

## SYNTHESIS AND PROPERTIES OF SUBSTITUTED RHODICINIUM SALTS

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### Summary

Rhodicinium salts with the following substituents; H, CH<sub>3</sub>, 1,1'-(CH<sub>3</sub>)<sub>2</sub>, CO<sub>2</sub>H, 1,1'-(CO<sub>2</sub>H)<sub>2</sub>, 1,1'-(COCl)<sub>2</sub>, 1,1'-(CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> and 1,1'-(NH<sub>2</sub>)<sub>2</sub> have been prepared as their hexafluorophosphate salts by the procedure previously employed for synthesis of the corresponding cobalticinium salts. The rhodicinium salts are paler in color but similar in stability and physical and chemical properties to the corresponding cobalticinium salts. IR, UV and <sup>1</sup>H and <sup>13</sup>C NMR spectra of the rhodicinium salts and their cobalticinium and ferrocene analogs are discussed. The basicity of 1,1'-diaminorhodicinium in aqueous acid,  $pK_1 = 13.36 \pm 0.06$ ,  $pK_2 = 17.04 \pm 0.06$ , was determined spectrophotometrically. The values for the corresponding 1,1'-diaminocobalticinium salt are  $pK_1 = 13.5 \pm 0.1$  and  $pK_2 = 18.1 \pm 0.1$ . The slightly greater basicity of the 1,1'-diaminorhodicinium is attributed to the greater separation of the cyclopentadienyl rings which moves the amino groups farther from the positively charged metal atom and from each other.

### Introduction

As an extension of our previous research on substituted cobalticinium salts [1–3] we have undertaken the synthesis and characterization of a series of substituted rhodicinium salts [4]. Rhodicinium salts have been prepared previously by reaction of cyclopentadienylmagnesium bromide or cyclopentadienylsodium with rhodium(III) acetylacetonate or anhydrous rhodium(III) chloride [5–8] but few substituted derivatives have been reported. Since cobalticinium salts can be prepared more easily in large quantities and in good yields from substituted cyclopentadienyl thallium derivatives [9], we utilized a similar procedure for rhodicinium salts.

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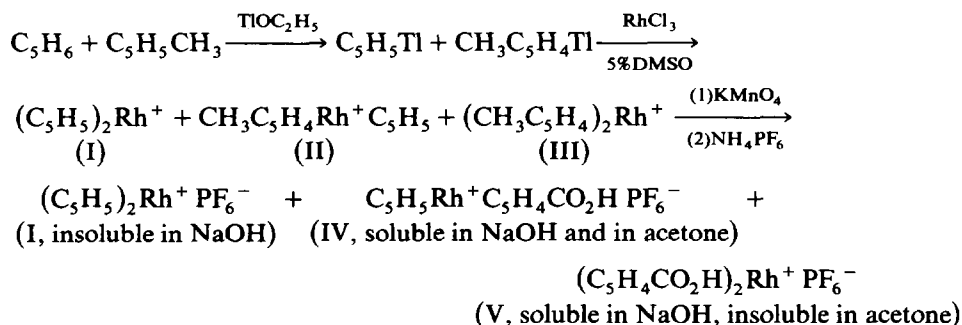
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## Results and discussion

The procedure for synthesis of the rhodicinium salts I–VIII is the same as that for corresponding cobalticinium salts [2,9]. Pure samples of I and III can be prepared in good yield from cyclopentadienylthallium and methylcyclopentadienylthallium, respectively. The only way we have been able to prepare II, the precursor for the monocarboxylic acid IV, was as a mixture with I and III. The yield for the mixture of I, II, and III is slightly better than for the corresponding cobalticinium salts because no change in oxidation state is necessary in converting  $\text{RhCl}_3$  to rhodicinium salts; whereas  $\text{CoCl}_2$  must be oxidized from the +2 to the +3 state concurrently with formation of the cobalticinium salts. No attempt was made to separate I, II and III since the three salts have very similar solubilities and retention times on most chromatographic supports. Instead the mixture was treated with sufficient alkaline  $\text{KMnO}_4$  to oxidize all of the methyl groups (determined by the ratio of  $\text{CH}_3$  protons to ring protons in the NMR) to carboxyls.

