

equivalently bonded between two iron atoms. At some temperature between 195 and 273°K, or perhaps over a range of temperatures, the crystal undergoes a transformation to a structure containing asymmetric bridging chloride ligands. It is possible that this asymmetric structure at low temperatures is similar to the structure of  $\text{Cu}(\text{py})_2\text{Cl}_2$ , which has been studied in detail by Dunitz<sup>7</sup> and found to possess asymmetric bridging chloride ligands (Cu-Cl distances, 2.28 and 3.05 Å; Cl-Cu-Cl bond angle, 88°). This structural change accounts for the Mössbauer spectral results for  $\text{Fe}(\text{py})_2\text{Cl}_2$  (A) because the decrease in symmetry about the iron atom with decreasing temperature would result in a large EFG and, hence, larger  $\Delta E_Q$  but would not necessarily change the total s-electron density at the iron nucleus. The additional set of lines observed in the Mössbauer spectrum of  $\text{Fe}(\text{py})_2\text{Cl}_2$  (B) at low temperatures can now be attributed to a portion of the polycrystalline sample which does not undergo this structural transformation and which retains the symmetric bridging structure at low temperature. This results in a smaller EFG for this particular portion of the sample and produces the additional low  $\Delta E_Q$  value observed at low temperatures. The method of preparing  $\text{Fe}(\text{py})_2\text{Cl}_2$  (B) *via* the decomposition of  $\text{Fe}(\text{py})_4\text{Cl}_2$  probably produces a crystal which has a large number of "defects." A high concentration of these "defects" possibly prevents a portion of the polycrystalline sample from undergoing the proposed crystal transformation at lower temperatures. If this is the case, the chemical isomer shift for each set of lines would be expected to be the same.

The proposed structural change is also consistent with the magnetic properties observed for  $\text{Fe}(\text{py})_2\text{Cl}_2$ . Anderson<sup>13,14</sup> has proposed a model for magnetic exchange (through a bridging atom) between paramagnetic metal ions, which, for the case under study, predicts ferromagnetic exchange if (1) the iron ions and chloride bridging ligands lie in the same plane, (2) the Fe-Cl-Fe and Cl-Fe-Cl bonding angles do not differ greatly from 90°, and (3) the bonds between the

bridging chloride ligand and the iron ions consists predominantly of chlorine p orbitals and iron d orbitals. Assuming that requirements 1 and 3 are met—which seems reasonable—it is clear that as the Cl-Fe-Cl bond angle approaches 90° the model predicts ferromagnetic exchange.  $\text{Fe}(\text{py})_2\text{Cl}_2$  is shown from the above-discussed X-ray work to have a Cl-Fe-Cl bond angle of 85.5° at room temperature. If the proposed asymmetric structure at low temperature is similar to  $\text{Cu}(\text{py})_2\text{Cl}_2$ ,<sup>7</sup> then its Cl-Fe-Cl bond angle will be of the order of 88°. This increase in bond angle toward 90° at lower temperatures results in the increasing possibility of ferromagnetic exchange which is indeed observed at temperatures below about 100°K. If the model proposed by Anderson<sup>13,14</sup> is valid for this system, it would appear that the structural transformation occurs over a range of temperatures since no discontinuous change is observed (see Figure 3) in the magnetic moment of either sample of  $\text{Fe}(\text{py})_2\text{Cl}_2$ . Of course, the possibility of "ferromagnetic impurities" still cannot be ruled out experimentally.

The authors conclude that the experimental properties of  $\text{Fe}(\text{py})_2\text{Cl}_2$  presented above are consistent with a temperature-dependent crystalline structure. They further conclude that  $\text{Fe}(\text{py})_2\text{Cl}_2$  contains symmetric bridging chloride ligands at room temperature and asymmetric bridging chloride ligands at temperatures of 195°K and lower. More detailed X-ray structural studies on  $\text{Fe}(\text{py})_2\text{Cl}_2$  at low temperatures and Mössbauer spectral studies at intermediate temperatures are planned hopefully to provide additional evidence in support of the proposed structural transformation.

**Acknowledgments.**—The authors wish to thank Dr. W. A. Baker, Jr., of Syracuse University for the use of the Faraday magnetic balance and the National Science Foundation for Grant No. GP-8653. A Department of Defense Project Themis Grant, No. AFOSR F-44620-69-C-0122, made possible the purchase of components for the Mössbauer spectrometer.

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## 1,2-Dithiolene Complexes of Ruthenium and Iron

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Received October 7, 1970

Physical characterization and chemical reactivity of  $(\text{CF}_3)_2\text{C}_2\text{S}_2\text{Fe}(\text{CO})_3$ , the initial product of the reaction between iron pentacarbonyl and bis(perfluoromethyl)dithietene, are reported. Bis(perfluoromethyl)dithietene reacts with triruthenium dodecacarbonyl at 100° to give an orange, carbonyl-containing substance and at higher temperatures to give a green, carbonyl-free material. Purification of the two substances has not been achieved. Reaction of the orange material with group V bases yields species of the type  $(\text{CF}_3)_2\text{C}_2\text{S}_2\text{Ru}(\text{CO})_n(\text{ER}_3)_{3-n}$ . The green material reacts with group V bases to yield  $(\text{base})\text{RuS}_4\text{C}_4(\text{CF}_3)_4$  and  $(\text{base})_2\text{RuS}_4\text{C}_4(\text{CF}_3)_4$  (base =  $(\text{C}_6\text{H}_5)_3\text{P}$ ,  $(\text{C}_6\text{H}_5)_3\text{As}$ ,  $(\text{C}_6\text{H}_5)_3\text{Sb}$ ). Magnetic, electrochemical, and electronic spectral characteristics of these new compounds are reported.

### Introduction

A variety of novel products have been obtained from the reaction of bis(perfluoromethyl)dithietene and

metal carbonyls.<sup>1</sup> As part of a study of the synthesis and properties of polynuclear dithiolene complexes, the reactions of bis(perfluoromethyl)dithietene with

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(1) E. W. Abel and B. C. Crosse, *Organometal. Chem. Rev.*, **2**, 443 (1967); J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).

