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Electrochemical and Chemical Properties of Dithiocarbamato Complexes of Ruthenium(II), Ruthenium(III), and Ruthenium(IV)

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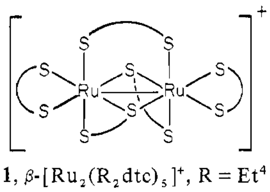
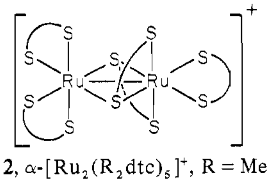
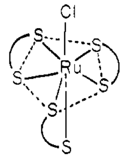
An electrochemical study of several *N,N*-diethyldithiocarbamato (Et_2dtc) complexes of Ru(II), Ru(III), and Ru(IV) was carried out. $[(CO)Ru(dtc)_2]_2$, $Ru(dtc)_3$, and $ClRu(dtc)_3$ were studied by dc, ac, and cyclic voltammetric techniques in the solvents acetonitrile, propylene carbonate, and methylene chloride. The results indicate that the bimetallic complexes α- and β-$[Ru_2(dtc)_5]^+$ are not formed as primary electrochemical oxidation products of $Ru(dtc)_3$ or reduction products of $ClRu(dtc)_3$. The electrochemical oxidation product of $Ru(dtc)_3$ in CH_3CN is $[(CH_3CN)Ru(dtc)_3]^+$, and the metal-containing reduction product of $ClRu(dtc)_3$, which exists as $[(CH_3CN)Ru(dtc)_3]^+Cl^-$ in CH_3CN, is $Ru(dtc)_3$. In propylene carbonate, $ClRu(dtc)_3$ is undissociated and exhibits a one-electron oxidation ($E_{1/2} = 0.97$ V) and a two-electron reduction ($E_{1/2} = -0.77$ V) to $Ru(dtc)_3^-$. $[(CO)Ru(dtc)_2]_2$ shows an irreversible one-electron oxidation with $E_{1/2} = 0.86$ V vs. SCE in CH_2Cl_2. The electrolysis products of these complexes are compared to chemical redox products and redox mechanisms are discussed. Various redox reactions of the mixed-valence complexes $Ru_2(dtc)_5$, $Ru(dtc)_5^+$, $ClRu(dtc)_3$, and $Ru(dtc)_3$ have been examined. Oxidation and isomerization reactions of $Ru(dtc)_3$ and α-$[Ru_2(dtc)_5]^+$ using BF_3 gas have been studied in detail, and reaction mechanisms are proposed. The ^1H NMR spectra of α- and β-$[Ru_2(Me_2dtc)_5]^+$ have been assigned by variable-temperature and ligand-exchange studies.

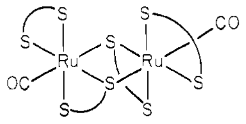
Introduction

A number of ruthenium(II), ruthenium(III), and ruthenium(IV) dithiocarbamate complexes have recently been well characterized by x-ray analysis.[1-6] Interesting redox and photoredox reactions have been used in the synthesis of many of these complexes. For example, the reaction of tris(*N,N*-diethyldithiocarbamato)ruthenium(III), $Ru(Et_2dtc)_3$, with BF_3 gas under aerobic conditions in benzene gives the novel bimetallic compound β-$[Ru_2(Et_2dtc)_5]BF_4$ (**1**) and oxidized ligand products,[4] whereas electrochemical oxidation of $Ru(Me_2dtc)_3$ in acetone with Et_4NBF_4 gives α-$[Ru_2(Me_2dtc)_5]BF_4$ (**2**, R = Me),[7] after chromatographic workup.[7,8] Compound **2** is more conveniently prepared as a chloride salt by reaction of $RuCl_3{\cdot}XH_2O$ with NaR_2dtc in aqueous solution and separation from $Ru(R_2dtc)_3$ by column chromatography.[3] Compounds **1** and **2** have been chemically reduced using $NaBH_4$ on mixed-valence Ru(II)–Ru(III) complexes.[4,7] Reaction of $Ru(Et_2dtc)_3$ with anhydrous HCl in benzene yields a novel seven-coordinate complex of Ru(IV), $ClRu(Et_2dtc)_3$ (**3**), in addition to **2** (R = Et).[9] Compounds **2** and **3** can also be synthesized by photolysis of $Ru(R_2dtc)_3$ in chlorine-containing solvents.[10] Stable mixed R_2dtc–carbonyl complexes of Ru(III) have been prepared by the photolysis of $Ru(Et_2dtc)_3$ in the presence of CO in various solvents.[11] This reaction gives a mixture of $[(CO)Ru(Et_2dtc)_2]_2$ (**4**) and *cis*-$(CO)_2Ru(Et_2dtc)_2$, in addition to oxidized ligand products.[11] Compound **4** is dimeric in the solid phase.[3]


1, β-$[Ru_2(R_2dtc)_5]^+$, R = Et[4]


2, α-$[Ru_2(R_2dtc)_5]^+$, R = Me


3, $ClRu(Et_2dtc)_3$[9]


4, $[(CO)Ru(Et_2dtc)_2]_2$[3]

Although many electrochemical studies have been reported on dithiocarbamato complexes,[4,7,12-14] only three have involved compounds of ruthenium in oxidation state III.[2,4,14] No studies have been reported using R_2dtc complexes of Ru(II) or -(IV). Since the mechanisms of the redox reactions described above involve complexes or intermediates in all three oxidation states, an electrochemical study of the above and related complexes has been undertaken. Solvents with different solvating abilities have been used since the stabilities of intermediates are expected to have a significant solvent dependence. In addition to the electrochemical study, the chemical and spectroscopic properties of the above complexes have been examined in detail and are reported in this paper. The results of this study give insight into the photochemical redox reaction mechanisms of ruthenium dithiocarbamate complexes.

Experimental Section

The complexes $Ru(Et_2dtc)_3$,[1] $ClRu(Et_2dtc)_3$,[5] α-$[Ru_2(R_2dtc)_5]Cl$ (R = Me and Et),[2,7] β-$[Ru_2(R_2dtc)_5]BF_4$ (R = Me and Et),[4] and $[(CO)Ru(Et_2dtc)_2]_2$[15] were prepared by published procedures.

Electrochemical Measurements. All measurements were made with a three-electrode Princeton Applied Research Model 170 instrument with platinum working and auxiliary electrodes. All potentials were determined at 0 or 25 °C vs. a saturated calomel reference electrode (SCE). The working electrode consisted of a 7-mm length of 24 gauge platinum wire sealed in an 8-mm Hg-filled glass tube. The wire was bent into a loop, and the electrode was rotated at 600 rpm. A glassy carbon electrode was also used for several experiments in order to check for Pt electrode poisoning. The platinum electrode was cleaned in concentrated nitric acid prior to use and prepolarized at the anodic and cathodic limits before each experiment. The SCE reference electrode was separated from the sample compartment by three nonaqueous salt bridges connected by glass frits. Solutions were ca. 1–2 mM in complex and 0.10 M in tetraethylammonium perchlorate as supporting electrolyte. All experiments were done under a nitrogen atmosphere. Cyclic voltammetric current–potential curves obtained at scan rates up to 200 mV/s were recorded on an X–Y recorder, while those obtained at faster scans were displayed on an oscilloscope. The phase-sensitive ac voltammograms were measured in phase with the input alternating potential. An ac potential (200 Hz) of 5 mV peak to peak and a scan rate of 10 mV/s were used unless stated otherwise. Burdick and Jackson "distilled in glass" acetonitrile, propylene carbonate ($C_3H_6O_3$), and methylene chloride solvents were dried over molecular sieves and used without further purification. Eastman reagent grade tetraethylammonium perchlorate was recrystallized six times from water and dried in vacuo. Eastman ultrapure tetrabutylammonium perchlorate was dried in vacuo and used without further purification for experiments using CH_2Cl_2 solvent.

Synthesis of $[(CH_3CN)Ru(Et_2dtc)_3]BF_4$. Electrochemical. Controlled-potential oxidative electrolysis at +0.50 V vs. SCE was carried out on a 10^{-3} M acetonitrile solution of $Ru(Et_2dtc)_3$. Tetraethylammonium tetrafluoroborate (0.1 M) was used as supporting electrolyte. The oxidation was continued until ca. 85% of the Ru-

Table I. ^{1}H NMR and Conductivity Data for Dithiocarbamato Complexes of Ruthenium

	^{1}H NMR data			Equivalent conductance	
		δ (mult, J)[a]			
Complex	Solvent	CH_3	CH_2	Solvent	Λ, $cm^2\ equiv^{-1}$
$ClRu(Et_2dtc)_3$	$CDCl_3$	1.31 (3, 7.2)	3.74 (4, 7.2)	$C_2H_4Cl_2$[e]	<0.125
	CD_2Cl_2	1.30	3.73	$C_4H_6O_3$[f]	0.952
	$(CD_3)_2CO$	1.31	3.78	$(CH_3)_2CO$	2.56
	CD_3CN	1.25	3.71	CH_3NO_2[g]	22.2
	$(CD_3)_2SO$	1.25	3.77	CH_3CN	70.5
$IRu(Et_2dtc)_3$	$CDCl_3$	1.38 (3, 7.2)	3.80 (4, 7.2)	CH_3NO_2[g]	69
$[(PPh_3)Ru(Et_2dtc)_3]Cl$	$CDCl_3$	1.17 (3, 7.2)	3.56 (4, 7.2)	$C_2H_4Cl_2$[e]	51
	CD_2Cl_2	1.14	3.52	CH_3CN	127
	$(CD_3)_2CO$	1.18	3.65		
	CD_3CN	1.09	3.52		
	$(CD_3)_2SO$	1.06	3.54		
$[(PPh_3)Ru(Et_2dtc)_3]BF_4$	CD_3CN	1.09 (3, 7.2)	3.52 (4, 7.2)	$C_2H_4Cl_2$[e]	33
				CH_3CN	125
$[(PPh_3)Ru(Me_2dtc)_3]BF_4$	CD_3CN	2.34			
$[(CD_3CN)Ru(Et_2dtc)_3]BF_4$[b]	CD_3CN	1.25 (3, 7.2)	3.71 (4, 7.2)		
$[(CD_3CN)Ru(Et_2dtc)_3]BF_4$[c]	CD_3CN	1.26	3.73		
$[(Me_2SO)Ru(Et_2dtc)_3]BF_4$[c]	$(CD_3)_2SO$	1.24	3.78		
α-$[Ru_2(Me_2dtc)_5]^+$[d]	CD_3CN	2.85, 3.11, 3.39, 3.45, 3.48		CH_3CN	109
β-$[Ru_2(Me_2dtc)_5]^+$[d]	CD_3CN	3.00, 3.11, 3.38, 3.44, 3.46		CH_3NO_2[g]	74

[a] Chemical shifts relative to Me_4Si (δ 0) at 30 °C; mult = multiplicity of multiplet; J in Hz. [b] Prepared by electrochemical oxidation of $Ru(Et_2dtc)_3$ in CH_3CN. [c] Prepared from $ClRu(Et_2dtc)_3$ by reaction with $AgBF_4$ in CH_3CN or $(CD_3)_2SO$. [d] The spectra are independent of anion; R = Et analogues have complex spectra. [e] 1,2-Dichloroethane. [f] Propylene carbonate. [g] Compare with Λ = 87 for $[Fe(Et_2dtc)_3]BF_4$ in CH_3NO_2.

$(Et_2dtc)_3$ had reacted as determined by the decrease in the limiting current. The CH_3CN solvent was distilled off and the remaining residue extracted with CH_2Cl_2. The small amount of $Ru(Et_2dtc)_3$ which was extracted was removed by column chromatography (silica gel) using CH_2Cl_2 eluent. The oxidation product which remained at the top of the column was then eluted using CH_3CN. The ^{1}H NMR and UV–vis spectra of the resulting complex recorded in CD_3CN and CH_3CN solvents, respectively, are identical with spectra of $ClRu(Et_2dtc)_3$ recorded in the same solvents (see Tables I and II). Since this latter complex is actually $[(CH_3CN)Ru(Et_2dtc)_3]Cl$ in CH_3CN solution (vide infra), the oxidation product is assigned as $[(CH_3CN)Ru(Et_2dtc)_3]BF_4$. This complex is not stable for very long in the solid state or in solvents other than CH_3CN.