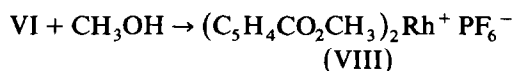
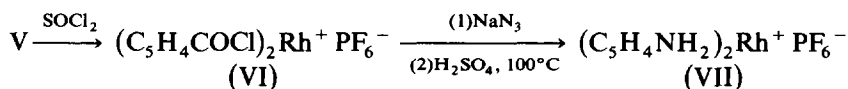
Upon oxidation with basic  $\text{KMnO}_4$ , compound I remains unchanged and precipitates from solution, while IV and V are soluble in alkaline solution. Upon acidification a mixture of IV and V precipitates. The monocarboxylic acid, IV, may be extracted into acetone but the dicarboxylic acid, V, is insoluble. With care quantitative separation can be achieved.



Compounds IV and V can be purified by dissolving in dilute base and reprecipitating as a fine powder with 10% HCl. Analytically pure samples can be obtained in large colorless plates by recrystallization from boiling water. The powdered form of V, however, reacts much more readily with  $\text{SOCl}_2$  than does the highly crystalline material, possibly because the dicarboxylic acid by analogy with the corresponding cobalticinium salt [10] is polymeric in the crystalline state.

The 1,1'-dicarboxylic acid V was converted to the diacyl chloride VI by refluxing for 3–6 h in excess thionyl chloride. The length of time needed for complete conversion varies, so the progress of the reaction is followed by infrared spectroscopy (see Experimental). Excessively long reaction times cause decomposition and decreased yields. The diacyl chloride VI was converted to the dimethyl ester VIII which can be analyzed more readily. The diacyl chloride was converted to the diacyl azide which readily undergoes a Curtius rearrangement in 96%  $\text{H}_2\text{SO}_4$  at  $100^\circ\text{C}$  to form the diamine VII in 20–40% yield. No 1-amino-1'-carboxyrhodicinium salt was obtained; whereas 1-amino-1'-carboxycobalticinium is formed in 20–40% yield under the same experimental conditions [16]. Owing to the small amount of monocarboxylic acid IV available, no attempt was made to prepare derivatives from

it. However, preparation should proceed smoothly by the same procedures used for the corresponding cobalticinium salts [2].



The rhodicinium salts bear a strong resemblance in their properties to the corresponding cobalticinium salts. They are paler in color, being white (V), cream colored (III) or light yellow (VII) rather than deep yellow or orange, and are slightly less soluble in water.

### Spectra of rhodicinium salts

The infrared spectra of substituted rhodicinium salts are almost identical to that of the corresponding cobalticinium salts (see Experimental and Ref. 2 and 16). The UV and proton and  $^{13}\text{C}$  NMR spectra are given in Tables 1-3. The shape of the UV absorption peaks is similar to that of the cobalticinium salts but the maxima are shifted to shorter wavelengths by 30–40 nm. The peaks in the proton NMR of rhodicinium salts lie within 0.1–0.2 ppm of the corresponding cobalticinium salts but coupling with  $^{103}\text{Rh}$ ,  $J \sim 1$  Hz, causes the spectra to be more complex.

The  $^{13}\text{C}$  NMR spectra are given in Table 3 along with data for the corresponding cobalticinium salts [14] and ferrocene derivatives [11,12]. The resonances for the rhodicinium salts lie 2–5 ppm downfield from the corresponding cobalticinium salts and 16–25 ppm downfield from the ferrocene derivatives. Coupling of 3–7 Hz is observed between  $^{103}\text{Rh}$  and  $^{13}\text{C}$ . In assigning the signals for C(2,5) and C(3,4) we have followed the convention of Slocum and Ernst [15] that electron-withdrawing substituents deshield C(2,5) more than C(3,4) and electron-donating substituents shield C(3,4) more than C(2,5). In all three classes of compounds electron-donating substituents cause an upfield shift of 5–10 ppm and electron-withdrawing sub-