TABLE I  
 PHYSICAL PROPERTIES OF COMPLEXES OF THE TYPE  $(CF_3)_2C_2S_2M(CO)_n(ER_3)_{3-n}$ 

Complex	% C		% H		% misc		-Mol wt <sup>a</sup>		$\nu_{CO}$ , $cm^{-1}$	Mp, °C
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found		
$(CF_3)_2C_2S_2Fe(CO)_2P(C_6H_5)_3$	48.02	48.05	2.52	2.67	10.68	10.63 (S)	600	606	2032, 1981 <sup>b</sup>	121-123
$(CF_3)_2C_2S_2Fe(CO)_2As(C_6H_5)_3$	44.75	44.60	2.35	2.32	9.96	9.82 (S)	644	648	2030, 1981 <sup>b</sup>	121.5-123.5
$(CF_3)_2C_2S_2Fe(CO)_2Sb(C_6H_5)_3$	41.71	41.88	2.19	2.19			690	702	2027, 1981 <sup>b</sup>	100-103
$(CF_3)_2C_2S_2Fe(CO)diphos^f$	52.56	52.39	3.42	3.64	9.05	9.13 (S)	708	700	1941 <sup>c</sup>	255-260 dec
					8.74	8.73 (P)				
$(CF_3)_2C_2S_2Fe(CO)_2(PC_6H_5(OCH_3)_2)_2$	33.08	33.35	2.19	2.41					2043, 1991 <sup>b</sup>	73-74
$(CF_3)_2C_2S_2Fe(CO)(PC_6H_5(OCH_3)_2)_2$	38.78	38.79	3.42	3.44			650	649	1972 <sup>b</sup>	119.5-120.5
$(CF_3)_2C_2S_2Fe(PC_6H_5(OCH_3)_2)_3$	42.43	42.61	4.20	4.37	11.72	11.44 (P)			None	148-149
$(CF_3)_2C_2S_2Ru(CO)(P(C_6H_5)_2)_2$ (violet)	55.96	55.92	3.44	3.59	7.30	7.50 (S)	880	882	1973 <sup>d</sup>	217-218
					7.04	7.39 (P)		855 <sup>e</sup>	1958 <sup>a,h</sup>	
$(CF_3)_2C_2S_2Ru(CO)(P(C_6H_5)_2)_2$ (orange)	55.96	55.72	3.44	3.84			880	824 <sup>e</sup>	1944 <sup>d</sup>	213-218 <sup>g</sup>
									1958 <sup>a,h</sup>	
$(CF_3)_2C_2S_2Ru(CO)(As(C_6H_5)_2)_2$	50.88	50.43	3.12	3.22					1934 <sup>e</sup>	208
$(CF_3)_2C_2S_2Ru(P(C_6H_5)_2OCH_3)_3$	52.91	52.47	4.03	4.14					None	188-189
$(CF_3)_2C_2S_2Ru(P(OCH_3)_2)_3$	22.32	22.52	3.90	3.74	9.16	9.13 (S)	700	708	None	166-167
					16.30	16.50 (F)				

<sup>a</sup> In chloroform solution. <sup>b</sup> In cyclohexane solution. <sup>c</sup> In dichloromethane solution. <sup>d</sup> In Nujol mull. <sup>e</sup> In benzene solution. <sup>f</sup> diphos =  $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ . <sup>g</sup> Turns violet at 213° and then melts. <sup>h</sup> Broad.

triruthenium dodecacarbonyl have been examined. Ruthenium dithiolene chemistry has received only scant attention. It has been briefly reported that both bis and tris species of the type  $Ru(S_2C_2(C_6H_5)_2)_n$  exist.<sup>2</sup> The products resulting from the reaction of bis(perfluoromethyl)dithietene with  $[(\pi-C_5H_5)M(CO)_2]_2$  ( $M = Ru, Fe$ ) have been described.<sup>3</sup>

In addition the reaction of bis(perfluoromethyl)dithietene with iron pentacarbonyl has been reexamined. Previous studies of this reaction have recorded the preparation of the carbonyl complex  $(CF_3)_2C_2S_2Fe_2(CO)_6$ <sup>4</sup> and the dimer  $Fe_2S_3C_8(CF_3)_8$ .<sup>5</sup> Reaction of  $(CF_3)_2C_2S_2Fe_2(CO)_6$  with sulfur produces the parent oxidized member ( $z = 0$ ) of a five-membered electron-transfer related series ( $z = 0, 1-, 2-, 3-, 4-$ ) based on the  $Fe_4S_4[S_2C_2(CF_3)_2]_4^z$  unit.<sup>6</sup> One of the major goals of this work was the preparation of the ruthenium analog of this tetramer; unfortunately this has not been achieved.

### Experimental Section

**Preparation of Compounds.**—Bis(perfluoromethyl)-1,2-dithietene<sup>7</sup> and methoxydiphenylphosphine<sup>8</sup> and dimethoxyphenylphosphine<sup>9</sup> were prepared as described in the literature. Unless specifically noted the new compounds reported herein are stable to the atmosphere both as solids and in solution.

$(CF_3)_2C_2S_2Fe(CO)_6$ .—A filtered solution containing 2 ml of  $S_2C_2(CF_3)_2$  and 3.2 ml of iron pentacarbonyl in 50 ml of pentane was allowed to stand, protected from the atmosphere but with provision for carbon monoxide evolution, for 48 hr. During this time the solution became violet, and large, well-formed, crystals were deposited. After filtration under nitrogen, 2.0 g of the air-sensitive product was obtained, mp 71-74°. *Anal.* Calcd: C, 22.97; H, 0.00; F, 31.14; S, 17.52. Found: C, 22.89; H, 0.33; F, 31.26; S, 16.72.

The infrared spectrum of the compound dissolved in cyclohexane shows three carbonyl stretching bands at 2099, 2046, and 2039  $cm^{-1}$  and a perturbed C=C stretch at 1481  $cm^{-1}$ . The mass spectrum exhibits a parent ion at 366 (for <sup>56</sup>Fe) and peaks

due to successive loss of CO at 338, 310, and 282. The compound is diamagnetic.

$(CF_3)_2C_2S_2Fe(CO)_n(ER_3)_{3-n}$ .—A stoichiometric quantity of the ligand  $ER_3$  dissolved in heptane was added to a slurry of 1.0 g of  $(CF_3)_2C_2S_2Fe(CO)_6$  in 50 ml of heptane. Carbon monoxide evolution generally ceased after 30 min and the solution was then filtered and cooled in a Dry Ice-acetone bath. The crystalline product was collected by filtration. Purification was achieved by recrystallization from petroleum ether (bp 20-40°). For the preparation of  $(CF_3)_2C_2S_2Fe(PC_6H_5(OCH_3)_2)_3$  it was necessary to reflux the initial mixture for 12 hr. The physical properties of the complexes are set out in Table I.

$[(C_{10}H_8N_2)Fe][Fe_2S_3C_8(CF_3)_8]$ .—A solution of 0.42 g (3.0 mmol) of  $\alpha, \alpha'$ -dipyridyl in 25 ml of acetone was added to an equimolar amount of either  $(CF_3)_2C_2S_2Fe(CO)_6$  or  $(CF_3)_2C_2S_2Fe_2(CO)_6$  dissolved in 50 ml of acetone. The red-brown solution which remained after CO evolution was filtered and sufficient ether was added to the filtrate to precipitate the complex as black crystals. Purification of the product was achieved by repeated precipitation from acetone solution by the addition of ether. Polarography of the complex in dichloromethane solution shows two oxidative waves ( $E_{1/2} = 0.71, 1.27$  V) with equal diffusion currents. These waves are indicative of the presence of  $Fe_2S_3C_8(CF_3)_8^{2-}$ . *Anal.* Calcd: C, 35.86; H, 1.57; N, 5.45. Found: C, 35.70; H, 1.42; N, 5.60.

