

Table III. Listing of Selected Bond Distances (Å) and Angles (deg) for $[\text{Mo}_2\text{O}_2\text{S}_2\text{Br}_4][(\text{nBu})_3\text{P}(\text{CH}_2)_4\text{P}(\text{nBu})_3]^{2+}$

Mo-Mo'	2.857 (2)	C(12)-C(13)	1.54 (3)
Mo-Br(1)	2.610 (2)	C(13)-C(14)	1.36 (6)
Mo-Br(2)	2.616 (3)	C(21)-C(22)	1.29 (3)
Mo-S	2.279 (5)	C(22)-C(23)	1.50 (4)
Mo-S'	2.259 (5)	C(23)-C(24)	1.40 (4)
Mo-O	1.67 (1)	C(31)-C(32)	1.50 (3)
P-C(11)	1.88 (2)	C(32)-C(33)	1.52 (4)
P-C(21)	1.75 (3)	C(33)-C(34)	1.44 (4)
P-C(31)	1.77 (2)	C(41)-C(42)	1.54 (2)
P-C(41)	1.82 (2)	C(42)-C(42)'	1.49 (2)
C(11)-C(12)	1.44 (4)		
Mo'-Mo-Br(1)	130.23 (7)	C(11)-P-C(31)	105 (1)
Mo'-Mo-Br(2)	127.78 (7)	C(11)-P-C(41)	105 (1)
Mo'-Mo-S	50.7 (1)	C(21)-P-C(31)	114 (2)
Mo'-Mo-S'	51.3 (1)	C(21)-P-C(41)	112 (1)
Mo'-Mo-O	102.7 (6)	C(31)-P-C(41)	112 (1)
Br(1)-Mo-Br(2)	79.41 (8)	P-C(11)-C(12)	117 (2)
Br(1)-Mo-S	147.5 (2)	C(11)-C(12)-C(13)	112 (2)
Br(1)-Mo-S'	81.0 (1)	C(12)-C(13)-C(14)	114 (3)
Br(1)-Mo-O	104.9 (5)	P-C(21)-C(22)	128 (2)
Br(2)-Mo-S	80.9 (1)	C(21)-C(22)-C(23)	122 (2)
Br(2)-Mo-S'	141.4 (2)	C(22)-C(23)-C(24)	115 (2)
Br(2)-Mo-O	109.3 (7)	P-C(31)-C(32)	115 (2)
S-Mo-S'	99.2 (2)	C(31)-C(32)-C(33)	110 (3)
S-Mo-O	105.9 (5)	C(32)-C(33)-C(34)	112 (3)
S'-Mo-O	107.7 (7)	P-C(41)-C(42)	118 (1)
Mo-S-Mo'	78.0 (2)	C(41)-C(42)-C(42)'	108 (1)
C(11)-P-C(21)	107 (1)		

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

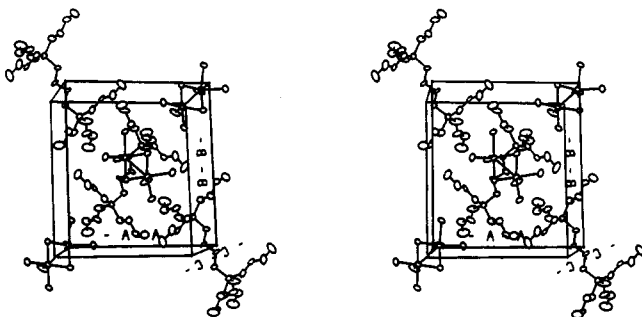


Figure 3. Unit cell drawing of $[\text{Mo}_2\text{O}_2\text{S}_2\text{Br}_4][(\text{nBu})_3\text{P}(\text{CH}_2)_4\text{P}(\text{nBu})_3]^{2+}$. Axes orientation: b, down; a, across; c, toward viewer. Atoms are represented by their ellipsoids at the 20% probability level.

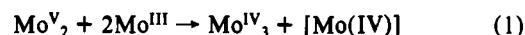
inserted at calculated positions and their thermal parameters constrained to one value, which was refined. The atomic positional parameters are listed in Table II, and selected bond distances and angles are listed in Table III.