TABLE 1  
UV SPECTRA OF RHODICINIUM AND COBALTICINIUM SALTS

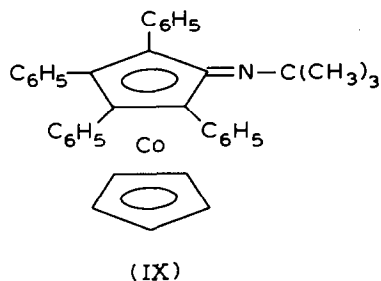
Substituent	Metal	$\lambda_{\text{max}}$ (nm) ( $\epsilon$ )		
H	Co	264 (33400)	300 sh (1200)	409 (200)
	Rh	232 (62000)	275 sh (1600)	
1,1'-(CH <sub>3</sub> ) <sub>2</sub>	Co	267 (34000)	308 sh (1200)	416 (255)
	Rh	283 (46800)	275 sh (2750)	
1,1'-(CO <sub>2</sub> H) <sub>2</sub>	Co	222 (7300) 271 (23200)	315 sh (1700)	414 (246)
	Rh	245 (31000)	285 sh (2500)	
1,1'-(NH <sub>2</sub> ) <sub>2</sub>	Co	269 (9900)	306 (13450)	365 (3300)
	Rh	257 (16750)	341 (6500)	
NH <sub>2</sub> , 1'-NH <sub>3</sub> <sup>+</sup>	Co	276 (16100)	358 (3720)	406 (1280)
	Rh	245 (44000)	330 (6600)	
1,1'-(NH <sub>3</sub> <sup>+</sup> ) <sub>2</sub>	Co	267 (39400)	310 (1120)	400 (260)
	Rh	237 (72700)	265 (6500)	

TABLE 2  
<sup>1</sup>H NMR OF SUBSTITUTED RHODICINIUM AND COBALTICINIUM SALTS

Substituent	Metal	$\delta$ (ppm) from TMS			
		C(2)	C(3)	C(1)	Other
H	Co <sup>a</sup>	6.25			
	Rh <sup>a</sup>	6.13 d			
1,1'-(CH <sub>3</sub> ) <sub>2</sub>	Co <sup>a</sup>	6.16			2.40 (CH <sub>3</sub> )
	Rh <sup>a</sup>	5.90	6.00		2.23 (CH <sub>3</sub> )
CO <sub>2</sub> H	Co <sup>a</sup>	6.33	6.09	6.04	
	Rh <sup>b</sup>	6.12 m		6.05 d	
1,1'-(CO <sub>2</sub> H) <sub>2</sub>	Co <sup>b</sup>	6.36	6.10		
	Rh <sup>b</sup>	6.50 m	6.25 m		
1,1'-(NH <sub>2</sub> ) <sub>2</sub>	Co <sup>a</sup>	5.04	5.22		4.76 (NH <sub>2</sub> )
	Rh <sup>a</sup>	5.48	5.50		

<sup>a</sup> Spectra in acetone-*d*<sub>6</sub>. <sup>b</sup> Spectra in 96% H<sub>2</sub>SO<sub>4</sub>.

stituents a downfield shift of comparable magnitude. The NH<sub>2</sub> group exerts a strong shielding effect on the 2- and 3-positions which is lost when protonation occurs in strong acid. The increase in chemical shift of C(1) produced by the amino groups, 41.7 ppm in the case of cobalticinium and 43.0 for rhodicinium, is much larger than the shift of approximately 20 ppm observed for aromatic amines [19], thus resonance between the amino group and the ring is more extensive than for simple aromatic amines, but not so extensive as in a true cyclopentadienoneimine such as compound IX in which C(1) appears at 154.12 ppm, a shift of 68.2 ppm from cobalticinium [20].



