Ruthenium(II)-Catalyzed Thioether Oxidation. 1. Synthesis of Mixed Sulfide and Sulfoxide Complexes

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$RuX_2(Me_2SO)_4$ complexes are excellent catalysts for the selective oxygen oxidation of thioethers. Under conditions designed to mimic a catalytic situation, i.e. in methanol at 100 °C, but in the absence of oxygen, a variety of $trans(X_2)$-$RuX_2(SR_2)_{4-n}(Me_2SO)_n$ complexes are formed; the value of n depends upon the steric bulk of the potential thioether donor, and $SR_2 = \overline{S(CH_2)_3CH_2}$ (X = Br, $n = 0$ (**7**); X = Cl, $n = 0$ (**8**)), Me_2S (X = Cl, $n = 0$ (**4**), 1 (**5**), 2 (**6**); X = Br, $n = 0$ (**1**), 1 (**2**), 2 (**3**)), Et_2S (X = Br, $n = 1$ (**10**), 2 (**11**)), or t-Bu_2S (X = Br, $n = 3$ (**9**)). Mixtures of two isomers containing S-bound sulfoxide, the *all-trans*- and the $trans,cis,cis$-$RuX_2(SR_2)_2(Me_2SO)_2$ complexes, are formed when $SR_2 = Me_2S$ (**3** and **6**) and Et_2S (**11**). The monosulfide complex containing S-bound sulfoxide, $RuX_2(SR_2)(Me_2SO)_3$, is observed only when $SR_2 = t$-Bu_2S (**9**). With multidentate thioether ligands, the S-bound sulfoxide complexes $trans(X_2)$-$RuX_2(EtSCH_2CH_2SEt)(Me_2SO)_2$ (X = Cl (**15**), Br (**12**)), *all-cis*-$RuCl_2$-$(EtSCH_2CH_2SEt)(Me_2SO)_2$ (**14**), $trans(X_2)$-$RuBr_2((EtSCH_2CH_2)_2S)(Me_2SO)$ (**13**), and cis-$RuCl_2(CH_3C(CH_2SEt_3)_3)(Me_2SO)$ (**16**) were prepared, and the structure of complex **16** was confirmed by single-crystal X-ray analysis. Crystals of **16** are monoclinic, $P2_1/n$, with $a = 15.110$ (2) Å, $b = 15.417$ (3) Å, $c = 9.040$ (1) Å, $\beta = 104.33$ (1)°, and $Z = 4$. The structure was refined to $R = 0.055$ ($R_w = 0.057$) by using 2247 unique reflections with $|F| > 4\sigma(|F|)$. The octahedral Ru(II) complex has tridentate fac-thioether and cis-dichloro ligands. The Me_2SO ligand is coordinated to the Ru(II) ion through the S atom. The six-membered rings of the tridentate ligand assume twist-boat conformations. The Ru–S(thioether) bond lengths range from 2.312 (2) to 2.342 (2) Å. The Ru–S bond length to the Me_2SO ligand is 2.277 (2) Å. The Ru–Cl bond lengths are 2.423 (3) and 2.456 (3) Å. Electrochemical studies of the isolated complexes reveal that the *all-trans*-$RuX_2(SR_2)_2(Me_2SO)_2$ complexes are very readily oxidized. This observation suggests that such a species is the most oxygen-active complex leading to catalysis in these systems.

Introduction

Our discovery that ruthenium(II) complexes of the type $RuX_2(Me_2SO)_4$ (X = Cl, Br, $SnCl_3$, SCN),[2] can function as effective catalysts for the selective autoxidation of thioethers to their sulfoxides prompted us to investigate this chemistry in greater detail. Our mechanistic and kinetic studies reveal that these catalyzed reactions are first order in $[Ru]_t$ and in $[O_2]$ at lower oxygen pressures (<150 psi O_2) and zero order in the substrate thioether concentration.[2] Thus, at lower O_2 pressures we observed that the rate-determining step is oxidation of a metal complex with O_2 to yield hydrogen peroxide plus oxidized metal. The net stoichiometry observed is shown in eq 1. An important obser-

$$R_1R_2CHOH + O_2 + SR_2 \longrightarrow R_1R_2C{=}O + \overset{O}{\underset{\uparrow}{S}}R_2 + H_2O \qquad (1)$$
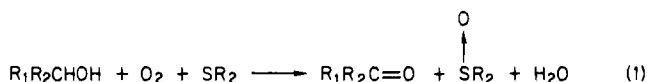
vation regarding the nature of the ruthenium catalyst in these systems is that different thioethers yield very different observed rates even though the reactions remain zero order in SR_2 substrate (Table I). This suggests that the nature of the complexes formed in situ and their relative concentrations are dependent upon the thioether substrate (potential ligand) present in large excess in these catalytic reactions. As can be seen in Table I, the observed rates increase as the steric bulk of the substrate (ligand) increases (rate increases in the order $\overline{S(CH_2)_3CH_2} < SMe_2 < SMe$-$(CH_2)_9CH_3 \ll SEt_2 < Bu_2S$), but then the rate decreases as steric demand in the substrate increases further (rate decreases in the order $Bu_2S > i$-$Bu_2S \gg t$-Bu_2S). These results imply that not only are various species formed in situ, but that more active species and/or greater concentrations of active species are formed when certain SR_2 ligands are present.

In order to learn more about the structures of the complexes formed in the catalytic system, a systematic study was made of the effect of the thioether substrate on the complexes formed in situ. Such studies were necessary to establish the nature of the oxygen activation in these systems. Several fundamental questions remain regarding this key interaction of O_2 and the as yet uncharacterized ruthenium(II) complex or complexes that lead to catalysis. For example, do peroxide adducts form (inner-sphere

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Table I. Turnover Numbers for Catalytic Autoxidation of Various Thioether Substrates

substrate	turnover no.,[a] mol of sub/(mol of cat h)	
	cis-$RuCl_2$-$(Me_2SO)_4$	*trans*-$RuBr_2$-$(Me_2SO)_4$
dimethyl sulfide	7.2	24
tetrahydrothiophene	4.0	9.5
decyl methyl sulfide	8.5	27
diethyl sulfide	52	121
di-n-butyl sulfide	78	172
diisobutyl sulfide	63	131
di-*tert*-butyl sulfide	0	0
thioanisole ($PhSCH_3$)	4	8

[a] $T = 105$ °C, 100 psi O_2 in MeOH.

electron transfer) or do outer-sphere processes occur, and are one- or two-electron-transfer processes operative. The answer to such fundamental issues can only be addressed by studying directly the oxygen reaction with the ruthenium(II) complex(es) that leads to productive catalytic chemistry in this system. Thus, we have begun to investigate this system by attempting to characterize all of the complexes formed in situ in model reactions (eq 2). The

$$RuX_2(Me_2SO)_4 + excess\ SR_2 \xrightleftharpoons{EtOH} RuX_2(SR_2)_n(Me_2SO)_{4-n} \qquad (2)$$
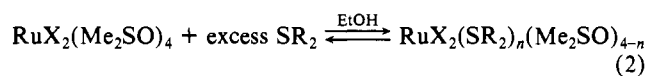
syntheses, characterizations, and electrochemistries of the complexes formed under conditions designed to mimic the catalytic case are described with the substrates (ligands) Me_2S, tetrahydrothiophene, Et_2S, and t-Bu_2S. We find that steric bulk indeed plays a major role in determining the distribution, as well as the concentration, of ruthenium(II) species present.

Experimental Section

General Procedures. All ruthenium syntheses were carried out under dry nitrogen by using conventional Schlenkware techniques and dry degassed solvents. Chemical analyses were performed in-house and also by Galbraith Laboratories, Knoxville, TN. Proton NMR spectra were recorded in $CDCl_3$ at 60 MHz on a Varian T-60 spectrometer and also at 270 MHz on a JEOL FX270 using $(CH_3)_4Si$ as an internal standard. Carbon-13 NMR spectra were recorded at 20 MHz in $CDCl_3$ on a Varian CFT-20 spectrometer using the center line of the chloroform triplet as the reference. Infrared spectra were recorded as Nujol mulls between CsBr windows on Perkin-Elmer Model 298 and 621 spectrophotometers. Electronic spectra were recorded in the UV/vis regions on

a Beckman DU-7 spectrophotometer using chloroform solutions in Teflon-stoppered quartz cells.

All cyclic voltammograms were measured in 0.10 M tetra-*n*-butylammonium tetrafluoroborate in methylene chloride. The methylene chloride was dried by passing through two columns of dry alumina and then distilling from CaH_2 under dry N_2. The supporting electrolyte was twice recrystallized from ethyl acetate–hexane. A single-compartment, three-electrode cell was used with a platinum working electrode, a platinum-wire auxiliary electrode, and a Ag/AgCl reference electrode in H_2O separated from the CH_2Cl_2 by a ceramic frit. The cyclic voltammetry experiments were performed with a PAR 173 potentiostat and a PAR universal programmer at sweep rates of 100–500 mV/s.

