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Synthesis of (π-Arene)metallacarbaboranes Containing Ruthenium or Osmium and a (π-Cyclohexadienyl)cobaltacarbaborane. Crystal Structure of 2,5,6-(η-C_6H_6)$RuC_2B_7H_{11}$

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Reaction of 3,1,2-(η-C_6H_6)$RuC_2B_9H_{11}$ with ethanolic KOH in refluxing ethylene glycol results in polyhedral contraction to form 1,2,4-(η-C_6H_6)$RuC_2B_8H_{10}$ and 2,5,6-(η-C_6H_6)$RuC_2B_7H_{11}$ in low yield. The latter was structurally characterized by a low-temperature single-crystal X-ray diffraction study and exists in the triclinic space group $P\bar{1}$, with $a = 12.718$ (5) Å, $b = 6.998$ (2) Å, $c = 9.200$ (3) Å, $\alpha = 123.04$ (1)°, $\beta = 74.26$ (2)°, $\gamma = 115.43$ (2)°, and $Z = 2$. The molecule possesses a 10-membered nido decaborane-like structure, in which the ruthenium atom resides in the closed portion of the polyhedron. The reaction of (η-C_6H_6)$OsCl_2 \cdot NCCH_3$ with Tl[3,1,2-$TlC_2B_9H_{11}$] in THF produces 3,1,2-(η-C_6H_6)$OsC_2B_9H_{11}$, the first reported (π-arene)osmacarbaborane. Bis(hexamethylbenzene)cobalt(I) hexafluorophosphate reacts with Tl[3,1,2-$TlC_2B_9H_{11}$] to yield 3,1,2-[*endo-H*-η^5-$(CH_3)_6C_6H$]$CoC_2B_9H_{11}$.

Introduction

Recently we reported that reaction of bis(arene)iron(II) salts or (benzene)dichlororuthenium dimer with Tl[3,1,2-$TlC_2B_8H_{11}$] formed air-stable (π-arene)(Fe,Ru)$C_2B_9H_{11}$ complexes in low or moderate yields.[1] Another route to (π-arene)Fe[2,3-$(CH_3)_2$-2,3-$C_2B_9H_9$] was reported concurrently.[2a] This synthesis involved the reaction of *closo*-2,3-$(CH_3)_2$-2,3-$C_2B_9H_9$ with (1,5-C_8H_{12})Fe(C_5H_5) in various aromatic solvents. Other groups have used a variety of synthetic methods, including metal vapor reactions, to prepare additional examples of (π-arene)ferracarbaboranes.[2b-d]

We report here some further chemistry of 3,1,2-(η-C_6H_6)$RuC_2B_9H_{11}$, the synthesis of the first (π-arene)osmacarbaborane, and the synthesis of a (η^5-cyclohexadienyl)Co($C_2B_9H_{11}$) derivative.

Experimental Section

Physical Measurements. Boron (^{11}B) NMR spectra were obtained either at 70.6 MHz (16 °C) with a Varian HR-220 spectrometer or at 115.8 MHz (22 °C) on a Nicolet NT 360 spectrometer and were externally referenced to $BF_3 \cdot O(C_2H_5)_2$ (positive values downfield). Proton NMR spectra were recorded on either a Nicolet NT 360 or a Varian HR 220 spectrometer and were referenced to internal Me_4Si. Infrared spectra were obtained as KBr disks with a Perkin-Elmer 283 spectrometer. Low-resolution mass spectral data were collected on a Varian CH 7 spectrometer. High-resolution mass spectral data were obtained on an AEI MS-9 at The Ohio State University, Columbus, OH. Melting points were determined in sealed, evacuated capillaries and are uncorrected.

Materials. All reactions were performed under an atmosphere of prepurified nitrogen. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl. 3,1,2-(η-C_6H_6)$RuC_2B_9H_{11}$,[1] (C_6H_6)$OsCl_2 \cdot NCCH_3$,[3] [$(CH_3)_6C_6]_2Co(PF_6)$,[4] and Tl[3,1,2-$TlC_2B_9H_{11}$][5] were prepared according to literature methods. All other commercially available reagents were used as received.

Polyhedral Contraction of 3,1,2-(η-C_6H_6)$RuC_2B_9H_{11}$. (a) Isolation of 2,5,6-(η-C_6H_6)$RuC_2B_7H_{11}$. Potassium hydroxide (2.4 g of 85% pellets, 36 mmol) was dissolved in a mixture of nitrogen-saturated ethylene glycol (20 mL), ethanol (8 mL), and distilled water (2 mL), after which 3,1,2-(η-C_6H_6)$RuC_2B_9H_{11}$ (0.366 g, 1.2 mmol) was added with stirring. The reaction mixture was heated under nitrogen to reflux for 32 h, cooled to room temperature, and then quenched with the addition of distilled water (50 mL). Hydrogen peroxide (30%, 2 mL) was added to the mixture, which was then extracted into CH_2Cl_2 (4 × 70 mL). The combined extracts were dried over $MgSO_4$ and filtered through a coarse glass frit. The filtrate was stripped onto silica gel (0.5 g, 100–200 mesh) and placed on a silica gel column (20 × 2 cm) packed with benzene/hexanes (1:1 v/v).

Initial elution with the benzene/hexanes mixture generated a pale yellow band, which on removal of the solvent and recrystallization from CH_2Cl_2/hexanes produced yellow plates of 2,5,6-(η-C_6H_6)$RuC_2B_7H_{11}$ (2 mg, 0.6%), mp 149–152 °C (dec). ^1H NMR (361 MHz, $CDCl_3$): δ 5.89 (s, 6 H), 4.9 (br s, 1 H), 3.7 (br s, 1 H), −1 to −2 (br, not integrable). The ^{11}B NMR data are given in Table I.

(b) 1,2,4-(η-C_6H_6)$RuC_2B_8H_{10}$. Elution of the column with benzene next developed an orange band. Removal of the solvent left a crude mixture of 3,1,2-(η-C_6H_6)$RuC_2B_9H_{11}$ and 1,2,4-(η-C_6H_6)$RuC_2B_8H_{10}$ (0.09 g). Attempted recrystallizations from CH_2Cl_2/hexanes mixtures and chromatography on a thick-layer preparative chromatography plate developed with toluene and then toluene/CH_2Cl_2 did not effect significant separation of the two compounds (approximately 1:1 by NMR). The data below refer to the resonances assignable to 1,2,4-(η-C_6H_6)$RuC_2B_8H_{10}$ in the mixture. ^1H NMR (361 MHz, $CDCl_3$): δ 5.92 (s, 6 H), 5.2 (br s, 1 H), 4.9 (br s, 1 H).