Further evidence that C(1) is bound to the metal in the case of both VII and its Co analog is that the signal for C(1) is split by <sup>103</sup>Rh although with a smaller coupling constant than the other ring carbons; whereas in  $\eta^4$ -cyclopentadienone and  $\eta^4$ -duroquinone complexes the carbonyl groups, which are bent out of the plane of the ring, are not split [13]. Whether C(1) in compound IX is also bent out of the plane of the ring is not known since no X-ray crystallographic study has been performed.

#### Basicity of 1,1'-diaminorhodicinium salts (VII)

In order to compare the influence of rhodium and cobalt on substituents we measured the values for  $pK_b$  for protonation of the two amino groups of VII in

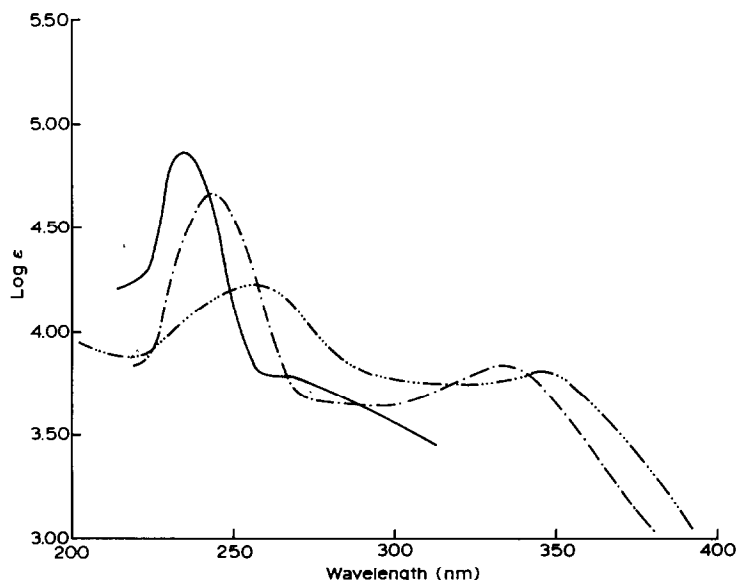


Fig. 1. UV spectra of unprotonated - · - · - ·, monoprotonated - - - and diprotonated — 1,1'-diaminorhodicinium salts in aqueous solution.

aqueous acid by the procedure previously employed for the cobalticinium analog [16]. Since the second amino group is at least a factor of  $10^3$  less basic than the first, it is possible to study the two equilibria separately and to observe the UV spectrum of the monoprotonated form in a solution where the concentration of unprotonated and diprotonated forms is negligible. (The NMR spectrum of the monoprotonated form cannot be observed since rapid proton exchange makes the two amino groups appear equivalent). The first stage of protonation is essentially complete in 0.5 *M* HCl while the second stage does not begin until concentration of HCl is greater than 2.0 *M*, so VII in 1.0–2.0 *M* HCl is monoprotonated. The second amino group is not sufficiently basic to be completely protonated in 12.0 *M* HCl but is completely protonated in 75–96%  $H_2SO_4$ . The UV spectra of the unprotonated, monoprotonated and diprotonated forms of VII are tabulated in Table 1 and shown in Fig. 1. From the known acid strength of HCl and  $H_2SO_4$  solutions [17], the values  $pK_1 = 13.36 \pm 0.06$  and  $pK_2 = 17.04 \pm 0.06$  were calculated, slightly more basic than the corresponding cobalticinium derivative,  $pK_1 = 13.5 \pm 0.1$   $pK_2 = 18.1 \pm 0.1$  [16].

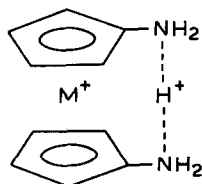
A similar trend was observed with the hydroxyrhodicinium salts, which are slightly less acidic than the corresponding hydroxycobalticinium salts [18]. Thus rhodium exerts a slightly weaker effect on substituents bound to the five-membered ring, either because rhodium is more electropositive or because the distance between the metal atom and the substituent is slightly greater. The increased distance between the rings moves the two amino groups further from the positively charged metal atom and also from each other. Thus an even larger effect would be expected on  $K_2$  than on  $K_1$ , since the three positive charges on the diprotonated species would be more widely dispersed. Intramolecular hydrogen bonding of the monoprotonated species which would hinder further protonation would be less likely for rhodium, Xa than for cobalt Xb because of the greater separation. Since the enhancement of