Results and Discussion

The structure consists of discrete $[\text{Mo}_2\text{O}_2\text{S}_2\text{Br}_4]^{2-}$ anions and $[(\text{nBu})_3\text{P}(\text{CH}_2)_4\text{P}(\text{nBu})_3]^{2+}$ cations lying on a 2-fold axis, which bisects the Mo-Mo' bond of the anion and the C(42)-C(42)' bond of the cation. ORTEP drawings of the anion and cation are shown in Figures 1 and 2, respectively, where the atom-numbering scheme is also defined. A stereoview of the unit cell diagram is shown in Figure 3. The Mo-Mo distance of 2.857 (2) Å is consistent with that reported for similar compounds, as are the Mo-S-Mo and S-Mo-S angles and the terminal Mo-O distance.⁴⁻⁶ The MoS₂Mo bridge is bent, but the average Mo-S distance of 2.269 [7] Å falls below the range reported for other compounds with Mo₂S₂ bridges.^{4,6}

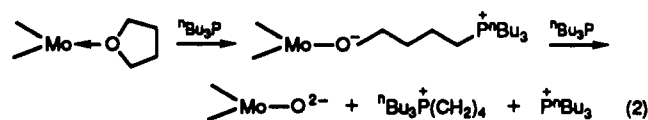
The infrared spectrum showed bands at 965 (m) and 954 (w) cm⁻¹, which are probably assignable to the terminal Mo-O stretching vibrations since this is consistent with reported data.⁸ A cyclic voltammogram in dimethyl sulfoxide (for comparison with previous results⁴ in that solvent) indicates that an irreversible reduction occurs at -1.672 V. The low solubility precluded the measurement of NMR spectra.

The syntheses of such M^V₂ compounds are usually carried out by the reduction of M(VI) compounds, such as MoO₄²⁻,⁸ MS₂²⁻,^{2,3,6} and Mo₇O₂₄⁶⁻.^{5,6} However, $[\text{Mo}_2\text{O}_2\text{S}_2\text{Br}_4]^{2-}$ resulted from the oxidation of Mo₃S₇Br₄. In 1987, Martinez et al. reported the formation of triangular molybdenum complexes from the reduction of molybdenum(V) dimers.¹³ They also proposed several reaction schemes by which this reaction might have occurred. The route to a μ₃-sulfido-capped trimer from the reduction of Mo₂O₂S₂²⁺ was shown to proceed via a cuboidal Mo₄S₄⁴⁺ intermediate. Equation 1 formally summarizes the overall reaction. The



$[\text{Mo}(\text{IV})]$ moiety is described as a "transient" that produces Mo^{IV}₃ or is reoxidized to Mo^V₂.¹³ We suggest that the oxidation of Mo₃S₇Br₄ can be regarded as the reverse of reaction 1. It is unclear, however, whether the trimer breaks down to give a dimer and monomer or if the oxidation step described below occurs first. It is doubtful that a cuboidal intermediate is formed.

The present reaction is effected by the transfer of an oxygen atom from THF and the participation of ⁿBu₃P, as indicated in reaction 2. While this scheme is speculative and intermediates were not



characterized, we do feel that this is a viable route and is the most probable for the products formed.

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Supplementary Material Available: Full listings of crystallographic data, bond distances and angles, positional and isotropic parameters, and anisotropic displacement parameters (8 pages); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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First Catalytic Sulfur Atom Transfer Reaction by a Novel (μ-Persulfido)ruthenium(IV) Complex, $[(\text{Edta-H})\text{Ru}^{\text{IV}}]_2\text{S}_2^{2-}$

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The interaction of $\text{K}[\text{Ru}^{\text{II}}(\text{Edta-H})\text{Cl}]\cdot 2\text{H}_2\text{O}$ (1) with elemental sulfur in 1:1 water-ethanol leads to the formation of the μ-persulfido complex $[\text{Ru}^{\text{IV}}(\text{Edta-H})]_2(\mu\text{-}\eta^1\text{-S}_2^{2-})$ (2) (Edta-H = protonated ethylenediaminetetraacetic acid). In the absence of a substrate the S₂²⁻ bond undergoes a heterolytic cleavage to give a μ-sulfido complex, $[\text{Ru}^{\text{IV}}(\text{Edta-H})]_2(\mu\text{-}\eta^1\text{-S}^{2-})$ (3), and elemental sulfur. Complexes 2 and 3 catalyze sulfur atom transfer to cyclohexene to form cyclohexene sulfide.