Preparation of 3,1,2-(η-C_6H_6)$OsC_2B_9H_{11}$. A slurry of (C_6H_6)$OsCl_2$-($NCCH_3$) (0.068 g, 0.18 mmol) was prepared in dry THF (50 mL), and Tl[3,1,2-$TlC_2B_9H_{11}$] (0.097 g, 0.18 mmol) was added with stirring. The reaction mixture was stirred under nitrogen for 50 h, after which time the mixture was opened to air and silica gel (0.5 g, 60–200 mesh) added. The solvent was removed in vacuo, and the solids were chromatographed on a silica gel column (~13 cm) packed with benzene. The column was eluted first with benzene, then with CH_2Cl_2, and finally with ethyl acetate. The eluates were stripped to dryness and recrystallized from acetone/hexanes, yielding 3,1,2-(η-C_6H_6)$OsC_2B_9H_{11}$ (11 mg, 15%). Slow recrystallization from the same solvent mixture produced colorless needles, mp 280–283 °C (dec). ^1H NMR (220 MHz, CD_3CN): δ 6.26 (s, 6 H), 4.7 (br s, 2 H).

Preparation of 3,1,2-[*endo-H*-η^5-$(CH_3)_6C_6H$]$CoC_2B_9H_{11}$. Bis(hexamethylbenzene)cobalt(I) hexafluorophosphate, [$(CH_3)_6C_6]_2Co(PF_6)$ (0.59 g, 1.1 mmol), was slurried in dry THF (50 mL), and Tl[3,1,2-$TlC_2B_9H_{11}$] (0.30 g, 0.56 mmol) was added with stirring. The reaction mixture was stirred under nitrogen for 14 h, after which dioxygen was bubbled through the solution for 45 min. Silica gel (0.5 g, 100–200 mesh) was added to the mixture, and the solvent was removed in vacuo. The solids were transferred to a short (~13 cm) silica gel column packed with benzene. Elution with benzene generated an orange-red band; enrichment of the eluent with CH_2Cl_2 produced a yellow band.

Removal of the solvent from the orange fraction yielded 3,1,2-[*endo-H*-η^5-$(CH_3)_6C_6H$]$CoC_2B_9H_{11}$. Recrystallization from benzene/toluene produced small brick red crystals (2 mg, 1%), mp 240–241 °C (dec). ^1H NMR (361 MHz, $CDCl_3$): δ 2.93 (q, 1 H, $J = 6.5$ Hz), 2.35 (s, 3 H), 2.2 (br s, 2 H), 1.88 (s, 6 H), 1.66 (s, 6 H), 0.57 (d, 3 H, $J = 6.5$ Hz). IR: 3026 (w), 2977 (w), 2883 (w), 255] (vs), 2531 (vs), 1616 (w, br), 1450 (m), 1420 (w), 1376 (s), 1301 (m, shp), 1278 (w), 1256 (w), 1202 (w), 1180 (w), 1132 (w), 1088 (m), 1049 (w), 1028 (w), 1011 (w), 979 (s), 936 (w), 916 (w), 874 (w), 669 (w), 598 (w), 414 (w) cm^{-1}.

On evaporation of the solvent, the yellow chromatographic fraction yielded crude Tl[1,2-$(C_2B_9H_{11})_2Co^{III}$] (up to 25% in a typical reaction), identified by its ^{11}B NMR spectrum.[6]

Crystallography of 2,5,6-(η-C_6H_6)$RuC_2B_7H_{11}$. A well-formed yellow crystal of maximum dimension 0.24 mm was used in the study. Data were collected at −162 °C by using a standard moving-crystal–moving-

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Table I. Boron (^{11}B) NMR Data

compd (MHz, solvent)	rel areas	δ_B (J_{BH}, Hz)
2,5,6-(η-C_6H_6)$RuC_2B_7H_{11}$ (115.8, C_6D_6)	1:1:1:1:1:1:1	12.5 (142), 9.8 (140), 5.3, 3.8, −2.4 (135), −5.7 (146), −38.5 (149)
1,2,4-(η-C_6H_6)$RuC_2B_8H_{10}$ (115.8, CH_2Cl_2)	1:1:1:1:1:1:1:1	62.5 (152), 11.7 (142), −0.8 (152), −2.0 (126), −14.0 (154), −20.7, −26.3 (146), −43.2 (149)
3,1,2-(η-C_6H_6)$OsC_2B_9H_{11}$ (70.6, CD_3CN)	1:1:2:2:2:1	−0.2 (142), −6.8 (138), −11.4 (127), −13.3 (144), −21.5 (151), −25.8 (164)
3,1,2-[*endo-H*-η^5-$(CH_3)_6C_6H$]$CoC_2B_9H_{11}$ (115.8, $CDCl_3$)	1:1:4:2:1	7.8 (139), −3.5 (142), −6.7 (136), −18.4 (154), −23.4 (167)

Table II. Crystal Data for 2,5,6-(η-C_6H_6)$RuC_2B_7H_{11}$

formula	$C_8H_{11}B_7Ru$
fw	289.96
space group	$P\bar{1}$
a, Å	12.718 (5)
b, Å	6.998 (2)
c, Å	9.200 (3)
α, deg	123.04 (1)
β, deg	74.26 (2)
γ, deg	115.43 (2)
V, Å^3	619.13
Z	2
D_{calcd}, g cm^{-3}	1.555
temp, °C	−162
μ, cm^{-1}	12.01
min-max transmission coeff	0.828–0.972
type of scan	θ–2θ
scan speed, deg/min	4
stationary bkgd counts, s	4
sample-detector dist, cm	22.5
sample-source dist, cm	23.5
data collecn range	$6° \leq 2\theta \leq 45°$
total no. of unique data	1632
total no. of data with $I \geq 2.33\sigma(I)$	1506
no. of params	213
R(*F*)	0.035
$R_w(F)$	0.036
error in an observn of unit wt, e	1.201
max Δ/σ for final cycle	0.05