TABLE 3  
 $^{13}\text{C}$  NMR OF SUBSTITUTED FERROCENES AND COBALTCINIUM AND RHODICINIUM SALTS

Substituent	Metal	$\delta(\text{ppm})$ from TMS					Ref.
		C(1)	C(2,5)	C(3,4)	C(1')	side chain	
H	Fe <sup>c</sup>	67.9					10
	Co <sup>a</sup>	85.89					14
	Rh <sup>a</sup>	87.84 88.25					
CH <sub>3</sub>	Fe <sup>c</sup>	84.00	69.2	67.2	68.7	14.8	11
	Rh <sup>a,e</sup>	not observed	88.21 87.78	87.09 86.57	88.41 87.95	13.70	
	Fe <sup>c</sup>	83.3 not observed	69.4	67.7		14.3	
1,1'-(CH <sub>3</sub> ) <sub>2</sub>	Co <sup>a</sup>	107.50	85.78	84.84		13.21	14
	Rh <sup>a</sup>	107.06	88.64	87.31		12.90	
	Fe <sup>c</sup>	90.3	88.17	86.79			
1,1'-(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	Fe <sup>c</sup>	90.3	67.2	67.5		22.0 15.1	12
	Co <sup>a</sup>	110.9	84.09	84.45		21.36 14.24	
	Fe <sup>c</sup>	90.3	67.2	67.5		22.0 15.1	
CO <sub>2</sub> <sup>-</sup>	Co <sup>d</sup>	96.1	86.41	overlap with C(1')	85.89	170.0	14
	Co <sup>d</sup>	96.21	87.90	86.49		169.47	
	Rh <sup>d</sup>	107.31 106.81 (7.5 Hz)	97.37 96.90 (6.9 Hz)	96.31 95.97 (6.6 Hz)		176.2	
1,1'-(CO <sub>2</sub> CH <sub>2</sub> - CH <sub>3</sub> ) <sub>2</sub>	Co <sup>a</sup>	91.54	89.06	87.76		163.13 63.57 14.35	14
	Co <sup>a</sup>	91.54	89.06	87.76		163.13 63.57 14.35	
	Co <sup>a</sup>	91.54	89.06	87.76		163.13 63.57 14.35	
NH <sub>2</sub>	Fe <sup>c</sup>	104.4	63.2	59.0	68.7		11
	Co <sup>a</sup>	125.5	78.94	66.26	84.68		
NH <sub>3</sub> <sup>+</sup>	Co <sup>b</sup>	98.7	83.64	80.77	87.37		14
	Co <sup>a</sup>	127.58	77.58	68.11			
1,1'-(NH <sub>2</sub> ) <sub>2</sub>	Rh <sup>a</sup>	131.51 131.29 (3.3 Hz)	80.32 79.74 (8.7 Hz)	71.32 70.82 (7.5 Hz)			14
	Rh <sup>a</sup>	131.51 131.29 (3.3 Hz)	80.32 79.74 (8.7 Hz)	71.32 70.82 (7.5 Hz)			
	Co <sup>b</sup>	100.59	86.40	83.08			

<sup>a</sup> Spectra in acetone-*d*<sub>6</sub>. <sup>b</sup> Spectra in 96% H<sub>2</sub>SO<sub>4</sub>. <sup>c</sup> Spectra in CDCl<sub>3</sub>. <sup>d</sup> Spectra in D<sub>2</sub>O containing 5% Na<sub>2</sub>CO<sub>3</sub>. <sup>e</sup> Spectrum was obtained from a mixture of H, CH<sub>3</sub> and 1,1'-(CH<sub>3</sub>)<sub>2</sub>.

basicity, Rh over Co, is greater for  $K_2$  than  $K_1$ , the ring separation appears to be of greater significance than the effect of the metal itself.