Materials. The syntheses of *cis*-RuCl$_2$(Me$_2$SO)$_4$[3] and *trans*-RuBr$_2$-(Me$_2$SO)$_4$[4] are reported elsewhere. Dimethyl sulfide, diethyl sulfide, di-*tert*-butyl sulfide, and tetrahydrothiophene were purchased from Aldrich Chemical Co. and distilled prior to use. The 3,6-dithiaoctane was purchased from Fairfield Chemical Co. and also distilled prior to use. The 2-mercaptoethyl sulfide precursor to bis(2-(ethylthio)ethyl) sulfide[5] was used as supplied from Aldrich Chemical Co. 1,1,1-Tris(bromomethyl)ethane was prepared by the method of Doering et al.[6] The 3,3'-thiodipropanol was used as supplied by Aldrich Chemical Co.

1,1,1-Tris((ethylthio)methyl)ethane. To a dry ethanol solution (150 mL) under N_2 containing 0.40 mol of sodium ethoxide was added ethanethiol (Aldrich) (29.8 mL, 0.402 mol) dropwise over 10 min. Then 30.7 g (0.0994 mol) of 1,1,1-tris(bromomethyl)ethane was added in a dropwise fashion for 5 min under N_2. The solution was then heated at reflux for 24 h. After this time, 30 mL of water was added and then ethanol was removed via a rotary evaporator to yield both oil and aqueous phases. The oily residue was extracted three times with 75-mL portions of Et_2O. The ether layers were combined and dried over $MgSO_4$ for 2 h. After filtration of the $MgSO_4$, the ether was removed by a rotary evaporator. The residual oil was distilled at 105–106 °C at 0.35 mmHg. The yield was 19.3 g (77%). Mass spectrum parent ion (*m/e*): 253 (calcd); 253 (found). Anal. Calcd for $C_{11}H_{24}S_3$: C, 52.32; H, 9.58; S, 38.10. Found: C, 52.49; H, 9.73; S, 38.01.

Bis(2-(ethylthio)ethyl) Sulfide. This material was prepared by a method analogous to that of Chatt et al.[5] In a typical preparation 17.5 g (0.113 mol) of bis-2-mercaptoethyl sulfide was added dropwise to 250 mL of a freshly prepared ethanolic solution containing 0.226 mol of NaOEt. The reaction was heated to reflux under dry N_2, and 35.2 g of ethyliodide (18.1 mL, 0.226 mol) was added dropwise. The reaction was refluxed for 3 h and then allowed to cool to room temperature. The ethanol was removed via a rotary evaporator. Water was then added to the oily solid to remove the salts, and the mixture was subsequently extracted with Et_2O. The ether layer was dried over Na_2SO_4 overnight and then filtered. The solvent was removed on a rotary evaporator. The oily mass was distilled under vacuum at 112 °C (0.7 mmHg) to afford 17.7 g (74% yield) of clear colorless oil, whose ^1H NMR, mass spectrum, and elemental analysis are in agreement with the proposed structure.

Dibromotetrakis(dimethyl sulfide)ruthenium(II) (1), Dibromo(dimethyl sulfoxide)tris(dimethyl sulfide)ruthenium(II) (2), and Dibromobis(dimethyl sulfoxide)bis(dimethyl sulfide)ruthenium(II) (3). To a 40-mL methanol solution containing 5.0 mL of dimethyl sulfide was suspended 1.20 g (2.1 mmol) of *trans*-RuBr$_2$(Me$_2$SO)$_4$. The solution was then transferred under N_2 to a Griffen–Worden pressure vessel[7] and shaken in an oil bath at 100 °C for 30 min. The solution was then cooled and the solvent removed on a rotary evaporator. The resultant yellow solid was dissolved under N_2 in 5 mL of 95% CH_2Cl_2/5% MeOH and then subjected to column chromatography under Ar (25 psi pressure) on silica gel (12 × 1 in., E. Merck Silica Gel 60) using the 95:5 CH_2Cl_2/MeOH solvent as the eluting agent. Three yellow-orange bands are eluted: band 1 ($R_f \sim 0.90$), broad band 2 ($R_f \sim 0.7$), and band 3 ($R_f \sim 0.6$). Each fraction was collected and taken to dryness. Addition of 10 mL of hot methanol to the solid obtained from either band 1 or 2 gave a yellow crystalline product on cooling. The yellow solid of band 3 was washed from the flask with Et_2O (10–15 mL) and collected by filtration. The following yields were obtained: (a) band 1 gave 0.51 g of compound 1 (48%); (b) band 2 gave 0.36 g of compound 2 (33%); (c) band 3 gave 0.14 g of compound 3 (12%). Anal. Calcd for $C_8H_{24}Br_2RuS_4$ (1): C, 18.86; H, 4.75; Br, 31.37; S, 25.18. Found: C, 18.61; H, 4.58; Br, 31.31; S, 25.11. Calcd for $C_8H_{24}Br_2ORuS_4$ (2): C, 18.29; H, 4.60; Br, 30.42; S, 24.41. Found: C, 18.08; H, 4.79; Br, 31.00; S, 24.63. Calcd for $C_8H_{24}Br_2O_2RuS_4$ (3): C, 17.75; H, 4.47; Br, 29.52; S, 23.69. Found:

C, 17.69; H, 4.31; Br, 29.22; S, 23.46.

Dichlorotetrakis(dimethyl sulfide)ruthenium(II) (4), Dichloro(dimethyl sulfoxide)tris(dimethyl sulfide)ruthenium(II) (5), and Dichlorobis(dimethyl sulfoxide)bis(dimethyl sulfide)ruthenium(II) (6). The preparation of these three complexes was carried out in a manner identical with that described for the preceding three bromo analogues. In this case 2.0 g (4.13 mmol) of the *cis*-RuCl$_2$(Me$_2$SO)$_4$ complex was used. The isolation of three complexes by chromatography was carried out as described in the preceding example. The following yields were obtained: (a) band 1 gave 0.89 g (51%) of complex 4; (b) band 2 gave 0.56 g (31%) of complex 5; (c) band 3 gave 0.24 g (13%) of complex 6. Anal. Calcd for $C_8H_{24}Cl_2RuS_4$ (4): C, 22.85; H, 5.75; Cl, 16.86; S, 30.50. Found: C, 22.69; H, 5.64; Cl, 17.11; S, 30.72. Calcd for $C_8H_{24}Cl_2ORuS_4$ (5): C, 22.01; H, 5.54; Cl, 16.24; S, 29.38. Found: C, 22.19; H, 5.38; Cl, 16.04; S, 29.21. Calcd for $C_8H_{24}Cl_2O_2RuS_4$ (6): C, 21.23; H, 5.35; Cl, 15.67; S, 28.34. Found: C, 21.44; H, 5.96; Cl, 14.38; S, 28.56.

Dibromotetrakis(tetrahydrothiophene)ruthenium(II) (7). To a hot ethanol solution containing 2.0 g (3.5 mmol) of *trans*-RuBr$_2$(Me$_2$SO)$_4$ was added 6.1 g (70 mmol) of tetrahydrothiophene. After the mixture was refluxed for several minutes under N_2, an orange precipitate formed, and after being refluxed for a total of $^1/_2$ h, the solution was cooled at −20 °C overnight. The solid was collected by filtration, washed with diethyl ether, and dried in vacuo to yield 1.92 g (90%) of orange microcrystalline solid. Anal. Calcd for $C_{16}H_{32}Br_2RuS_4$: C, 31.32; H, 5.26; Br, 26.05; S, 20.90. Found: C, 31.61; H, 5.12; Br, 26.36; S, 21.07.

Dichlorotetrakis(tetrahydrothiophene)ruthenium(II) (8). This complex was synthesized by the same method as outlined for preceding complex 7. The yield of complex 8 from 2.0 g (4.13 mmol) of *cis*-RuCl$_2$(Me$_2$SO)$_4$ was 1.83 g (85%). Anal. Calcd for $C_{16}H_{32}Cl_2RuS_4$: C, 36.63; H, 6.15; Cl, 13.51; S, 24.45. Found: C, 36.91; H, 6.40; Cl, 13.33; S, 24.19.

Dibromo(di-*tert*-butyl sulfide)tris(dimethyl sulfoxide)ruthenium(II) (9). To a hot ethanol solution (60 mL) containing 1.0 g (1.74 mol) of *trans*-RuBr$_2$(Me$_2$SO)$_4$ was added 2.5 g (17.0 mmol) of di-*tert*-butyl sulfide. The solution was refluxed under N_2 for an additional 30 min. At this point TLC on silica-gel plates using 95:5 CH_2Cl_2/MeOH indicated only one product. The solution was taken to dryness and the solid dissolved in a minimum volume of hot acetone (7 mL). While the mixture was still hot, an equivolume amount of diethyl ether was slowly added. The cloudy solution was then cooled and stored at −40 °C overnight. A pale orange solid was collected by filtration, washed with Et_2O, and dried in vacuo. The yield of complex 9 was 0.63 g (58%). TLC analyses of the filtrate and of the redissolved solid were identical and show that only one ruthenium-containing species is present. Anal. Calcd for $C_{14}H_{36}Br_2O_3RuS_4$: C, 26.21; H, 5.66; Br, 24.91; S, 19.99. Found: C, 26.04; H, 5.77; Br, 24.83; S, 20.15.