The activation of diatomic molecules such as H₂, O₂, N₂, and CO has attained significant relevance in chemistry and homogeneous catalysis.^{1,2} Despite several papers and monographs,^{3,4}

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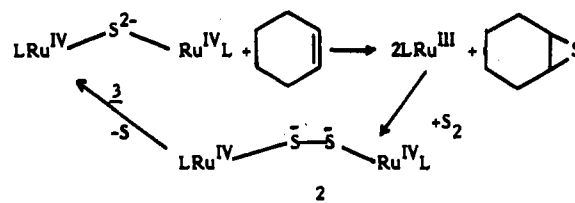
on dioxygen complexes only a few on the disulfur complexes⁵⁻¹⁵ have been reported. Some of these complexes include $[M-(dppe)_2(S_2)]Cl$ ($M = Ir(I), Rh(I)$; $dppe = 1,2$ -bis(diphenylphosphino)ethane) and its selenium analogue. A μ - η^1 -disulfur complex of ruthenium pentaamine with the composition $[(NH_3)_5RuSSRu(NH_3)_5]^{4+}$ was reported by Taube and co-workers⁶ and characterized as a supersulfido-bridged mixed-valence Ru(II), Ru(III) compound by Elder and Trkula.⁷ Disulfur and diselenium complexes of ruthenium and osmium were reported by Clark et al.^{8,9} A complex of the composition $[(H_2O)_5CrSSCr(H_2O)_4]^{4+}$ was obtained¹⁰ by the oxidation of $(H_2O)_5CrSH$ by iodine in solution. A μ - η^2 - Se_2 complex of Ni has been recently reported.¹¹ The S_2 moiety also enters the cluster configuration of molybdenum,¹² tungsten,^{13,14} and iron¹⁵ complexes.

Recently diselenium and disulfur complexes of Rh(I) have been synthesized¹⁶ by the photodecomposition of dithio- and diselenocarbonates to coordinated disulfur or diselenium with the evolution of CO. In the S_2 complexes synthesized so far several formulations can be adapted for coordinated S_2 ranging from neutral disulfur S_2 and supersulfide ion S_2^- to disulfide S_2^{2-} . Electrochemical and other physicochemical studies to confirm the nature of coordinated sulfur or the cleavage of S_2^{2-} bonds were not reported in these complexes. In the present paper we report the synthesis and characterization of the water-soluble μ - η^1 -persulfido complex of Ru(IV) of the composition $[Ru(Edta-H)]_2S_2^{2-}$ (**2**). Complex **2** on prolonged refluxing in solution gives the μ -sulfido complex of Ru(IV) of the composition $[Ru(Edta-H)]_2S^{2-}$ (**3**). In the presence of a substrate such as cyclohexene, complexes **2** and **3** catalyze sulfur atom transfer to the substrate to form cyclohexene sulfide. To our knowledge this is the first report of a sulfur atom transfer reaction catalyzed by a μ -persulfido complex, a reaction analogous to oxygen atom transfer¹⁷ in peroxo and oxo complexes.

Experimental Section

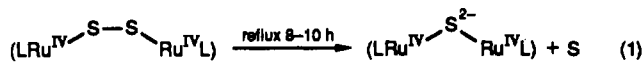
Synthesis of the μ -Persulfido and μ -Sulfido Complexes. The μ -persulfido complex **2** was prepared by the interaction of the Ru(III) complex¹⁸ $K[Ru(EDTA-H)Cl] \cdot 2H_2O$ (**1**) with elemental sulfur in a 1:1 water-ethanol medium. The reaction solution was refluxed for a period of 3–4 h in argon atmosphere when the color of the solution changed from yellow to orange. The solution was then concentrated under reduced pressure and complex **2** precipitated by addition of ethanol. The orange precipitate was then filtered off, washed several times with a 9:1 ethanol-water mixture, and dried under vacuum. Anal. Calcd (found): C, 24.12 (24.66); H, 3.22 (3.25); N, 5.62 (5.14); S, 6.43 (6.60).

Scheme I



L = Edta-H

The μ -sulfido complex $[Ru^{IV}(EDTA-H)]_2S^{2-}$ (**3**) was obtained by the disproportionation of complex **2** according to reaction 1.



Complex **2** was dissolved in a 1:1 water-ethanol solution and refluxed for 8–10 h when the orange color changed to dark brown with the precipitation of elemental sulfur. The dark brown complex was then precipitated and isolated in a manner similar to that for complex **2**. Complex **3** can also be prepared by the interaction of complex **1** with elemental sulfur in a 1:1 water-ethanol mixture with prolonged refluxing for 8–10 h when the color of the solution turns to orange and then to the brown solution of **3**. Complex **3** was precipitated from solution by the addition of alcohol, washed several times with a 9:1 alcohol-water mixture, and dried. Anal. Calcd (found): C, 27.12 (27.02); H, 3.84 (4.02); N, 6.33 (6.23); S, 3.62 (3.61).