(Xa, M = Rh ;

Xb, M = Co )

## Experimental

The following instruments were used to obtain spectroscopic data: IR, Perkin-Elmer 237B Grating Infrared Spectrometer; UV, Cary 15 Ultraviolet-Visible Spectrophotometer;  $^1\text{H}$  NMR, Hitachi-Perkin-Elmer R20A NMR Spectrometer,  $^{13}\text{C}$  NMR, JEOL FX60 Fourier Transform NMR Spectrometer at 15.03 MHz and Varian CFT-20 Fourier Transform NMR Spectrometer at 20 MHz.

### *Preparation of rhodicinium (I), methylrhodicinium (II) and 1,1'-dimethylrhodicinium salts (III)*

Cyclopentadiene, b.p.  $43^\circ\text{C}$ , and methylcyclopentadiene, b.p.  $75^\circ\text{C}$ , were prepared by cracking the commercially available dimers immediately before use. Cyclopentadiene, 1.06 g (0.0160 mol) and methylcyclopentadiene, 1.30 g (0.016 mol) were dissolved in 150 ml of ethanol under nitrogen with continuous stirring and 8.33 g (0.033 mol) thallium ethoxide added. After 30 min a white precipitate formed. Then 5.0 g (0.016 mol) of rhodium trichloride hexahydrate dissolved in 60 ml of 10% DMSO was added and stirring was continued overnight. The reaction mixture was filtered and the residue was washed several times with 5 ml portions of water. The combined solution and washings were acidified with 10 ml of 6.0 M HCl and a small amount of thallium chloride which precipitated was filtered out. The solution was washed with ether, decolorized with charcoal and concentrated to half its original volume. Addition of a solution of 2.8 g of  $\text{NH}_4\text{PF}_6$  in 10 ml of water, and chilling at  $0^\circ\text{C}$  produced a curdy white precipitate of a mixture of I, II and III. Yield 3.7 g (55%). Pure I could be prepared by the same procedure from cyclopentadiene and pure III from methylcyclopentadiene (Chemical Samples Co., redistilled). Found C, 31.70; H, 2.72; F, 30.31; P, 8.24.  $\text{C}_{10}\text{H}_{10}\text{RhPF}_6$  calcd.: C, 31.77; H, 2.67; F, 30.15; P, 8.19%. IR max (KBr) 3100, 1410, 830  $\text{cm}^{-1}$ . UV max ( $\text{H}_2\text{O}$ ) 232 nm ( $\epsilon$  62000) 275 nm shoulder ( $\epsilon$  1600). NMR (acetone- $d_6$ )  $\delta$ (ppm) 6.13 d ( $J$  1 Hz coupling to  $^{103}\text{Rh}$ ). Found C, 35.73; H, 3.41; P, 7.35; F, 27.01.  $\text{C}_{12}\text{H}_{14}\text{RhPF}_6$  calcd.: C, 35.49; H, 3.47; P, 7.63; F, 28.07%. IR max (KBr) 3120, 2950, 2850, 1460, 1370, 1230, 1030 and 830  $\text{cm}^{-1}$ . UV max ( $\text{H}_2\text{O}$ ) 238 nm ( $\epsilon$  46800) 275 nm ( $\epsilon$  2750). NMR (acetone- $d_6$ )  $\delta$ (ppm) 6.00 m (4) 5.90 m (4).

### *Preparation of rhodicinium carboxylic acid (IV) and rhodicinium-1,1'-dicarboxylic acid (V)*

A 2.7 g sample of the mixture of I, II and III (0.007 mol) was added to a solution of 3.22 g (0.021 mol) potassium permanganate and 0.30 g (0.0075 mol) sodium hydroxide in 100 ml of water. The solution was stirred for 5 h at  $90\text{--}100^\circ\text{C}$ , cooled and a few mg of sodium bisulfite added to remove unreacted permanganate. The solution was filtered through asbestos to remove the slimy precipitate of  $\text{MnO}_2$  and 1.5 g of  $\text{NH}_4\text{PF}_6$  in 10 ml water added. After chilling and filtering out unreacted I (0.5 g) the solution was acidified with 6 M HCl and 1.53 g of white crystals of IV and V obtained (50% yield). The precipitate was stirred for 3 h with two successive 250 ml portions of acetone. The insoluble material is V which can be purified by dissolving in 10% NaOH and reprecipitating with 6 M HCl, yield 0.6 g (25%). The acetone solutions were combined, stripped and the residue redissolved in 50 ml acetone. Insoluble material was filtered out and the solution stripped. The residue was IV which was dissolved in 10% NaOH, precipitated with 6 M HCl and dried in

