Perhaps the higher pH at which our incubations were performed[14] deprotonates this lysine (p$K_a \sim$ 9–10) and renders it sufficiently nucleophilic to compete with other nucleophilic residues in the active site. To our knowledge, this is the first report of a lysine residue in E_2-HSD modified by an active-site-directed alkylating agent.

Acknowledgment. This work was supported by NIH Grants CA-23582, Research Career Development Award CA-00829 (D.F.C.), and National Research Service Award GM-07805 (R.J.A.). Assistance was provided by the Washington University High Resolution NMR Facility, supported in part by NIH 1 S10 RR00204 and a gift from Monsanto Co. We thank Mary Ann Sullivan, R.N., and her staff at St. John's Mercy Medical Center, St. Louis; Dr. Gene Z. Chiao; and Patrick C. McMullan for assistance in obtaining human term placenta.

---

(14) High pH was necessary to drive the equilibrium toward oxidation of alcohol to ketone (see Scheme I and ref 2a).

(15) Midland, M. M. *J. Org. Chem.* **1975**, *40*, 2250–2252.

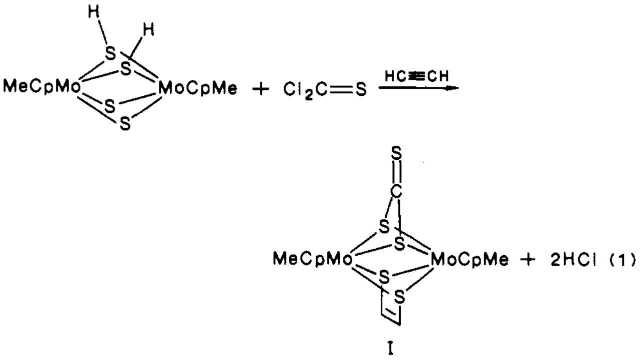
Expansion of the Molybdenum Coordination Sphere in Dinuclear Tetrasulfur-Bridged Complexes with the $Cp_2Mo_2S_4$ Core

L. L. Wright, R. C. Haltiwanger, J. Noordik, and
M. Rakowski DuBois*

Department of Chemistry and Biochemistry
University of Colorado, Boulder, Colorado 80309

Received July 24, 1986

The reaction of the dinuclear hydrosulfido-bridged molybdenum complex with thiophosgene has been reported to yield a Mo(III) derivative with a μ-η^2-trithiocarbonate ligand (eq 1).[1] Although several mononuclear and dinuclear trithiocarbonate complexes have been prepared,[2–7] we have not found previous reports of the η^2-bridging mode for this ligand. We have, therefore, begun a study of the reactivity of the thiocarbonyl functional group in complex I. We report here an interesting result which reveals reactivity characteristics of the molybdenum ions in these systems in which sulfur ligand reactivity normally dominates the chemistry.[8–10]



I

Unlike the thiocarbonyl functional group in organic molecules, the C═S bond of the trithiocarbonate ligand is resistant to hydrolysis. Complex I was recovered nearly quantitatively from an aqueous/THF solvent mixture which had been refluxed for 3 weeks. The addition of a small amount of trifluoroacetic acid did not alter these results. However, when complex I was reacted with 2–3 equiv of methyl iodide at room temperature in THF, a reaction did occur to form an 80% yield of an orange product.[11] The complex was formulated as the salt $[(MeCpMo)_2(SC_2H_2S)S_2CSMe]I$ (II). Elemental analyses are consistent with the proposed composition.[11] The room temperature proton NMR spectrum in $CDCl_3$ shows sharp resonances at 2.87 and 7.2 ppm which are consistent with a SMe group and the alkenedithiolate ligand, respectively. However, the methylcyclopentadienyl resonances at 6.06 and 2.2 ppm are broad singlets at room temperature. A variable-temperature NMR study confirms that there is a fluxional process occurring in solution. At -54 °C, two singlets are observed for the Cp ring protons at 6.41 and 5.66 ppm and for the Cp–Me protons at 2.49 and 1.89 ppm. As the temperature is increased, these resonances broaden with coalescence for the Cp–Me resonances occurring at 0 °C and for the Cp signals at 6 °C. On the basis of these coalescence temperatures, the free energy of activation for the fluxional process is calculated to be 56 kJ/mol.[12] The ^{13}C NMR spectrum also shows a variation with temperature.[13]