Chemical. Reaction of $ClRu(Et_2dtc)_3$ with an equimolar amount of $AgBF_4$ in CD_3CN yielded an immediate precipitate of AgCl. ^{1}H NMR and UV–vis analysis of the solution after filtration gave spectra which were identical with those of $ClRu(Et_2dtc)_3$ in CD_3CN (Tables I and II). Satisfactory elemental analysis of this complex has not been obtained due to its instability when removed from CH_3CN solvent for extended periods of time.

Synthesis of $[(PPh_3)Ru(R_2dtc)_3]X$ (X = Cl or BF_4, R = Me or Et). Slow quantitative addition of triphenylphosphine, PPh_3, to a CD_3CN solution of $ClRu(Et_2dtc)_3$ produced a second set of ethyl resonances in the ^{1}H NMR spectrum. The resonances due to $[(CD_3CN)Ru(Et_2dtc)_3]Cl$ vanished when exactly an equimolar amount of PPh_3 had been added. ^{1}H NMR, conductivity, and UV–vis data (Tables I and II) suggest that the complex is $[(PPh_3)Ru(Et_2dtc)_3]Cl$. Crystals of this complex have not been obtained. The tetrafluoroborate salt of this complex has also been prepared. $ClRu(R_2dtc)_3$ (R = Et and Me) (0.014 mmol) was mixed with PPh_3 (0.015 mmol) in CH_3CN solution. To this solution was added 0.84 mmol of $NaBF_4$ (dissolved in 20 mL of CH_3CN), and the white precipitate of NaCl which formed was removed by filtration. The CH_3CN solvent was pumped off, and the remaining residue was thoroughly washed with heptane and then extracted with CH_2Cl_2. Pure samples of $[(PPh_3)Ru(R_2dtc)_3]BF_4$ were isolated upon CH_2Cl_2 evaporation and dried in vacuo. The spectroscopic properties of these compounds are identical with their chloride analogues (Tables I and II). Anal. Calcd for $[(PPh_3)Ru(Me_2dtc)_3]BF_4$: C, 40.00; H, 4.10; N, 5.18. Found: C, 40.19; H, 4.28; N, 5.11. Calcd for $[(PPh_3)Ru(Et_2dtc)_3]BF_4$: C, 44.29; H, 5.07; N, 4.70. Found: C, 44.88; H, 5.32; N, 4.62. Infrared (KBr disk) for R = CH_3: 1625 (w, br), 1519 (s, br), 1465 (w, sh), 1436 (s), 1382 (w), 1354 (m), 1277 (s), 1206 (s), 1151 (m), 1060 (s, br), 848 (m), 777 (w), 747 (m), 692 cm^{-1} (s).

Synthesis of α- and β-$[Ru_2(R_2dtc)_5]$ (R = Me and Et). Electrochemical reduction of α- or β-$[Ru_2(Et_2dtc)_5]^+$ in CH_3CN leads to air-sensitive solutions of the neutral mixed-valence bimetallic complexes. Due to the difficulty of purification in the presence of supporting electrolyte, however, the neutral complexes were synthesized by chemical reduction of **1** or **2** using $NaBH_4$.[4] To a filtered degassed ethanol solution (50 mL) of α- or β-$[Ru_2(R_2dtc)_5]X$ (X = Cl or BF_4) (0.1 mmol) was added 100 mL of a $NaBH_4$ solution (5 mmol) under nitrogen. The resulting solution quickly became deep purple (β isomer) or olive green (α isomer) and a precipitate formed. The purple or green solid was removed by filtration under nitrogen and thoroughly washed with degassed ethanol. The vacuum-dried slightly air-sensitive solids gave satisfactory elemental analyses without further purification. UV–vis data are reported in Table II. The ^{1}H NMR spectra of these paramagnetic complexes consisted of very broad resonances. Anal. Calcd (R = Et) for $Ru_2S_{10}C_{25}H_{50}N_5$: C, 31.83; H, 5.34; N, 7.42. Found (α): C, 30.83; H, 5.24; N, 6.61. Found (β): C, 31.62; H, 5.14; N, 7.03. Magnetic susceptibility at 25 °C for solid: (R = Et, α) $\chi_m^{uncorr} = 997 \times 10^{-6}$ cgsu mol^{-1}, $\mu_{eff} = 1.91\ \mu_B$; (R = Et, β), $\chi_m^{uncorr} = 1078 \times 10^{-6}$ cgsu mol^{-1}, $\mu_{eff} = 1.96\ \mu_B$. Diamagnetic correction $= 520 \times 10^{-6}$ cgsu mol^{-1}.

Oxidation of α- and β-$[Ru_2(Me_2dtc)_5]$ with I_2. A degassed benzene solution containing iodine was slowly added to a degassed benzene solution of pure α- or β-$[Ru_2(Me_2dtc)_5]$ at 20 °C until the purple (or green) color just changed to a red-brown. The benzene solvent was immediately pumped off while the temperature was maintained below 20 °C. ^{1}H NMR analysis in CD_3CN solution indicated that the α isomer was converted into ca. 70% α- and 30% β-$[Ru_2(Me_2dtc)_5]^+I^-$, while the β isomer was converted into 100% β-$[Ru_2(Me_2dtc)_5]^+I^-$.

Reaction of β-$[Ru_2(Et_2dtc)_5]$ with CO. CO was bubbled through a degassed toluene solution of β-$[Ru_2(Et_2dtc)_5]$, and upon UV irradiation through a quartz vessel (450-W Hg vapor lamp) the color changed from purple to yellow. Evaporation of the solvent yielded a residue which was analyzed by IR to consist of *cis*-$(CO)_2Ru(Et_2dtc)_2$ (ν(CO) 2030 and 1963 cm^{-1}) and $[(CO)Ru(Et_2dtc)_2]_2$ (ν(CO) 1920 cm^{-1}).[11] The reaction did not occur in the dark.

Reaction of α-$[Ru_2(Me_2dtc)_5]Cl$ with BF_3 Gas. A 90:10 (v/v) C_6H_6/CH_2Cl_2 solution of α-$[Ru_2(Me_2dtc)_5]Cl$ was reacted with BF_3 gas (slow bubbling) for 15 s at 20 °C in the presence of oxygen and under essentially oxygen-free conditions (N_2 atmosphere).[16] In the presence of oxygen the α isomer was quickly and quantitatively converted into the β isomer, whereas with trace oxygen present ca. 60% α and 40% β resulted. The product distribution was determined by ^{1}H NMR analysis in CD_3CN of the residue remaining after solvent removal. The identity of the anion was not determined.

Reaction of α-$[Ru_2(Me_2dtc)_5]Cl$ with I_2. A 100-fold molar excess of iodine (in CD_3CN solution) was added to a CD_3CN solution of

Table II. Electronic Spectral Data for Dithiocarbamato Complexes of Ruthenium

Complex	Solvent	λ_{max}, nm (log ϵ)						
$Ru(Et_2dtc)_3$	$CHCl_3$		260 (sh, 4.57)	280 (sh, 4.44)	370 (4.01)	400 (sh, 3.82)	467 (3.47)	563 (3.23)
	CH_3CN	237 (4.64)	254 (sh, 4.57)	280 (sh, 4.39)	364 (4.03)	400 (sh, 3.78)	469 (3.47)	558 (3.25)
$ClRu(Et_2dtc)_3$	$CHCl_3$	270 (4.65)	315 (sh, 4.19)	360 (3.95)	435 (sh, 2.91)	500 (sh, 2.40)	560 (2.40)	
	CH_3CN	264 (4.65)	320 (4.23)	400 (sh, 3.19)	470 (sh, 2.58)		550 (2.38)	
	$C_4H_6O_3$^{a}	267 (4.65)	315 (sh, 4.19)	355 (sh, 3.98)	435 (sh, 2.96)	510 (sh, 2.46)	550 (2.44)	
	$(CH_3)_2SO$	272 (4.54)	310 (sh, 4.23)	380 (sh, 3.41)	460 (sh, 2.79)		550 (2.40)	
$[(Me_2SO)Ru(Et_2dtc)_3]BF_4$^{c}	$(CH_3)_2SO$	272 (*e*)	310 (sh, *e*)	385 (sh, *e*)	460 (sh, *e*)		550 (*e*)	
$[(CH_3CN)Ru(Et_2dtc)_3]BF_4$^{b}	CH_3CN	260 (*e*)	320 (*e*)	390 (sh, *e*)	470 (sh, *e*)		540 (*e*)	
$[(CH_3CN)Ru(Et_2dtc)_3]BF_4$^{c}	CH_3CN	260 (*e*)	315 (*e*)	400 (sh, *e*)	470 (sh, *e*)		550 (*e*)	
$[(PPh_3)Ru(Et_2dtc)_3]BF_4$	CH_3CN	263 (4.48)	298 (4.33)	390 (sh, 3.59)	460 (sh, 2.84)		554 (2.46)	
$[(PPh_3)Ru(Et_2dtc)_3]Cl$	CH_2Cl_2	265 (*e*)		400 (sh, *e*)	460 (sh, *e*)		555 (*e*)	
	CH_3CN	267 (*e*)		390 (sh, *e*)	460 (sh, *e*)		555 (*e*)	
α-$[Ru_2(Et_2dtc)_5]^{+}$^{d}	$CHCl_3$	265 (4.73)	290 (sh, 4.61)	330 (4.32)		450 (3.70)		1040 (2.4)^f
β-$[Ru_2(Et_2dtc)_5]^{+}$^{d}	$CHCl_3$	269 (4.62)	290 (4.63)	340 (4.20)	400 (sh, 3.59)	470 (3.29)	555 (2.82)	950 (2.18)^f
α-$[Ru_2(Et_2dtc)_5]$	$C_6H_5CH_3$^{g}			362 (4.34)	465 (3.86)	595 (3.56)	783 (3.58)	920 (sh, 3.4)
β-$[Ru_2(Et_2dtc)_5]$	$C_6H_5CH_3$	300 (4.69)	336 (sh, 4.41)	365 (sh, 4.26)	515 (3.86)	585 (3.74)	735 (sh, 3.42)	988 (sh, 3.20)

[a] Propylene carbonate. [b] Prepared by electrochemical oxidation of $Ru(Et_2dtc)_3$ in CH_3CN. [c] Prepared from $ClRu(Et_2dtc)_3$ by reaction with $AgBF_4$ in CH_3CN or $(CH_3)_2SO$. [d] Me_2SO spectra are independent of anion. [e] Unknown concentration. [f] Broad bands. [g] Recorded at 5 °C.

Table III

Reaction condition	Endpoint time, s	Mol % $[Ru_2(Me_2dtc)_5]^+$
Dry nitrogen[16]	30	85 α, 15 β
Air	15	16 α, 84 β
Pure oxygen	5	20 α, 80 β

α-$[Ru_2(Me_2dtc)_5]Cl$ at 20 °C. After 5 min ca. 50% of the α isomer had reacted, producing the β isomer and some $Ru(Me_2dtc)_3I$.[6] After ca. 1.5 hr the conversion was 90% complete. The final product distribution was 74 mol % β isomer and 26 mol % $Ru(Me_2dtc)_3I$, as determined by ^1H NMR signal integration.