Table III. Fractional Coordinates and Isotropic Thermal Parameters for 2,5,6-(η-C_6H_6)$RuC_2B_7H_{11}$[a,b]

atom	*x*	*y*	*z*	B_{iso}, Å^2
Ru	2116.6 (4)	490 (1)	1728 (1)	19
C(5)	3538 (5)	−371 (11)	−139 (8)	25
C(6)	3875 (6)	2249 (11)	1087 (8)	27
C(11)	2083 (7)	−691 (13)	3571 (8)	32
C(12)	2192 (6)	1725 (14)	4523 (8)	33
C(13)	1423 (6)	2551 (13)	4573 (8)	33
C(14)	503 (6)	869 (15)	3286 (9)	35
C(15)	358 (6)	−1603 (13)	2347 (8)	33
C(16)	1145 (7)	−2378 (13)	2469 (8)	36
B(1)	2267 (6)	−1557 (13)	−1047 (9)	24
B(3)	1933 (7)	1187 (13)	−220 (9)	26
B(4)	2520 (7)	−338 (14)	−2445 (9)	27
B(7)	3131 (7)	3481 (13)	1111 (10)	30
B(8)	3022 (7)	2859 (15)	−1145 (11)	36
B(9)	3953 (7)	1310 (16)	−2718 (11)	36
B(10)	3634 (6)	−1120 (14)	−2309 (10)	29
H(1)	176 (5)	348 (11)	−167 (7)	26 (12)
H(3)	115 (5)	135 (10)	−14 (7)	26 (13)
H(4)	199 (5)	−139 (11)	−351 (8)	27 (13)
H(5)	387 (4)	−129 (10)	6 (6)	16 (11)
H(6)	443 (6)	300 (11)	183 (8)	29 (14)
H(7)	322 (6)	527 (13)	202 (9)	41 (15)
H(8)	281 (6)	406 (13)	−139 (9)	52 (18)
H(9)	435 (6)	135 (13)	−396 (9)	49 (17)
H(10)	393 (5)	−268 (12)	−328 (8)	34 (14)
H(11)	258 (6)	−123 (13)	352 (9)	37 (17)
H(12)	281 (6)	271 (12)	505 (8)	27 (14)
H(13)	154 (6)	412 (14)	497 (9)	43 (17)
H(14)	11 (6)	133 (13)	321 (9)	33 (18)
H(15)	−31 (6)	−273 (13)	162 (9)	39 (15)
H(16)	106 (5)	−403 (12)	184 (8)	27 (13)
H(17) [Hb_1]	403 (7)	334 (13)	−114 (10)	50 (17)
H(18) [Hb_2]	447 (6)	82 (12)	−202 (8)	39 (15)

[a] Fractional coordinates are ×10^4 for non-hydrogen atoms and ×10^3 for hydrogen atoms. B_{iso} values are ×10. [b] Isotropic values for those atoms refined anisotropically are calculated from the formula given in Hamilton, W. C. *Acta Crystallogr.* 1959, *12*, 609.

detector technique. Data collection and reduction techniques for the Picker goniostat have been described in detail previously.[7] Data were corrected for absorption by using an analytical technique. Pertinent crystal and diffractometer parameters for the present study are given in Table II.

The structure was solved by use of an interactive Patterson interpreter written locally.[8] Hydrogen atoms were located and refined isotropically, and all other atoms were assigned anisotropic thermal parameters. A final difference Fourier synthesis was featureless, the largest peak being 0.45 e/Å^3. Positional and isotropic thermal parameters are listed in Table III. Anisotropic thermal parameters are presented in Table IV.

Results and Discussion

Polyhedral Contraction of 3,1,2-(η-C_6H_6)$RuC_2H_9H_{11}$. (a) Formation of 2,5,6-(η-C_6H_6)$RuC_2B_7H_{11}$. The controlled basic degradation of metallacarbaboranes is probably the least studied and most complex of the reactions involving transformation of the polyboron cage.[9-11] Such "polyhedral contractions" are inherently derivative in nature and depend for their success on the accessibility and stability of the parent metallacarbaborane. Furthermore, the fairly harsh conditions generally employed (e.g., 1 M EtO^- in refluxing ethylene glycol[10]) may generate a plethora of products from a single reaction, including various isomers and alkoxy-substituted derivatives of metallacarbaboranes that have lost either one, two, or three boron atoms (and possibly a carbon atom[11b,d]) from the original cage.

Despite its experimental complexity, polyhedral contraction offers a forum in which electronic effects of the incorporated metal should manifest themselves in the extent and stereochemistry of the cage degradation.[11b] To date, only (cyclopentadienyl)cobaltacarbaboranes have been successfully studied under the conditions producing contraction, and hence the availability of an isoelectronic (π-arene)ruthenacarbaborane offered an ideal test of the comparative influences of two transition metals on the reaction.

The polyhedral contraction of 3,1,2-(C_5H_5)$CoC_2B_9H_{11}$ yields three major products, characterized as 1,2,4-(C_5H_5)$CoC_2B_8H_{10}$ (63%), 2,6,7-(C_5H_5)$CoC_2B_7H_9$ (8%), and an unknown, but unsymmetrical, isomer of (C_5H_5)$CoC_2B_7H_9$ (2%);[10] this reaction served as our reference for the degradation studies of the icosahedral ruthenium system. When 3,1,2-(η-C_6H_6)$RuC_2B_9H_{11}$ is refluxed for 32 h in an ethylene glycol/water/ethanol mixture containing KOH (effectively 1.2 M in EtO^-) and afterward ox-

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Table IV. Anisotropic Thermal Parameters for 2,5,6-(η-C_6H_6)$RuC_2B_7H_{11}$[a]

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru	24.7 (3)	22.7 (3)	23.1 (3)	11.7 (2)	−1.0 (2)	8.0 (2)
C(5)	28 (3)	30 (3)	42 (4)	12 (3)	1 (3)	20 (3)
C(6)	31 (3)	33 (4)	39 (4)	9 (3)	−4 (3)	18 (3)
C(11)	54 (4)	54 (5)	30 (4)	34 (4)	10 (3)	25 (4)
C(12)	41 (4)	52 (5)	28 (4)	12 (4)	−8 (3)	18 (3)
C(13)	62 (5)	38 (4)	22 (3)	32 (4)	5 (3)	5 (3)
C(14)	37 (4)	76 (6)	30 (4)	38 (4)	13 (3)	26 (4)
C(15)	28 (4)	54 (5)	27 (3)	0 (3)	−4 (3)	21 (3)
C(16)	71 (5)	33 (4)	23 (3)	16 (4)	13 (3)	14 (3)
B(1)	32 (4)	30 (4)	25 (4)	9 (3)	−1 (3)	13 (3)
B(3)	38 (4)	1 (4)	37 (4)	25 (4)	1 (3)	23 (4)
B(4)	39 (4)	43 (4)	29 (4)	18 (4)	0 (3)	21 (4)
B(7)	42 (4)	24 (4)	44 (5)	10 (3)	−4 (4)	14 (4)
B(8)	45 (5)	48 (5)	53 (5)	16 (4)	−3 (4)	30 (4)
B(9)	42 (5)	53 (5)	46 (5)	17 (4)	5 (4)	31 (4)
B(10)	37 (4)	36 (4)	35 (4)	18 (4)	3 (3)	15 (4)