The process which results in inequivalent cyclopentadienyl resonances at low temperatures was proposed to involve the interaction of the methylated ligand with a molybdenum ion in the cation. The nature of this interaction has been established by an X-ray diffraction study. The complex crystallized in space group $P21/c$ with four molecules per unit cell.[14] A perspective drawing of the molecule is shown in Figure 1. The structure consists of discrete cations and anions. The structure of the cationic dinuclear molybdenum complex confirms that the terminal sulfur atom of the trithiocarbonate ligand has been methylated. The C–S bond distances around this terminal sulfur atom lie within the normal range for single bonds. The ligand is coordinated to Mo_1 through the other two sulfur atoms S_2 and S_3 and to Mo_2 through sulfur atoms 2 and 3 and the carbon atom (C_1) of the ligand. The Mo–C distance of 2.195 (6) Å is typical of a single bond between these atoms.[15] The CS_3 portion of the ligand retains its planarity, and by chelating to Mo_1, the ligand forms a planar four-membered metallocycle. All three of the C–S distances in the ligand are identical within standard deviation. The structure, therefore, involves an unusual bridging coordination mode for a thioxanthate ligand.[16] Upon expanding the coordination sphere around Mo_2, all the Mo–S and Mo–C_{Cp} distances have increased slightly. For

---

(1) McKenna, M.; Wright, L. L.; Miller, D. J.; Tanner, L.; Haltiwanger, R. C.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1983**, *105*, 5329.

(2) Fackler, J. P., Jr.; Coucouvanis, D. *J. Am. Chem. Soc.* **1966**, *88*, 3913.

(3) Bianchini, C.; Mealli, C.; Meli, A.; Scapacci, G. *J. Chem. Soc., Dalton Trans.* **1982**, 799.

(4) Fehlhammer, W. P.; Mayr, A.; Stolzenberg, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 626.

(5) Benson, I. B.; Hunt, J.; Knox, S. A. R.; Oliphant, V. *J. Chem. Soc., Dalton Trans.* **1978**, 1240.

(6) Thiele, G.; Liehr, G.; Lindner, E. *J. Organomet. Chem.* **1974**, *70*, 427.

(7) Brunner, H. *Z. Naturforsch, B* **1969**, *24B*, 275.

(8) Casewit, C. J.; Haltiwanger, R. C.; Noordik, J.; Rakowski DuBois, M. *Organometallics* **1985**, *4*, 119.

(9) Casewit, C. J.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 5482.

(10) DuBois, D. L.; Miller, W. K.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1981**, *103*, 3429 and references therein.

(11) After the reaction was stirred for 15 h, the precipitated product was filtered and washed with THF. Mass spectrum (EI), m/e^+ 548 ($P - CH_3I$), 478 ($MeCp_2Mo_2S_4$), 142 (CH_3I). Anal. Calcd for $C_{16}H_{19}Mo_2S_5I$: C, 27.84; H, 2.77; S, 23.22. Found: C, 27.89; H, 2.66; S, 23.19.

(12) Gunther, H. *NMR Spectroscopy*; translated by Gleason, R. W.; Wiley: New York, 1980; p 243.

(13) ^{13}C NMR ($CDCl_3$, 250 MHz, $T = -50$ °C) 16.6, 16.3 (Me groups); 92.1, 96.9, 101.8, 105.4 (Cp's); 147.3 ppm (SC_2H_2S); a very weak resonance at 174 ppm is tentatively assigned to *C*–Mo; ($T = 30$ °C) 16.5 (SMe); 147.4 (SC_2H_2S); 174 ppm (C–Mo). Resonances associated with the MeCp ligands are not observed at this temperature.

(14) A single crystal of $[(MeCpMo)_2(SCHCHS)(S_2CSMe)]I$, obtained by slow evaporation of a CH_2Cl_2 solution, had cell dimensions $a = 11.676$ (3) Å, $b = 13.992$ (4) Å, $c = 14.286$ (2) Å, and $\beta = 116.26$ (1)°; $V = 2093.0$ (8) Å^3, $Z = 4$, $\rho_{calcd} = 2.19$ g/cm^3. By use of a crystal of dimensions 0.3 × 0.3 × 0.2 mm, 8119 reflections were measured at values of $\pm h$, $+k$, and $\pm l$ in the range $3.0° \leq 2\theta < 50°$; 3122 of the 3707 unique reflections had $F_o \geq 6\sigma F_o$. The structure was solved by the heavy atom method and Fourier techniques. Full-matrix least-squares refinement on 229 variables with all non-hydrogen atoms anisotropic converged with residuals of $R = 0.046$ and $R_w = 0.061$. Atomic parameters and observed and calculated structure factors are included in the supplementary material.

(15) Schrauzer, G. N.; Hughes, L. A.; Strampach, N.; Robinson, P. R.; Schlemper, E. O. *Organometallics* **1982**, *1*, 44 and references therein.