Dibromo(dimethyl sulfoxide)tris(diethyl sulfide)ruthenium(II) (10) and Dibromobis(diethyl sulfide)bis(dimethyl sulfoxide)ruthenium(II) (11). In an ethanol solution containing 2.0 g (22 mmol) of diethyl sulfide was suspended 1.0 g (1.74 mmol) of *trans*-RuBr$_2$(Me$_2$SO)$_4$. The solution was refluxed for 1 h to give an orange-red solution, which was cooled and then taken to dryness. The orange solid was dissolved in 7 mL of 95:5 CH_2Cl_2/MeOH and subjected to the same chromatographic workup as described above for compounds 1–3.

Two orange bands were apparent on the column: a narrow leading component, band 1 ($R_f \sim 0.65$), and a second broader band ($R_f \sim 0.5$). Both fractions were collected separately and then stripped to dryness to give pale orange crystalline products. The yields of these two complexes are as follows: for band 1, complex 10, 0.30 g (28%); for band 2, complex 11, 0.68 g (65%). Anal. Calcd for $C_{14}H_{36}Br_2ORuS_4$ (10): C, 27.58; H, 5.95; Br, 26.22; S, 21.04. Found: C, 27.71; H, 6.07; Br, 26.59; S, 20.79. Calcd for $C_{12}H_{32}Br_2O_2RuS_4$ (11): C, 24.12; H, 5.40; Br, 26.75; S, 21.46. Found: C, 24.37; H, 5.61; Br, 26.83; S, 21.59.

trans-**Dibromobis(dimethyl sulfoxide)[1,2-bis(ethylthio)ethane]ruthenium(II) (12).** In a chloroform solution (75 mL) containing 0.26 g (1.75 mmol) of 1,2-bis(ethylthio)ethane was added 1.0 g of RuBr$_2$(Me$_2$SO)$_4$. The mixture was refluxed for 1 h to give a yellow-orange solution, which was cooled and then taken to dryness. The yellow solid was dissolved in a minimum volume of 95% CH_2Cl_2/5% MeOH and subjected under Ar to medium-pressure (20 psi) column chromatography (12 × 1 in. column) with silica gel (E. Merck Silica Gel 60, less than 230 mesh) and 95% CH_2Cl_2/5% MeOH as the eluting solvent. One major yellow band eluted with an $R_f \sim 0.8$. After this band was collected, the solvent was removed and the resulting solid was recrystallized from 10 mL of hot methanol under Ar. Yellow crystals were obtained, collected by filtration, washed with diethyl ether, and dried in vacuo. A total yield of 0.64 g (65%) was obtained. Anal. Calcd for $C_{10}H_{26}Br_2O_2RuS_4$: C, 21.17; H, 4.62; Br, 28.16; S, 22.60. Found: C, 20.87; H, 4.78; Br, 27.96; S, 22.48.

Dibromo(dimethyl sulfoxide)[bis(2-(ethylthio)ethyl) sulfide]ruthenium(II) (13). To 25 mL of 2-methoxyethanol were added 1.0 g (1.74 mmol) of *trans*-RuBr$_2$(Me$_2$SO)$_4$ and 0.37 g (1.76 mmol) of bis(2-

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Table II. Complexes Formed and Isolated from the Reaction of $RuX_2(Me_2SO)_4$ with Excess SR_2 at 100 °C under Ar in Methanol

catalyst	sulfide	products (% yield)
cis-RuCl$_2$(Me$_2$SO)$_4$	SMe$_2$	RuCl$_2$(SMe$_2$)$_4$ (50)^a
		RuCl$_2$(SMe$_2$)$_3$(Me$_2$SO) (33)^a
		RuCl$_2$(Me$_2$S)$_2$(Me$_2$SO)$_2$ (12)^b
trans-RuBr$_2$-(Me$_2$SO)$_4$	S(CH$_2$)$_3$CH$_2$	RuBr$_2$(S(CH$_2$)$_3$CH$_2$)$_4$ (85)^c
trans-RuBr$_2$-(Me$_2$SO)$_4$	SMe$_2$	same distribution as chloro
trans-RuBr$_2$-(Me$_2$SO)$_4$	SEt$_2$	RuBr$_2$(Et$_2$S)$_3$(Me$_2$SO) (28)^a
		RuBr$_2$(Et$_2$S)$_2$(Me$_2$SO)$_2$ (65)^b
trans-RuBr$_2$-(Me$_2$SO)$_4$	*t*-Bu$_2$S	RuBr$_2$(Me$_2$SO)$_3$(*t*-Bu$_2$S) (>90)

^{a} trans-Dihalo complex from far-IR and/or ^{1}H NMR data. ^{b} 2:1 Mixture of two isomers: trans,cis,cis and trans,trans,trans complexes. ^{c} trans-Dibromo complex; other compounds present but in low levels.

(ethylthio)ethyl) sulfide. This suspension was refluxed for 90 min under Ar to give an orange solution, which was cooled and then taken to dryness. The yellow solid was dissolved in a minimum volume of 95% CH$_2$Cl$_2$/5% MeOH and subjected to column chromatography (conditions the same as for the synthesis of **1**). A dark green polar material was retained at the origin while a yellow band ($R_f \sim 0.6$) was collected and this solution taken to dryness. The resultant orange solid was recrystallized from hot methanol under Ar to yield 0.55 g (60%) of yellow-orange microcrystalline product **13**. Anal. Calcd for C$_{10}$H$_{24}$Br$_2$ORuS$_4$: C, 21.86; H, 4.40; Br, 29.09; S, 23.34. Found: C, 21.91; H, 4.45; Br, 28.76; S, 23.25.

Preparation of Two Isomers of Dichlorobis(dimethyl sulfoxide)[1,2-bis(ethylthio)ethane]ruthenium(II) (14 and 15). To a chloroform solution (70 mL) containing 0.31 g (2.06 mmol) of 1,2-bis(ethylthio)ethane was added 1.0 g (2.06 mmol) of *cis*-RuCl$_2$(Me$_2$SO)$_4$. The suspension was refluxed for 2 h. After this time, the reaction mixture was unchanged by TLC. The solution was cooled and taken to dryness and the resultant yellow solid dissolved in 5 mL of 98% CH$_2$Cl$_2$/2% MeOH. The reaction mixture was then subjected to an identical column chromatography workup as described above. Two bands were eluted, with the major band possessing an $R_f \sim 0.55$ and the minor band possessing an $R_f \sim 0.4$. The two fractions were worked up independently by removing the solvent and dissolving the resultant yellow solid in a minimum volume of hot MeOH under Ar. Addition of diethyl ether and cooling afforded 0.61 g (63%) of yellow needles of the major isomer, compound **14**, and afforded 0.17 g (20%) of orange cubic crystals of the minor isomer, compound **15**. Anal. Calcd for each isomer of C$_{10}$H$_{26}$Cl$_2$O$_2$RuS$_4$: C, 25.10; H, 5.48; Cl, 14.81; S, 26.80. Found for major isomer **14**: C, 25.13; H, 5.37; Cl, 14.72; S, 26.77. Found for minor isomer **15**: C, 25.19; H, 5.57; Cl, 14.67; S, 26.73.

Dichloro(dimethyl sulfoxide)[1,1,1-tris((ethylthio)methyl)ethane]ruthenium(II) (16). This complex was prepared and chromatographed in a manner identical with that described above for **13**, except that 1.23 g (2.54 mmol) of *cis*-RuCl$_2$(Me$_2$SO)$_4$ and 0.65 g (2.6 mmol) of H$_3$CC-

(CH$_2$SEt)$_3$ were used. Only one band eluted from the silica gel column (95:5, CH$_2$Cl$_2$/MeOH solvent) with an $R_f \sim 0.65$, although some greenish material was retained at the origin. The orange-yellow band was collected and taken to dryness on a rotary evaporator. The resultant solid was dissolved in a minimum volume of hot methanol (5 mL), and diethyl ether was added till cloudy (40 mL). After storage at −40 °C overnight, yellow-orange crystals formed. The product was collected by filtration and dried in vacuo. The yield of **16** was 0.81 g (63%). Anal. Calcd for C$_{13}$H$_{30}$Cl$_2$ORuS$_4$: C, 31.07; H, 6.02; Cl, 14.11; S, 25.52. Found: C, 31.11; H, 5.96; Cl, 14.38; S, 25.86.

***trans*-Dibromobis[1,2-bis(ethylthio)ethane]ruthenium(II) (17).**^{5} This complex was prepared by reacting 0.5 g (0.87 mmol) of *trans*-RuBr$_2$-(Me$_2$SO)$_4$ with 0.26 g (1.75 mmol) of 3,6-dithiaoctane in refluxing chloroform under Ar. After 1 h the solution volume was reduced to a few milliliters and hot EtOH added with stirring. After the mixture was allowed to cool, a pink-red solid formed, which was collected via filtration, washed with EtOH and Et$_2$O, and dried in vacuo. A yield of 0.37 g (76%) was obtained. Anal. Calcd for C$_{12}$H$_{28}$Br$_2$RuS$_4$: C, 25.67; H, 5.03; Br, 28.46; S, 22.84. Found: C, 25.71; H, 4.91; Br, 28.66; S, 22.73.

Results

Syntheses and Characterizations. In general the syntheses described here were carried out under conditions designed to mimic the catalytic situation when monodentate ligands were used. As a consequence, each reaction was carried out in alcoholic solvents using a large excess of the thioether ligand (substrate). The only difference from the catalytic situation was that the synthetic reactions were carried out in the absence of oxygen. Also, in several instances model complexes using multidentate ligands were synthesized to aid our characterizations. These syntheses were carried out under conditions that utilized the ligands in stoichiometric amounts.