$(CF_3)_2C_2S_2Fe_2(CO)_6[P(C_6H_5)_3]_3$ .—A solution of 1.0 g (4.0 mmol) of triphenylphosphine in 5 ml of acetone was added to a slurry of 2.0 g (4.0 mmol) of  $(CF_3)_2C_2S_2Fe_2(CO)_6$  in 5 ml of acetone. After gas evolution had ceased, the green solution was filtered and cooled to 0°. Dropwise addition of water to the cold solution caused the complex to separate as violet crystals. Additional purification was effected by dissolving the complex in acetone, filtering, and precipitating it by the addition of water; mp 114-116°. *Anal.* Calcd: C, 43.81; H, 2.05; P, 4.18; mol wt 740. Found: C, 43.74; H, 2.13; P, 4.07; mol wt 745 (in  $CHCl_3$  solution).

The infrared spectrum obtained from a cyclohexane solution shows carbonyl bands at 2082, 2061, 2027, 2018, 2006, 1982, and 1948  $cm^{-1}$ . The mass spectrum does not exhibit a parent ion; however ions corresponding to  $(CF_3)_2C_2S_2Fe(CO)_n[P(C_6H_5)_3]_3$  ( $n = 4-0$ ) and  $(CF_3)_2C_2S_2Fe_2(CO)_n$  ( $n = 5-0$ ) are observed.

**Reaction of  $(CF_3)_2C_2S_2$  with  $Ru_3(CO)_{12}$ . Species A.**—A solution of 200 mg (0.31 mmol) of  $Ru_3(CO)_{12}$  and 240 mg (1.07 mmol) of  $S_2C_2(CF_3)_2$  in 75 ml of *n*-heptane was heated under reflux for 30 min. An orange solid formed while carbon monoxide was evolved. The solution was cooled and the solid A was collected by filtration, washed with *n*-heptane, and vacuum dried. It has been impossible to achieve any further purification of this material because of its limited solubility in common organic solvents. Thin layer chromatography of A suggests that it is a mixture of at least two components; however, attempts to scale up this separation failed due to decomposition of the complex(es). In a KBr pellet CO stretching bands are observed at 2139, 2084, and 2035  $cm^{-1}$ . Analysis suggests an approximate composition

(2) G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *J. Amer. Chem. Soc.*, **88**, 5174 (1966); G. N. Schrauzer, V. Mayweg, H. W. Finck, U. Müller-Westerhoff, and W. Heinrich, *Angew. Chem.*, **76**, 345 (1964).

(3) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **6**, 469 (1967).

(4) R. B. King, *J. Amer. Chem. Soc.*, **85**, 1584 (1963).

(5) A. L. Balch, I. G. Dance, and R. H. Holm, *ibid.*, **90**, 1139 (1968); A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **3**, 814 (1964).

(6) A. L. Balch, *J. Amer. Chem. Soc.*, **91**, 6962 (1969).

(7) C. G. Krespan, *ibid.*, **83**, 3434 (1961).

(8) H. J. Harwood and D. W. Grisley, Jr., *ibid.*, **82**, 423 (1960).

TABLE II  
 PHYSICAL PROPERTIES OF COMPLEXES OF THE TYPE  $(R_3E)_nRu[S_2C_2(CF_3)_2]_2^a$ 

Complex	-% C -		-% H -		-% S -		-% misc -		-Mol wt <sup>a</sup> -		Mp, °C
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
$(C_6H_5)_3P)_2RuS_4C_4(CF_3)_4$	38.27	38.22	1.85	1.84	15.76	15.61	3.80	3.88 (P)	816	802	175.5-177.5
$(C_6H_5)_3P)_2RuS_4C_4(CF_3)_4$	49.01	48.95	2.80	2.91	11.92	12.01	5.75	5.71 (P)	1078	599 <sup>b</sup>	196-197
$(C_6H_5)_3As)_2RuS_4C_4(CF_3)_4$	36.31	36.68	1.76	1.89							172.5-173.5
$(C_6H_5)_3As)_2RuS_4C_4(CF_3)_4$	45.33	45.23	2.59	2.41	11.02	10.94	12.86	13.32 (As)	1166	583	217-220
$(C_6H_5)_3Sb)_2RuS_4C_4(CF_3)_4$	41.94	41.94	2.40	2.29			18.10	17.90 (F)	1260	631	156-158
$(C_6H_5)_3P(OCH_3)_2)_2RuS_4C_4(CF_3)_4$	26.56	26.26	1.53	1.55					724	710	163.5-164.5
$[(C_6H_5)_4As][[(C_6H_5)_3P)_2RuS_4C_4(CF_3)_4]$	50.09	49.84	2.94	2.94	10.70	11.54	2.58	2.52 (P)			142.5-144

<sup>a</sup> In benzene solution. <sup>b</sup> Incomplete dissociation in benzene; verified by the electronic spectra.

of  $(CF_3)_2C_2S_2Ru_2(CO)_6$ . *Anal.* Calcd: C, 20.1; H, 0.0; S, 10.7. Found: C, 19.4; H, 0.4; S, 10.6.

**Species B.**—Bis(perfluoromethyl)dithietene (480 mg, 2.1 mmol) was added to a solution of 200 mg (0.31 mmol) of  $Ru_2(CO)_{12}$  in 50 ml of *n*-decane. The solution was heated under reflux until gas evolution ceased. The dark green solution was filtered while hot and the solvent was removed under reduced pressure. A dark green amorphous solid, B, was obtained. No method of purification of the substance has been found. It will not crystallize, it decomposes on chromatographic columns, and it does not sublime. Consequently, thorough characterization has been thwarted. The infrared spectrum of B indicates an absence of coordinated carbon monoxide.

$(CF_3)_2C_2S_2Ru(CO)_n(ER_3)_{3-n}$ .—A solution of 5.5 mmol of the appropriate base dissolved in 50 ml of *n*-heptane was added to 100 mg of solid A. The solution was heated under reflux for 12 hr, filtered, and cooled at 0°. The crystalline complex was collected by filtration. Purification was achieved by dissolution in a minimum of dichloromethane, filtration, and addition of 125 ml of petroleum ether to the filtrate. On cooling to 0° the complex crystallized and was collected. Characterization of the complexes is given in Table I. With triphenylphosphine a mixture of orange and violet crystals was obtained; the mixture was separated mechanically.

$(R_3E)RuS_4C_4(CF_3)_4$ .—A solution of 0.15 mmol of the base in 80 ml of *n*-heptane was added to 100 mg of solid B. The resulting solution was heated under reflux for 2 hr. The solution was filtered and its volume was reduced to 15 ml. Upon cooling to 0° the solution yielded the crystalline complex. Purification was affected by recrystallization from petroleum ether. Characterization of the individual complexes is set out in Table II.