[a] Form of the anisotropic thermal parameter: $\exp[-2\pi^2[h^2(a^*)^2U_{11} + \ldots + hka^*b^*U_{12} + \ldots]]$. All values are $\times 10^3$.

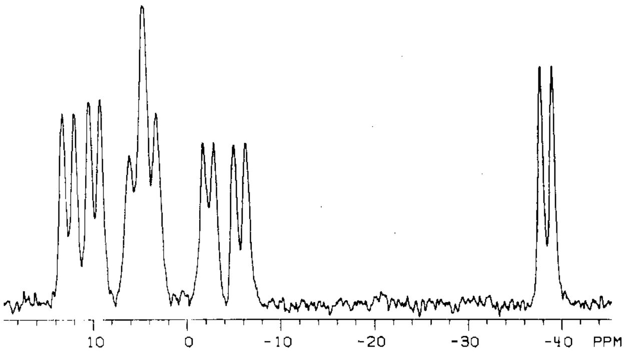

Figure 1. Boron-11 NMR spectrum (115.8 MHz) of 2,5,6-(η-C_6H_6)-$RuC_2B_7H_{11}$ (C_6D_6). For exact chemical shifts and coupling constants, see Table I.

idized with hydrogen peroxide, a mixture of products is produced, which can be partially separated by column chromatography.

The initial and least polar substance isolated from the reaction is a neutral, yellow air-stable sublimable solid. Its ^{11}B NMR spectrum consists of seven distinct equal-area resonances (Figure 1), indicating that two boron atoms have been removed from the original icosahedral complex in such a way as to destroy the symmetry of the cage. The asymmetry is confirmed in the proton NMR spectrum, which contains a singlet assignable to an η^6-C_6H_6 ring and two distinct resonances from the cage C–H units; in addition, a broad, diffuse peak that was not possible to integrate meaningfully is evident from ca. −1 to −2 ppm, i.e., in the region normally associated with bridging hydrogen resonances.

If allowance is made for some difference of resolution from the different magnetic field strengths employed, the ^{11}B NMR spectrum of the complex is nearly superimposable on that of the metallacarbaborane characterized as an isomer of *closo*-(C_5H_5)$CoC_2B_7H_9$ (compound IB in ref 10), isolated from the polyhedral contraction of 3,1,2-(C_5H_5)$CoC_2H_9H_{11}$. Although several symmetrical structures for both MC_2B_7 cages can be eliminated from the NMR data, 15 possible isomers remain that cannot be assigned by spectroscopic means alone. In order to determine the location of the ruthenium and carbon atoms in the cage, as well as to confirm whether bridging hydrogens were in fact present, a low-temperature X-ray crystal structure determination was completed.

(b) Solid-State Structure of 2,5,6-(η-C_6H_6)$RuC_2B_7H_{11}$. The crystal contains monomeric units of the complex, which, as expected from the NMR data, contain no symmetry. A view of the molecule indicating the coordination geometry and numbering scheme is presented in Figure 2. Selected interatomic bond distances and angles are listed in Tables V and VI, respectively. Average bond distances are collected in Table VII.

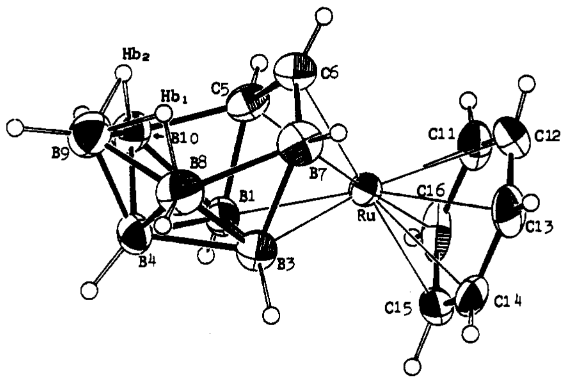

Figure 2. ORTEP view of the 2,5,6-(η-C_6H_6)$RuC_2B_7H_{11}$ molecule with the atom-numbering scheme used in the tables. Hydrogen atoms are represented as open circles.

Table V. Bond Distances (Å) for the 2,5,6-(η-C_6H_6)$RuC_2B_7H_{11}$ Molecule

A	B	dist	A	B	dist
Ru	C(5)	2.169 (6)	C(12)	C(13)	1.399 (10)
Ru	C(6)	2.139 (6)	C(13)	C(14)	1.387 (10)
Ru	C(11)	2.240 (7)	C(14)	C(15)	1.398 (11)
Ru	C(12)	2.238 (6)	C(15)	C(16)	1.380 (10)
Ru	C(13)	2.209 (6)	C(5)	B(1)	1.681 (9)
Ru	C(14)	2.189 (7)	C(6)	B(7)	1.518 (10)
Ru	C(15)	2.208 (6)	B(1)	B(3)	1.838 (10)
Ru	C(16)	2.219 (7)	B(3)	B(7)	1.780 (10)
Ru	B(1)	2.142 (7)	B(8)	B(9)	1.769 (12)
Ru	B(3)	2.188 (7)	B(9)	B(10)	1.795 (11)
Ru	B(7)	2.255 (8)	B(8)	H(17) [Hb_1]	1.18 (8)
C(5)	C(6)	1.466 (9)	B(9)	H(17) [Hb_1]	1.36 (7)
C(11)	C(12)	1.377 (10)	B(9)	H(18) [Hb_2]	1.28 (7)
C(11)	C(16)	1.410 (10)	B(10)	H(18) [Hb_2]	1.25 (7)