(16) For a previous structural study of a thioxanthate complex, see: Coucouvanis, D.; Lippard, S. J.; Zubieta, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 761.

0002-7863/87/1509-0282$01.50/0

J. Am. Chem. Soc. 1987, 109, 283-285

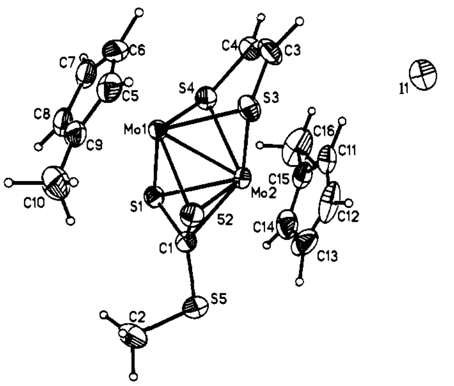


Figure 1. Perspective view and numbering scheme for $[(MeCpMo)_2(SC_2H_2S)(S_2CSMe)]I$. Thermal ellipsoids are shown at the 50% probability level. Selected bond distances (Å): Mo_1–Mo_2, 2.623 (1); Mo_2–C_1, 2.195 (6); C_1–S_1, 1.749 (7); C_1–S_2, 1.754 (6); C_1–S_5, 1.755 (6); S_5–C_2, 1.789 (8); Mo_1–S_1, 2.423 (2); Mo_1–S_2, 2.438 (2); Mo_2–S_1, 2.452 (2); Mo_2–S_2, 2.442 (2). Angles (deg): S_1–C_1–S_2, 108.4 (3); S_1–C_1–S_5, 124.3 (4); S_2–C_1–S_5, 125.7 (4); Mo_2–C_1–S_5, 126.5 (3).

example, the average Mo_2–C_{Cp} distance of 2.327 Å is approximately 0.03 Å longer than the Mo_1–C_{Cp} average distance (2.292 Å); Mo_2–$S_{3(4)}$ (2.473 (2) Å) is 0.04 Å longer than Mo_1–$S_{3(4)}$. Other structural features of the $Cp_2Mo_2S_4$ core are similar to those observed for related cations, including the Mo–Mo distance of 2.623 (1) Å.[8,17]

In a somewhat related example of unusual coordination geometries, a 1,2-alkenedithiolate ligand has been found to display an μ-η^2,η^4-bonding interaction in a neutral dinuclear ruthenium complex.[18] The dithiolene ligand bonds to one Ru ion through the two sulfur atoms and to the second Ru ion through the two sulfur and two carbon atoms. In this system, the formation of the dithiolate ligand with the unusual bonding mode was induced by phosphine abstraction of a disulfido ligand. In contrast, the formation of complex II appears to be induced by the generation of a positive charge on the dithio ligand and results in an expansion of the molybdenum coordination sphere.[19] The complex provides a rare example of verified reactivity of a molybdenum ion in these tetrasulfur-bridged complexes and suggests that the characteristic reactivity of the Mo ion in complexes of this type is that of a Lewis base. This permits the stabilization of unusual types of electron-deficient ligands. The basicity of the metal ion may also have important implications for the reactions of related molybdenum complexes which result in the heterolytic cleavage of the hydrogen molecule.[20]

Acknowledgment. Support from the National Science Foundation and, in part, from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is acknowledged. M.R.D. is grateful for a Dreyfus Fellowship, 1981–1986, and a Guggenheim Fellowship, 1984–1985.

Supplementary Material Available: Crystal data and details of the structural determination and tables of bond distances, bond angles, and atomic and thermal parameters for $[(MeCpMo)_2(SC_2H_2S)(S_2CSMe)]I$ (5 pages); observed and calculated structure factor table for $[(MeCpMo)_2(SC_2H_2S)(S_2CSMe)]I$ (13 pages). Ordering information is given on any current masthead page.

---

[17] Rakowski; BuBois, M.; Haltiwanger, R. C.; Miller, D. J.; Glatzmaier, G. *J. Am. Chem. Soc.* **1979**, *101*, 5245.

[18] Rauchfuss, T. B.; Rodgers, D. P. S.; Wilson, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 3114.

[19] Previous examples of an expanded molybdenum coordination sphere have been reported in cluster syntheses. See, for example: Cowans, B.; Noordik, J.; Rakowski DuBois, M. *Organometallics* **1983**, *2*, 931.

[20] Laurie, J. C. V.; Duncan, L.; Weberg, R. T.; Haltiwanger, R. C.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 6234.