Reaction of $Ru(Me_2dtc)_3$ with BF_3 Gas. BF_3 gas (unpurified, Matheson) was slowly bubbled through a benzene solution of $Ru(Me_2dtc)_3$ (ca. 10^{-3} M) at 23 °C until the green color just disappeared and a fine suspension of product (red-brown) formed (qualitative endpoint). For the given reaction conditions the endpoint times and Ru-containing product distributions are given in Table III. The benzene solvent was freshly distilled from benzophenone ketyl radical anion under nitrogen which was purified by passage through a hot BASF catalyst column. ^1H NMR analysis in CD_3CN of the Ru-containing products was carried out on the residues which remained after benzene and excess BF_3 removal (see Table I for ^1H NMR data). The spectra were recorded in the presence of air. In addition to the products tabulated above, two organic compounds were identified but not separated by ^1H NMR in CD_3CN. These compounds are tentatively assigned as the ones shown in structures **6** and **8** (R = Me) (vide infra) and have ^1H NMR shifts of δ 2.56 and 2.70 ppm and 2.63 ppm, respectively. The ^1H NMR spectra of these compounds formed by another reaction are shown in the top trace of Figure 7. These compounds may also be identified by their $S_2C\overset{\cdots}{-}N$ IR stretching frequencies which occur in the 1580–1590 cm^{-1} region for a mixture of both compounds.

Reaction of $Ru(Et_2dtc)_3$ with $Et_2O·BF_3$. Freshly distilled $Et_2O·BF_3$ was thoroughly deoxygenated by vigorous bubbling with purified N_2. Enough $Et_2O·BF_3$ was added via a cannular tube to a benzene solution of $Ru(Et_2dtc)_3$ (~10^{-3} M) under nitrogen at 25 °C in order to keep all reaction products in solution. The color lightened immediately upon addition, and UV–vis examination of the solution under nitrogen showed complete conversion into α-$[Ru_2(Et_2dtc)_5]^+$. The spectrum did not change upon standing for at least 24 h. The same experiment was repeated in the presence of oxygen, and complete conversion into the β isomer occurred. The UV–vis spectral properties of these complexes are reported in Table II.

Spectral Measurements. Electronic absorption spectra were recorded with a Cary 14 spectrophotometer using 1-cm quartz cells. Infrared spectra were recorded on a Perkin-Elmer Model 237 grating instrument. ^1H NMR spectra were obtained on a Varian XL-100 instrument operated in the FT mode or on a Varian CFT 20 instrument. A Yellow Springs Instrument Co. Model 31 conductivity bridge was used for conductivity measurements. Complex concentrations used in the conductivity experiments were ca. 1 × 10^{-3} M. Magnetic measurements were made at 23 °C using the Faraday technique, and $Hg[Co(SCN)_4]$ was used as a calibrant.

Results and Discussion

The experiments reported in this paper have been designed to give results which should assist in an understanding of the redox mechanisms between dithiocarbamate complexes of Ru(II), Ru(III), and Ru(IV). The experiments are divided into electrochemical and chemical ones and are discussed in the following sections.

Electrochemical Study. $Ru(Et_2dtc)_3$. Several electrochemical studies have been reported which deal at least in part with the tris(dithiocarbamato) complexes of ruthenium(III).[4,13,14] In all of these studies, however, the existence of the recently discovered seven-coordinate complexes of ruthenium(IV),[5,6] $Ru(Et_2dtc)_3X$, where X = Cl or I, was unknown. Since the interpretation of the electrochemical results depends markedly on a knowledge of the Ru(IV) complexes and since the results of cyclic voltammetry have never been completely reported or interpreted, we report here the details of our electrochemical study.

Table IV. Electrochemical Data for *N,N*-Diethyldithiocarbamato Complexes of Ruthenium[a]

				Dc voltammetry		Ac voltammetry		Cyclic voltammetry	
Complex[b]	Process	Product	Solvent	$E_{1/2}$, V	$(E_{3/4} - E_{1/4})$, mV	E_s, V	$\Delta E_{s/2}$	ΔE_p, mV	$i_{p,c}/i_{p,a}$
$Ru(dtc)_3$	Redn	$[Ru(dtc)_3^-]$	CH_3CN	−0.73	54	−0.74	93	70	1.1
			$C_4H_6O_3$	−0.73	58	−0.73	98	67	1.2
			CH_2Cl_2	−0.74	60	−0.74	105	84	1.0
$Ru(dtc)_3$	Oxidn	$[Ru(dtc)_3S^+]$[c]	CH_3CN	+0.33	64	+0.33	130	*d*	*d*
			$C_4H_6O_3$[h]	+0.38	59	+0.40	110	*d*	*d*
			CH_2Cl_2	+0.46	65	+0.47	110	*d*	*d*
$[(CH_3CN)Ru(dtc)_3]^+$[e]	Redn	$[Ru(dtc)_3]$	CH_3CN[h]	−0.55[f]	*f*	*g*	*g*	*e*	*e*
$ClRu(dtc)_3$	Redn	$[Ru(dtc)_3 + Cl^-]$	CH_3CN	−0.50	52	*g*	*g*		
		$[Ru(dtc)_3^-]$	CH_3CN	−0.72	59	−0.71	95	73	
		$[Ru(dtc)_3^- + Cl^-]$	$C_4H_6O_3$	−0.77	130	−0.72	78	120	1.5
$ClRu(dtc)_3$	Oxidn	$[Ru(dtc)_3S^+ + Cl]$	CH_3CN	+0.97	62	+1.01	100	*d*	*d*
			$C_4H_6O_3$	+0.97	51	+0.99	84	*d*	*d*
β-$[Ru_2(dtc)_5]^+$	Redn	$[\beta$-$Ru_2(dtc)_5]$	CH_3CN[h]	−0.56	60	−0.54	84	59	1.1
		$[Ru_2(dtc)_5^-]$	CH_3CN[h]	−1.18	125	−1.12			
α-$[Ru_2(dtc)_5]^+$	Redn	$[\alpha$-$Ru_2(dtc)_5]$	CH_3CN[h]	−0.54	55	−0.56	96		
		$[Ru_2(dtc)_5^-]$	CH_3CN[h]	−1.01	90	−0.98			
$[(CO)Ru(dtc)_2]_2$	Oxidn	$[(CO)Ru(dtc)_2]_2^+$[i]	CH_2Cl_2	+0.86	76	+0.84[j]	135[j]	102	0.95[i]

[a] All potentials were determined at 0 °C vs. SCE using a rotating platinum electrode. Ac voltammetry: 200 Hz. Cyclic voltammetry scan rate 200 mV s^{-1}. [b] Parent complex in solution. [c] S is a solvent molecule or an anion from the supporting electrolyte, in which case the complex is neutral. [d] The cathodic peak appeared far removed from the anodic peak and results from the process: $Ru(dtc)_3S^+ \rightarrow Ru(dtc)_3$. The cathodic $E_{p,c}$ values for this process are −0.60, −0.19, and −0.20 V, respectively, for CH_3CN, $C_4H_6O_3$, and CH_2Cl_2 solvents (see Figures 1 and 2). [e] Complex generated by controlled-potential oxidation of $Ru(dtc)_3$ at +0.50 V in CH_3CN. $E_{p,c}$ is −0.60 V (see Figure 1). [f] Wave not well formed due to overlapping with the wave from the process: $Ru(dtc)_3 \rightarrow Ru(dtc)_3^-$. [g] Ac peak absent. [h] 25 °C. [i] Two new peaks appeared during the cathodic scan of the cyclic voltammetry at $E_{p,c}$ of +0.56 and −0.15 V but only for scans started at potentials ≥0.80 V. [j] 10 Hz using a glassy carbon electrode.

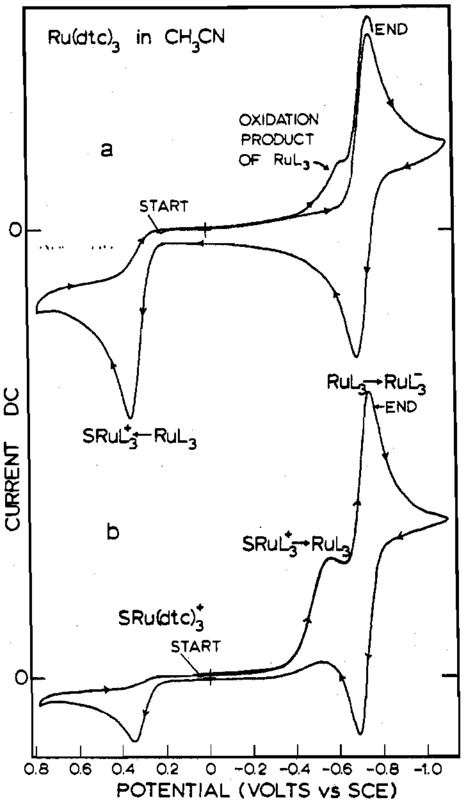


Figure 1. (a) Cyclic voltammogram of $Ru(Et_2dtc)_3$ in CH_3CN (~0.1 M $[NEt_4][ClO_4]$). (b) Cyclic voltammogram of the above solution in (a) (but with $[NEt_4][BF_4]$ as supporting electrolyte) after controlled-potential electrolysis at 0.50 V. Approximately 85% of the $Ru(Et_2dtc)_3$ has been oxidized. The zero-current–zero-potential position is marked by a cross (scan rate 200 mV s^{-1}).

The electrochemical behavior of $Ru(Et_2dtc)_3$ was examined by conventional dc, ac, and cyclic voltammetry using the solvents acetonitrile, propylene carbonate ($C_4H_6O_3$), and dichloromethane. The numerical results are given in Table IV. A one-electron cathodic wave (reduction) at $E_{1/2}$ or E_p of −0.74 V vs. SCE is observed in all three solvents and corresponds to process I. This process is reversible as evidenced by the data in Table IV and by the cyclic voltammograms shown in Figures 1a and 2. The anionic complex, $[Ru(Et_2dtc)_3]^-$, is analogous to the known iron species $[Fe(Et_2dtc)_3]^-$ but has not been isolated. Hendrickson et al.[7] reported the electronic spectrum of $[Ru(Me_2dtc)_3]^-$, which was electrochemically synthesized but not isolated.

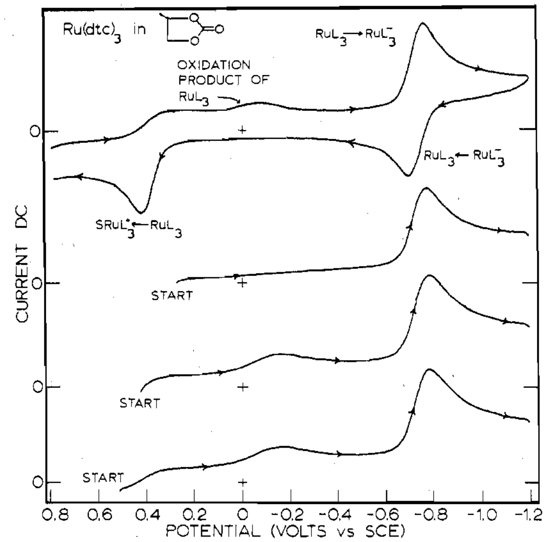


Figure 2. Cyclic voltammogram of $Ru(Et_2dtc)_3$ in propylene carbonate (~0.25 M $[NEt_4][ClO_4]$). The linear scan voltammograms (200 mV s^{-1}) show the effect of the starting potential on the appearance of the peak at ca. −0.2 V.

$$Ru(Et_2dtc)_3 + e^- \underset{E_{1/2} = -0.74\ V}{\rightleftarrows} [Ru(Et_2dtc)_3]^- \qquad (I)$$

A one-electron anodic wave (oxidation) is also observed at ca. +0.40 V. This wave has been assigned to process II in

$$Ru(Et_2dtc)_3 \rightleftarrows [Ru(Et_2dtc)_3]^+ + e^- \qquad (II)$$

previous studies.[4,7,14] However, the wave is not reversible by cyclic voltammetry (Figures 1a and 2 and Table IV), and the cationic complex $[Ru(Et_2dtc)_3]^+$ is not observed or isolated after controlled potential oxidation. Hendrickson et al.[7] have found some degree of reversibility for this process in acetone by cyclic voltammetry (100 mV s^{-1}) with certain N,N substituents (e.g., Me and Ph); however, in the diethyl analogue the process is irreversible up to scan rates of 200 mV s^{-1} in all solvents examined including acetone. Representative cyclic voltammograms are shown in Figures 1a and 2. Hendrickson et al.[7] claimed that after exhaustive oxidative electrolysis of $Ru(Me_2dtc)_3$ in acetone α-$[Ru_2(Me_2dtc)_5]^+$ was not present,[18] but after chromatographic workup a mixture of α-$[Ru_2(Me_2dtc)_5]^+$ and $Ru(Me_2dtc)_3$ was isolated. We have not verified this result with the diethyl derivative using CH_3CN solvent; however, we find that the immediate oxidation product of $Ru(Et_2dtc)_3$ is a reasonably stable complex of Ru(IV), $[(CH_3CN)Ru(Et_2dtc)_3]^+$. This diamagnetic seven-coordinate complex was isolated after exhaustive electrolysis at +0.50 V by column chromatography and identified by ^1H NMR and UV-vis spectroscopy in CH_3CN (see Experimental Section, Tables I and II, and the section on the electrochemistry of $ClRu(Et_2dtc)_3$).