Table VI. Bond Angles (deg) for 2,5,6-(η-C_6H_6)$RuC_2B_7H_{11}$

A	B	C	angle
C(5)	Ru	C(6)	39.8 (2)
C(6)	Ru	B(7)	40.7 (2)
B(7)	Ru	B(3)	47.6 (3)
B(3)	Ru	B(1)	50.2 (3)
B(1)	Ru	C(5)	45.9 (3)
C(11)	Ru	C(12)	35.8 (3)
C(12)	Ru	C(13)	36.7 (3)
C(13)	Ru	C(14)	36.8 (3)
C(14)	Ru	C(15)	37.1 (3)
C(15)	Ru	C(16)	36.3 (3)
C(16)	Ru	C(11)	36.9 (3)
C(11)	C(12)	C(13)	121.6 (7)
C(12)	C(13)	C(14)	118.8 (7)
C(13)	C(14)	C(15)	120.4 (7)
C(14)	C(15)	C(16)	120.1 (6)
C(15)	C(16)	C(11)	120.2 (7)
C(16)	C(11)	C(12)	118.9 (7)
C(5)	C(6)	B(7)	115.2 (6)
C(6)	B(7)	B(3)	108.2 (5)
B(7)	B(3)	B(1)	101.1 (5)
B(3)	B(1)	C(5)	101.6 (5)
B(1)	C(5)	C(6)	113.4 (5)
B(8)	B(9)	B(10)	101.9 (5)
Ru	C(6)	H(6)	120 (4)
C(5)	C(6)	H(6)	121 (4)
B(7)	C(6)	H(6)	124 (4)
B(8)	B(9)	H(17) [Hb_1]	42 (3)
B(9)	H(17) [Hb_1]	B(8)	88 (5)
B(9)	B(8)	H(17) [Hb_1]	50 (4)
B(9)	B(10)	H(18) [Hb_2]	45 (3)
B(10)	H(18) [Hb_2]	B(9)	91 (4)
B(10)	B(9)	H(18) [Hb_2]	44 (3)
H(17) [Hb_1]	B(9)	H(18) [Hb_2]	84 (4)

The geometry of the molecule is loosely based on that of decaborane(14), which may be viewed crudely as consisting of a four-membered diamond "butterfly" capped by a six-membered

Table VII. Average Bond Lengths

atoms	no.	range, Å	av, Å
Ru-C(ring)	6	2.189 (7)-2.240 (7)	2.22 (2)
Ru-C(cage)	2	2.139 (6)-2.169 (6)	2.15 (2)
Ru-B(cage)	3	2.142 (7)-2.225 (8)	2.19 (4)
B-B	12	1.726 (11)-1.907 (11)	1.80 (5)
B-C	3	1.518 (10)-1.748 (10)	1.65 (12)
C-C(ring)	6	1.377 (10)-1.410 (10)	1.39 (1)
C-H(ring)	6	0.74 (7)-0.98 (7)	0.87 (8)
B-H(terminal)	7	1.03 (7)-1.13 (8)	1.08 (4)
B-H(bridging)	4	1.18 (8)-1.36 (7)	1.27 (7)

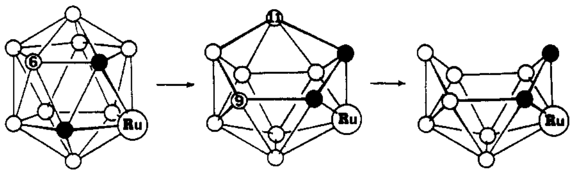

Figure 3. Proposed degradative formation of (η-C_6H_6)$RuC_2B_7H_{11}$. For illustrative purposes, the coordinated benzene has been omitted and the 2,6,7-enantiomer is represented.

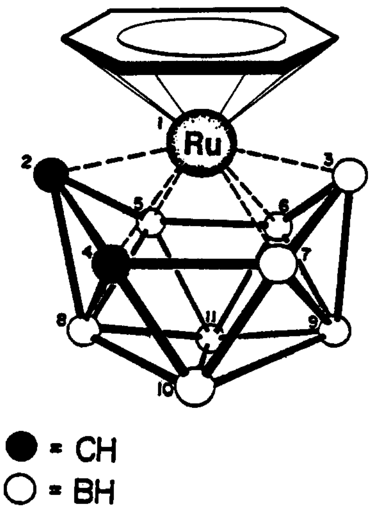

Figure 4. Proposed structure of 1,2,4-(η-C_6H_6)$RuC_2B_8H_{10}$.

cyclohexane-like "boat".[12] The ruthenium atom occupies position 2 in the butterfly, while the carbon atoms lie adjacent to each other in the boat at positions 5 and 6, where they are formally 5- and 4-coordinate, respectively. Two hydrogen atoms (Hb_1 and Hb_2) were unambiguously determined to bridge borons B8/B9 and B9/B10, respectively. With the exception of the ruthenium residue in position 2, the structure of the compound is thus analogous to that proposed for the isoelectronic carbaborane 5,6-$C_2B_8H_{12}$.[13]

As an examination of Table VII indicates, most of the distances in the molecule are typical for metallacarbaborane cages and require no elaborate comment. The geometry about the ruthenium is unexceptional; the C–C lengths in the ring are experimentally equal, and the ring itself is planar to within 0.016 Å. The metal–ring distance of 2.22 Å (average) is well within the range normally observed for (η-C_6H_6)Ru^{II} complexes.[14]

The uniqueness of the molecule lies in the placement of its heteroatoms; specifically, it is the first 24-e 10-membered nido metallacarbaborane with a decaborane geometry in which the metal is not located on the six-membered open "boat".[15,16] It thus stands in contrast to the structurally characterized 8,6,7-(C_5H_5)$CoC_2B_7H_{11}$[17] and 6,5,9-$(Et_3P)_2NiMe_2C_2B_7H_9$[18] complexes, formed respectively from the degradation of 1,2,4-(C_5H_5)$CoC_2B_8H_{10}$ and the reaction of *arachno*-5,9-Me_2-5,9-$C_2B_7H_{11}$ with Et_3P and $(COD)_2Ni$.