Reactions with Dimethyl Sulfide. With both *cis*-RuCl$_2$(Me$_2$SO)$_4$ and *trans*-RuBr$_2$(Me$_2$SO)$_4$ the reaction with excess dimethyl sulfide produced at least three different complexes, as observed via silica-gel chromatography. The complexes were resolved by preparative-scale medium-pressure column chromatography under Ar to afford in each case three fractions corresponding to three different stoichiometries RuX$_2$(SMe$_2$)$_{4-n}$(Me$_2$SO)$_n$, where X = Cl or Br and n = 0, 1, or 2. These stoichiometries were confirmed by elemental analyses. The identity of each fraction (see Table II) was established from the ^{1}H NMR spectra (Table III) and the infrared spectra (Table IV) of the isolated materials. For both X = Cl and Br the same complexes were formed in similar ratios, so the discussion will be limited to one case, where X = Cl. From this reaction the major material (50%) has the stoichiometry RuCl$_2$(SMe$_2$)$_4$, whose ^{1}H NMR spectrum shows only one resonance at δ 2.30 and whose ^{13}C NMR spectrum shows only one resonance at δ 19.5, consistent only with the symmetrical *trans*-RuCl$_2$(SMe$_2$)$_4$ complex. This is also consistent with the far-IR spectrum, which shows only one weak Ru–Cl stretching absorption

Table III. ^{1}H NMR Spectra of Selected Ru(II) Complexes

compound	chemical shifts (intensity)^a	
	Me$_2$SO	sulfide ligand
RuBr$_2$(SMe$_2$)$_4$ (**1**)		2.40
RuBr$_2$(SMe$_2$)$_3$(Me$_2$SO) (**2**)	3.36 (1)	2.45 (1), 2.40 (2)
RuBr$_2$(SMe$_2$)$_2$(Me$_2$SO)$_2$ (**3**)	3.15 (2)^b	2.33 (1), 2.29 (1)
RuCl$_2$(SMe$_2$)$_4$ (**4**)		2.30
RuCl$_2$(SMe$_2$)$_3$(Me$_2$SO) (**5**)	3.30 (1)	2.40 (1), 2.35 (2)
RuCl$_2$(SMe$_2$)$_2$(Me$_2$SO)$_2$ (**6**)	3.10 (1), 3.20 (1)	2.10 (1), 2.30 (1)
RuCl$_2$(S(CH$_2$)$_3$CH$_2$)$_4$ (**8**)		2.09 (1),^{c} 1.9 (1)^c
RuBr$_2$(S-*t*-Bu$_2$)(Me$_2$SO)$_3$ (**9**)	3.41 (1), 3.33 (2)	1.50 (3)
RuBr$_2$(SEt$_2$)$_3$(Me$_2$SO) (**10**)	3.29 (1)	3.2 (2),^{d} 1.4 (3)^e
RuBr$_2$(SEt$_2$)$_2$(Me$_2$SO)$_2$ (**11**)	3.47 (2), 3.40 (1)	3.2 (2),^{d} 1.37 (3)^f
RuBr$_2$(EtSCH$_2$CH$_2$SEt)(Me$_2$SO)$_2$ (**12**)	3.43 (6)^g	2.9 (4),^{b} 1.38 (3)^h
RuBr$_2$(EtSCH$_2$CH$_2$SCH$_2$CH$_2$SEt)(Me$_2$SO) (**13**)	3.52 (3)^g	3.11 (6),^{d} 1.42 (3)
RuCl$_2$(EtSCH$_2$CH$_2$SEt)(Me$_2$SO)$_2$ (**14**)	3.42, 3.38 (6)^i	3.0 (4),^{d} 1.47 (1.5),^{j} 1.42 (1.5)^j
RuCl$_2$(EtSCH$_2$CH$_2$SEt)(Me$_2$SO)$_2$ (**15**)	3.4 (3)^g	1.38 (3),^{h} 2.93 (4)^d
RuCl$_2$(CH$_3$C(CH$_2$SEt)$_3$)(Me$_2$SO) (**16**)	3.4 (2)^g	1.3 (3),^{j} 2.56 (1),^{k} 3.1 (4)^l
RuBr$_2$(EtSCH$_2$CH$_2$SEt)$_2$ (**17**)		1.40 (3),^{h} 3.0 (4)^d

^{a} Chemical shifts in ppm relative to Me$_4$Si. ^{b} Broad. ^{c} Splitting pattern identical with that of free tetrahydrothiophene. ^{d} Broad multiplet. ^{e} Broadened triplet. ^{f} Two overlapping triplets, $J_{CH} \sim 8$ Hz. ^{g} Sharp singlet. ^{h} Sharp triplet, J_{CH} = 8 Hz. ^{i} Unresolved doublet. ^{j} Sharp triplet, J_{CH} = 7 Hz. ^{k} Quartet, J_{CH} = 6 Hz. ^{l} Complex multiplet (at least 7 lines).

Table IV. Selected Infrared Absorption Frequencies[a]

	frequency, cm^{-1} (intensity)	
compound	Me_2SO	Ru–X
$RuCl_2(SMe_2)_4$ (4)		332 (w)[b]
$RuCl_2(SMe_2)_3(Me_2SO)$ (5)	1085 (s);[b,d] 1015 (s);[b] 965[b,e]	334 (w)[b]
$RuCl_2(SMe_2)_2(Me_2SO)_2$ (6)	1083 (s); 1021, 1010;[g] 970[c,e]	326 (w)[c]
$RuCl_2(S(CH_2)_3CH_2)_4$ (8)		337 (w)[b]
$RuBr_2(t\text{-}Bu_2S)_2(Me_2SO)_3$ (9)	1090, 1017 (s);[f] 1021, 1000;[g] 970[c,e]	
$RuBr_2(EtSCH_2CH_2SEt)(Me_2SO)_2$ (12)	1074 (s);[b,d] 1020 (s);[b,e] 969[c,e]	
$RuBr_2(EtSCH_2CH_2SCH_2CH_2SEt)(Me_2SO)$ (13)	1080 (s);[b,d] 1022 (s),[b,e] 970[e]	
$RuCl_2(EtSCH_2CH_2SEt)(Me_2SO)_2$ (14)	1087, 1072;[f] 1018, 1009;[g] 971[e]	338, 311 (m)
$RuCl_2(EtSCH_2CH_2SEt)(Me_2SO)_2$ (15)	1079 (s);[b,d] 1005 (s);[b,e] 960[b,e]	337 (w)[b]
$RuCl_2(CH_3C(CH_2SEt)_3)(Me_2SO)$ (16)	1080 (s);[b,d] 990 (s);[b,e] 961[b,e]	341, 316 (m)

[a] s = strong, m = medium, and w = weak. [b] Singlet. [c] Broad. [d] γ_{SO}, S-bound. [e] CH rock, S. [f] Intense doublet, γ_{SO}, S-bound. [g] Doublet, CH rock, S.

Table V. Selected Electronic Absorption Spectra and Half-Wave Potentials ($E_{1/2}$) for Pseudoreversible One-Electron Oxidations of Selected Ruthenium(II) Complexes

compound	λ_{max}, 10^3 cm^{-1} (ϵ)	$E_{1/2}$, V
$RuBr_2(SMe_2)_4$ (1)	20.2 (85), 27.4 (142), 37.9 (3030)	+0.65
$RuBr_2(SMe_2)_3(Me_2SO)$ (2)	22.6 (105), 28.3 (240), 39.0 (2990)	+0.86
$RuBr_2(SMe_2)_2(Me_2SO)_2$ (3)	27.2 (broad, 279), 39.1 (2660)	+0.77, +1.02
$RuCl_2(SMe_2)_4$ (4)	22.6 (180), 26.4 (290), 38.8 (2890)	+0.61
$RuCl_2(SMe_2)_3(Me_2SO)$ (5)	23.1 (91), 26.9 (192), 37.7 (3150)	+0.85
$RuBr_2(S(CH_2)_3CH_2)_4$ (7)	21.7 (216), 27.6 (270), 37.5 (3040)	+0.59
$RuCl_2(S(CH_2)_3CH_2)_4$ (8)	23.5 (209), 26.7 (370), 35.2 (2020)	+0.58
$RuBr_2(S\text{-}t\text{-}Bu_2)(Me_2SO)_3$ (9)	21.6 (92), 27.7 (260), 38.1 (2760)	+1.34
$RuBr_2(SEt_2)_3(Me_2SO)$ (10)	22.1 (71), 27.9 (220), 38.6 (3310)	+0.84
$RuBr_2(SEt_2)_2(Me_2SO)_2$ (11)	21.5 (220), 32.05 (sh)	+0.79, +1.01
$RuBr_2(EtSCH_2CH_2SEt)(Me_2SO)_2$ (12)	22.1 (73), 31.7 (360), 38.2 (2280)	+1.07[a]
$RuCl_2(EtSCH_2CH_2SCH_2CH_2SEt)(Me_2SO)$ (13)	23.0 (470), 26.3 (370), 28.9 (321), 37.9 (2130)	+0.92
$RuCl_2(EtSCH_2CH_2SEt)(Me_2SO)_2$ (14)	26.3 (510), 31.4 (550), 38.8 (1460)	+1.22
$RuCl_2(EtSCH_2CH_2SEt)(Me_2SO)_2$ (15)	23.5 (80), 33.1 (290), 39.2 (1730)	+1.05
$RuCl_2(CH_3C(CH_2SEt)_3)(Me_2SO)$ (16)	23.5 (sh), 25.75 (250), 29.9 (240), 38.6 (1860)	+0.89
$RuBr_2(EtSCH_2CH_2SEt)_2$ (17)	20.0 (61), 28.2 (150)	+0.69
$RuCl_2(SMe_2)_2(Me_2SO)_2$ (6)		+0.75, +1.04[a]
$cis\text{-}RuCl_2(Me_2SO)_4$		+1.55[a]
$trans\text{-}RuBr_2(Me_2SO)_4$		+1.55[a]