$(R_3E)_2RuS_4C_4(CF_3)_4$ .—The preparation of the bisadducts follows that of the monoadducts except that additional base (0.50 mmol for 100 mg of solid B) was employed. The complexes were purified by recrystallization from dichloromethane-hexane. Despite the fact that these bisadducts are essentially completely dissociated into the monoadducts in solution, it is not necessary to add additional base during the recrystallization. The less soluble bisadduct crystallizes preferentially. Some properties of the complexes are set out in Table II.

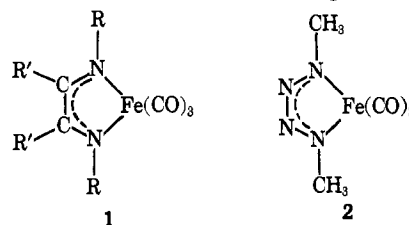
$[(C_6H_5)_4As][[(C_6H_5)_3PRuS_4C_4(CF_3)_4]$ .—One drop of hydrazine hydrate was added to a mixture of 8.4 mg of  $(C_6H_5)_3PRuS_4C_4(CF_3)_4$  in 30 ml of ethanol. Tetraphenylarsonium chloride (18 mg) was added to the blue solution. The solvent volume was reduced to 2 ml by use of a rotary evaporator. One-hundred milliliters of water was added and the resulting mixture was extracted with four 15-ml portions of dichloromethane. The dichloromethane solution was dried over magnesium sulfate and then filtered. Hexane (30 ml) was added to the filtrate and the dichloromethane was distilled off. On cooling, the product formed violet crystals. These were collected by filtration and recrystallized from dichloromethane-hexane. On prolonged exposure to air, the monoanion, both in solution and as a solid, is oxidized. In nitromethane solution the salt behaves as a 1:1 electrolyte ( $\Lambda = 75 \text{ cm}^2 \text{ mol}^{-1} \text{ ohm}^{-1}$  at  $\sim 10^{-3} M$ ). Other characterization is given in Table II.

**Physical Measurements.**—Molecular weights were measured in chloroform or benzene solution with a Mechrolab osmometer standardized with triphenylstibine. A Picker MS-9 spectrometer using 70-eV ionizing electrons with direct insertion of the complex was employed for mass spectral studies. Infrared spectra were recorded on a Perkin-Elmer 421 spectrophotometer. Electronic spectra were recorded on a Cary Model 14 spectrophotometer. Polarographic measurements were made using an ORNL Model 1988 polarograph equipped with a three-electrode

configuration in conjunction with a rotating platinum working electrode. The technique for recording polarograms in dichloromethane has been described previously.<sup>9,10</sup> Magnetic moments were measured on solid samples using a Faraday balance with  $HgCo(CNS)_4$  as the standard.

## Results and Discussion

**$(CF_3)_2C_2S_2Fe(CO)_3$  and Related Species.**—The initial product of the reaction between iron pentacarbonyl and bis(perfluoromethyl)-1,2-dithietene is violet, diamagnetic  $(CF_3)_2C_2S_2Fe(CO)_3$ . This formulation is supported by the mass spectrum which exhibits a parent ion and ions due to successive loss of three carbonyl groups and the infrared spectrum which contains three  $\nu_{CO}$  absorptions.<sup>10a</sup> The perturbed C=C stretching frequency occurs at  $1481 \text{ cm}^{-1}$  which is well below that of the free ligand ( $1622 \text{ cm}^{-1}$ ) or that of the dithiolate complex  $(CF_3)_2C_2S_2Fe_2(CO)_6$  ( $1631 \text{ cm}^{-1}$ ). Polarographic measurements indicate that  $(CF_3)_2C_2S_2Fe(CO)_3$  does not undergo any well-defined redox reactions in dichloromethane solution. No other organosulfur complexes analogous to  $(CF_3)_2C_2S_2Fe(CO)_3$  are known; however the nitrogen donor analogs 1<sup>11a,b</sup> and 2<sup>11b</sup>



have been reported. In addition  $(CF_3)_2C_2S_2Fe(CO)_3$  is isoelectronic in the valence sense with the iron tricarbonyl complexes of various substituted butadienes although the mode of coordination in these two types of complexes is most certainly different. The dithiolene group in  $(CF_3)_2C_2S_2Fe(CO)_3$  is undoubtedly attached to iron in the same manner as found in  $(CF_3)_2C_2S_2Ru(CO)(P(C_6H_5)_3)_2$  (*vide infra*).

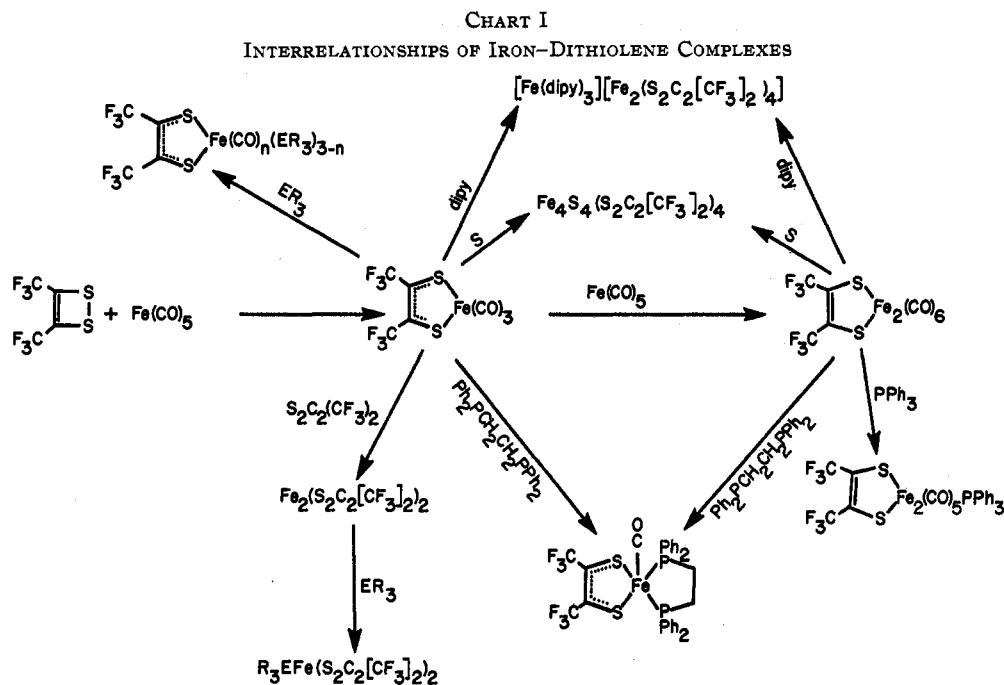
The chemical reactions of  $(CF_3)_2C_2S_2Fe(CO)_3$  are summarized in Chart I. This compound reacts with

(9) F. Röhrscheid, A. L. Balch, and R. H. Holm, *Inorg. Chem.*, **5**, 1542 (1966).

(10) A. L. Balch, *ibid.*, **6**, 2158 (1967).