Although the ruthenametallacarbaborane is formed in very low yield, its unique stereochemistry allows us to propose a plausible mechanism of formation. Of pivotal structural importance is the persistence of the C–Ru–C triangle of the parent icosahedral molecule in the framework of the degraded metallacarbaborane. In fact, since the ruthenium is still bound to a B_3C_2 "face" of the polyhedron, there is no need to postulate the breakage of any M–C or M–B bonds during the contraction. The simplest scheme that will lead to the observed isomer is detailed in Figure 3. The first boron likely to be extracted is B(6) in the original icosahedron; it is adjacent to both carbon atoms and is probably the most electrophilic boron in the cage.[19] Its loss from the skeleton would produce the *nido*-3,7,8-(η^6-C_6H_6)$RuC_2B_8H_{10}^{2-}$ ion. Subsequent removal of B(9) (or, equivalently, B(11)) from this anion followed by protonation yields the observed 2,5,6-(η-C_6H_6)$RuC_2B_7H_{11}$.

It may be worthwhile to reconsider the structure of the nonsymmetrical degradation product of 3,1,2-(C_5H_5)$CoC_2B_9H_{11}$ formulated as an isomer of *closo*-(C_5H_5)$CoC_2B_7H_9$.[10] We think it likely that the compound in question may in fact be a *nido*-(C_5H_5)$CoC_2B_7H_{11}$ complex, perhaps even the 2,5,6-isomer. To begin with, the nearly identical ^{11}B NMR spectra of the cobalt and ruthenium compounds suggest a far closer relationship between them than would be expected if one molecule had a nido geometry while the other had a closo geometry. In addition, the low-resolution mass spectral cutoff of *m/e* 235 reported for the cobaltacarbaborane corresponds to the $^{12}C_7{}^1H_{15}{}^{11}B_7{}^{59}Co^+$ ion, i.e., $(C_5H_5)CoC_2B_7H_{10}^+$, which contains one too many hydrogens for the closo species but might result from the loss during ionization of a hydrogen from a nido cage.[22] Finally, the elemental composition calculated for the nido complex is in better agreement with the experimental analysis than is that calculated for the closo configuration.[23] Although no proton NMR resonances were reported that could be attributed to bridging hydrides, such signals are not always obvious; they are only weakly observed in the present ruthenium complex and are not detected at all in the spectrum of 6,5,9-$(Et_3P)_2NiMe_2C_2B_7H_9$.[18]

If in fact the cobalt and ruthenium compounds are isostructural, we have the first preliminary evidence that the isoelectronic $(C_5H_5)Co^{2+}$ and (η-C_6H_6)Ru^{2+} moieties are functionally equivalent during polyhedral contraction. This tentative conclusion is reinforced by the detection of a second product from the contraction of 3,1,2-(η-C_6H_6)$RuC_2B_9H_{11}$ (vide infra).

(c) **1,2,4-(η-C_6H_6)$RuC_2B_8H_{10}$.** After the elution of 2,5,6-(η-C_6H_6)$RuC_2B_7H_{11}$, an orange band develops that is found to consist of an approximately 1:1 mixture of the starting material and an unknown compound. Unfortunately, the solubilities of the two substances are nearly identical in common organic solvents, and we have been unable to effect their complete separation by either column or thick-layer preparative chromatography. Spectroscopically, however, eight distinct equal-area resonances, which are distinct from those of 3,1,2-(η-C_6H_6)$RuC_2B_9H_{11}$ (see Table I), are clearly detectable in the ^{11}B NMR spectrum of the mixture.

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The ^{1}H NMR spectrum of the mixture contains, besides the peaks expected for the starting material, a singlet of area 6 at δ 5.92 and two broad, unit-area resonances at δ 5.2 and 4.9. The data are consistent with an (η-C_6H_6)Ru complex of a nonsymmetrical B_8C_2cage, i.e., (η-C_6H_6)$RuC_2B_8H_{10}$. The similarity of the ^{11}B NMR spectrum to that of 1,2,4-(C_5H_5)$CoC_2B_8H_{10}$[10] suggests that we are dealing with the same structural species (Figure 4), formed presumably via an analogous degradative pathway.[11a]

Since at least two products from the degradation of 3,1,2-(η-C_6H_6)$RuC_2B_9H_{11}$ are probably related to those obtained from its isoelectronic cobalt counterpart, we have no reason to believe that the degradation mechanisms are fundamentally different for the two cases. Indeed, the chief difference between the polyhedral contraction reactions appears to be the somewhat greater chemical robustness of the ruthenium complex: after 32-h reflux in 1.2 M KOH, appreciable amounts of the starting material are recovered (up to ca. 10%), whereas the degradation of the cobalt complex appears to be essentially complete after 25 h.[10]

Synthesis of 3,1,2-(η-C_6H_6)$OsC_2B_9H_{11}$. In an effort to determine whether the parallelisms tentatively established between the (η-C_6H_6)Ru^{2+} and (C_5H_5)Co^{2+} moieties would be maintained with a third-row transition metal, an attempt was made to prepare the parent 3,1,2-(η-C_6H_6)$OsC_2B_9H_{11}$ by the reaction of (C_6H_6)$OsCl_2{\cdot}NCCH_3$ with Tl[3,1,2-$TlC_2B_9H_{11}$] in THF. Workup of the reaction mixture indeed produced the desired compound, albeit in low (15%) yield. The complex forms colorless, air-stable crystals that dissolve in a variety of organic solvents. Its ^{11}B NMR spectrum (Table I) is indicative of a closo icosahedral cage, and the ^{1}H NMR spectrum exhibits a singlet at δ 6.26, as anticipated for an η^6-C_6H_6 ring. The low-resolution mass spectrum cutoff of *m/e* 404 corresponds to the molecular ion $^{12}C_8{}^1H_{17}{}^{11}B_9{}^{192}Os^+$; its composition was confirmed by the measured high-resolution mass of *m/e* 404.1788 (calcd *m/e* 404.1780).

The osmium complex is noteworthy in that it represents the first reported (π-arene)osmacarbaborane and thus completes the iron triad of arene complexes. The disappointingly low yield of its preparation, however, meant that it was not available in sufficient quantities for detailed study of its reactivity.