[a] Irreversible.

at 332 cm^{-1}, consistent with a *trans*-dihalo geometry. This is in contrast to the case of the starting material *cis*-RuCl$_2$(Me$_2$SO)$_4$, which possesses two prominent bands in this region.[3,4]

The second material (~30%) to elute from the column has the stoichiometry of RuCl$_2$(SMe$_2$)$_3$(Me$_2$SO); the infrared spectrum again shows only one weak Ru–Cl stretch and an S–O stretch at 1085 cm^{-1} corresponding to S-bound sulfoxide. The ^{1}H NMR spectrum shows three singlet resonances at δ 3.30, 2.40, and 2.35 in a relative intensity ratio of 1:1:2. The downfield resonance is typical for S-bound sulfoxide methyl hydrogens,[8,9] while the two higher field methyl hydrogen resonances correspond to two unique dimethyl sulfides. The ^{13}C NMR spectrum of this complex (5) also reveals the same symmetry, namely, a downfield resonance at δ 43.3 corresponding to the sulfoxide carbons and two resonances at δ 19.8 and 18.8 corresponding to two dimethyl sulfide ligands in different environments. These spectral results are consistent with a trans formulation for complex 5, RuCl$_2$(SMe$_2$)$_3$(Me$_2$SO). The bromo analogue, 2, possesses virtually identical NMR parameters and is assumed to have the same structure, although the far-infrared Ru–Br stretch was not observed. The similarity between the electronic spectra (Table V) of these two complexes, 2 and 5, also suggests that they possess identical structures. The intensities of the two "d–d" absorptions observed in the spectra of complexes 2 and 5 are very similar to those observed with the *trans*-RuX$_2$(Me$_2$S)$_4$ complexes. This fact also suggests that
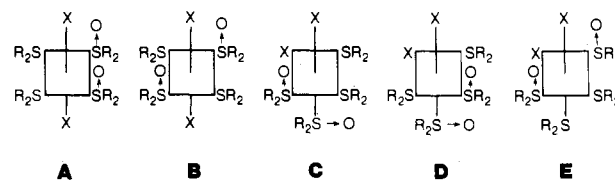
(8) (a) Ruiz-Ramirez, L.; Stephenson, T. A.; Switkes, E. S. *J. Chem. Soc., Dalton Trans.* **1973**, 1770. (b) Horrocks, W. D.; Cotton, F. A. *Spectrochim. Acta* **1961**, *17*, 134. (c) Drago, R. S.; Meek, D. W. *J. Phys. Chem.* **1961**, *65*, 1446.

(9) Evans, I. P.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 204.

Figure 1. Structures of the five possible geometric isomers of the stoichiometry RuX$_2$(SR$_2$)$_2$(R$_2$SO)$_2$.

complexes **2** and **5**, RuX$_2$(SMe$_2$)$_3$(Me$_2$SO), also are trans, since cis complexes of lower symmetry could be expected to have "d–d" bands of greater intensity,[9] as observed in cis complex **16** (vide infra) and in other complexes of this type (see the following two papers in this issue).

The third fraction to be eluted from the chromatographic workup of this reaction (when X = Cl or Br) reveals a much more complicated infrared spectrum. Instead of a sharp singlet absorption in the S–O stretching region, there is a well-defined doublet. The far-infrared spectrum reveals only one absorption in the Ru–Cl stretching region, consistent with a *trans*-dihalo arrangement. The elemental analyses of materials **6** and **3** agree with the formulation RuX$_2$(SMe$_2$)$_2$(Me$_2$SO)$_2$.

The ^{1}H NMR spectra of these mixtures have been especially helpful regarding the composition of the fractions both where X = Cl, **6**, and where X = Br, **3**. When X = Cl, the ^{1}H NMR spectrum reveals four different singlet resonances of equal intensity. When X = Br, three different singlet resonances are observed but in a 2:1:1 ratio, with the more intense downfield resonance showing considerable broadening. To determine if these resonances were indeed singlets or coupled doublets, the spectra were also recorded at 270 MHz. This clearly showed that the

splittings are due to chemical shift differences, not coupling constants. Consequently, there are only two logical explanations: (1) both fractions **3** (X = Br) and **6** (X = Cl) are mixtures containing two different symmetrical geometric isomers, present in a 1:1 ratio with the stoichiometry $RuX_2(Me_2S)_2(Me_2SO)_2$, or (2) there is a single dissymmetric isomer formed that has the 2,2,2 stoichiometry. Even though there are five different isomers possible with four of them affording a symmetrical structure (Figure 1), it is possible to assign structures to **3** and **6** unequivocally. The far-IR spectrum of **6** indicates that a trans complex is present and suggests that complexes **3** and **6** are mixtures of two complexes with the all-trans (isomer B) and trans(X_2), cis,cis (isomer A) structures. This is also consistent with the electrochemical studies (vide infra).

Reactions with Tetrahydrothiophene. When the complexes $RuX_2(Me_2SO)_4$ (X = Cl or Br) react with tetrahydrothiophene in alcohol solvents, a single major species forms, and in both cases elemental analysis indicates that it is the $RuX_2(\overline{S(CH_2)_3CH_2})_4$ complex. This complex accounts for over 80% of the ruthenium in this system. Infrared spectra of both **7** (X = Br) and **8** (X = Cl) reveal that no dimethyl sulfoxide is present, and the far-infrared spectrum of **8** shows only one weak Ru–Cl stretch at 337 cm^{-1}, indicative of a trans formulation. In addition, this structure assignment is confirmed by the ^1H NMR and ^{13}C NMR of these complexes. Both **7** and **8** exhibit identical ^1H and ^{13}C NMR spectra. The ^1H NMR spectra show peaks at δ 2.9 and 1.9 in 1:1 intensity and with shapes identical with those of free tetrahydrothiophene. The ^{13}C NMR of each complex exhibits two sharp singlet resonances, at δ 36.8 and 30.4. These NMR and IR results are consistent with the trans formulation for complexes **7** and **8**. The electronic spectra are also very similar to those of the $trans$-$RuX_2(SMe_2)_4$ complexes.

Reaction with Di-*tert*-butyl Sulfide. The complex $trans$-$RuBr_2(Me_2SO)_4$ reacts with the bulky thioether di-*tert*-butyl sulfide to produce only one complex, **9**, in solution, as indicated by TLC. The elemental analysis of this complex reveals a stoichiometry of $RuBr_2(t$-$Bu_2S)(Me_2SO)_3$—where only one dimethyl sulfoxide is replaced by a thioether ligand. The solid-state infrared spectrum of this complex reveals two different types of S-bound Me_2SO ligands. The ^1H NMR spectrum reveals that there are indeed two different Me_2SO ligands present in solution in the ratio 1:2. Since there are three different geometric isomers possible with the formulation $RuBr_2(t$-$Bu_2S)(Me_2SO)_3$ (two cis isomers and one trans isomer) and since each isomer would be expected to have the same ^1H NMR pattern, we cannot be positive of the structure of this complex on the basis of NMR and IR spectra alone. The electronic spectrum of **9** is very similar to those of the $trans$-$RuBr_2(SR_2)_4$ complexes (where X = SMe$_2$ or $\overline{S\text{-}(CH_2)_3CH_2}$) that show two "d–d" bands with an extinction coefficient of 90 M^{-1} cm^{-1} for the lower energy band and 150–270 M^{-1} cm^{-1} for the higher energy band. The two bands observed in the t-Bu$_2$S complex have extinction coefficients of 92 and 260 M^{-1} cm^{-1}. These results suggest that **9** is also the trans isomer.[10]

**Reactions with Diethyl Sulfide.** The reaction of $trans$-$RuBr_2(Me_2SO)_4$ with excess diethyl sulfide in ethanol produces an apparent mixture of two species in an approximately 2:1 ratio. Column chromatographic separation gives two fractions. The first fraction accounts for about 30% of the ruthenium, while the second fraction accounts for about 65% of the ruthenium. The elemental analysis of the material that crystallizes from the first fraction agrees with the stoichiometry $RuBr_2(SEt_2)_3(Me_2SO)$. The ^1H NMR spectrum of this material indicates that it is a single pure isomer (complex **10**) and not a mixture of different geometric isomers. Without a single-crystal structural determination, the assignment of the structure of this isomer is difficult. But in analogy with the case of the dimethyl sulfide complex, it would seem logical that this diethyl sulfide complex also is the $trans$-dibromo isomer. The electronic spectrum of **10** also provides

support for this assignment. As in the case with dimethyl sulfide complex **2**, two "d–d" bands are observed, which occur at very nearly the same energies and with low extinction coefficients ($\sim$70 and 220 M^{-1} cm^{-1}) similar to that observed for **2**. The higher symmetry associated with the $trans$-dibromo structure is consistent with the lower extinction coefficients.[10]

