1040 *Inorg. Chem.* **1999,** *38,* 1040−1041

Synthesis, Structure, and Reactivity of Novel Dithiolato(oxo)rhenium(V) Complexes

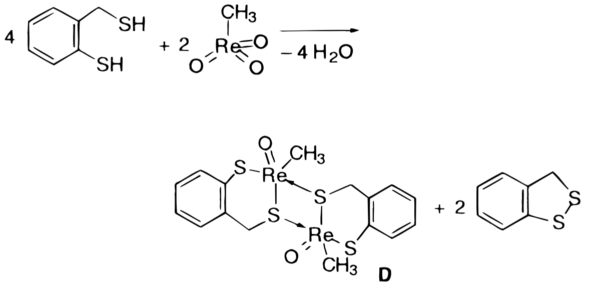
Josemon Jacob, Ilia A. Guzei, and James H. Espenson*

Ames Laboratory and Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa 50011

Received November 30, 1998

Oxygen atom transfer catalyzed by transition metal complexes holds great interest owing to its chemical and biological relevance.[1−8] The intriguing mechanisms of certain of these reactions catalyzed by organorhenium oxides have been revealed.[9,10] As we became involved in certain sulfur atom transfer reactions, it became important to synthesize stable thiolato complexes derived from methyltrioxorhenium (CH_3ReO_3 or MTO), in that they are related to important catalytic intermediates. A tetrathiophenylato complex, unstable above 15 °C, has been reported,[11] as have anionic dithiolato complexes of rhenium(V)-sulfides.[12] Prompted by these reports, we sought to prepare new, thermally stable thiolato complexes derived from MTO.

The reaction of MTO (0.8 mmol, 200 mg) with a twofold excess of the dithiol[13,14] was carried out at 0 °C in toluene (10 mL); after 15 min, 5 mL of hexane was added, and the mixture was kept in a freezer overnight. The product was a dimeric dithiolato−dirhenium complex, **D**, that forms fine needles, isolated in 88% yield. Its structure was determined from spectroscopic[15] and X-ray data,[16,17] as shown in eq 1 and Figure 1.



(1)

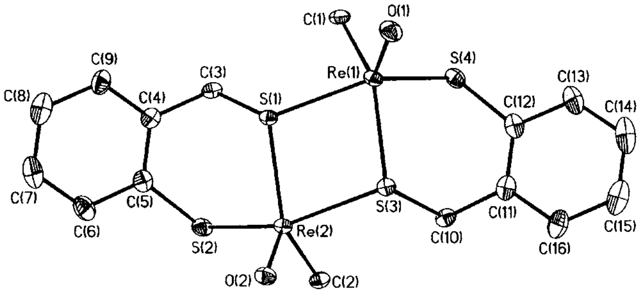


Figure 1. Perspective view of the dinuclear rhenium(V) compound **D** with thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): Re(1)−S(1) 2.386; Re(1)−S(3) 2.362; Re(1)−S(4) 2.299; Re(1)−O(1) 1.670; Re(1)−C(1) 2.120; S(3)−Re(1)−S(1) 75.2; S(3)−Re(1)−S(4) 90.8; S(4)−Re(1)−S(1) 146.2; S(3)−Re(1)−O(1) 112.7; S(3)−Re(1)−C(1) 143.2; O(1)−Re(1)−C(1) 103.8.

As depicted, **D** is a dinuclear compound held together with coordinate bonds from the sulfur of one ligand to the rhenium of the other. A dithiolate ligand chelates Re(V), which is also coordinated by single oxo and methyl groups. Accompanying this product is the cyclic organic disulfide, required to balance the reduction of Re(VII) to Re(V). **D** contains a four-membered heteroatomic ring composed of two rhenium and two sulfur atoms. The two {Re, S, S} planes within the central Re_2S_2 core define a dihedral angle of 19.2(2)°. The rhenium atoms exist in a severely distorted trigonal bipyramid: two sulfur atoms lie in apical positions, at an average angle of 148(2)°, considerably off linearity. Sulfur, oxygen, and carbon atoms are found in the equatorial plane. The distortions are such that, alternatively, the coordination sphere of the rhenium atoms can be described as distorted square pyramidal with a carbon and three sulfur atoms in the basal plane and an oxygen atom at the apex. One set of three sulfur atoms and carbon is coplanar within 0.01(1) Å; the second within 0.09(1) Å. The rhenium−oxo vectors are almost normal to those planes, at angles of 84.5(1)° and 83.9(1)°. Although the rhenium−sulfur distance between the monomeric units (av 2.373(11) Å) exceeds that found within each monomer (av 2.294(8) Å), it falls well within similar rhenium−sulfur bond

---

(1) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401.