S Atom Transfer Reaction. The stoichiometric sulfur atom transfer to cyclohexene in the presence of a 10^{-2} M concentration of **2** and an excess of cyclohexene ($\sim 10^{-1}$ M) was studied in a 1:1 ethanol-water mixture at 80 °C. The amount of cyclohexene sulfide formed per unit time was studied directly by GC analysis by comparing the area under the peak with an authentic sample of cyclohexene sulfide.

Results and Discussion

The infrared spectrum of complex **2** shows peaks at 1710, 1620, 375, and 480 cm^{-1} , which have been assigned to $\nu(COOH)$, $\nu(COO^-)$, $\nu(Ru-S)$, and $\nu(S-S)$ ⁷ frequencies, respectively.

The magnetic susceptibility measurement of complex **2** by the Faraday method at 300 K gave a value of $\mu_{eff} = 4.32 \mu_B$ and by the Evan¹⁹ method gave a value of $4.7 \mu_B$, corresponding to an overall four unpaired spins per complex or two unpaired spins per metal ion, conforming to the formulation of Ru(IV) with the $(t_{2g})^4$ configuration. The CV of complex **2** in aqueous $HClO_4/ClO_4^-$ medium with a glassy-carbon electrode gave peaks corresponding to $E_{1/2}$ values of +0.84, +0.06, -0.18, and -0.42 V. The peaks at +0.84 are assigned to the potential for the Ru^{4+}/Ru^{3+} couple.²⁰ The peaks at +0.06 and -0.18 V are split peaks assigned to the reduction of the Ru^{3+}/Ru^{2+} couple.²² The peak at -0.42 V is not well resolved and is assigned to the reduction of coordinated S_2^{2-} group.

The IR spectrum of complex **3** shows peaks corresponding to $\nu(COOH)$, $\nu(COO^-)$, and $\nu(Ru-S)$ at 1715, 1620, and 360 cm^{-1} , respectively. The magnetic susceptibility measurement of **3** gave a μ_{eff} value of $3.76 \mu_B$ in the solid state by the Faraday method and $4.9 \mu_B$ by the Evans method in solution, corresponding to two unpaired spins per metal ion in solution, confirming a Ru(IV) formulation with the $(t_{2g})^4$ configuration. The value of μ_{eff} of the complex is lower than expected for four free spins per complex in the solid state, which may be due to some extent of antiferromagnetism and pairing of spins as the ruthenium centers are close to each other in **3** as compared to complex **2**.

The CV of complex **3** gave peaks corresponding to $E_{1/2}$ value of +0.53, +0.08, -0.2, and -0.42 V, which are assigned to the $Ru^{4+}/Ru^{3+}/Ru^{2+}$ couples and to the reduction of coordinated sulfur, respectively, as in complex **2**.

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The UV-vis spectrum of complex **2** shows peaks at 280 ($\epsilon = 4.87 \times 10^3$), 356 (1.1×10^3), 488 (5.9×10^1), and 747 nm ($19.5 \text{ M}^{-1} \text{ cm}^{-1}$). Complex **3** gives bands at 249 (1.24×10^4), 478 (1.4×10^3), and 755 nm ($1.2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). The bands at 280 and 249 nm in complexes **2** and **3** are assigned to the ligational bands¹⁷ due to EDTA. The characteristic peaks at 356 nm in complex **2** and 478 nm in complex **3** are due to a $1\pi^* \rightarrow d$ LMCT transition from S_2^{2-} and S^{2-} groups, respectively, to Ru(IV). As expected these transitions are observed at lower energy²³ as compared to O_2^{2-} and O^{2-} because of a larger size of $1\pi^*$ orbitals of sulfur as compared to oxygen.

The reaction of complex **2** or **3** in a 1:1 EtOH-water mixture in the absence of excess sulfur takes place in a stoichiometric manner with the formation of cyclohexene sulfide and complex **1**. In the presence of excess sulfur, however, the reaction becomes catalytic. A mechanism for the sulfur atom transfer to cyclohexene is shown in Scheme I.