The second fraction eluted by chromatography contained nearly 65% of the ruthenium, and the elemental analysis of this material, fraction **11**, agrees with the formulation $RuBr_2(SEt_2)_2(Me_2SO)_2$. The ^1H NMR of fraction **11** shows a complicated pattern with two types of S-bound dimethyl sulfoxide ligands in a 2:1 ratio and two types of methyl triplets from diethyl sulfide in about a 2:1 ratio. These results indicate that two geometric isomers of $RuBr_2(SEt_2)_2(Me_2SO)_2$ composition are formed in the fraction but are not separated by the chromatographic methods. Numerous attempts to perform this separation have not been successful. This is partly due to the air sensitivity of this material. As a consequence, we are restricted to working in an inert atmosphere. The ^1H NMR spectrum also reveals that these two isomers are symmetrical, namely, the two Me_2SO ligands and the two SEt_2 ligands in each isomer are equivalent. As in the case of the dimethyl sulfide complex, there are five geometric isomers possible for $RuBr_2(SEt_2)_2(Me_2SO)_2$ (Figure 1), and four of these (isomers A, B, D, and E) are symmetrical. As a consequence, the assignment of the structure of the isomers present in mixture **11** is not possible without additional data.

Syntheses with Multidentate Ligands. In order to make structure assignments for the unknown isomers produced in the reaction of $RuX_2(Me_2SO)_4$ with monodentate thioethers, an attempt was made to synthesize and characterize complexes with multidentate ligands. With use of multidentate ligands, fewer geometrical isomers are possible and greater control of product geometry could be realized with the properly designed ligand. Reaction of the potentially bidentate 3,6-dithiaoctane ligand with the cis-$RuCl_2(Me_2SO)_4$ complex resulted in the formation of two isomeric complexes whose elemental analyses revealed the stoichiometry $RuCl_2(EtSCH_2CH_2SEt)(Me_2SO)_2$. The two isomers, **14** and **15**, were produced in about 65% and 20% yields, respectively.

The infrared spectra of these two complexes have been very useful for determining the structures of these two complexes. The infrared spectrum of the major isomer, **14**, shows two different

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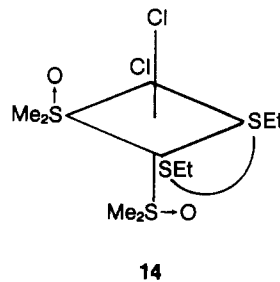
S-bound sulfoxide ligands and a medium-intensity doublet Ru–Cl stretching absorption. These observations are only consistent with a cis-dichloro structure with nonequivalent dimethyl sulfoxide ligands. Additionally, the ^1H NMR spectrum of **14** reveals the presence of two nonequivalent dimethyl sulfoxide ligands and shows that the terminal methyl groups (triplets) of the bidentate ligand are nonequivalent. Of the five possible geometric isomers (Figure 1), only the all-cis isomer (C) would give the unsymmetric IR or ^1H NMR spectrum. The electronic spectrum of this complex also agrees with this formulation. This complex has two "d–d" bands, as do the other complexes discussed above, but the extinction coefficients are greater than 500 M^{-1} cm^{-1}, indicating considerably lower symmetry at the ruthenium(II) center, consistent with the cis-dihalo geometry—not the $trans$-dihalo geometry.[10]

The minor isomer, **15**, possesses a symmetrical ^1H NMR spectrum with one type of Me_2SO ligand and a symmetric 3,6-dithiaoctane ligand. Also, the infrared spectrum of this complex possesses one type of S-bound sulfoxide (equivalent Me_2SO lig-

(10) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 658.

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18
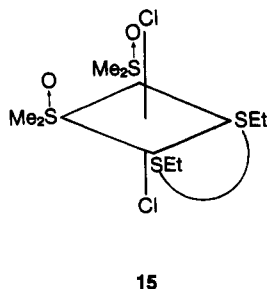
ands) and a weak singlet Ru–Cl stretching absorption at 337 cm^{-1}. The electronic spectrum reveals two "d–d" bands with low extinction coefficients, which suggests the *trans*-dihalo ligand arrangement.[10] These spectral results and the presence of the bidentate thioether ligands allow us to identify the structure of this product as isomer A of Figure 1 (shown as **15**).
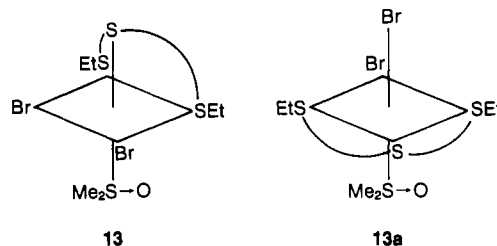
The reaction of *trans*-RuBr$_2$(Me$_2$SO)$_4$ with the same bidentate 3,6-dithiaoctane ligand produces only one isomer, **12**, whose ^{1}H NMR, IR, and electronic spectra are virtually identical with those of the minor isomer, **15**; consequently, complex **12** must also possess the same geometry (trans-dihalo, cis-sulfoxide, cis-thioether) as **15**.

The reaction of *cis*-RuCl$_2$(Me$_2$SO)$_4$ with the tripod thioether ligand H$_3$CC(CH$_2$SEt)$_3$ affords only one product whose elemental analysis confirms the formulation of complex **16** as RuCl$_2$-(CH$_3$C(CH$_2$SEt)$_3$)(Me$_2$SO). If all three thioether substituents coordinate to ruthenium, the ligand will be constrained to a facial array. The infrared spectrum reveals two medium-intensity Ru–Cl stretching bands, consistent with a *cis*-dichloro arrangement. Solution molecular weight measurements in chloroform confirm the monomeric nature of this complex. Confirmation of the structure of **16** as a *cis*-dichloro, S-bound sulfoxide, facial tridentate thioether ruthenium(II) complex was made by a single-crystal X-ray diffraction study (cf. the perspective drawing of the complex given in Figure 2). The details of the structure determination and the atomic parameters have been deposited as supplementary material.[11]

The reaction of the *trans*-RuBr$_2$(Me$_2$SO)$_4$ complex with the linear tridentate ligand bis(2-(ethylthio)ethyl) sulfide (EtSCH$_2$CH$_2$SCH$_2$CH$_2$SEt) produces only one isomeric product, **13**, whose elemental analysis and ^{1}H NMR spectrum confirm the formulation RuBr$_2$(EtSCH$_2$CH$_2$SCH$_2$CH$_2$SEt)(Me$_2$SO). The sulfoxide is S-bound (^{1}H NMR and IR spectra), and the structure is symmetrical due to the equivalency of the terminal methyl groups of the tridentate ligand. This eliminates one structural candidate for this complex—namely, structure **18**, in which the
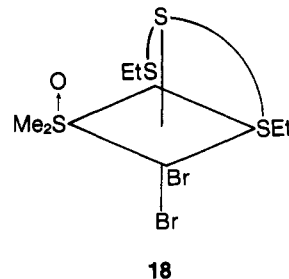
thioether ligand has folded so as to coordinate facially. Unfortunately, the structure of this product cannot be deduced from the ^{1}H NMR or infrared spectrum alone since there are three other symmetrical isomers possible. The electronic spectrum of this complex shows three "d–d" transitions with large extinction coefficients. In addition, the electronic spectrum is virtually identical with that observed for *cis*-dichloro complex **16**, in which the thioether ligand occupies three facial sites. Due to the similarity in the electronic spectra of these two complexes, it is very likely that complex **13** possesses the *cis*-dibromo structure shown as **13**, although the *cis*-dibromo geometry of **13a** cannot be ruled out.

13   **13a**

The reaction of the *trans*-RuBr$_2$(Me$_2$SO)$_4$ complex with 2 equiv of 3,6-dithiaoctane produces the previously synthesized complex *trans*-RuBr$_2$(EtSCH$_2$CH$_2$SEt)$_2$ (**17**).[5] The ^{1}H NMR spectrum of this complex is symmetrical and supports the trans formulation. In addition, the electronic spectrum of **17** is virtually identical with that of *trans*-RuBr$_2$(SMe$_2$)$_4$, thus providing additional support for the trans formulation for complex **17**.

Electrochemical Studies. The Ru(II,III) oxidation potentials for all the complexes described here were measured in methylene chloride, since in acetonitrile ligand dissociation occurs. The oxidation potentials of the complexes are listed in Table V and reveal two very significant trends. First, the oxidation potential is dependent on the degree of substitution (magnitude of n) in the complexes RuX$_2$(SR$_2$)$_{n-4}$(R$_2$SO)$_n$. Second, for the groups of complexes where $n = 2$, we have isolated three different geometric isomers in this work and examples of the other two possible isomers are reported in the following two papers in this issue, and each isomer has its own unique oxidation potential.[12] For the complexes with monodentate ligands, RuX$_2$(SR$_2$)$_2$(Me$_2$SO)$_2$ (where X = Cl or Br and SR$_2$ = Me$_2$S or Et$_2$S), **3**, **6**, and **11**, we isolated, in each instance, mixtures of two complexes whose structures have been tentatively assigned as the all-trans (**3a**, **6a**, **11a**) and trans,cis,cis isomers (**3b**, **6b**, **11b**) (B and A of Figure 1). The cyclic voltammograms of each of these three mixtures of **3**, **6**, and **11** show two oxidation waves, which for **3** and **11** are both pseudoreversible. These results support our previous assignment that these materials are mixtures of two geometric isomers.