Synthesis and Properties of 3,1,2-[*endo-H*-η^5-$(CH_3)_6C_6H$]-$CoC_2B_9H_{11}$. The chemistry of (π-arene)metallacarbaboranes incorporating the group 9[29] metals (Co, Rh, Ir) is inherently less predictable than that of compounds incorporating the iron metals, since the neutral (η^6-arene)$M^{II}C_2B_9H_{11}$ complexes isolable for the latter elements are not likely to be stable with d^7 metal centers. On the one hand, oxidation to the trivalent metal state should be strongly favored in order to relieve the 1-e excess and form diamagnetic 18-e [(η^6-arene)$M^{III}C_2B_9H_{11}$]$^+$ species. Cationic metallacarbaboranes, however, are not particularly stable compounds. The Co(I) complex [$(HMB)_2Co$](PF_6) reacts with Tl[3,1,2-Tl-$C_2B_9H_{11}$], forming substantial amounts of the $(C_2B_9H_{11})_2Co^-$ ion and a low yield of an air-stable dull red crystalline solid. The latter is readily soluble in hydrocarbon solvents and can be recrystallized without decomposition from hot benzene/toluene mixtures. Its ^{11}B NMR spectrum (Table I) is typical of *closo*-$LMC_2B_9H_{11}$ metallacarbaboranes, and the observation of normal chemical shifts and B–H coupling constants (J = 155 ± 20 Hz) suggests that the complex is diamagnetic and probably contains formal Co(III). Both the low-resolution mass spectrum cutoff at *m/e* 356, corresponding to the $^{12}C_{14}{}^1H_{30}{}^{11}B_9{}^{59}Co^+$ ion, and the high-resolution mass (*m/e* 356.2524 (calcd *m/e* 356.2517)) indicate that the compound contains one more hydrogen atom than is required by the formulation (HMB)$CoC_2B_9H_{11}$.

The proton NMR spectrum clearly indicates that the HMB ring no longer possesses a C_6 axis and that the additional hydrogen is a component of a hexamethylcyclohexadienyl ligand (Figure 5).

Although coupling between the extra hydrogen and the geminal methyl group is readily apparent from the spectrum, the configuration of the hydrogen on the ring (exo or endo) is not immediately obvious and was deduced from both spectroscopic and chemical evidence.

A compilation of reported proton NMR chemical shifts of methylated cyclohexadienyl complexes reveals that, despite variations in other parts of the spectra, the resonances of exo methyl groups on the saturated carbons nearly always occur at higher field than +1 ppm; conversely, endo methyl protons resonate below 1 ppm.[24] The correlation is observed across a wide range of complexes and is most dramatic with exo–endo pairs of compounds, such as in [*exo-Me*-η^5-Me_6C_6H]Ir(Me_5C_5)$^+$ and [*endo-Me*-η^5-Me_6C_6H]Ir(Me_5C_5)$^+$, for which the methyl doublets are detected at δ 0.48 and 1.08,[24b] respectively. The shift of 0.57 ppm observed for the cobaltacarbaborane complex thus places it in the exo-Me (endo-H) class.

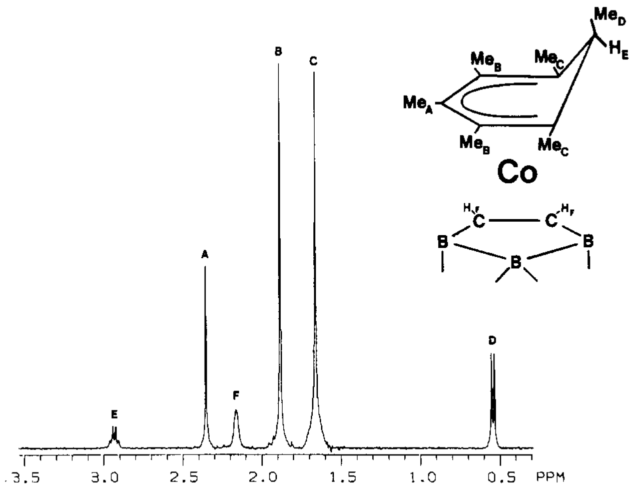

Figure 5. Proton NMR spectrum (361 MHz) and assignments for 3,1,2-[*endo-H*-η^5-$(CH_3)C_6H$]$CoC_2B_9H_{11}$. For exact chemical shifts and the coupling constants, see the Experimental Section.

The molecule does not react with Ph_3C^+, a reagent that fails to abstract a hydride from cyclohexadienyl complexes only when the hydrogen is endo.[25] When the complex is dissolved in the presence of the less selective reagents *N*-bromosuccinimide (CD_3OD)[27] or HNO_3 ($CDCl_3$),[28] however, the orange-red solution immediately becomes yellow and the ^{1}H NMR spectrum collapses to a singlet at δ 2.50 (18 H) and a broad resonance at δ 4.1 (2 H). Such a spectrum is consistent with the presence of an η^6-HMB ring and two equivalent carbaborane CH groups and suggests that the species present in solution is in fact the cation (η^6-HMB)-$CoC_2B_9H_{11}{}^+$. As might be expected of a cationic metallacarbaborane, the solution is stable only for ca. 30 min, after which solids begin to precipitate.

All of the evidence obtained thus far strongly favors formulation of the original cobaltacarbaborane as 3,1,2-[*endo-H*-η^5-$(CH_3)_6C_6H$]$CoC_2B_9H_{11}$.

Intermolecular nucleophilic attack on the arene ring of the complex by a hydride source would add the hydrogen exo to the coordinated ring. The apparent endo configuration of the added hydrogen in the cobaltacarborane derivative is uncommon and suggests that at some point in the reaction a cobalt hydride intermediate is present that subsequently transfers the hydrogen to the ring. Further studies will be needed to confirm and strengthen these initial results.

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(29) 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 an 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

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Synthesis of Pentaammine(phosphato)rhodium(III) and Kinetics of Formation of Its Diprotonated Form

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The compound $[Rh(NH_3)_5PO_4]\cdot 3H_2O$ has been prepared in pure form and characterized. The kinetics of formation of its diprotonated form, $[Rh(NH_3)_5H_2PO_4]^{2+}$ from $[Rh(NH_3)_5H_2O]^{3+}$ and $H_2PO_4^-/H_3PO_4$, has been studied in aqueous solution at 80, 90, and 97 °C ($[H^+] = 0.8 \times 10^{-3}$–$1.3 \times 10^{-1}$); $I = 1.0$ ($LiClO_4$)). Both H_3PO_4 (k_1 path) and $H_2PO_4^-$ (k_2 path) are reactive, but no evidence for outer-sphere association has been found. Values of the rate constants at 80, 90, and 97 °C are as follows: 10^4k_1 ($M^{-1}\ s^{-1}$) = 2.1, 5.4, 14; 10^3k_2 ($M^{-1}\ s^{-1}$) = 1.7, 5.5, 10. The results are interpreted in terms of a mechanism with associative activation. A comparison with existing data for anation of $[Rh(NH_3)_5H_2O]^{3+}$ is made.

