1:5. The product was redissolved in 20 ml of absolute ethanol and filtered. The undissolved material was I while the filtrate consisted mainly of II and a small amount of I. The filtrate was passed through a 2 × 10 cm polyamide chromatography column and eluted with ethanol. If the extraction of the aqueous phase had been incomplete, a pale yellow-green band was first to be eluted. A dark green band was then eluted which, upon removal of the solvent, afforded 0.060 g (0.19 mmol, 36%) of black crystals of II.

$(\pi\text{-}C_5H_5)Co^{IV}(\pi\text{-}2\text{-}B_7CH_8)$, III. A 50-mg (0.17-mmol) sample of I was dissolved in 50 ml of dichloromethane. A 28-mg (0.17-mmol) amount of anhydrous, sublimed ferric chloride was added as a slurry in 25 ml of dichloromethane *via* an addition funnel. The solution was stirred under nitrogen for 0.5 hr during which time the color had become intensely green and a white precipitate had formed. The reaction mixture was transferred to a vacuum line where the solvent was removed. A dark green, nearly black, solid was sublimed at room temperature to a −80° cold finger. The sublimer was opened in a nitrogen-fillex drybox yielding approximately 25 mg (0.11 mmol, 65%) of III.

$(\pi\text{-}C_5H_5)Co^{IV}\{\pi\text{-}2\text{-}B_7CH_7(CH_3)\}$, IV. A 52-mg (0.17-mmol) sample of II was oxidized by 28 mg (0.17 mmol) of ferric chloride as described immediately above. Approximately 25 mg (0.10 mmol, 60%) of IV was removed from the sublimer in the drybox.

Registry No. $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}6,7\text{-}B_{10}C_2H_{12})$, 37333-32-7; $[(CH_3)_4N][(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_8)]$, 38882-84-7; $Cs[(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_8)]$, 38882-83-6; $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}6,7\text{-}B_{10}C_2H_{11}\text{-}6\text{-}CH_3)$, 37333-33-8; $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}6,7\text{-}B_{10}C_2H_{11}\text{-}7\text{-}CH_3)$, 37333-34-9; $[(CH_3)_4N][(\pi\text{-}C_5H_5)Co^{III}\{\pi\text{-}2\text{-}B_7CH_7(CH_3)\}]$, 38882-82-5; $(\pi\text{-}C_5H_5)Co^{IV}(\pi\text{-}2\text{-}B_7CH_8)$, 38882-81-4; $(\pi\text{-}C_5H_5)Co^{IV}\{\pi\text{-}2\text{-}B_7CH_7(CH_3)\}$, 38882-80-3.

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Raman Spectra of Some Xenon(II) Compounds[1]

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The Raman spectra of the Xe(II) compounds $Xe_2F_3\cdot AsF_6$, $Xe_2F_3\cdot SbF_6$, $XeF\cdot AsF_6$, $XeF\cdot SbF_6$, $XeF\cdot Sb_2F_{11}$, $XeF\cdot Nb_2F_{11}$, $XeF\cdot Ta_2F_{11}$, $FXe(SO_3F)$, and $Xe(SO_3F)_2$ have been measured. Characteristic frequencies are assigned for the XeF^+ and $Xe_2F_3^+$ ions. In the spectra of $FXe\cdot MF_6$ and $FXe\cdot M_2F_{11}$ bands are observed in addition to those due to XeF^+ and the anion and these are assigned to the fluorine bridge Xe- - -F-M. The spectra of $FXe(SO_3F)$ and $Xe(SO_3F)_2$ are compared with those of other fluorosulfates.

Introduction

A variety of adducts of XeF_2 with pentafluorides such as SbF_5, AsF_5, TaF_5, NbF_5, PtF_5, RuF_5, IrF_5, and OsF_5 have been prepared. The majority have 2:1, 1:1, and 1:2 stoichiometries, *e.g.*, $2XeF_2\cdot SbF_5$, $XeF_2\cdot AsF_5$, and $XeF_2\cdot 2RuF_5$.[2-7] X-Ray crystallographic studies of $XeF_2\cdot 2SbF_5$, $XeF_2\cdot RuF_5$, and $2XeF_2\cdot AsF_5$ have shown that they may be formulated as $XeF^+\cdot Sb_2F_{11}^-$, $XeF^+\cdot RuF_6^-$, and $Xe_2F_3^+\cdot AsF_6^-$, respectively.[8-10] In $XeF\cdot Sb_2F_{11}$ the XeF^+ ion is bonded to the $Sb_2F_{11}^-$ ion by a relatively short fluorine bridge (2.35 Å) which Peacock, *et al.*, regarded as having considerable covalent character. In $Xe_2F_3\cdot AsF_6$ the $Xe_2F_3^+$ ion has the bent structure II. In $XeF^+\cdot RuF_6^-$ the bridging XeF bond length is 2.19 Å which is between the XeF bond lengths in $XeF\cdot Sb_2F_{11}$ and in $Xe_2F_3^+$.

From their spectroscopic studies Sladky, *et al.*,[7] concluded

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