(2) Espenson, J. H.; Abu-Omar, M. M. *Adv. Chem. Ser.* **1997**, *253*, 99−134.

(3) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981.

(4) Abrams, M. J.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1984**, *82*, 125.

(5) Begnan, I. A.; Behm, J.; Cook, M. R.; Herrmann, W. A. *Inorg. Chem.* **1991**, *30*, 2165.

(6) Conry, R. R.; Mayer, J. M. *Inorg. Chem.* **1990**, *29*, 4862−4867.

(7) Schultz, B. E.; Gheller, S. F.; Muetterties, M. C.; Scott, M. J.; Holm, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 2714.

(8) Moyer, B. A.; Sipe, B. K.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 1475.

(9) Abu-Omar, M. M.; Appleman, E. H.; Espenson, J. H. *Inorg. Chem.* **1996**, *35*, 7751−7757.

(10) Abu-Omar, M. M.; Espenson, J. H. *Inorg. Chem.* **1995**, *34*, 6239−6240.

(11) Takacs, J.; Cook, M. R.; Kiprof, P.; Kuchler, J. G.; Herrmann, W. A. *Organometallics* **1991**, *10*, 316.

(12) Goodman, J. T.; Rauchfuss, T. B. *Inorg. Chem.* **1998**, *37*, 5040−5041.

(13) Klingsberg, E.; Schreiber, A. M. *J. Am. Chem. Soc.* **1962**, *84*, 2941−2944.

(14) Hortmann, A. G.; Aron, A. J.; Bhattacharya, A. K. *J. Org. Chem.* **1978**, *43*, 3374−3378.

(15) Spectroscopic data for the dinuclear compound **D** are as follows. ^{1}H NMR: δ 7.52 (d, 2H, J = 8 Hz), 7.03 (m, 2H), 6.91(m, 4H), 4.05 (d, 2H, J = 10.8 Hz), 3.53 (d, 2H, J = 10.8 Hz), and 2.91 (s, 6H) ppm. ^{13}C NMR: δ 141.94, 135.81, 130.62, 130.56, 130.18, 127.87, 36.91, 17.10 ppm. Elemental anal. Calcd: C, 25.85; H, 2.44; S, 17.27. Found: C, 26.68; H, 2.53; S, 17.33.

(16) X-ray crystal data for $C_{16}H_{18}O_2Re_2S_4{\cdot}C_7H_8$: monoclinic, $P2_1/c$, a = 14.6264(8) Å, b = 18.7219(10) Å, c = 9.3664(5) Å, β = 93.393(1)°, V = 2560.3(2) Å^3, Z = 4, T = 163(2) K, D_{calcd} = 2.166 Mg/m^3, $R(F)$ = 1.98% for 4407 independently observed ($I \geq 2\sigma(I)$ reflections ($4° \leq 2\theta \leq 53°$).

(17) All atoms other than hydrogen were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-Ray Systems, Madison, WI). Absorption corrections were carried out by programs SADABS (Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−38) for **D** and DIFABS (Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158) for **M**−**L**.

(18) Tisato, F.; Bolzati, C.; Duatti, A.; Bandoli, G.; Refosco, F. *Inorg. Chem.* **1993**, *32*, 2042−2048.

(19) Tanner, L. D.; Haltiwanger, R. C.; DuBois, M. R. *Inorg. Chem.* **1988**, *27*, 1741−1746.