(10a) NOTE ADDED IN PROOF.—A recent note [C. J. Jones, J. A. McCleverty, and D. G. Orchard, *J. Organometal. Chem.*, **26**, C19 (1971)] reports an independent preparation of  $(CF_3)_4C_4S_4Fe(CO)_3$  and suggests a dimeric, sulfur-bridged structure for this complex on the basis of solution molecular weight data. Because of the sensitivity of this complex to air, we did not attempt similar measurements. However, it is clear that the various substitution products obtained from  $(CF_3)_4C_4S_4Fe(CO)_3$  are monomeric. Also no ions containing two iron atoms are found in the mass spectrum obtained from  $(CF_3)_4C_4S_4Fe(CO)_3$ . Consequently, if dimerization does occur, it appears to be a rather weak interaction compared to the situation in  $Fe_2S_8C_8(CF_3)_8$  and  $Fe_4[S_2C_2(CF_3)_2]_4$ .

(11) (a) S. Otsuka, T. Yoshida, and A. Nakamura, *Inorg. Chem.*, **6**, 20 (1967); (b) H. tom Dieck and H. Bock, *Chem. Commun.*, 678 (1968); (c) R. J. Doedens, *ibid.*, 1271 (1968); M. Dekker and G. R. Knox, *ibid.*, 1243 (1967).

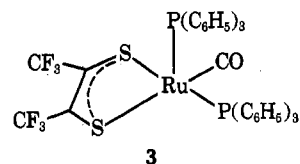


iron pentacarbonyl to give  $(\text{CF}_3)_2\text{C}_2\text{S}_2\text{Fe}_2(\text{CO})_6^4$  and with the dithietene to yield  $\text{Fe}_2\text{S}_8\text{C}_8(\text{CF}_3)_8$ .<sup>5</sup> With sulfur it gives  $\text{Fe}_4\text{S}_4[\text{S}_2\text{C}_2(\text{CF}_3)_2]_4$ .<sup>6</sup> With  $\alpha, \alpha'$ -dipyridyl both  $(\text{CF}_3)_2\text{C}_2\text{S}_2\text{Fe}(\text{CO})_3$  and  $(\text{CF}_3)_2\text{C}_2\text{S}_2\text{Fe}_2(\text{CO})_6$  react to produce the tris(dipyridyl)iron(II) salt of  $\text{Fe}_2\text{S}_8\text{C}_8(\text{CF}_3)_8^{2-}$ . The substitution reactions of  $(\text{CF}_3)_2\text{C}_2\text{S}_2\text{Fe}(\text{CO})_3$  with phosphines, arsines, and stibenes occur rapidly under mild conditions. This reactivity is unusual for iron pentacarbonyl derivatives. For example 1 ( $\text{R}' = \text{CH}_3$ ,  $\text{R} = \text{C}_6\text{H}_5$ ) can be recovered unchanged after treatment with triphenylphosphine at  $80^\circ$  for 5 hr. (Substituted butadiene)-iron tricarbonyl complexes also require considerably more drastic conditions to affect carbonyl substitution.<sup>12</sup>

Only one reaction has been found which converts  $(\text{CF}_3)_2\text{C}_2\text{S}_2\text{Fe}_2(\text{CO})_6$  into a derivative of  $(\text{CF}_3)_2\text{C}_2\text{S}_2\text{Fe}(\text{CO})_3$ . Reaction of the former with bis(diphenylphosphino)ethane (diphos) gives  $(\text{CF}_3)_2\text{C}_2\text{S}_2\text{Fe}(\text{CO})(\text{diphos})$ . With triphenylphosphine  $(\text{CF}_3)_2\text{C}_2\text{S}_2\text{Fe}_2(\text{CO})_6$  yields the simple substitution product  $(\text{CF}_3)_2\text{C}_2\text{S}_2\text{Fe}_2(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3$ . Similar substitution reactions of other  $(\text{RS})_2\text{Fe}_2(\text{CO})_6$  species have been reported.<sup>13</sup>

**Ruthenium Species Analogous to  $(\text{CF}_3)_2\text{C}_2\text{S}_2\text{Fe}(\text{CO})_3$ .**—Reaction of bis(perfluoromethyl)dithietene with triruthenium dodecacarbonyl in refluxing heptane produces a yellow-orange solid which, because of its low solubility, we assume to be a polymer of approximate composition  $(\text{CF}_3)_2\text{C}_2\text{S}_2\text{Ru}_2(\text{CO})_6$ .<sup>14</sup> Because of its intractability a thorough characterization of this substance has not been possible. It does react with phosphines and arsines to yield well-defined, diamagnetic species of the type  $(\text{CF}_3)_2\text{C}_2\text{S}_2\text{Ru}(\text{CO})_n(\text{ER}_3)_{3-n}$ . With triphenylphosphine two different solids (orange and violet) of composition  $(\text{CF}_3)_2\text{C}_2\text{S}_2\text{Ru}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$  have been obtained. While as solids these two species

have different infrared and electronic spectra, they each dissolve in a common solvent to give solutions with identical infrared and electronic spectra. The two forms, which appear to be structural isomers are in equilibrium in solution; the position of this equilibrium is solvent dependent. It is possible to interconvert the two forms: crystallization of the orange form from dichloromethane-hexane yields a mixture of the orange and violet crystals; crystallization of the violet form from acetonitrile yields the orange species. The structure of the violet form has been determined by X-ray crystallography<sup>15</sup> to have the square-pyramidal configuration 3. A more detailed analysis of the struc-



tures and dynamics of structural rearrangements of both the iron and ruthenium monodithioleene species will be presented once the structure of the orange isomer is determined. None of these ruthenium complexes react with sulfur to yield tractable materials; consequently the ruthenium analog of  $\text{Fe}_4\text{S}_4[\text{S}_2\text{C}_2(\text{CF}_3)_2]_4$  remains to be synthesized.

**Ruthenium Bisdithioleenes.**—Refluxing triruthenium dodecacarbonyl with excess bis(perfluoromethyl)dithietene at  $170^\circ$  yields a deep green solution. It has been impossible to isolate a crystalline product from this solution but treatment of the solid obtained by evaporation of this solution with Lewis bases yields two series of adducts. With an excess of base, diamagnetic bisadducts of the type  $(\text{base})_2\text{Ru}_4\text{C}_4(\text{CF}_3)_4$  are formed. With a deficiency of base, monoadducts  $(\text{base})\text{Ru}_4\text{C}_4(\text{CF}_3)_4$ , which also are diamagnetic, are produced. Iron analogs of the monoadducts have been prepared by the cleavage of  $\text{Fe}_2\text{S}_8\text{C}_8(\text{CF}_3)_8$  with bases;

(12) T. A. Manuel and F. G. A. Stone, *J. Amer. Chem. Soc.*, **82**, 386 (1960); E. Weiss and W. Hübel, *J. Inorg. Nucl. Chem.*, **11**, 42 (1959); F. Faraone, F. Zingales, P. Uguagliati, and U. Belluco, *Inorg. Chem.*, **7**, 2362 (1968).