vacuo at 60°C, yield 0.50 g (20%). Found C, 31.35; H, 2.48; P, 7.08; F, 26.75.  $C_{11}H_{10}O_2RhPF_6$  calcd.: C, 31.30; H, 2.39; P, 7.58; F, 27.01%. IR max (KBr) 3110, 1720(s), 1500, 1420, 1400, 1375, 1180, 1040(w) and 825 (vs)  $cm^{-1}$ . NMR  $\delta$ (ppm) ( $H_2SO_4$ ) 6.05 d ( $J$  1 Hz) (5) 6.12 m (2).

Analysis of V proved difficult so it was converted to the dimethyl ester, VIII for analysis (see next section). IR max (KBr) 3120, 3300–2400 broad, 1710, 1490, 1410, 1400, 1370, 1290, 1180, 820, 750  $cm^{-1}$ . NMR ( $H_2SO_4$ )  $\delta$ (ppm) 6.25 m (4) 6.50 m (4).

#### *Preparation of 1,1'-diaminorhodicinium (VII)*

A 1.3 g sample ( $2.8 \times 10^{-3}$  mol) of V was refluxed for 3–6 h in 100 ml of thionyl chloride and 1 ml of pyridine. As the reaction progressed the solid V dissolved and reprecipitated as the diacyl chloride VI. The progress of the reaction could be followed by withdrawing samples of the solid at intervals. Upon completion of the reaction the carbonyl peak at 1710  $cm^{-1}$  and the broad, strong OH stretch at 3200–2500  $cm^{-1}$  had disappeared and new peaks had appeared at 1740 and 1810  $cm^{-1}$ . Upon completion half of the thionyl chloride was distilled off and the suspension chilled and filtered. The diacyl chloride is obtained as nearly colorless crystals, yield 0.89 g (63%). Evaporation of the mother liquor produced a tarry residue containing organic polymers and inorganic rhodium salts which was saved for reclamation of the rhodium. The diacyl chloride was converted to the diacyl azide by stirring for 1 h with 15 ml of a 25% aqueous solution of sodium azide at 0°C. The diacyl azide was collected as a colorless powder in 60–80% yield. Although some hydrolysis back to the carboxylic acid undoubtedly occurred, the predominant product was the diacyl azide. Use of a quarternary ammonium azide in an aprotic solvent would probably improve the yield of the diacyl azide but would complicate the isolation and purification of the final products, since quarternary ammonium salts have solubilities similar to the rhodicinium salts. Any carboxylic acid formed either from incomplete conversion to the diacyl chloride or by hydrolysis can be recovered in the final work-up and recycled.

The solid diacyl azide, 0.5–0.6 g, is dissolved in 10 ml of 96% sulfuric acid. Sodium azide, 1.0 g, is added and the solution is heated for 1 h on the steam bath in a well ventilated hood. Evolution of nitrogen gas, probably containing some hydrazoic acid vapors, begins almost immediately. The solution is chilled and neutralized carefully with 6 *M* potassium hydroxide (avoid excess). Ethanol, 250 ml, was added and the heavy precipitate of potassium sulfate filtered out. The volume was reduced to 50 ml and 1.0 g of  $NH_4PF_6$  in 10 ml of water added. Upon chilling 0.20 g (28%) of the diamine, VII, was obtained.