A careful examination of the cyclic voltammograms of $Ru(Et_2dtc)_3$ in CH_3CN solvent (see Figure 1a) reveals a new cathodic wave at ca. −0.60 V, which appears only after oxidation of $Ru(Et_2dtc)_3$. After controlled-potential electrolysis of $Ru(Et_2dtc)_3$ at +0.50 V such that ca. 85% of the $Ru(Et_2dtc)_3$ was oxidized, the cyclic voltammogram shown in Figure 1b was recorded. The new wave at −0.60 V is now initially present and remains on standing for at least 12 h. Since the complex $[(CH_3CN)Ru(Et_2dtc)_3]^+$ is isolated from this solution in good yield, the new cathodic wave must result from process III. The entire cyclic process in CH_3CN solvent

$$[(CH_3CN)Ru(Et_2dtc)_3]^+ \xrightarrow[E_{p,c} = -0.60\ V]{+e^-} Ru(Et_2dtc)_3 + CH_3CN \tag{III}$$

is shown in Figure 1 and represented by IV. The chemical

$$\begin{tikzcd}
{[Ru(Et_2dtc)_3]^+} \arrow[r, shift right, "{+e^-\ E_{1/2} = 0.33\ V}"'] \arrow[d, "CH_3CN"', "(fast)"] & Ru(Et_2dtc)_3 \arrow[l, shift right, "-e^-"'] \arrow[r, shift left, "+e^-"] & {[Ru(Et_2dtc)_3]^-} \arrow[l, shift left, "{-e^-\ E_{1/2} = -0.74\ V}"] \\
{[(CH_3CN)Ru(Et_2dtc)_3]^+} \arrow[ur, "+e^-", "{-CH_3CN\ E_{p,c} = -0.60\ V}"'] & &
\end{tikzcd} \tag{IV}$$

step which converts the presumably paramagnetic $[Ru(Et_2dtc)_3]^+$ (d^4 low spin) into the diamagnetic CH_3CN adduct must be fast. The lifetime of $[Ru(Et_2dtc)_3]^+$ is less than 10^{-3} s since the reverse cathodic wave expected at ca. +0.29 V, assuming a reversible process, is completely absent even for scan speeds of 200 V s^{-1}. The cationic complex of Ru(IV), $[(CH_3CN)Ru(Et_2dtc)_3]^+$, is somewhat stable in the solid state as a BF_4^- salt but is not stable in solvents other than CH_3CN, and its decomposition products have not been identified.

Cyclic voltammetry of $Ru(Et_2dtc)_3$ using the weakly coordinating solvent propylene carbonate at 25 °C shows a behavior which is qualitatively similar to that using CH_3CN solvent. However, the new cathodic wave which appears after oxidation of $Ru(Et_2dtc)_3$ is anodically shifted to ca. −0.19 V from its value of −0.60 V observed using CH_3CN. The results for propylene carbonate are shown in Figure 2. The peak at −0.19 V only appears after prepolarization at potentials $\gtrsim$0.40 V. Controlled-potential oxidation at +0.50 V shows a growth of the −0.19-V peak with a corresponding decrease in the +0.40-V oxidation wave of $Ru(Et_2dtc)_3$. Due to the low solubility of $Ru(Et_2dtc)_3$ in propylene carbonate, attempts were not made to isolate the oxidation products. The cathodic wave could be due to process V, where coordinated $C_4H_6O_3$ stabilizes

$$[(C_4H_6O_3)Ru(Et_2dtc)_3]^+ + e^- \xrightarrow[E_{p,c} = -0.19\ V]{} Ru(Et_2dtc)_3 + C_4H_6O_3 \tag{V}$$

the Ru(IV) cation in a similar fashion to CH_3CN. However, it is also possible that the seventh coordination site is occupied by ClO_4^- or H_2O, especially since the corresponding cathodic wave in noncoordinating CH_2Cl_2 and acetone solvents occurs at −0.20 and −0.17 V, respectively. In either case, these results indicate that the electrochemical oxidation of $Ru(Et_2dtc)_3$ in a variety of solvents yields a solvent- or "anion"-stabilized seven-coordinate complex of Ru(IV). This conclusion is supported by the results reported in the next section.

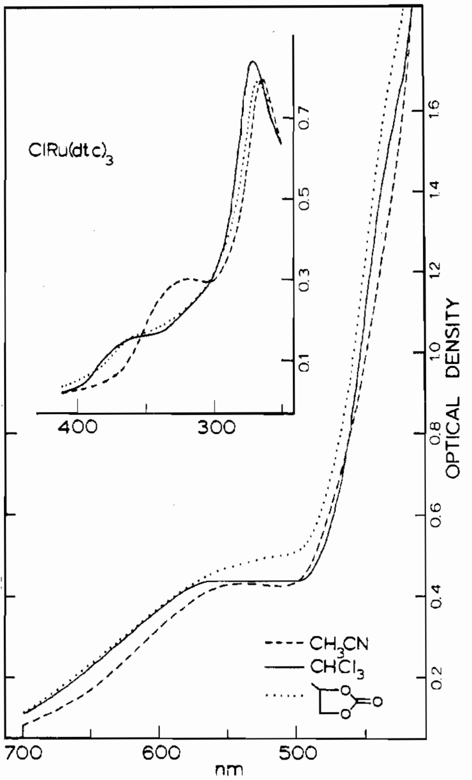


Figure 3. The electronic absorption spectrum of $ClRu(Et_2dtc)_3$ recorded in CH_3CN, $CHCl_3$, and propylene carbonate solvents at 25 °C. Complex concentrations are 1.79×10^{-5} and 1.79×10^{-3} M in the 250–400 and 400–700 nm ranges, respectively.

ClRu(Et₂dtc)₃. The electrochemistry of this pentagonal-bipyramidal complex of Ru(IV) has not previously been reported. Since the results are quite different for CH_3CN and propylene carbonate solvents, the form of the complex in these solvents will be established first. In CH_3CN solution the Cl^- ion is completely dissociated (1:1 electrolyte) and a CH_3CN molecule is coordinated in an axial site to give $[(CH_3CN)Ru(Et_2dtc)_3]^+Cl^-$, while in propylene carbonate and $CHCl_3$ the complex is undissociated. Evidence for this comes from conductivity, spectroscopic, chemical, and electrochemial data (see Experimental Section and Tables I, II, and IV). The UV-vis spectrum of $ClRu(Et_2dtc)_3$ in CH_3CN differs considerably in the 300–400 nm range from spectra recorded in propylene carbonate and $CHCl_3$ solvents (Figure 3 and Table II). The band shift of ca. 60 nm indicates a major change in coordination composition or geometry. Reaction of $ClRu(Et_2dtc)_3$ with $AgBF_4$ in CH_3CN yields AgCl(s) and $[(CH_3CN)Ru(Et_2dtc)_3]^+BF_4^-$ immediately on mixing (Experimental Section). The complex $[(CH_3CN)Ru(Et_2dtc)_3]^+BF_4^-$ has identical chemical, ^1H NMR, and UV–vis

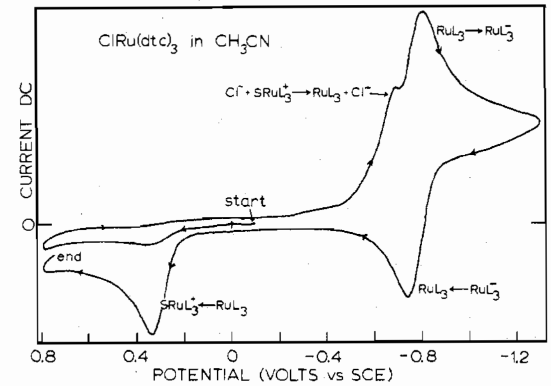


Figure 4. Cyclic voltammogram of $ClRu(Et_2dtc)_3$ in CH_3CN (~0.1 M $[NEt_4][ClO_4]$); the scan rate is 500 mV s^{-1}.

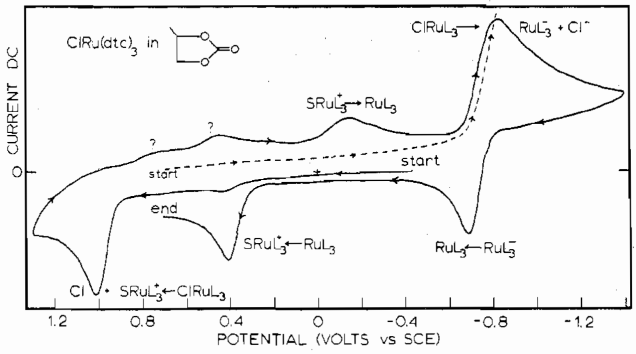


Figure 5. Cyclic voltammogram of $ClRu(Et_2dtc)_3$ in propylene carbonate (~0.25 M $[NEt_4][ClO_4]$); the scan rate is 200 mV s^{-1}.

properties in CH_3CN solvent, as does $ClRu(Et_2dtc)_3$. $ClRu(Et_2dtc)_3$ is diamagnetic in solution (CH_3CN, propylene carbonate, acetone, CH_2Cl_2, and $CHCl_3$) and has essentially identical ethyl ^1H NMR spectra in these solvents (Table I), which suggests that the pentagonal-bipyramidal geometry is maintained.[19] Finally, the electrochemical results (vide infra) are entirely consistent with the conclusion that a CH_3CN-stabilized seven-coordinate Ru(IV) cation exists in CH_3CN solution while $ClRu(Et_2dtc)_3$ maintains its structural integrity in propylene carbonate and methylene chloride.

In CH_3CN the complex $[(CH_3CN)Ru(Et_2dtc)_3]Cl$ shows two one-electron reduction waves with $E_{1/2}$ values of −0.50 and −0.72 V. The less cathodic wave is irreversible while the other is reversible by ac and cyclic voltammetry. The cyclic voltammogram is shown in Figure 4 and is very similar in appearance to the cyclic voltammogram of oxidized $Ru(Et_2dtc)_3$ shown in Figure 1b. Since it is apparent that $ClRu(Et_2dtc)_3$ and oxidized $Ru(Et_2dtc)_3$ both exist as $[(CH_3CN)Ru(Et_2dtc)_3]^+$ in CH_3CN solution, the cyclic process of Figures 1b and 4 are represented by IV. Note that the anodic peak at ca. 0.4 V in Figure 4 only appears after the reduction of $[(CH_3CN)Ru(Et_2dtc)_3]^+$ to $Ru(Et_2dtc)_3$ and corresponds to the oxidation of $Ru(Et_2dtc)_3$. An irreversible anodic wave at $E_{1/2}$ = 0.97 V also occurs for $[(CH_3CN)Ru(Et_2dtc)_3]^+Cl^-$ in CH_3CN and probably corresponds to process VI. Process VI

$$[(CH_3CN)Ru(Et_2dtc)_3]^+Cl^- \xrightarrow[E_{p,a} = 1.0\ V]{-e^-} [(CH_3CN)Ru(Et_2dtc)_3]^+ + Cl \qquad (VI)$$

actually corresponds to the oxidation of Cl^- to a chlorine radical. The oxidation of chloride from KCl in CH_3CN occurs at the same potential. The products of reaction VI have not been isolated.