(13) W. Hieber and A. Zeidler, *Z. Anorg. Allg. Chem.*, **329**, 92 (1964).

(14) Both a monomeric and a polymeric form of the analogous  $(\text{C}_6\text{H}_5)_2\text{Ru}_2(\text{CO})_6$  have been reported: G. Cetini, O. Gambino, E. Sappa, and M. Valle, *J. Organometal. Chem.*, **18**, P4 (1968).

(15) I. Bernal, private communication.

however, these iron adducts show no evidence for addition of further base.<sup>10</sup>

The electronic spectra of the ruthenium complexes are set out in Table III. The monoadducts retain

TABLE III  
ELECTRONIC SPECTRA

Compd	State	$\nu_{\max}$ , $\text{cm}^{-1}$ ( $\epsilon$ )
$(\text{C}_6\text{H}_5)_3\text{PRuS}_4\text{C}_4(\text{CF}_3)_4$	$\text{CH}_2\text{Cl}_2$ soln	16,900 (11,300), 22,150 sh (2750), 23,900 (3490), 30,750 (8270)
	Solid <sup>a</sup>	16,950, 22,000 sh, 23,800
$(\text{C}_6\text{H}_5)_2\text{AsRuS}_4\text{C}_4(\text{CF}_3)_4$	$\text{CH}_2\text{Cl}_2$ soln	17,100 (11,000), 22,000 sh (2850), 23,650 (3920), 30,750 (10,300)
	Solid <sup>a</sup>	17,100, 21,750 sh, 23,550
$(\text{C}_6\text{H}_5)_2\text{SbRuS}_4\text{C}_4(\text{CF}_3)_4$	$\text{CH}_2\text{Cl}_2$ soln <sup>b</sup>	17,200 (11,910), 22,150 sh (2640), 24,250 (3620), 30,850 (11,700)
	Solid <sup>a</sup>	16,050 (6150), 18,850 sh (2290), 24,750 (3000), 27,700 sh (4670), 32,550 (8400), 36,900 (18,300)
$(\text{C}_6\text{H}_5)_3\text{PRuS}_4\text{C}_4(\text{CF}_3)_4^-$	$\text{CH}_2\text{Cl}_2$ soln	16,050 (6150), 18,850 sh (2290), 24,750 (3000), 27,700 sh (4670), 32,550 (8400), 36,900 (18,300)
	Solid <sup>a</sup>	16,100, 18,850 sh, 23,000, 27,400 sh
$((\text{C}_6\text{H}_5)_3\text{P})_2\text{RuS}_4\text{C}_4(\text{CF}_3)_4$	$\text{CH}_2\text{Cl}_2$ soln <sup>c</sup>	14,800 (435), 21,350 (8100), 25,850 sh (5440), 28,350 (6860)
	Solid <sup>a</sup>	14,750, 16,850, 20,650 sh, 22,150, 28,100
$((\text{C}_6\text{H}_5)_3\text{As})_2\text{RuS}_4\text{C}_4(\text{CF}_3)_4$	$\text{CH}_2\text{Cl}_2$ soln <sup>c</sup>	14,400 (412), 20,900 (9840), 25,700 sh (5250), 28,150 (7120)
	Solid <sup>a</sup>	14,500, 21,100, 25,750 sh, 28,000
$((\text{C}_6\text{H}_5)_3\text{Sb})_2\text{RuS}_4\text{C}_4(\text{CF}_3)_4$	$\text{CH}_2\text{Cl}_2$ soln <sup>c</sup>	23,500 (2480)
	Solid <sup>a</sup>	18,850, 20,800 sh, 24,700 sh, 27,800

<sup>a</sup> Recorded in fluorocarbon mull. <sup>b</sup> Data reported for a solution of  $((\text{C}_6\text{H}_5)_3\text{Sb})_2\text{RuS}_4\text{C}_4(\text{CF}_3)_4$  which is completely dissociated into  $(\text{C}_6\text{H}_5)_3\text{Sb}$  and  $(\text{C}_6\text{H}_5)_3\text{SbRuS}_4\text{C}_4(\text{CF}_3)_4$ . <sup>c</sup> Data recorded in the presence of sufficient excess base component to ensure essentially complete conversion into the bisadduct.

their integrity in solution as shown by the consistency of their electronic spectra in the solid and in solution. In dichloromethane solution the spectra of the monoadducts obey Beer's law over the concentration range  $10^{-5}$ – $10^{-3}$  M. Molecular weight measurements indicate that they are monomeric in solution.

Polarographic data for the  $(\text{base})\text{RuS}_4\text{C}_4(\text{CF}_3)_4$  species are set out in Table IV. A well-defined one-

TABLE IV  
POLAROGRAPHIC DATA FOR THE REDUCTION  
 $\text{E}_3\text{EMS}_4\text{C}_4(\text{CF}_3)_4 + \text{e}^- = \text{E}_2\text{EMS}_4\text{C}_4(\text{CF}_3)_4^-$

Compd	$E_{1/2}$ , <sup>a</sup> V	$i_d/C$ , $\mu\text{A}/\text{mM}$
$(\text{C}_6\text{H}_5)_3\text{PRuS}_4\text{C}_4(\text{CF}_3)_4$	+0.26 <sup>d</sup>	25 <sup>d</sup>
$(\text{C}_6\text{H}_5)_2\text{AsRuS}_4\text{C}_4(\text{CF}_3)_4$	+0.21	28
$(\text{C}_6\text{H}_5)_2\text{SbRuS}_4\text{C}_4(\text{CF}_3)_4$ <sup>b</sup>	+0.19	24
$\text{C}_6\text{H}_5\text{P}(\text{OCH}_3)_2\text{RuS}_4\text{C}_4(\text{CF}_3)_4$	+0.25	27
$(\text{C}_6\text{H}_5)_2\text{PF}_2\text{S}_4\text{C}_4(\text{CF}_3)_4$	+0.30 <sup>c</sup>	...
$(\text{C}_6\text{H}_5)_2\text{AsFeS}_4\text{C}_4(\text{CF}_3)_4$	+0.43	24
$(\text{C}_6\text{H}_5)_2\text{SbFeS}_4\text{C}_4(\text{CF}_3)_4$	+0.41 <sup>c</sup>	...