10.1021/ic981367w CCC: $18.00

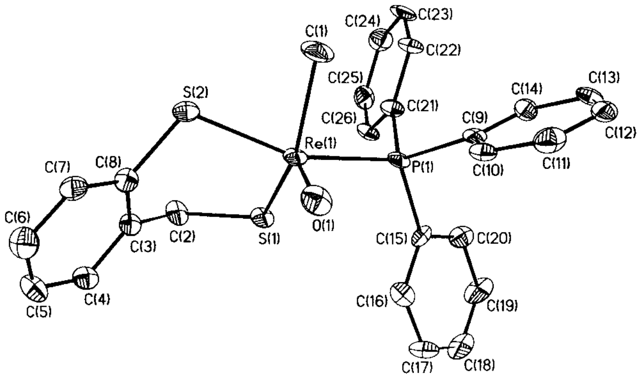
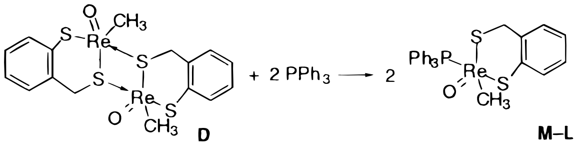


Figure 2. Perspective view of **M−L** with thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg) (corresponding parameters for the second molecule in parentheses): Re(1)−S(1) 2.283 (2.275); Re(1)−S(2) 2.329 (2.340); Re(1)−P(1) 2.452 (2.447); Re(1)−O(1) 1.677 (1.696); Re(1)−C(1) 2.125 (2.131); S(2)−Re(1)−S(1) 91.0 (90.6); S(2)−Re(1)−C(1) 78.6 (78.8); S(2)−Re(1)−O(1) 108.9 (109.1); C(1)−Re(1)−P(1) 83.3 (83.0).

lengths.[12,18] Mixed sulfido−oxo complexes of rhenium[18] and molybdenum[19] have been reported.

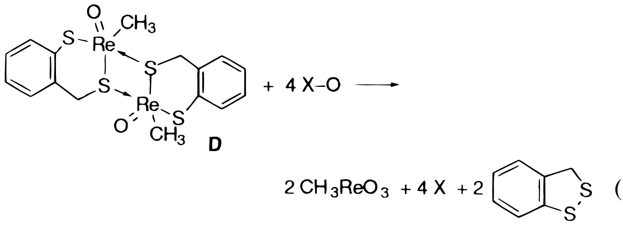
Most likely, a first-formed mononuclear Re(VII) chelate then undergoes reductive elimination. Further ligand coordination and dimerization yields the Re(V) dithiolato complex **D**. Although excess dithiol was used in the synthesis, it did not monomerize **D** and remained unreacted. A tetrathiophenolato complex of MTO,[11] stable at low temperatures, undergoes reductive elimination at higher temperature. In our study, low-temperature NMR experiments did not detect any intermediary Re(VII) species. However, the reactivity of **D** toward various two-electron oxidants (vide infra) suggests the intermediacy of a Re(VII) species.

Given the dimeric structure, it seemed possible that a Re(V) monomer might be formed by coordination of an exogenous Lewis base, L. The addition of 2 equiv of Ph_3P to the yellow dimer resulted in the quantitative formation of the intensely green mononuclear dithiolato complex ($\epsilon_{606} = 1.9 \times 10^2$ L mol^{-1} cm^{-1}), eq 2. The rhenium(V) phosphine compound **M−L** was characterized by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and (despite quite small crystals grown by the slow diffusion of hexane into a toluene solution) single-crystal X-ray analysis.[17,20,21] Its molecular structure, presented in Figure 2, shows two independent molecules with virtually identical parameters in the asymmetric unit; only one is shown. In the following discussion the structural parameters have been averaged between two molecules. As in the case of **D**, the molecular geometry of **M−L** can be viewed as highly distorted trigonal bipyramidal with one sulfur and one phosphorus atom in the apical positions (av P−Re−S angle is 149.4(4)°). Sulfur, carbon, and oxygen atoms lie in the equatorial plane. Alternatively, the rhenium atom is in a distorted square pyramidal environment with a phosphorus, a carbon, and two sulfur atoms in the basal plane (planarity within 0.14(1) Å) and an oxygen atom at the vertex. The oxygen−rhenium vector intersected the basal plane at 84.6(1)°. The bond distances to rhenium fall in the usual ranges. The similar structural features of both complexes are noteworthy because the one is a dimer, the other a monomer.