The dc and ac voltammograms of $ClRu(Et_2dtc)_3$ in propylene carbonate show only two waves in the range ±1.5 V vs. SCE. The reduction wave ($E_{1/2}$ = −0.77 V and E_s = −0.72 V) has exactly double the diffusion-limiting current (dc voltammetry) of the oxidation wave ($E_{1/2}$ = 0.97 V and E_s = 0.99 V), and both waves are irreversible by cyclic voltammetry (Figure 5). The cathodic peak has a return anodic peak with $i_{p,c}/i_{p,a} \approx 1.5$, which suggests that the cathodic reaction is a more-than-one-electron process. A second anodic peak at ca. +0.4 V which only appears after cycling through the −0.80-V peak also occurs in the cyclic voltammogram and corresponds to the oxidation of $Ru(Et_2dtc)_3$. The entire process is represented by VII, where S = $C_4H_6O_3$, ClO_4^-, or H_2O. The

$$\begin{gathered} ClRu(Et_2dtc)_3 \xrightarrow[E_{p,c} = -0.80\ V]{+2e^-} Cl^- + [Ru(Et_2dtc)_3]^- \\ [Ru(Et_2dtc)_3]^- \xrightarrow[E_{p,a} = -0.68\ V]{-e^-} Ru(Et_2dtc)_3 \xrightarrow[E_{p,a} = 0.40\ V]{-e^-} \\ [SRu(Et_2dtc)_3]^+ \end{gathered} \qquad (VII)$$

irreversible oxidation of $ClRu(Et_2dtc)_3$ which occurs at $E_{p,a}$ = 1.00 V has a "return" cathodic peak at −0.19 V, which corresponds exactly to the peak observed after oxidation of $Ru(Et_2dtc)_3$ in propylene carbonate (see Figures 2 and 5). Therefore, the data are most reasonably explained by process VIII. The exact sequence of chemical and electrochemical

$$\begin{gathered} S + ClRu(Et_2dtc)_3 \xrightarrow[E_{p,a} = 1.00\ V]{-e^-} Cl + [SRu(Et_2dtc)_3]^+ \\ [SRu(Et_2dtc)_3]^+ \xrightarrow[E_{p,c} = -0.19\ V]{+e^-} Ru(Et_2dtc)_3 + S \end{gathered} \qquad (VIII)$$

steps in VIII is not known.

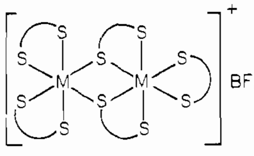
The electrochemical results for the α and β forms of $[Ru(Et_2dtc)_5]^+$ in CH_3CN are also reported in Table IV. The results are essentially identical with those in acetone reported by Hendrickson et al.[7] and will not be discussed here. The important point is that the potentials found in these bimetallic species are never observed in the above electrochemical studies on $Ru(Et_2dtc)_3$ and $ClRu(Et_2dtc)_3$ using CH_3CN and propylene carbonate solvents. Therefore, electrochemical oxidation of $Ru(Et_2dtc)_3$ and oxidation or reduction of $ClRu(Et_2dtc)_3$ do not yield known bimetallic species as primary products. It is possible, however, that the bimetallic complexes are formed during workup of the primary electrochemical products as reported by Hendrickson et al.[7]

$[(CO)Ru(Et_2dtc)_2]_2$. An electrochemical study of this compound was undertaken because it was expected that oxidation would lead to $Ru(Et_2dtc)_2^+$, which should react with $Ru(Et_2dtc)_3$ to yield bimetallic complexes **1** or **2**. In CH_2Cl_2 the complex is dimeric as shown in **4** since the ^1H NMR recorded in CD_2Cl_2 at 30 °C consists of complex overlapping multiplets in the CH_2 region and four overlapping triplets in the CH_3 region. Note that four nonequivalent C_2H_5 groups are expected for structure **4** in the limit of slow $S_2C \overset{...}{-} N$ bond rotation. Dc voltammetry in CH_2Cl_2 solution at 0 °C in the range 1.6 to −1.4 V vs. SCE shows a poorly shaped one-electron oxidation wave with $E_{1/2}$ = 0.86 V (Table IV). The cyclic voltammogram showed both cathodic ($E_{p,c}$ = +0.80 V) and anodic ($E_{p,a}$ = +0.90 V) peaks. Upon repeated cycling, additional peaks grew in at $E_{1/2}$ = +0.61 and −0.12 V where $E_{1/2} = (E_{p,c} + E_{p,a})/2$. Controlled-potential oxidative electrolysis at 1.3 V produced a dark green solution (the starting solution is light yellow) which had four distinct sets of cyclic voltammetric peaks with $E_{1/2}$ values of 0.83, 0.58, 0.37, and −0.12 V. Addition of $NaEt_2dtc$ to the oxidized solution gave $Ru(Et_2dtc)_3$ immediately ($E_{p,a}$ = 0.46 and $E_{1/2}$ = −0.74 V), and the $E_{1/2}$ = −0.12 V couple vanished. Addition of $Ru(Et_2dtc)_3$ to another oxidized solution had no noticeable effect on the four waves except that a small wave appeared at $E_{1/2}$

= −0.53 V; this could be due to formation of some bimetallic complex **1** or **2**.

The above results show that several species are formed upon oxidation of $[(CO)Ru(Et_2dtc)_2]_2$ in CH_2Cl_2 and that the formation of bimetallic complexes **1** or **2** upon addition of $Ru(Et_2dtc)_3$ to the oxidation products is only a minor reaction. Further work is needed to elucidate the nature of the oxidation products. Attempts at isolation of these compounds are currently in progress; however, it can be assumed that $Ru(Et_2dtc)_2^+$ is not produced as a major product.

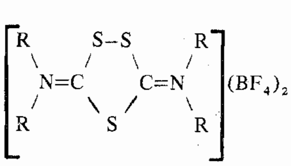
Chemical Redox Reactions. Boron Trifluoride Oxidations. Reactions of $M(R_2dtc)_3$ complexes with boron trifluoride gas or $Et_2O{\cdot}BF_3$ under aerobic conditions have been reported for M = Fe,[13,20] Co,[21] Mn,[20,22] Rh,[23] Ru,[4] and Bi.[24] The metal-containing products of these reactions are well characterized, they are $[Fe(R_2dtc)_3]BF_4$, $[Co_2(R_2dtc)_5]BF_4$ (**5**), $[Mn(R_2dtc)_3]BF_4$, $[Rh_2(R_2dtc)_5]BF_4$ (**5**), β-$[Ru_2(R_2dtc)_5]BF_4$ (**1**), and $[Bi(R_2dtc)_2]BF_4$, respectively. Increase in the formal oxidation state of the metal occurs only with complexes of Fe and Mn, whereas ligand oxidation has been suggested in the case of Ru[4] and presumably occurs also with complexes of Co, Rh, and Bi. The Co and Rh bimetallic complexes, **5**, do not have a M–M bond (M–M distance = 3.372 (s) and 3.556 (1) Å, respectively[21,23]) but are otherwise structurally similar to α-$[Ru_2(R_2dtc)_5]BF_4$ (**2**) which has a Ru–Ru distance of 2.789 (4) Å.[2]



5, $[M_2(R_2dtc)_5]BF_4$, M = Co (R = Et)[21] or Rh (R = Me)[23]

The mechanism of these oxidation reactions has not previously been discussed; however, several facts may be gleaned from careful reading of the above referenced papers: (1) the presence of oxygen or air (either stated or implied) along with gaseous BF_3 or $Et_2O{\cdot}BF_3$ is necessary for oxidation; (2) a noncoordinating solvent such as benzene is always used; and (3) high yields usually much greater than 50% are common. Efforts to systematically vary the conditions of these reactions have not been made. Before discussing our attempts to elucidate the reaction mechanism for the Ru complexes, it is useful to briefly review several other procedures which have been used for preparing the oxidized complexes from $M(R_2dtc)_3$. In the case of Fe and Mn, where simple one-electron oxidized cationic complexes $M(R_2dtc)_3^+$ result, several oxidizing agents, including electrochemical oxidation, have been successfully employed. For example, $Fe(ClO_4)_3{\cdot}6H_2O$ reacts with $Fe(R_2dtc)_3$ in acetone/benzene solution to give $[Fe(R_2dtc)_3]ClO_4$,[25] and $Mn(ClO_4)_2{\cdot}6H_2O$ has been used to oxidize $Mn(R_2dtc)_3$ to $[Mn(R_2dtc)_3]ClO_4$ in benzene solution.[22] Pasek and Straub[20] prepared $[Fe(Et_2dtc)_3]PF_6$ by bubbling air through an acetone solution of $Fe(Et_2dtc)_3$ which was acidified with H_2SO_4 and contained PF_6^-. $[Fe(Et_2dtc)_3]ClO_4$ has been prepared in ca. 50% yield by the reaction of $Fe(Et_2dtc)_3$ in acetone containing Et_4NClO_4 with $HClO_4$ (with or without air present).[13] The $M(R_2dtc)_3^+$ complexes react rapidly with R_2dtc^- in acetone, yielding $M(R_2dtc)_3$ and $^1/_2$(R_4-thiuram disulfide).[13,22]

The bimetallic complexes, $[M_2(R_2dtc)_5]^+$, are generally synthesized via the BF_3/air route; however, an electrochemical synthesis has been reported for **2** (R = Et)[7] (but **2** is not a primary electrochemcial product—see Electrochemistry Section). The non-metal-containing byproducts of these reactions are generally unknown; however, synthesis of **1** by reaction of $Ru(Et_2dtc)_3$ with BF_3 in aerated benzene solution yielded at least some 3,5-bis(*N*,*N*-diethyliminium)-1,2,4-trithiolane bis(tetrafluoroborate), $[Et_4bitt](BF_4)_2$ (**6**).[4] The boron-containing byproducts of these reactions other than BF_4^- have not been isolated or identified. The bimetallic complexes of Ru (**1** and **2**) do not react with R_2dtc^- even after refluxing in CH_3CN, whereas the complexes of Co and Rh (**5**) are rapidly converted to the $M(R_2dtc)_3$ complexes in the presence of R_2dtc^-.[21,23]



6, R = Et

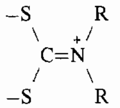
From the above observations it would appear that O_2 is a necessary component of the BF_3 oxidation reaction. Experiments carried out under air-free conditions, however, gave immediate products. For example, the reaction of $Ru(Et_2dtc)_3$ with $Et_2O{\cdot}BF_3$ in benzene under rigorously oxygen-free conditions (purified N_2 atmosphere) yielded complete and fast conversion into α-$[Ru_2(Et_2dtc)_5]^+$ (**2**, R = Et). The same reaction carried out in the presence of O_2 yielded complete conversion into β-$[Ru_2(Et_2dtc)_5]^+$ (**1**). These reactions were monitored by UV–vis spectroscopy (see Experimental Section). The same results were obtained by ^1H NMR spectroscopy of the products of the reaction of $Ru(Me_2dtc)_3$ with BF_3 gas in C_6H_6 solution. The formulas of the anions were not determined in these reactions. An additional experiment showed that α-$[Ru_2(Me_2dtc)_5]^+$ was quickly converted into β-$[Ru_2(Me_2dtc)_5]^+$ by reaction with BF_3 gas in aerated C_6H_6/CH_2Cl_2 (v/v, 90:10), whereas the isomerization only occurred partially with trace O_2 present (see Table III). Two conclusions can be drawn from these observations. Firstly, O_2 is not necessary for the conversion of $Ru(R_2dtc)_3$ into bimetallic species in the presence of BF_3. Secondly, O_2 has an important effect on the stereochemistry of the product. These conclusions can be rationalized by reaction process IX There is good evidence

$$Ru(R_2dtc)_3 + BF_3 \xrightarrow[\text{benzene}]{N_2} Ru(R_2dtc)_2^+ + R_2dtcBF_3^- \qquad (IXa)$$

$$Ru(R_2dtc)_2^+ + Ru(R_2dtc)_3 \xrightarrow[\text{benzene}]{N_2} \alpha\text{-}[Ru_2(R_2dtc)_5]^+ \qquad (IXb)$$

$$\alpha\text{-}[Ru_2(R_2dtc)_5]^+ \xrightarrow{BF_3/O_2} \beta\text{-}[Ru_2(R_2dtc)_5]^+ \qquad (IXc)$$

for step IXa since it is exactly the observed reaction with $Bi(R_2dtc)_3$,[24] and we have evidence that this is the first step in the reaction of $Fe(R_2dtc)_3$ with $Et_2O{\cdot}BF_3$ in the absence of O_2.[26] Step IXb is reasonable, but the complex $Ru(R_2dtc)_2^+$ has not been isolated or studied. It is important to note that formation of the bimetallic complexes **1** and **2** does not require oxidation. The dissociation of R_2dtc^- which is promoted by formation of a BF_3 adduct is a sufficient cause for reaction. It is well-known that BF_3 forms Lewis adducts with sulfur compounds,[27] and the enhanced nucleophilicity of the R_2dtc^- ligand due to resonance structure **7** is expected to add stability to a $R_2dtcBF_3^-$ adduct. The ultimate fate of the $R_2dtcBF_3^-$ anion in the presence of BF_3 and O_2 appears to be a redox reaction which gives a mixture of **6** and **8**. A mixture of these dications (R = Me) has been observed by ^1H NMR and IR spectroscopy as a reaction product of the $Ru(Me_2dtc)_3$ +