Facile Reductive Cleavage of the C=O Bond of Acyl Halides and the C≡N Bond of Nitriles by Hydrogen in the Presence of Sulfido-Bridged Molybdenum Complexes

D. E. Coons, J. C. V. Laurie, R. C. Haltiwanger, and
M. Rakowski DuBois*

Department of Chemistry and Biochemistry
University of Colorado, Boulder, Colorado 80309

Received July 24, 1986

We have recently reported that cationic dinuclear molybdenum complexes of the type $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SR)]^+$ undergo unusual reactions with molecular hydrogen to form protons and types of molybdenum and organic products which vary depending on the nature of R.[1,2] We report here extensions of this reactivity which result in the reductive cleavage of the C=O and C≡N bonds in acyl halides and nitriles, respectively, under mild homogeneous conditions.

Although many organic halides react with $(CpMo\mu\text{-}S)_2S_2CH_2$ (I) to form the cationic derivatives of the type discussed above,[1,3] acyl halides do not form isolable sulfur-acylated cations. However, when a solution containing complex I and excess acyl halide is placed under an atmosphere of hydrogen at room temperature, two competing reactions are observed by ^1H NMR spectroscopy. One is the hydrogenolysis of the acyl halide to the corresponding aldehyde catalyzed by I. The second competing reaction eventually consumes all of I to form a catalytically inactive molybdenum product. The final molybdenum products have been isolated (in ca. 80% yield) from reactions with acetyl halides and benzoyl chloride and identified by NMR as derivatives of low symmetry. For example, the NMR spectrum for the product of the reaction with acetyl bromide shows two cyclopentadienyl resonances at 6.74 and 5.69 ppm. The methanedithiolate ligand is represented by an AX pattern with doublets at 7.16 and 5.31 ppm. A singlet at 2.57 ppm is assigned as the methyl resonance.

Single crystals of the bromide salt of this product were obtained by addition of pentane to an ethanol solution, and an X-ray diffraction study has been completed.[4] The product, which is pictured in Figure 1, is a salt of composition $[(CpMo)_2(S_2CH_2)(S_2CCH_3)]Br\cdot{}^1/_2EtOH$ (II). The cation contains a bridging dithioacetate ligand which is coordinated to Mo(2) through the two sulfur atoms and to Mo(1) through the two sulfur atoms and the chelated carbon atom of the ligand. The ligand is approximately planar. Selected bond distances and angles are presented with Figure 1. The structural parameters are similar to those observed for a related cationic complex.[5] The structure provides another example of the ability of the molybdenum ion in these complexes to function as a Lewis base and thereby stabilize the formation of an unusual electron-deficient dithiolate ligand.[5]

A possible mechanism for the cleavage of the carbon–oxygen bond in the acyl group is shown in Scheme I. The cationic derivative A has been detected by NMR spectroscopy in the presence of excess acyl halide and in the absence of hydrogen. Intermediate A is proposed to react with hydrogen by a pathway analogous to those of related cations.[1,2] Intramolecular S–H addition to the carbonyl group would form a ethanol-1,1-dithiolate

---

[1] Laurie, J. C. V.; Duncan, L.; Weberg, R. T.; Haltiwanger, R. C.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 6234.

[2] Weberg, R. T.; Laurie, J. C. V.; Haltiwanger, R. C.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 6242.

[3] Casewit, C. J.; Haltiwanger, R. C.; Noordik, J.; Rakowski DuBois, M. *Organometallics* **1985**, *4*, 119.

[4] $[(CpMo)_2(S_2CH_2)(S_2CCH_3)]Br$ crystallized in space group $P2_1/c$ with cell dimensions a = 13.9834 (32) Å, b = 8.1974 (15) Å, c = 15.9709 (34) Å, β = 90.721 (18)°, and V = 1830.6 Å^3, Z = 4, ρ_{calcd} = 2.13 g/cm^3. From a crystal of dimensions 0.27 × 0.38 × 0.50 mm, 11 139 reflections were measured at values of $\pm h$, $+k$, and $\pm l$ over a 2θ range of 4.0–60.0°. These were averaged to 5379 independent reflections (R_{av} = 0.016). Full-matrix least-squares calculations on 204 variables using 3522 observed reflections ($F_o > 6.0\sigma(F_o)$) converged with residuals of R = 0.033 and R_w = 0.041.

[5] Wright, L. L.; Haltiwanger, R. C.; Noordik, J.; Rakowski DuBois, M. *J. Am. Chem. Soc.*, preceding paper in this issue.

0002-7863/87/1509-0283$01.50/0