The use of a chelating bidentate thioether affords the trans(X$_2$), cis, cis complexes **12** and **15**. Each of these complexes has an oxidation wave (pseudoreversible) near 1.05 V. This oxidation occurs at the same potential as one of the oxidations present in the mixtures of trans(X$_2$), cis,cis and all-trans complexes. Thus, since this structure has also been assigned to one of the two isomers

(11) Compound **16** crystallizes in the monoclinic space group P2$_1$/n (No. 14), with a = 15.110 (2) Å, b = 15.417 (3) Å, c = 9.042 (1) Å, β = 104.33 (1)°, Z = 4, D$_{calcd}$ = 1.64 g cm^{-3}, μ(Mo Kα) = 14.0 cm^{-1}. Intensities of 3926 (3613 unique) reflections (2.5 < 2θ < 50.0°), were collected at 17 °C from a crystal with dimensions 0.10 × 0.12 × 0.20 mm on a Syntex P2$_1$ diffractometer in ω–2θ scan mode using Mo Kα (λ = 0.710 73 Å) radiation and a graphite incident-beam monochromator. Data were corrected for absorption by an empirical method based on a pseudoellipsoidal treatment of azimuthal (ψ) scans of selected intense reflections (transmission factors: max = 0.672; min = 0.624). The structure was solved by the automatic Patterson solution method and was refined by using 2247 reflections with F$_o$ > 4σ(F$_o$). One methyl group was disordered and was treated as two fractional atoms, C(11a) and C11(b), with fixed occupancy factors of 0.56 and 0.44, respectively. The final least-squares cycles by the blocked-cascade method employed anisotropic thermal parameters for all non-hydrogen atoms of the structure. Twenty-one hydrogen atoms were included as fixed contributions at their idealized positions or positions from a difference density map. Completion of refinement gave R = $\sum(||F_o| - |F_c||/|F_o|$ = 0.055, R$_w$ = $\sum(w(|F_o| - |F_c|)^2/w|F_o|^2)^{1/2}$ = 0.057, w^{-1} = σ^2(F$_o$) + 0.0005|F$_o$|^2, S = 1.38, and mean (max) shift/σ = 0.024 (0.210). A final difference Fourier contained peaks below ± 0.5 e Å^{-3}, except for three peaks with densities <1 e Å^{-3} near the Ru atom. Atomic scattering factors and anomalous dispersion corrections were taken from: *International Tables of X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol IV. All calculations were performed on a Data General Eclipse S-250 computer using the SHELXTL package: Sheldrick, G. M. *SHELXTL: An integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*; Nicolet: Madison, WI, 1984.

(12) In the following two papers in this issue, we describe how we have isolated and characterized examples of the remaining two isomers possible for RuX$_2$(R$_2$S)$_2$(R$_2$SO)$_2$ complexes. These two complexes also possess their own unique oxidation potentials: *cis*-dihalo,*trans*-sulfoxide,*cis*-thioether, E$_{1/2}$ ~ 0.91 V; *cis*-dihalo,*cis*-sulfoxide,*trans*-thioether, E$_{1/2}$ ~ 1.45 V.
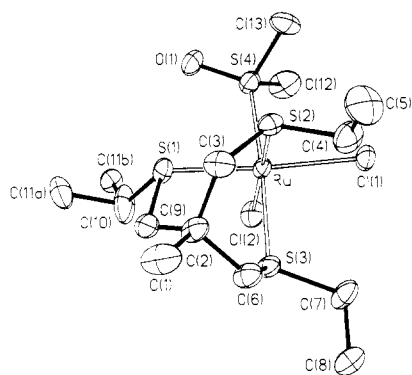
Figure 2. Perspective illustration of complex **16**, dichloro(dimethyl sulfoxide)[1,1,1-tris((ethylthio)methyl)ethane]ruthenium(II).

present, we can assign the oxidation at 1.05 V in mixtures **3**, **6**, and **11** to the trans,cis,cis isomer A (compounds **3b**, **6b**, and **11b**). This means that the other isomer, all-trans (isomer B) (compounds **3a**, **6a**, **11a**), must oxidize at ~0.75 V. The third 2,2,2 isomer, the all-cis complex **14**, oxidizes at an even higher potential, 1.22 V.

As noted above, stoichiometry has a large effect on the oxidation potential of the Ru(II,III) couple. The tetrakis(sulfoxide) complexes (n = 4) are very difficult to oxidize, while the tetrakis-(thioether) complexes (n = 0) are relatively easy to oxidize (their solutions are air-sensitive). For each replacement of an S-bound sulfoxide with a thioether ligand, the oxidation potential decreases by about 0.2 V, except when n = 2, where structure plays a significant role in the oxidation potential.

Discussion

As discussed above, the $RuX_2(Me_2SO)_4$ complexes are excellent catalysts for the selective O_2 oxidation of thioethers to sulfoxides in alcohol solvents. The overall mechanism suggested in ref 2 implies that the thioether simply "traps" the peroxide as it is generated and that these Ru(II) catalysts are actually alcohol oxidation catalysts. But no oxidation of alcohol occurs unless thioether is added to reactions with the $RuX_2(Me_2SO)_4$ complexes. Further, this mechanistic picture predicts that the thioether substrate should have no effect on the rate, because the reaction is essentially a catalytic alcohol oxidation. Since the thioether does have a profound effect on the rate (Table I), the active catalyst must be generated in situ by reaction with the thioether.

Our synthetic efforts were designed to mimic a catalytic situation so that information regarding the types of species formed could be obtained. These synthetic results are summarized in Table II for several different monodentate thioethers varying primarily only in their steric bulk. The smallest of the potential coordinating thioethers is tetrahydrothiophene.[13] The other thioethers studied in order of increasing steric bulk are Me_2S < Et_2S < *t*-Bu_2S. The effect of steric bulk upon the product distributions in these reactions is dramatic. With the smallest ligand, tetrahydrothiophene, the major species is the tetrakis(thioether) complex. While with dimethyl sulfide the tetrakis(thioether) complex is still the major species, there are significant amounts of tris(thioether) complex and of a mixture of two bis(thioether) complexes. When the ligand size is increased with Et_2S, the tetrakis(thioether) complex does not form—apparently due to steric effects. Finally, with a very bulky thioether, di-*tert*-butyl sulfide, only one complex forms, the mono(thioether) complex.

These distribution results enable us to make some qualitative statements concerning the likelihood that a specific structure is an oxygen-active species leading to catalysis in these oxidations. First, a mono(thioether) complex can likely be ruled out, since no activity is observed in the di-*tert*-butyl sulfide system and since this is the only complex formed in this system. If complexes of

the stoichiometry *trans*-$RuX_2(SR_2)_4$ were the most active species leading to catalysis in these systems, then the greatest activity should be observed with tetrahydrothiophene or dimethyl sulfide as a substrate. This is inconsistent with experimental results. Consequently, these complexes can also be ruled out as the most oxygen-active species leading to catalysis, especially since these reactions are rate-limiting in the oxygen oxidation step. This then leaves the two *trans*-dihalo bis(thioether) bis(sulfoxide) complexes and the *trans*-$RuX_2(SR_2)_3(Me_2SO)$ complex as the likely candidates for the most oxygen-active species leading to catalysis in these systems.

To obtain a better understanding of the redox properties of these various complexes, their electrochemistry was studied with standard cyclic voltammetry. As can be seen in Table V, the sulfoxide ligand appears to stabilize the ruthenium(II) to oxidation very effectively. Apparently, the S-bound sulfoxide ligand is either an excellent π-acceptor or weak σ-donating ligand (or both) when coordinated to low-spin Ru(II). Each replacement of a sulfoxide ligand with a thioether ligand decreases the oxidation potential by about 0.2–0.3 V. A break in this trend is observed with the unusually low oxidation potential exhibited by one of the $RuX_2(R_2S)_2(R_2SO)_2$ complexes. Since we have not been able to separate this mixture of two isomers of stoichiometry *trans*-(X_2)-$RuX_2(SR_2)_2(R_2SO)_2$, we independently made and characterized two model complexes with a bidentate ligand, 3,6-di-thiaoctane. These complexes have the *trans*(X_2)-*cis,cis*-RuX_2-$(SR_2)_2(Me_2SO)_2$ structure and possess a reversible oxidation wave at 1.05 V when X = Cl and at 1.07 V when X = Br. This indicates that the structure which possesses the anomalously low oxidation potential is the *all-trans*-RuX_2(sulfoxide)$_2(SR_2)_2$ complex.