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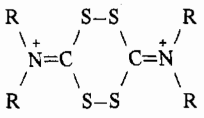

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BF_3/O_2 reaction (Experimental Section). Evidence for the existence of **8** has recently been published.[28,29] Work in progress is directed at determining the mechanism of the redox decomposition of $R_2dtcBF_3^-$; however, our data indicate that tetraalkylthiuram disulfides are converted into oxidized cationic species such as **6** and **8** by reaction with BF_3 and O_2 so that the initial reaction of $R_2dtcBF_3^-$ could well involve formation of $R_2dtc\cdot$ and $BF_3^{-}\cdot$. There is a precedent for radical anion formation with triarylboranes[30] but not with BF_3. More work is needed to verify this and to determine that exact role of O_2.

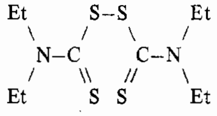
Step IXc is interesting and provides clear evidence for the importance of O_2. This step has been carried out by the reaction of α-$[Ru_2(Me_2dtc)_5]Cl$ with BF_3/O_2 in C_6H_6/CH_2Cl_2 solution at room temperature, in which case complete conversion to the β isomer is achieved, but in the absence of O_2 that α isomer does not isomerize. It is known that the α → β isomerization occurs thermally (60 °C in $CHCl_3$, first-order rate constant $k \approx 1 \times 10^{-4}\ s^{-1}$),[7] but at room temperature the conversion is extremely slow. Since a bond rupture occurs during the α → β isomerization,[23] it is most reasonable to assume that the BF_3/O_2 combination promotes bond rupture through partial ligand oxidation. To test this idea, excess I_2 was reacted with α-$[Ru_2(Me_2dtc)_5]Cl$ in CH_3CN at room temperature, and indeed the same α → β conversion occurred but with some formation of $IRu(Me_2dtc)_3$[6] (Experimental Section). Metal–sulfur bond rupture upon ligand oxidation has been proposed to occur in photochemical reactions of $M(R_2dtc)_3$ complexes, where M = Fe[11] or Ru.[10]

Reduction of α- and β-$[Ru(R_2dtc)_5]^+$. The α and β isomers of the bimetallic complexes, **1** and **2**, can be reduced to neutral mixed-valence Ru(II)–Ru(III) complexes by reaction with $NaBH_4$ in ethanol.[4] These complexes are paramagnetic ($S = {}^1/_2$) and mildly air-sensitive in toluene solution. Spectroscopic and magnetic data are presented in Table II and the Experimental Section. The reduction product of α-$[Ru_2(E_2dtc)_5]^+$ is green in toluene solution, while the reduced β isomer is purple (Table II). The solution absorption spectrum of the green complex which is due to α-$Ru_2(Et_2dtc)_5$ slowly converts into the spectrum of the purple complex, β-$Ru_2(Et_2dtc)_5$. The α → β isomerization is complete in toluene solution at 25 °C in ca. 15 min, which indicates that the isomerization is much faster than with the cationic complexes **1** and **2**.[7] The rate constant for the α → β isomerization was measured by spectroscopic monitoring of the interconversion and is $8 \times 10^{-4}\ s^{-1}$ at 30 °C. These results show that the BH_4^- reduction occurs without isomerization. The fact that the neutral mixed-valence complexes isomerize faster than their cationic Ru(III) counterparts suggests that bond rupture and rearrangement occur faster in the paramagnetic mixed-valence complexes. Martin[7] has reported that the anionic complexes, $[Ru_2(R_2dtc)_5]^-$, prepared electrochemically in acetone solution by one-electron reduction of $Ru_2(R_2dtc)_5$ are only stable in the α form. This is consistent with there being no Ru–Ru bond, as expected for Ru(II) which is d^6 and low spin. In fact, this complex is isoelectronic with the dirhodium compound $Rh_2(R_2dtc)_5$ (**5**), which has the α stereochemistry but without a M–M bond.[23]

Reactions of α- and β-$Ru_2(R_2dtc)_5$. The reaction chemistry of α- or β-$Ru_2(R_2dtc)_5$ is consistent with the presence of a weakened Ru–Ru bond compared with the cationic complexes, as would be expected if the added electron occupies a σ^* orbital of the M–M bond. For example, NO does not react with α- or β-$[Ru_2(Et_2dtc)_5]^+$ but reacts rapidly with α- or β-$Ru_2(Et_2dtc)_5$ in toluene solution, giving some of the known complex $(NO)Ru(Et_2dtc)_3$.[31] Photolysis of the cationic complexes using unfiltered UV radiation from a 450-W Hg vapor lamp in $CHCl_3$ saturated with CO shows no reaction, whereas the neutral complexes give $(CO)_2Ru(Et_2dtc)_2$ and $[(CO)Ru(Et_2dtc)_2]_2$[11,32] in good yield when irradiated in toluene saturated with CO.[33] Surprisingly, the α- and β-$Ru_2(R_2dtc)_5$ complexes slowly react with $CHCl_3$ and CH_2Cl_2 in the dark (rapidly in UV light), yielding their respective cationic complexes **1** and **2** with a Cl^- counterion. This oxidation reaction is similar to the dark reaction of $Fe(Et_2dtc)_2$ with $CHCl_3$ which gives $ClFe(Et_2dtc)_2$[11] and the photochemical chlorine abstraction reactions of $Fe(R_2dtc)_3$[11] and $Ru(R_2dtc)_3$[10] which give $ClFe(R_2dtc)_2$ and a mixture of α-$[Ru_2(R_2dtc)_5]Cl$ and $ClRu(R_2dtc)_3$, respectively. This observation also makes the recently reported UV–vis spectra of α- and β-$Ru_2(Me_2dtc)_5$ in CH_2Cl_2[7] subject to some doubt.

The complexes α- or β-$Ru_2(Me_2dtc)_5$ can be oxidized to their respective cationic complexes by reaction with a stoichiometric amount of I_2 (Experimental Section).

Reactions of $ClRu(Et_2dtc)_3$. Several redox reactions of this novel complex of Ru(IV) have previously been reported.[5] Reaction with $NaEt_2dtc$ in acetone gave $Ru(Et_2dtc)_3$ and Et_4tds (**9**), while reaction with excess $AgBF_4$ in acetone in the presence of O_2 gave the bimetallic complex $[Ru_2(Et_2dtc)_5]BF_4$ and **9**.[5] Both reactions occurred immediately on mixing, and the stereochemistry of the diruthenium complex was not determined. Careful ^1H NMR analysis in CD_3CN of the second reaction using $Ru(Me_3dtc)_3Cl$ showed that a mixture of α- and β-$[Ru_2(Me_2dtc)_5]BF_4$ and **8** was present upon removal of the acetone solvent. Compound **8** is presumed to have δ 2.63 (vide supra).[29] We believe this to be the correct product analysis for the Et complex as well, which indicates that our previous qualitative result was partly in error.[5] A proposed mechanism of this reaction is shown in eq X. The species



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$$ClRu(R_2dtc)_3 + AgBF_4 \xrightarrow{S} \underline{AgCl} + SRu(R_2dtc)_3{}^+ + BF_4{}^-$$

$$SRu(R_2dtc)_3{}^+ \xrightarrow{-S} Ru(R_2dtc)_2 + dtc^+ \ (\equiv {}^1/_2 8) \qquad (X)$$

$$Ru(R_2dtc)_2 + SRu(R_2dtc)_3{}^+ \xrightarrow{-S} [Ru_2(R_2dtc)_5]^+$$

$SRu(R_2dtc)_3{}^+$ where S is acetone or water has been observed in electrochemical experiments of $Ru(Et_2dtc)_3$ and $ClRu(R_2dtc)_3$ (see Electrochemical Study). The formation of **8** most simply results from R_2dtc^+ dissociation from $SRu(R_2dtc)_3{}^+$ as shown in eq X, but it could also involve $R_2dtc\cdot$ dissociation to **9** and subsequent $2e^-$ oxidation of **9** to **8** by the reduction 2[Ru(IV) → Ru(III)]. The latter reaction sequence is unlikely since **9** does not reduce $ClRu(R_2dtc)_3$. In addition, Willemse[34] has postulated the importance of R_2dtc^+ as an intermediate in redox reactions of Ni- and $Cu(R_2dtc)$ complexes.

It has been established that $ClRu(Et_2dtc)_3$ is completely dissociated into $SRu(Et_2dtc)_3{}^+$ and Cl^- in donor-type solvents, S, such as CH_3CN and $(CH_3)_2SO$ (Electrochemical Study and Tables I and II). To further establish the nature of these Ru(IV) compounds, PPh_3 was added to $ClRu(Et_2dtc)_3$ and to $[(CH_3CN)Ru(Et_2dtc)_3]BF_4$ in CH_3CN. In both cases, the ion $[(PPh_3)Ru(Et_2dtc)_3]^+$ was immediately formed. Characterization data for this complex are presented in Tables I and II and in the Experimental Section.

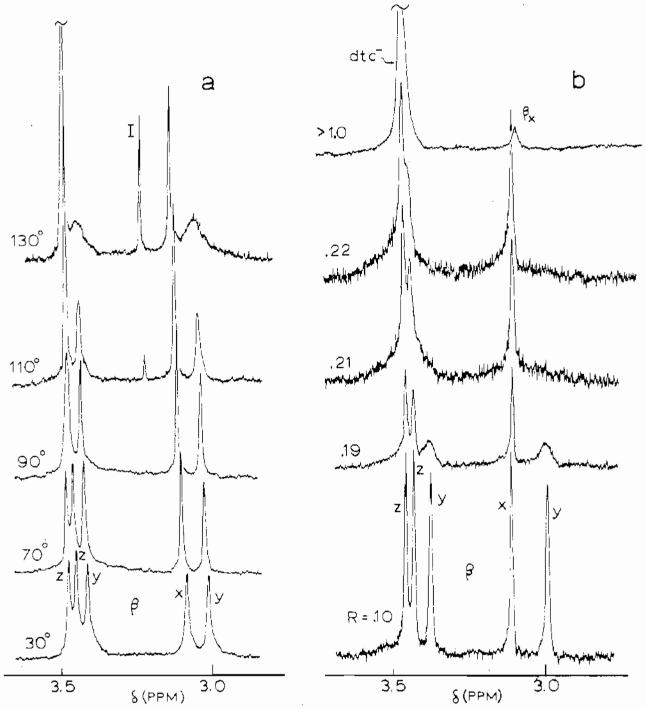


Figure 6. ^{1}H NMR traces of β-[$Ru_2(Me_2dtc)_5$]BF_4 recorded in (a, left) $(CD_3)_2SO$ as a function of temperature and (b, right) CD_3CN at 30 °C as a function of added $NaMe_2dtc$ (R = mole ratio $NaMe_2dtc/\beta$-[$Ru_2(Me_2dtc)_5$]BF_4). The letters x, y, and z refer to ligand environments defined in structure **11**, and I is due to the complex $Ru(Me_2dtc)_2(Me_2SO)_2$ (see text). The spectra were recorded at 100.1 MHz.