Unreacted V can be recovered by acidification of the mother liquor, yield 0.1–0.2 g (15–30%). Found C, 29.69; H, 3.11; N, 7.05; P, 7.73.  $C_{10}H_{12}N_2RhPF_6$  calcd.: C, 29.42; H, 3.11; N, 6.86; P, 7.60%. IR max (KBr) 3450, 3380, 3250, 3120, 1630, 1510 (s), 1390, 1230, 830 (s). NMR (acetone- $d_6$ )  $\delta$ (ppm) 5.48 s(4), 5.50 s(4).

#### *Preparation of 1,1'-bis(carbomethoxyrhodicinium) hexafluorophosphate (VIII)*

A 0.25 g sample of the diacyl chloride, VI, prepared as previously described was dissolved in 100 ml of methanol and refluxed for 30 min. The dimethyl ester, VIII, was precipitated in 75% yield by dropwise addition of a saturated solution of  $NH_4PF_6$  in methanol. Found. C, 33.70; H, 2.78; P, 6.48.  $C_{14}H_{14}O_4RhPF_6$  calcd.: C,



34.23; H, 2.86; P, 6.26%. IR max (KBr) 3120, 2970, 1730(s), 1475, 1340, 1375, 1285, 1208, 1158, 1050, 1025, 970, 952, 875, 830(vs), 820, 790, and 780  $\text{cm}^{-1}$ .

#### *Basicity of 1,1'-diaminorhodicinium salts (VII)*

To study the first equilibrium a  $1.00 \times 10^{-3}$  M stock solution of VII was prepared in distilled water and diluted tenfold with pH 7 buffer and 0.10, 0.20, 0.30, 0.50, 1.0, 1.5, 2.0, 3.0, 6.0 and 12.0 M HCl. The UV spectra were scanned and extinction coefficients calculated at 5 nm intervals from 230–420 nm. As acidity increased above pH 7, absorbance at 300 nm decreased and the maximum at 257 nm ( $\epsilon$  16750) shifted to 245 nm ( $\epsilon$  44000) for the solutions in 1.0–2.0 M HCl. Since no change in the spectrum occurred between 1.0 and 2.0 M HCl, this represents the spectrum of the completely monoprotonated species. Above 2.0 M HCl further changes were observed corresponding to the second stage of protonation. Beer's Law plots were performed for the unprotonated species in distilled water and the monoprotonated species in 1.5 M HCl. The concentrations of the two species in the 0.1–0.5 M HCl solutions were calculated from the extinction coefficients of the two species at 245 and 300 nm and checked using other pairs of wavelengths. Compound VII was approximately 50% protonated in 0.3 M HCl. An average of three calculations of  $pK_b$  using different pairs of wavelengths in each of the four acid solutions 0.1–0.5 M HCl gave  $pK_1$   $13.36 \pm 0.06$ .

Aqueous HCl is not sufficiently acidic for complete diprotonation, so sulfuric acid solutions were used for the second equilibrium. The spectrum of VII is the same in 10–20%  $\text{H}_2\text{SO}_4$  as in 1.0–2.0 M HCl so it also represents the monoprotonated species. Solutions  $1.00 \times 10^{-4}$  M in VII were prepared in 30, 50, 55, 60, 65, 70, 75, 85 and 96% sulfuric acid. A gradual shift of the maximum at 245 nm ( $\epsilon$  44000) to 237 nm ( $\epsilon$  72700) and a disappearance of the maximum at 330 nm ( $\epsilon$  6600) were observed as acidity increased. The shift was half completed in 50%  $\text{H}_2\text{SO}_4$  and no further change was observed above 75%  $\text{H}_2\text{SO}_4$ , indicating complete diprotonation. The acidity of each solution was checked by titrating a weighed portion with standard sodium hydroxide. The monoprotonated species in 20%  $\text{H}_2\text{SO}_4$  and the diprotonated species in 97%  $\text{H}_2\text{SO}_4$  were shown to follow Beer's Law. Calculations were performed as described for the first equilibrium, using initially absorbances at 290 and 330 nm and checking with several other pairs of wavelengths. From the known acidities of sulfuric acid solutions [17] a value  $pK_2 = 18.1 \pm 0.1$  was obtained.

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