The relative ease of oxidation of the all-trans isomer indicates that it is indeed unusual electronically. An inspection of the oxidation potentials of the *all-trans*-$RuX_2(R_2S)_2(R_2SO)_2$ isomers **3a**, **6a**, and **11a** shows that they are, in fact, oxidized at nearly 0.3 V lower potential than the *trans*(X_2)-*cis,cis*-$RuX_2(R_2S)_2$-$(R_2SO)_2$ isomers **3b**, **6b**, and **11b** and at potentials between 0.1 and 0.17 V lower than the potentials observed for various structures obtained with the tris(thioether)-containing complexes RuX_2-$(R_2S)_3(R_2SO)$. Since the all-trans complex $RuX_2(R_2S)_2(R_2SO)_2$ is the most easily oxidized of the likely complexes leading to catalysis and since oxygen oxidation of a ruthenium(II) species is rate-determining at lower O_2 pressures, it is very likely that the all-trans complex is the most oxygen-active species leading to catalysis in these systems. All our examples of complexes with the stoichiometry $RuX_2(R_2S)_3(Me_2SO)$ (**2**, **5**, **10**, **13**, and **16**) and the *trans*(X_2)-*cis,cis*-$RuX_2(EtSCH_2CH_2SEt)(R_2SO)_2$ complexes (**12** and **15**) are not air-sensitive. This also lends support to our belief that the ground-state catalyst species is the *all-trans*-$RuX_2(R_2S)_2(R_2SO)_2$ complex in these systems.

Since the all trans complex is the most likely candidate for a catalyst in these systems, we believe that in order to understand the intimate details of the oxygen oxidation step, it would be desirable to synthesize examples of *all*-trans-$RuX_2(R_2S)_2(R_2SO)_2$ complexes containing polydentate ligands.

In this way we hope to not only make very active catalysts but at the same time control the stereochemistry about the Ru(II) center so the detailed mechanism of the reaction of Ru(II) with O_2 can be studied. Attempts to synthesize and study the chemistry of the *all-trans*-$RuX_2(R_2S)_2(R_2SO)_2$ complexes are detailed in the following two papers in this issue. Also, additional synthetic, electrochemical, and catalytic reactivity studies are in progress so that a more substantial understanding of these catalytic systems can be developed.

(13) This statement is based on a treatment similar to that in ref 14 but assumes the lone pair occupies a constant volume in all thioethers and can hence be ignored in comparisons of steric bulk.

(14) Tolman, C. A. *Chem. Rev.* **1977**, *77*(3), 313.

49-1; EtSH, 75-08-1; CH$_3$C(CH$_2$Br)$_3$, 60111-68-4; EtSCH$_2$CH$_2$SCH$_2$CH$_2$SEt, 6052-45-5; HSCH$_2$CH$_2$SCH$_2$CH$_2$SH, 3570-55-6; EtI, 75-03-6; SMe$_2$, 75-18-3; SEt$_2$, 352-93-2; S̄(CH$_2$)$_3$CH$_2$, 110-01-0; S-*n*-Bu$_2$, 544-40-1; S-*i*-Bu$_2$, 592-65-4; S-*t*-Bu$_2$, 107-47-1; PhSCH$_3$, 100-68-5; decyl methyl sulfide, 22438-39-7.

Supplementary Material Available: Tables of crystallographic details,

atomic coordinates, bond lengths and bond angles, and anisotropic temperature factors for compound **16** (7 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (22 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

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Ruthenium(II)-Catalyzed Thioether Oxidation. 2. Syntheses and Crystal Structures of Two Ruthenium(II) Complexes with the New Linear Tridentate Ligand 3-(Ethylthio)-1-((3-(ethylthio)propyl)sulfinyl)propane

Dennis P. Riley[1] and Joel D. Oliver*

Syntheses of a new tridentate mixed sulfur-donor ligand, 3-(ethylthio)-1-((3-(ethylthio)propyl)sulfinyl)propane (EESP) (**3**), and two of its ruthenium(II) complexes, RuX$_2$(Me$_2$SO)[EtS(CH$_2$)$_3$SO(CH$_2$)$_3$SEt] (X = Cl, (**4**), Br (**5**)), are described. Only one geometric isomer is produced when **3** reacts with either *cis*-RuCl$_2$(Me$_2$SO)$_4$ or *trans*-RuBr$_2$(Me$_2$SO)$_4$; X-ray structures show that the two products, **4** and **5**, contain the same geometric isomer. Complexes **4** and **5** possess a symmetrical structure, as deduced from ^{13}C and ^{1}H NMR spectra. Single-crystal structure determinations were carried out for **4** and **5**. Crystals of **5**: monoclinic, space group $P2_1$ (No. 4), with $a = 8.715$ (2) Å, $b = 13.342$ (3) Å, $c = 9.030$ (2) Å, $\beta = 105.47$ (2)°, and $Z = 2$. Crystals of **4**: $a = 8.718$ (2) Å, $b = 13.182$ (3) Å, $c = 8.912$ (2) Å, and $\beta = 105.87$ (2)°. The absolute configuration of **5** was determined by the Bijvoet method. Least-squares refinement of **5** resulted in $R = 0.030$ and $R_w = 0.029$ on the basis of 2264 reflections with $|F_o| > 5.0\sigma(|F_o|)$ including the Bijvoet pairs. Least-squares refinement of **4** gave $R = 0.023$ and $R_w = 0.029$ on the basis of 1777 unique reflections with $|F_o| > 2.5\sigma(|F_o|)$. The coordination geometry in both **4** and **5** is trans-thioether, cis-halo, and cis-sulfoxide. The tridentate, chelate ligand coordinates meridionally to the Ru(II) ion. In both structures, the two six-atom chelate rings have different conformations: one ring has a distorted chair conformation and the other ring has a twist-boat conformation. The major geometrical details for **5** are Ru–Br(1) = 2.601 (1) Å, Ru–Br(2) = 2.578 (1) Å, Ru–S(1) = 2.275 (2) Å, Ru–S(2) = 2.393 (2) Å, Ru–S(3) = 2.235 (2) Å, Ru–S(4) = 2.372 (2) Å, and Br(1)–Ru–Br(2) = 86.4 (1)°. The related details for the chloro complex, **4**, are Ru–Cl(1) = 2.467 (1) Å, Ru–Cl(2) = 2.444 (1) Å, Ru–S(1) = 2.269 (1) Å, Ru–S(2) = 2.386 (1) Å, Ru–S(3) = 2.218 (1) Å, Ru–S(4) = 2.365 (1) Å, and Cl(1)–Ru–Cl(2) = 86.4 (1)°.

Introduction

In the preceding paper in this series, we presented the evidence and arguments indicating that in the RuX$_2$(Me$_2$SO)$_4$-catalyzed oxygen oxidation of thioethers the most oxygen-active species leading to catalysis is generated in situ and is the *all-trans*-RuX$_2$(R$_2$S)$_2$(R$_2$SO)$_2$ complex. These results suggest that we could in principle (depending on the rates of ligand exchange) develop more active catalysts by the presynthesis of the all-trans complex rather than rely on an equilibrium process to generate some of the catalyst structure in solution. Additionally, in order to gain a complete understanding of the details of the electron-transfer mechanism involving ruthenium(II) and molecular oxygen, we need to be able to study discrete, stable complexes in solution. Model complexes containing multidentate ligands should be good candidates since they would be less susceptible to the loss of geometric integrity by dissociative processes. For these reasons, an effort has been made to synthesize examples of all-trans complexes with multidentate ligands.

In this report we describe the synthesis of the new symmetrical tridentate ligand **3** and the details of our attempts to make the all-trans complex with this new ligand. The results of our X-ray structure determinations reveal that complexes **4** and **5** correspond to the cis-X$_2$,cis-R$_2$SO, trans-R$_2$S geometry (isomer D of Figure

1 of the first article in this series). Surprisingly, this geometry forms when either *trans*-RuBr$_2$(Me$_2$SO)$_4$ or *cis*-RuCl$_2$(Me$_2$SO)$_4$ reacts with ligand **3** under a variety of conditions.

Experimental Section

General Considerations. The majority of the experimental procedures used in this work have been described in the first paper in this series. Mass spectra were obtained on a Hewlett-Packard Model 5985B mass spectrometer. All X-ray measurements were made at room temperature with a Syntex P2$_1$ autodiffractometer that was equipped with a Mo target X-ray tube and an incident-beam graphite monochromator.

Materials. 3-(Ethylthio)-1-((3-(ethylthio)propyl)sulfinyl)propane. Ten grams (0.065 mol) of 3,3′-thiodipropanol (Aldrich) was converted to its corresponding ditosylate by standard procedures in 125 mL of dry pyridine at 0 °C by using 25 g (0.133 mol) of *p*-toluenesulfonyl chloride.[4] The solution was stirred at 0 °C for 16 h. The reaction workup proceeded by pouring the pyridine solution onto 400 g of crushed ice with vigorous stirring. The crude ditosylate compound precipitated and was collected by filtration. The crude product was redissolved in 100 mL of methylene chloride. This solution was washed with 150 mL of 0.1 N HCl, followed by two water washings. The methylene chloride layer was dried over Na$_2$CO$_3$, treated with activated charcoal, and filtered. The methylene chloride was removed on a rotary evaporator, and the clear, colorless oil was redissolved in diethyl ether. The ethereal solution was cooled to −78 °C, whereupon crystals formed that were collected and dried in vacuo to yield 20 g (66%) of the desired ditosylate, **1**.

1 was oxidized to yield the sulfoxide **2**. In a standard preparation 5 g (10.9 mmol) of ditosylate **1** was dissolved in 50 mL of methylene chloride at 10° C. To this stirred solution was added, in a dropwise

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