^{1}H NMR Properties. $LRu(R_2dtc)_3{}^n$ (L = CH_3CN, PPh_3 or $(CH_3)_2SO$, n = +; L = Cl or I, n = 0). All of the seven-coordinate complexes of Ru(IV) are stereochemically nonrigid, even at temperatures approaching the freezing points of the solvents CD_2Cl_2, $CDCl_3$, CD_3CN, and $(CD_3)_2SO$ (Table I, ref 5 and 6). Complexes where L = CH_3CN and $(CH_3)_2SO$ can only be examined in CD_3CN and $(CD_3)_2SO$, respectively. The nonrigidity of these complexes is unexpected since another d^4 complex, $(NO)Mo(Me_2dtc)_3$, which has the same solid-state geometry as $ClRu(Et_2dtc)_3$ and $IRu(Me_2dtc)_3$, is rigid up to ~60 °C.[35] In a previous paper we suggested that rapid halide dissociation and recombination was probably responsible for the nonrigid nature of the complexes where L = Cl and I.[5] This seems likely because of the substitutionally labile nature of the Ru–halide bond. Axial L exchange is also probably responsible for the nonrigidity in complexes where L = CH_3CN and $(CH_3)_2SO$. Additional support for this mechanism derives from halide-exchange experiments. Equimolar $CDCl_3$ solutions of $ClRu(Et_2dtc)_3$ and $IRu(Etdtc)_3$ were mixed at 25 °C and examined by ^{1}H NMR. The ethyl resonances were averaged even though the signals due to the two complexes should be well resolved if halide exchange was slow (Table I). This experiment clearly demonstrates that rapid halide exchange is occurring and is the most probable cause for the nonrigid nature of the compounds. Previous experiments have shown that R_2dtc^- ligand exchange is slow on the ^{1}H NMR time scale.[5]

Although the above mechanism is most reasonable for the complexes where L = Cl, I, CH_3CN, and $(CH_3)SO$, the PPh_3 adduct has properties which suggest that a different rearrangement mechanism is operative. Most importantly, L exchange is slow on the ^{1}H NMR time scale between complexes of L = Cl and PPh_3 in $CDCl_3$ solution at 30 °C. Therefore, rapid PPh_3 exchange cannot account for the nonrigidity for the L = PPh_3 complex. Other mechanisms including nondissociative polyhedral rearrangements[35] and partial R_2dtc ligand dissociation[5] have also been discussed for complexes of this type and of course could be operative here.

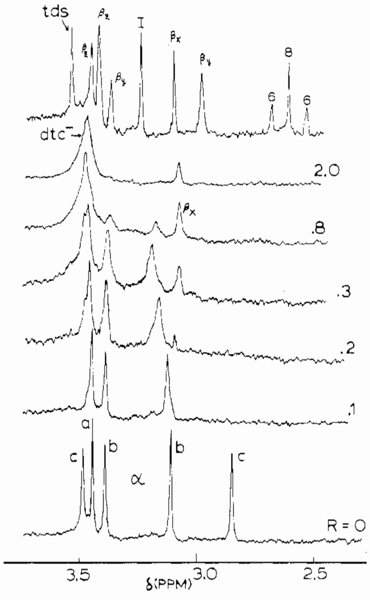
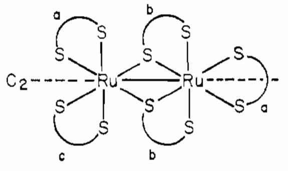


Figure 7. ^{1}H NMR traces of α-[$Ru_2(Me_2dtc)_5$]Cl recorded in CD_3CN at 30 °C as a function of added $NaMe_2dtc$ (R = mole ratio $NaMe_2dtc/\alpha$-[$Ru_2(Me_2dtc)_5$]Cl). The letters a, b, c, β_x, β_y, and β_z refer to ligand environments defined in structures **10** and **11**. I is due to the complex $IRu(Me_2dtc)_3$, and 6 and 8 are due to compounds **6** and **8** shown in the text. The spectra were recorded at 79.54 MHz. The top trace resulted upon addition of excess iodine to the R = 2.0 solution.

α- and β-[$Ru_2(R_2dtc)_5$]X (X = Cl or BF_4). ^{1}H NMR spectra of the α and β isomers with R = CH_3 and C_2H_5 have been recorded in various solvents.[4,7] Only the results with R = CH_3 using CD_3CN and $(CD_3)_2SO$ solvents will be discussed here. The R = Et compounds have complex ^{1}H NMR spectra. Both isomers possess five well-resolved methyl singlets at 30 °C which result from the C_2 symmetry of the compounds in solution and slow $S_2C{\overset{\dots}{-}}N$ bond rotation.[4,7,36] Actual spectra are shown in Figures 6 and 7, and chemical shifts are listed in Table I. The approximate C_2 symmetry in the solid state must be exact on the time average in solution, and therefore the α and β isomers can be represented by **10** and **11**, respectively. The letters refer to the nonequivalent Me_2dtc ligands. Note that the ligands labeled a and x contain the C_2 symmetry axis in each isomer, respectively, and therefore possess only one CH_3 environment, whereas the other ligands each possess two nonequivalent CH_3 environments; hence, five signals result.



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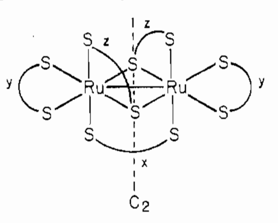

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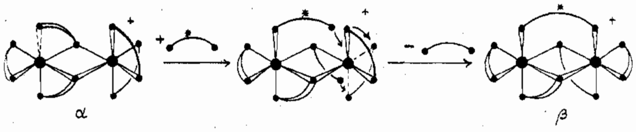
The results of variable-temperature and ligand-exchange experiments can be used to assign the ^{1}H NMR resonances to the various ligands a–c and x–z, respectively. The high-temperature ^{1}H NMR traces for the β complex recorded in $(CD_3)_2SO$ are shown in Figure 6a. The five CH_3 environments are labeled by the letters x, y, and z, and their assignment to **11** goes as follows. Increasing the temperatures should cause $S_2C{\overset{\dots}{-}}N$ bond rotation to become fast on the ^{1}H NMR time scale, and coalescence of the signals due to the two nonequivalent CH_3 groups of ligands y and z should occur separately. Figure 6a clearly shows the coalescence of the z pair at ~90° and the start of the y pair coalescence at 130°. These spectral changes are reversible; however, at temperatures >100° the complex slowly and irreversibly decomposes into the known compound $Ru(Me_2dtc)_2(Me_2SO)_2$,[37] which accounts for the ^1H NMR resonance labeled I in Figure 6a. From the high-temperature data, resonance which remains sharp is assigned to the unique bridging ligand which contains the C_2 symmetry axis as shown in **11**. The assignment of y and z as pairs is obvious from these data, but their correspondence to **11** requires the ligand-exchange results given below. Hendrickson et al.[7] have assigned the z doublet coalescence to an accidental degeneracy of the resonances; however, the reversible broadening of the y peaks at a higher temperature, exactly as expected if the rate of $S_2C\dashrightarrow N$ bond rotation for the y and z ligands is the same, argues against their assignment.[38] They[7] apparently did not monitor the ^1H NMR at high enough temperatures to observe the broadening of the y resonances.

Experiments with added $NaMe_2dtc$ in CD_3CN confirm the above conclusions and provide good evidence for the ligand labeling shown in **11**. The ligand-exchange ^1H NMR data are shown in Figure 6b for the β isomer. In this figure, R denotes the mole ratio of added $NaMe_2dtc$ to β-$[Ru_2Me_2dtc]BF_4$. For small amounts of $NaMe_2dtc$ added ($R \lesssim 0.1$), the five-line pattern is unaffected and appears virtually identical with the 30 °C $(CD_3)_2SO$ spectrum of Figure 6a. As the amount of ligand is increased, the y resonances broaden and eventually average with free ligand. Finally, when $R = 0.22$, the z resonances also coalesce, and for $R = 1.0$ only the average signal (composed of y, z, and free-ligand methyl groups) and the unique ligand x resonance remain. The bridging z ligands are expected to be more inert to ligand exchange than the terminal y ligands because the average Ru–S(bridge) distance is 0.11 Å shorter than the average Ru–S(terminal) distance.[4] Therefore, the assignment of y and z in **11** is reasonable, and the assignment of x is certain.

A similar ligand-exchange argument is used to assign the resonances in the α isomer. The assignment is shown in **10** and Figure 7. The five-line pattern ($R = 0$, Figure 7) is similar to but easily distinguishable from that of the β isomer. Upon additions of a small amount of $NaMe_2dtc$ ($R < 0.1$) in CD_3CN solution, the c resonances coalesce with free ligand. Eventually, when $R \simeq 0.8$, the a resonance coalesces; however, the b peaks also broaden and begin averaging for about the same R value. For the α isomer, the b ligands should be most resistant to exchange because the average bridging Ru–S distance is 0.09 Å shorter than the average nonbridging distance;[2] however, the distinction between the a and b resonances is not clear from this experiment, and the a and b ligand assignment in **10** depends on arguments in the next paragraph.

Hendrickson et al.[7] added lanthanide shift reagents to the α and β isomers in CD_2Cl_2 solution. Since the five-line CH_3 patterns of both isomers in CD_2Cl_2 are very similar to those in CD_3CN and $(CD_3)_2SO$, the shift reagent data can be used to confirm the above assignments. Figure 1 of ref 7 shows plots of the CH_3 chemical shifts for the α and β isomers as a function of added shift reagent. It is obvious from these plots that the pairs of resonances due to ligands y and z of the b isomer and b and c of the α isomer give lines with similar slopes, whereas the x and a peaks, respectively, have quite different sloped lines, thus establishing them as belonging to the ligands which contain the C_2 symmetry axes. The combination of all of these arguments places the assignments on rather firm ground.

In Figure 7 a new resonance (β_x) grows in as R increases. This resonance is due to the presence of the β isomer (recall that the x ligand is resistant to ligand exchange), which forms from the α isomer in the presence of excess ligand. The presence of free ligand must therefore increase the rate of effective bond rupture in the α isomer so that conversion to β is significantly accelerated. Since thermal bond rupture occurs and results in slow α → β conversion (see above), the accelerated rate in the presence of free ligand probably involves a mechanism similar to the one shown in eq XI. In XI the α → β conversion can be achieved by initial rupture of a nonbridging Ru–S bond (dashed line) followed by attack of monodentate free ligand and subsequent chelation and displacement as shown in XI. The thermal mechanism has been proposed to involve rupture of the stronger Ru–S(bridge) bond followed by major rearrangement and reattachment.[23] Finally, the top ^1H NMR trace in Figure 7 resulted upon addition of iodine to the $R = 2.0$ solution which reacts with excess ligand giving compounds **6**, **8**, and **9**[28] ($R = CH_3$). Resonances due to these compounds, the β isomer, and some $IRu(Me_2dtc)_3$ (I) are evident in the ^1H NMR PMR trace. No α isomer remains.



(XI)

Summary

The chemical redox and electrochemical experiments reported here on dithiocarbamato complexes of ruthenium clearly show that the novel bimetallic complexes α- and β-$[Ru_2(R_2dtc)_5]^+$ are not formed by electrochemical oxidation of $Ru(R_2dtc)_3$ in a variety of solvents as previously thought, and that chemical oxidation using boron trifluoride gas does yield the bimetallic α isomer directly in the absence of oxygen. Oxidation of $Ru(R_2dtc)_3$ using boron trifluoride gas in the presence of oxygen yields the β isomer. Electrochemical oxidation of $Ru(R_2dtc)_3$ in CH_3CN irreversibly yields a stable seven-coordinate complex of Ru(IV), $[(CH_3CN)Ru(R_2dtc)_3]^+$. Similarly, oxidation using I_2 or anhydrous HCl yields $IRu(R_2dtc)_3$ and $ClRu(R_2dtc)_3$, respectively. These pentagonal-bipyramidal complexes are stereochemically nonrigid on the ^1H NMR time scale.