The product cyclohexene sulfide was isolated from the reaction mixture by fractional distillation under reduced pressure so that the temperature did not exceed 80 °C. The fraction boiling between 70 and 75 °C at 21 mm of Hg pressure was collected. The product was characterized by ¹H NMR and IR spectral analysis. The ¹H NMR spectrum of the product gave peaks at δ 3.2 (broad singlet, 2 H, C1 H and C2 H) δ 2.2 (broad singlet, C3 2 H, C6 2 H) and δ 1.38 (multiplet, C4 2 H, C5 2 H), which is in agreement with the spectrum taken for authentic sample of cyclohexene sulfide prepared by following the reported procedure.²⁴ The IR spectrum of the product gave characteristic strong bands at 1360, 1020, and 885 cm^{-1} for the episulfide ring. Reaction **1** proceeds at 80 °C with a turnover rate of the product cyclohexene sulfide of about (7 mol/mol of catalyst)/h. The reaction is 1 order of magnitude slower than the O atom transfer reaction of cyclohexene to the epoxide catalyzed¹⁷ by Ru(III)-EDTA in the presence of O_2 . This is expected on the basis of a weaker electrophilicity of S as compared to O.

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Insertion Reaction of Acetone- d_6 into the Os-H Bond of $[\text{OsHCl}(\text{CO})(\text{P}^i\text{Pr}_3)_2]$: Experimental Evidence for the Hydrogen-Transfer Mechanism from Alcohols to Ketones

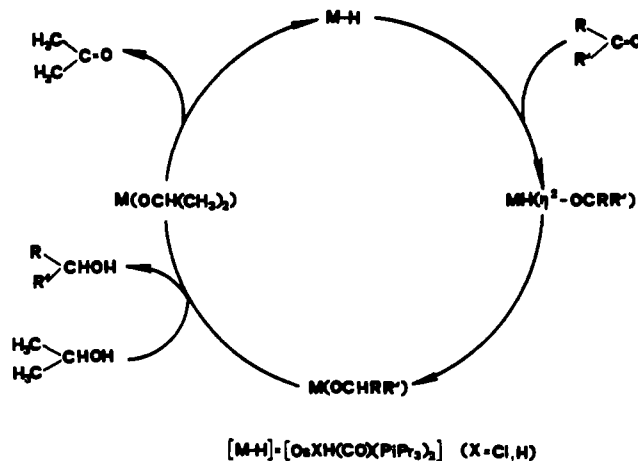
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Transfer hydrogenation reactions catalyzed by transition-metal complexes have received a great deal of attention.^{1,2} However, direct experimental evidence for possible reaction intermediates remains scarce, and no detailed proof of the mechanism has as yet been obtained.

We have recently postulated³⁻⁵ that the hydrogen transfer from propan-2-ol to ketones involves four steps (Scheme I): (i) coor-

Scheme I. Catalytic Cycle for the $\text{OsHX}(\text{CO})(\text{P}^i\text{Pr}_3)_2$ -Catalyzed Hydrogen Transfer from Propan-2-ol to Ketones



dination of the ketone to the coordinatively unsaturated metal center, (ii) formation of an alkoxy metal intermediate by hydrogen migration from the metal to the ketonic double bond, (iii) exchange of the alkoxy group by reaction with the alcohol, which acts as solvent, and (iv) a β -elimination process. We have now found, under noncatalytic conditions, by using the five-coordinate hydrido osmium complex $[\text{OsHCl}(\text{CO})(\text{P}^i\text{Pr}_3)_2]$ (**1**) as starting material experimental evidence for the coordination, insertion, and β -elimination steps. Exchange between the hydrogen-bonded alcohol and the coordinated alkoxy has been previously demonstrated.⁶ This exchange proceeds most probably via a hydrogen-bonded adduct, some examples of which have been characterized.⁷

The ¹H NMR spectrum of **1** shows, in C_6D_6 , at room temperature a triplet at δ -31.9 with P-H coupling of 14 Hz.⁸ In acetone- d_6 , this triplet disappears and a broad signal at δ -28.3 is observed.⁹ When the temperature is lowered, a new compound is formed by insertion of the coordinated ketone into the Os-H bond. Thus, the ¹H NMR spectrum in acetone- d_6 at -60 °C shows the signals of the phosphine ligands together with a new signal at δ 3.43, which is characteristic of a $\text{OCH}(\text{CD}_3)_2$ group linked to the metal.⁶

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