Introduction

Whereas anation reactions of pentaammineaquocobalt(III) and pentaammineaquochromium(III) have been well studied,[1-6] the corresponding reactions of pentaammineaquorhodium(III) are not so well-known.[7] Following our interest in complexes containing phosphorus oxoanions,[8,9] we report in this paper the synthesis of pure $[Rh(NH_3)_5PO_4]\cdot 3H_2O$ (hereafter referred to as the phosphato complex) and its characterization and a study of the kinetics of formation of its diprotonated form from the corresponding aquo complex (eq 1) in order to provide more data on the reactivity and substitution mechanisms of pentaammine complexes of Rh(III).

$$[Rh(NH_3)_5H_2O]^{3+} + H_2PO_4^- = [Rh(NH_3)_5H_2PO_4]^{2+} + H_2O \qquad (1)$$

Experimental Section

Materials. Stock solutions of phosphoric acid, lithium dihydrogen phosphate, and lithium perchlorate were prepared as previously described.[3] $RhCl_3(aq)$ (Johnson Matthey Chemicals) was used as a source of rhodium. $[Rh(NH_3)_5H_2O](ClO_4)_3$ was prepared[10] from $[Rh(NH_3)_5Cl]Cl_2$.[11] The spectrum of the aquo complex, maxima at 315 nm ($\epsilon = 111\ M^{-1}\ cm^{-1}$) and 263 nm ($\epsilon = 98\ M^{-1}\ cm^{-1}$), was in good agreement with literature values.[12] $[Rh(NH_3)_5CO_3]ClO_4$ was prepared by the method of Palmer et al.[13] and characterized spectrophotometrically.

Preparation of $[Rh(NH_3)_5PO_4]\cdot 3H_2O$. $[Rh(NH_3)_5CO_3]ClO_4$ (0.4 g) and 85% phosphoric acid (40 mL) were heated at 80–85 °C on a water bath for 7 h. The resulting syrup was allowed to cool to room temperature and treated with distilled methanol (ca. 350 mL) under constant stirring until a precipitate started to form. The suspension was left in the refrigerator overnight and then centrifuged. The solid, which easily becomes an oil, was dissolved in the minimum amount of water and poured onto a 150 × 15 mm column of Lewatit MP 64 weakly basic anion-exchange resin (OH^- form) and the effluent collected. The column was washed with water until the washings gave no basic reaction. The combined effluent and washings were treated with a 1/10 volume of concentrated ammonia and then with an excess of distilled ethanol that had been previously treated with activated charcoal (the ethanol used should be very pure, otherwise the UV bands of the impurities mask the bands of the phophato complex). The yellow-white solid that precipitated was filtered and washed with ethanol and air-dried. Anal. Calcd for $[Rh(NH_3)_5PO_4]\cdot 3H_2O$: PO_4, 28.19; NH_3, 25.22. Found: PO_4, 28.1; NH_3, 25.1. A solution of the diprotonated phosphato complex was obtained by dissolving the neutral species in 0.1 M $HClO_4$.

Analyses. Phosphates were determined gravimetrically as quinolinium phosphomolybdate.[14] Ammonia was determined by distillation in the presence of Devarda alloy.

Kinetic Runs. The reaction was followed in situ at 340 nm in the cell compartment of a Beckman UV 5230 spectrophotometer that was thersmostated by circulating water (80, 90 ± 0.1 °C) or ethylene glycol (97 ± 0.1 °C) from a Hetto 05 ultrathermostat. The temperature control was achieved with a copper–constantan thermocouple directly connected to the cell. Absorbance values were read from the recording chart. In the acidity range used ($[H^+] = 0.8 \times 10^{-3}$–$1.3 \times 10^{-1}$) the only relevant species derived from phosphoric acid are H_3PO_4 and $H_2PO_4^-$; furthermore, given the low acidity constant of $[Rh(NH_3)_5H_2O]^{3+}$, $pK_a = 6.9$ at 25 °C, the contribution of $[Rh(NH_3)_5OH]^{2+}$ can be neglected since even at the lowest acidity the concentration ratio of $[Rh(NH_3)_5OH]^{2+}$ to $[Rh(NH_3)_5H_2O]^{3+}$ is ca. 2×10^{-4}. The reaction was carried out with a great excess of total phosphate concentration, $[PO_4]_T = [H_3PO_4] + [H_2PO_4^-]$, over that of aquo complex, 7.00×10^{-3} M in all runs, thus ensuring pseudo-first-order conditions. Values of $[H^+]$, $[H_3PO_4]$, and $[H_2PO_4^-]$ were calculated from added $HClO_4$, H_3PO_4, and LiH_2PO_4. The ionic strength was adjusted to 1.0 with $LiClO_4$ in all runs. The runs carried out at low $[PO_4]_T$ and/or low temperature (i.e., most at 80 °C, about half at 90 °C, and a few at 97 °C) do not reach 100% completion as can be shown by comparing experimental and calculated A_∞ values. To eliminate the contribution of the back-reaction (the aquation reaction) (see below), only the values of absorbance/time corresponding to the first approximately 20% of the reaction were used in computing first-order rate constants (k_{obsd}).[2] These were obtained from the slopes of the plots of $-\ln (A_\infty - A)$ vs. time, which were linear, thereby

$$-d[Rh(NH_3)_5H_2O^{3+}]/dt = k_{obsd}[Rh(NH_3)_5H_2O^{3+}] \qquad (2)$$

The A_∞ values used in this formula correspond to those calculated on the assumption of 100% conversion. Errors quoted are standard deviations.

Results and Discussion

Characterization of the Phosphato Complex. Seel and Bohnstedt[15] prepared the neutral phosphato complex, heavily contaminated by ammonium carbonate, and did not report spectra. We have been able to prepare it in a pure form, using a different procedure. $[Rh(NH_3)_5PO_4]\cdot 3H_2O$ is a yellow-white stable solid, easily soluble in water. The IR spectrum (Figure 1) clearly shows the presence of monodentate phosphate group (C_{3v} symmetry) and is very similar to that of the cobalt[16] and chromium[8] analogues. Conductivity measurements (10^{-3} M, 25 °C) give $\Lambda = 23\ \Omega^{-1}\ cm^2\ mol^{-1}$, a value somewhat high due to partial protonation of the neutral species but consistent with its formulation as a nonelectrolyte. The compound does not give an immediate precipitate

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