The bimetallic complexes can be electrochemically or chemically ($NaBH_4$) reduced to mixed-valence compounds which maintain the α and β stereochemistries at low temperature. The neutral α isomer thermally converts into the neutral β isomer at 30 °C with a first-order rate constant of $8 \times 10^{-4}\ s^{-1}$. The mixed-valence complexes are more reactive than their cationic counterparts. Reaction with CO under UV irradiation yields *cis*-$(CO)_2Ru(R_2dtc)_2$ and $[(CO)Ru(R_2dtc)_2]_2$, while photolysis in $CHCl_3$ yields the oxidized cations with chloride counterions and retained α and β stereochemistry.

Acknowledgment. This research was supported by the National Science Foundation.

Registry No. $Ru(Et_2dtc)_3$, 31656-15-2; **3**, 60490-51-9; α-$[Ru_2(Me_2dtc)_5]Cl$, 61695-23-6; α-$[Ru_2(Et_2dtc)_5]Cl$, 63912-30-1; β-$[Ru_2(Me_2dtc)_5]BF_4$, 57774-53-5; β-$[Ru_2(Et_2dtc)_5]BF_4$, 55326-22-2; **4**, 58320-56-2; $[(CH_3CN)Ru(Et_2dtc)_3]BF_4$, 64799-64-0; $[(PPh_3)Ru(Et_2dtc)_3]Cl$, 64784-38-9; $[(PPh_3)Ru(Me_2dtc)_3]BF_4$, 64784-37-8; $[(PPh_3)Ru(Et_2dtc)_3]BF_4$, 64784-35-6; $ClRu(Me_2dtc)_3$, 63994-96-7; α-$[Ru_2(Me_2dtc)_5]$, 64825-44-1; α-$[Ru_2(Et_2dtc)_5]$, 64825-41-8; β-$[Ru_2(Me_2dtc)_5]$, 64825-45-2; β-$[Ru_2(Et_2dtc)_5]$, 64825-42-9; I_2, 7553-56-2; *cis*-$(CO)_2Ru(Et_2dtc)_2$, 64784-39-0; $Ru(Me_2dtc)_3I$, 64784-40-3; BF_3, 7637-07-2; **6** (R = Me), 64771-40-0; **8** (R = Me), 64771-41-1; $Et_2O \cdot BF_3$, 109-63-7; $[(Me_2SO)Ru(Et_2dtc)_3]BF_4$, 64825-50-9; $IRu(Et_2dtc)_3$, 64784-44-7; $[(CD_3CN)Ru(Et_2dtc)_3]BF_4$, 64784-46-9; $[(CH_3CN)Ru(Et_2dtc)_3]Cl$, 64784-47-0.

References and Notes

(1) (a) L. H. Pignolet, *Inorg. Chem.*, **13**, 2051 (1974); (b) A. Domenicano, A. Vaciago, L. Zambonelli, P. L. Loader, and L. M. Venanzi, *Chem. Commun.*, 476 (1966); (c) C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 2418 (1975).

(2) C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 2410 (1975).

(3) C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 2418 (1975).

(4) B. M. Mattson, J. R. Heiman, and L. H. Pignolet, *Inorg. Chem.*, **15**, 564 (1976); L. H. Pignolet and B. M. Mattson, *J. Chem. Soc., Chem. Commun.*, 49 (1975).

(5) K. W. Given, B. M. Mattson, and L. H. Pignolet, *Inorg. Chem.*, **15**, 3152 (1976).

(6) B. M. Mattson and L. H. Pignolet, *Inorg. Chem.*, **16**, 488 (1977).

(7) A. R. Hendrickson, J. M. Hope, and R. L. Martin, *J. Chem. Soc., Dalton Trans.*, 2032 (1976).

(8) The designation of α and β to the bimetallic complexes **2** and **1** is due to Martin (ref 7).

(9) (a) K. W. Given, B. M. Mattson, and L. H. Pignolet, *Inorg. Chem.*, **15**, 3152 (1976). (b) The bimetallic product of this reaction is the α isomer at room temperature (vide infra).

(10) K. W. Given, B. M. Mattson, M. F. McGuiggan, G. L. Miessler, and L. H. Pignolet, *J. Am. Chem. Soc.*, **99**, 4855 (1977).

(11) G. L. Miessler, G. Stuk, T. P. Smith, K. W. Given, M. C. Palazzotto, and L. H. Pignolet, *Inorg. Chem.*, **15**, 1982 (1976).

(12) For example, see the following papers and references cited therein: (a) T. H. Randle, T. J. Cardwell, and R. J. Magee, *Aust. J. Chem.*, **29**, 1191 (1976); (b) A. R. Hendrickson, R. L. Martin, and N. M. Rohde, *Inorg. Chem.*, **14**, 2980 (1975); (c) H. C. Brinkoff, *Recl. Trav. Chim. Pays-Bas*, **90**, 377 (1971); (d) J. G. M. van der Linden, *J. Inorg. Nucl. Chem.*, **34**, 1645 (1972); (e) G. Cauquis and D. Lachenal, *Inorg. Nucl. Chem. Lett.*, **9**, 1095 (1973); (f) R. M. Golding and K. Lehtonen, *Aust. J. Chem.*, **27**, 2083 (1974); (g) A. M. Bond, A. T. Casey, and J. R. Thackeray, *Inorg. Chem.*, **13**, 84 (1974).

(13) R. Chant, A. R. Hendrickson, R. L. Martin, and N. M. Rohde, *Inorg. Chem.*, **14**, 1894 (1975).

(14) G. S. Patterson and R. H. Holm, *Inorg. Chem.*, **11**, 2285 (1972).

(15) J. V. Kingston and G. Wilkenson, *J. Inorg. Nucl. Chem.*, **28**, 2709 (1966).

(16) It is very difficult to completely remove all oxygen, especially since it is a likely impurity in the BF_3 gas. Therefore, this experiment most certainly was done in the presence of trace amounts of oxygen.

(17) J. L. K. F. de Vries, J. M. Trooster, and E. de Boer, *Inorg. Chem.*, **12**, 2730 (1973).

(18) Hendrickson et al.[7] do not show actual cyclic voltammetric scans nor do they report what species or electrochemical waves or peaks were actually present after the electrolysis.

(19) Coordinated CH_3CN has not been directly observed by ^1H NMR or IR due to interference from free CH_3CN; however, its presence is inferred by the data presented. In addition, triphenylphosphine can be added to $[(CH_3CN)Ru(Et_2dtc)_3]X$, where X = Cl or BF_4, to give $[(PPh_3)Ru(Et_2dtc)_3]X$, which also has very similar ^1H NMR properties. The stereochemically nonrigid nature of these complexes strongly suggests that they will have the same stereochemistry.[5,6]

(20) E. A. Pasek and D. K. Straub, *Inorg. Chem.*, **11**, 259 (1972).

(21) A. R. Hendrickson, R. L. Martin, and D. Taylor, *J. Chem. Soc., Dalton Trans.*, 2182 (1975).

(22) A. R. Hendrickson, R. L. Martin, and N. M. Rohde, *Inorg. Chem.*, **13**, 1933 (1974).

(23) A. R. Hendrickson, R. L. Martin, and D. Taylor, *Aust. J. Chem.*, **29**, 269 (1976).

(24) G. E. Manoussakis, M. Lalia-Kantouri, and R. B. Huff, *J. Inorg. Nucl. Chem.*, **37**, 2330 (1975).

(25) R. M. Golding, C. M. Harris, K. J. Jessop, and W. C. Tennant, *Aust. J. Chem.*, **25**, 2567 (1972).

(26) L. H. Pignolet, observations to be published.

(27) P. Labarbe and M. T. Forel, *Spectrochim. Acta, Part A*, **31a**, 525 (1975).

(28) E. W. Ainscough and A. M. Brodie, *J. Chem. Soc., Dalton Trans.*, 565 (1977).

(29) We have repeated the reaction of Me_4-thiuram disulfide with I_2 in $CHCl_3$ solution as reported in ref 28, and we find that a mixture of **6** and **8** is formed. See the Experimental Section for the ^1H NMR shifts of these compounds. The same ^1H NMR resonances result from reaction of Me_4-thiuram disulfide with BF_3/O_2 in benzene and with Hg_2I_2 and I_2 in $CHCl_3/EtOH$. The last reaction is known to give compound **6** (J. Willemse and J. A. Cras, *Recl. Trav. Chim. Pays-Bas*, **91**, 1309 (1972), and apparently compound **8** is also formed. We have also obtained MS evidence for both **6** and **8** where R = Et. It should be mentioned that none of these reactions are clean (e.g., oxygen is able to replace sulfur), and further work is needed to unambiguously characterize these compounds. Results will be published in a further paper.

(30) T. L. Chu and T. J. Weismann, *J. Am. Chem. Soc.*, **78**, 23 (1956).

(31) $(NO)Ru(Et_2dtc)_3$ (ref 1b) is isolated in ~10% yield along with α- or β-$[Ru_2(Et_2dtc)_5]^+$. The anion appears to be NO_2^- by IR analysis. The details of this reaction warrant further study.

(32) J. V. Kingston and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 2709 (1966).

(33) The details of these experiments will be published in a separate paper.

(34) J. Willemse, Ph.D. Thesis, University of Nijmegen, 1974, pp 73–74.

(35) R. Davis, M. N. S. Hill, C. E. Holloway, B. F. G. Johnson, and K. H. Al-Obaidi, *J. Chem. Soc. A*, 994 (1971).

(36) The conclusion that $S_2C\underset{\cdots}{-}N$ bond rotation in these complexes is slow is based on the fact that no further peak splittings occur at low temperatures.[4,7]

(37) I. P. Evans, A. Spencer, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 204 (1973), and B. Edgar, Ph.D. Thesis, University of Minnesota, 1974.

(38) This follows because the closely spaced doublet z (peak separation ≈ 2.60 Hz) should coalesce at a lower temperature than the more widely spaced doublet y (peak separation ≈ 38.4 Hz), as is well-known from NMR theory (see, e.g., L. H. Pignolet, in "Chemical Applications of NMR in Paramagnetic Molecules," R. H. Holm, W. D. Horrocks, and G. N. LaMar, Ed., Academic Press, New York, N.Y., 1973, Chapter 8) and the y doublet coalescence occurs where predicted for a similar activation energy process.

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B-Alkyl and *B*-Aryl Derivatives of 1,2,3,4,5,6-Hexahydro-1,1,3,3,5,5-hexamethylcyclotriboraphosphane[2,3]

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A new synthetic method for *B*-organo-substituted 1,2,3,4,5,6-hexahydrocyclotriboraphosphane derivatives has been developed based on the replacement of *B*-halogen substituents using organometallic reagents. Reported herein are the limitations of the method, with regard to competing degradation, reduction, and halogenation reactions, which influence product yield, degree of alkylation, and isomerization.

Introduction

All reported syntheses of *B*-alkyl-substituted boraphosphane oligomers or polymers have utilized precursors already containing the *B*-alkyl group. The first examples were reported by Burg and Wagner[5] who dehydrobrominated phosphine dimethylbromoborane with triethylamine to obtain an initially monomeric product which polymerized in solution giving rise to $[H_2PB(CH_3)_2]_n$, considered to have a linear structure. The monomer $H_2PB(n\text{-}C_4H_9)_2$, similarly prepared,[6] appeared to polymerize more slowly but like the *B,B*-dimethyl polymer was reactive with oxygen and probably had a linear structure. Attempted pyrolytic dehydrogenation of dimethylphosphine–dimethylborane, $(CH_3)_2PH{\cdot}BH(CH_3)_2$, was preceded by disproportionation so that the principal product was not a polymeric $(CH_3)_2PB(CH_3)_2$ species but an inhomogeneous material assumed to consist principally of $(CH_3)_2PBHCH_3$ units with lesser amounts of $(CH_3)_2PBH_2$ and $(CH_3)_2PB(CH_3)_2$ units.[5] The volatility of the mixture suggested that