<sup>a</sup> Measured in dichloromethane solution with 0.1 M  $(\text{C}_6\text{H}_5)_4\text{NPF}_6$  as supporting electrolyte. <sup>b</sup> Measured in a solution prepared from  $((\text{C}_6\text{H}_5)_3\text{Sb})_2\text{RuS}_4\text{C}_4(\text{CF}_3)_4$  which dissociates. <sup>c</sup> Data from ref 10. <sup>d</sup> For the reverse reaction  $((\text{C}_6\text{H}_5)_3\text{P})\text{RuS}_4\text{C}_4(\text{CF}_3)_4^- + \text{e}^- + (\text{C}_6\text{H}_5)_3\text{PRuS}_4\text{C}_4(\text{CF}_3)_4$ ,  $E_{1/2} = +0.25$  V,  $i_d/C = 24$   $\mu\text{A}/\text{mM}$ .

electron reductive wave was observed for each complex; no one-electron oxidative process was found. The half-wave potentials for the cathodic process indicate that the ruthenium complexes are more difficult to reduce than are their iron counterparts.<sup>10</sup> As was found for the iron complexes the potential for reduction is not very sensitive to the nature of the base component. Reduction of  $(\text{C}_6\text{H}_5)_3\text{PRuS}_4\text{C}_4(\text{CF}_3)_4$  with hydrazine produces  $(\text{C}_6\text{H}_5)_3\text{PRuS}_4\text{C}_4(\text{CF}_3)_4^-$ , which has been isolated as the tetraphenylarsonium salt.

Polarography of this salt shows an oxidative wave at 0.25 V; thus the redox process is reversible. Attempts to isolate other monoanions were hampered by their oxygen sensitivity. As expected for an odd-electron system  $[(\text{C}_6\text{H}_5)_4\text{As}][(\text{C}_6\text{H}_5)_3\text{PRuS}_4\text{C}_4(\text{CF}_3)_4]$  is paramagnetic with  $\mu_{\text{eff}} = 1.79$  BM.

The electronic spectrum of  $(\text{C}_6\text{H}_5)_3\text{PRuS}_4\text{C}_4(\text{CF}_3)_4^-$  in solution corresponds well to the spectrum of the solid  $[(\text{C}_6\text{H}_5)_4\text{As}][(\text{C}_6\text{H}_5)_3\text{PRuS}_4\text{C}_4(\text{CF}_3)_4]$ . In addition the solution spectrum of the anion is not affected by the presence of additional quantities of triphenylphosphine. Consequently it is concluded that  $(\text{C}_6\text{H}_5)_3\text{PRuS}_4\text{C}_4(\text{CF}_3)_4^-$  unlike  $(\text{C}_6\text{H}_5)_3\text{PF}_2\text{S}_4\text{C}_4(\text{CF}_3)_4^-$ <sup>10,16</sup> does not undergo extensive base dissociation in solution. Moreover  $(\text{C}_6\text{H}_5)_3\text{PRuS}_4\text{C}_4(\text{CF}_3)_4^-$  does not appear to add a second mole of base to become six-coordinate.

The bisadducts  $(\text{base})_2\text{RuS}_4\text{C}_4(\text{CF}_3)_4$  exhibit, as solids, electronic spectra which are distinct from those of the monoadducts (Figure 1). Consequently both bases

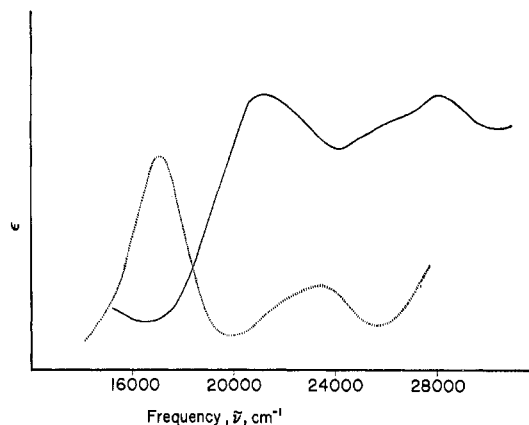


Figure 1.—Electronic spectra of (—)  $((\text{C}_6\text{H}_5)_3\text{As})_2\text{RuS}_4\text{C}_4(\text{CF}_3)_4$  and (· · ·)  $((\text{C}_6\text{H}_5)_3\text{Sb})_2\text{RuS}_4\text{C}_4(\text{CF}_3)_4$  in a fluorocarbon mull (absorbance scale arbitrary).

of the bisadducts are assumed to coordinate the metal. In solution, however, these are almost completely dissociated into the monoadducts. This dissociation is reflected by the molecular weight measurements of the bisadducts which give values half those calculated for  $(\text{base})_2\text{RuS}_4\text{C}_4(\text{CF}_3)_4$ . The equilibrium between the mono- and bisadducts can be followed spectrophotometrically. Figure 2 shows the electronic spectrum of  $((\text{C}_6\text{H}_5)_3\text{As})_2\text{RuS}_4\text{C}_4(\text{CF}_3)_4$  in the presence of varying amounts of triphenylarsine. The existence of isosbestic points indicates that there are only two species present which are chromophoric over the region of the spectrum utilized. The initial spectrum observed with no additional triphenylarsine present is identical with that obtained from  $(\text{C}_6\text{H}_5)_3\text{AsRuS}_4\text{C}_4(\text{CF}_3)_4$ . The limiting spectrum reached in the presence of a large excess of triphenylarsine correlates well with the spectrum of solid  $((\text{C}_6\text{H}_5)_3\text{As})_2\text{RuS}_4\text{C}_4(\text{CF}_3)_4$  (Figure 1). Similar observations have been made for the complexes with triphenylphosphine and triphenylstibine<sup>17</sup> as bases. From these data it has been possible to obtain equilib-

(16) E. F. Epstein, I. Bernal, and A. L. Balch, *Chem. Commun.*, 136 (1970); A. L. Balch, *Inorg. Chem.*, **10**, 276 (1971); J. A. McCleverty, N. M. Atherton, N. G. Connelly, and J. C. Winscom, *J. Chem. Soc. A*, 2242 (1969).

(17) In the case of  $((\text{C}_6\text{H}_5)_3\text{Sb})_2\text{RuS}_4\text{C}_4(\text{CF}_3)_4$  the limiting spectrum, obtained in the presence of a large excess of triphenylstibine, does not correspond to the spectrum of solid  $((\text{C}_6\text{H}_5)_3\text{Sb})_2\text{RuS}_4\text{C}_4(\text{CF}_3)_4$ . The reason for this difference is unknown.