(2)

Since complexes of methyldioxorhenium are known to abstract oxygen from various oxidants to form MTO,[9,22] we investigated the reactivity of **D** toward various oxygen donors, XO. Addition of 4 equiv of XO in benzene solution caused both the rhenium and its dithiolate ligand to be oxidized:[23,24]



(3)

The reactions were monitored by ^{1}H NMR.[25] With XO = pyridine *N*-oxide, Me_3NO, or Ph_3AsO, complete reaction occurred within 5 min. Me_2SO required 1.5 days for 81% conversion, whereas Ph_3SbO gave only 50% reaction in 3 days. The disulfide isolated from this reaction and from eq 1 showed ^{1}H and ^{13}C NMR spectra identical to those of a sample prepared independently.[26] Perhaps initial O transfer to form the Re(VII) thiolato is rate controlling; detailed studies are now underway to define the differences in reactivity of various oxidants.

In summary, we have synthesized, analyzed, and characterized new oxorhenium(V) complexes containing a dithiolato ligand. The dinuclear version of this complex is monomerized upon reaction with triphenylphosphine. The dimer readily reacts with several O-atom donors, undergoing oxidation both at the metal and at the ligand. We are currently investigating the scope and mechanism of this reaction and further studying the reactivity of this binuclear complex.

Acknowledgment. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract W-7405-Eng-82.

Supporting Information Available: Spectroscopic and analytical data for the new complexes, X-ray diffraction data for **D** and **M−L**, and the UV−vis changes accompanying the reaction between **D** and PPh_3. This material is available free of charge via the Internet at http://pubs.acs.org.

IC981367W

---

(20) ^{1}H NMR: δ 7.84 (d, 1H, J = 7.6 Hz), 7.67 (m, 6H), 7.11 (t, 1H, J = 7.6 Hz), 7.04 (d, 1H, J = 7.6 Hz), 6.90 (m, 10H), 4.80 (d, 1H, J = 10.6 Hz), 3.25 (d, 1H, J = 10.6 Hz), 2.97(d, 3H, J = 8.4 Hz) ppm. ^{13}C NMR: δ 142.66, 140.37, 137.84 (d, J = 9.2 Hz), 134.62 (d, J = 7.7 Hz), 133.99 (d, J = 14.7 Hz), 131.14 (d, J = 1.7 Hz), 130.98, 130.47, 129.29, 126.29, 42.54 (d, J = 7.1 Hz,) 15.45 (d, J = 3 Hz) ppm. ^{31}P NMR: δ 27.82 ppm. Elemental anal. Calcd: C, 49.25; H, 3.82; S, 10.12. Found: C, 49.25; H, 3.60; S, 9.78.

(21) X-ray crystal data for $C_{26}H_{24}O_2PReS_2$: triclinic, $P\bar{1}$, $a = 11.7741(5)$ Å, $b = 13.9288(6)$ Å, $c = 14.7608(7)$ Å, $\alpha = 83.860(1)°$, $\beta = 84.093(1)°$, $\gamma = 81.878(1)°$, $V = 2373.23(18)$ Å^3, $Z = 4$, $T = 163(2)$ K, $D_{\text{calcd}} = 1.774$ Mg/m^3, $R(F) = 5.01\%$ for 7178 independent observed ($I \geq 2\sigma(I)$ reflections ($4° \leq 2\theta \leq 56°$).

(22) Zhu, Z.; Espenson, J. H. *J. Mol. Catal.* **1995**, *103*, 87.

(23) Arterburn, J. B.; Perry, M. C.; Nelson, S. L.; Dible, B. R.; Holguin, M. S. *J. Am. Chem. Soc.* **1997**, *119*, 9309.

(24) Abu-Omar, M. M.; Khan, S. I. *Inorg. Chem.* **1998**, *37*, 4979.

(25) In the case of Me_3NO, the reaction proceeds with decomposition of the product, MTO. Although free MTO has δ 1.20 ppm in C_6D_6, in all these cases the MTO formed in the reaction showed a chemical shift $1.50 \leq \delta \leq 1.70$ ppm due to the coordination of X formed in the reaction. See also: Wang, W.-D, Espenson, J. H. *J. Am. Chem. Soc.* **1998**, *120*, 11335.

(26) Wallace, T. J. *J. Org. Chem.* **1966**, *31*, 1217−1221.