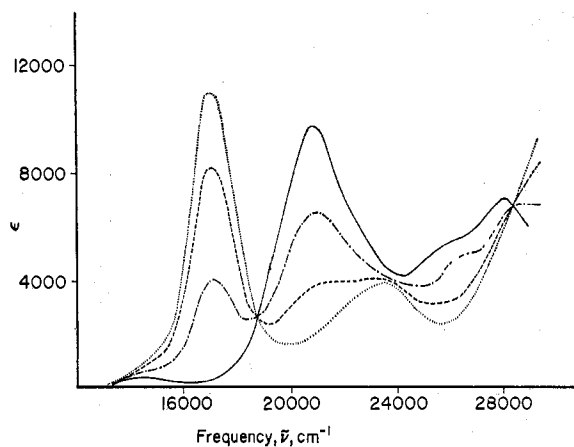
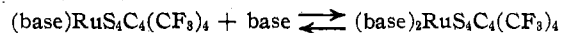


Figure 2.—Electronic spectra of  $((\text{C}_6\text{H}_5)_3\text{As})_2\text{RuS}_4\text{C}_4(\text{CF}_3)_4$  in dichloromethane solution in the presence of  $(\text{C}_6\text{H}_5)_3\text{As}$ . Concentration of  $((\text{C}_6\text{H}_5)_3\text{As})_2\text{RuS}_4\text{C}_4(\text{CF}_3)_4$  is  $7.52 \times 10^{-6} F$  throughout. Concentrations of  $(\text{C}_6\text{H}_5)_3\text{As}$ :  $\cdots$ , no excess added;  $\cdots\cdots$ ,  $5.18 \times 10^{-4} M$ ;  $-\cdot-\cdot-$ ,  $2.64 \times 10^{-3} M$ ;  $—$ ,  $\geq 1.00 \times 10^{-1} M$ .

rium constants for the reaction



These equilibrium constants decrease, as is generally the case with group V donors, down the following series:  $(\text{C}_6\text{H}_5)_3\text{P}$  ( $K = 153 \pm 7 \text{ l. mol}^{-1}$ )  $>$   $(\text{C}_6\text{H}_5)_3\text{As}$  ( $K = 68 \pm 3$ )  $>$   $(\text{C}_6\text{H}_5)_3\text{Sb}$  ( $K = 9 \pm 2$ ).

The great similarity in chemical and physical properties between  $(\text{base})\text{RuS}_4\text{C}_4(\text{CF}_3)_4$  and  $(\text{base})\text{FeS}_4\text{C}_4(\text{CF}_3)_4$  suggests that they have very similar structures. X-Ray crystallographic study of  $(\text{C}_6\text{H}_5)_3\text{AsFeS}_4\text{C}_4(\text{CF}_3)_4$  reveals that it is a square pyramid with triphenylarsine in the axial position;<sup>18</sup> a similar geometry is proposed for  $(\text{base})\text{RuS}_4\text{C}_4(\text{CF}_3)_4$ . The bisadducts probably have a pseudooctahedral structure with the bases in trans positions; a five-coordinate structure with a nonchelating dithiolene appears most unlikely.

**Acknowledgment.**—We thank the National Institutes of Health (Grant AM 12182) and the Research Committee of the University of California, for support of this research.

(18) E. F. Epstein and I. Bernal, *Inorg. Chem.*, in press.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, WESTERN ILLINOIS UNIVERSITY, MACOMB, ILLINOIS 61455, AND NORTH CAROLINA STATE UNIVERSITY, RALEIGH, NORTH CAROLINA 26707

## Kinetics of the Acid and Base Hydrolysis of Di- $\mu$ -hydroxo-tetrakis(ethylenediamine)dnicobalt(III) Cation<sup>1</sup>

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Received April 27, 1970

The acid hydrolysis of di- $\mu$ -hydroxo-tetrakis(ethylenediamine)dnicobalt(III) cation (hereafter called dimer) was studied using spectrophotometry and the base hydrolysis of this same complex was investigated using a pH-Stat method. The data were found to be well fitted by the assumption of two successive first-order reactions. The apparent first-order rate constants for the acid hydrolysis show a complex dependence on hydrogen ion concentration of the following form:  $k_1(\text{apparent}) = (C_{10} + C_{11}(\text{H}^+))/(1 + K_1(\text{H}^+))$  and  $k_2(\text{apparent}) = (C_{21}(\text{H}^+) + C_{22}(\text{H}^+)^2)/(1 + K_2(\text{H}^+))$ . For the base hydrolysis, the apparent rate constant for the first step as a function of pH was satisfactorily fitted by the equation  $k_3(\text{apparent}) = (C_{30} + C_{31}(\text{OH}^-))/(1 + K_3(\text{OH}^-))$ , while the value of  $k_4$  showed but slight change with pH. A mechanism is proposed in which a singly bridged species acts as an intermediate in the course of the reaction. The acid hydrolysis was studied at nine wavelengths, six hydrogen ion concentrations, and two temperatures, *viz.*,  $25.00 \pm 0.02$  and  $35.00 \pm 0.05^\circ$ , while the base hydrolysis was studied at  $25.00 \pm 0.01^\circ$  and over the pH range 9.3–10.4. At  $25.00^\circ$  and  $0.1127 F \text{ HClO}_4$  ( $\mu = 1.0 M$ ,  $\text{NaClO}_4$ ) the rate constants for the acid hydrolysis are  $k_1(\text{apparent}) = (11.82 \pm 0.08) \times 10^{-4} \text{ sec}^{-1}$  and  $k_2(\text{apparent}) = (3.76 \pm 0.01) \times 10^{-4} \text{ sec}^{-1}$ . For the base hydrolysis at  $25.00^\circ$  and  $2.43 \times 10^{-4} F \text{ NaOH}$  ( $\mu = 1.0 M$ ,  $\text{NaNO}_3$ ) the values for the rate constants are  $k_3 = (3.53 \pm 0.08) \times 10^{-3} \text{ sec}^{-1}$  and  $k_4 = (0.373 \pm 0.01) \times 10^{-4} \text{ sec}^{-1}$ . Values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for the various kinetic parameters in the acid hydrolysis are reported.

### Introduction

The doubly bridged cobalt(III) dimeric species  $\text{Co}_2(\text{en})_4(\text{OH})_2^{4+}$  decomposes in acid solutions to give the diaquo ion  $\text{Co}(\text{en})_2(\text{OH}_2)_2^{3+}$  and in basic solutions to give the dihydroxo ion  $\text{Co}(\text{en})_2(\text{OH})_2^+$ .

Rasmussen and Bjerrum<sup>2</sup> studied these reactions spectrophotometrically. They indicated that the accuracy in the case of the basic hydrolysis is rather low due to the similarity of the visible and near-ultraviolet spectra of the dimer to those of the dihydroxo ion. No final results nor detailed study of the basic hydrolysis was given by them.

Although a detailed study and a mechanism were

given for the acid hydrolysis, it was observed that a representative run given in ref 2 has the first experimental point taken after 1 hr from the time of mixing the reactants. It was also observed that their experiments were done at only three wavelengths, *viz.*, 560, 540, 520 nm, all in the visible region. This indicated that a repetition of the study of Rasmussen and Bjerrum was desirable.

### Experimental Section

**Materials.**—All chemical reagents used were analytical reagent grade. The water was first deionized by passing it through a mixed-bed cation-anion-exchange resin and then distilled from very dilute potassium permanganate-sodium hydroxide solution. Sodium hydroxide stock solutions were prepared from carbonate-free concentrated NaOH.<sup>3</sup> Sodium perchlorate was pre-

(1) Based on the Ph.D. thesis of A. A. El-Awady, University of Minnesota, Minneapolis, Minn. 55455.

(2) S. E. Rasmussen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 735 (1955).

(3) I. M. Kolthoff and E. B. Sandell, "Text Book of Quantitative Inorganic Analysis," Macmillan, New York, N. Y., 1952.