Inorg. Chem. **1996,** *35,* 3022−3030

Oxidation at a Dimolybdenum(V) Sulfur Bridge. Formation of SO and SO_2 Bridges. Facile Extrusion of SO from the SO_2 Bridge

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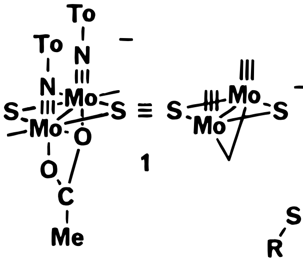
Received November 29, 1995⊗

Peroxide oxygenation of μ-thiolate−μ-sulfide Mo(V) dimer complexes of the type $[Mo_2(NAr)_2(S_2P(OEt)_2)_2(\mu\text{-}O_2CMe)(\mu\text{-}SR)(\mu\text{-}S)]$ yielded $Mo_2(\mu\text{-}SO)$ and $Mo_2(\mu\text{-}SO_2)$ complexes, demonstrating the reactivity sequence μ-S > μ-SO ≫ μ-SR. Inversion isomers of the pyramidal sulfur site in the μ-SO bridge were observed, and the pyramidicity was confirmed crystallographically. Visible light photolysis of the $Mo_2(\mu\text{-}SO_2)$ complex liberated SO from the SO_2 bridge and produced $Mo_2(\mu\text{-}O)$ compounds. Crystallography of analogous $Mo_2(\mu\text{-}S)$, $Mo_2(\mu\text{-}SO)$, $Mo_2(\mu\text{-}SO_2)$, and $Mo_2(\mu\text{-}O)$ complexes provided structural comparisons related to variations in the bridge functionality. For **2**, $Mo_2C_{31}H_{44}N_2O_6P_2S_6$: $a = 13.604(5)$ Å, $b = 15.280(4)$ Å, $c = 12.502(2)$ Å, $\alpha = 93.36(2)°$, $\beta = 112.00\ (2)°$, $\gamma = 76.01(2)°$, triclinic, $P\bar{1}$, $Z = 2$. For **3**, $Mo_2C_{31}H_{44}N_2O_7P_2S_6$: $a = 12.535(2)$ Å, $b = 25.299(9)$ Å, $c = 13.989(5)$ Å, $\beta = 99.99(2)°$, monoclinic, $P2_1/n$, $Z = 4$. For **4**, $Mo_2C_{31}H_{44}N_2O_8P_2S_6$: $a = 12.591(9)$ Å, $b = 25.34(1)$ Å, $c = 14.048(3)$ Å, $\beta = 100.79(4)°$, monoclinic, $P2_1/n$, $Z = 4$. For **5**, $Mo_2C_{31}H_{44}N_2O_7P_2S_5$: $a = 13.731(5)$ Å, $b = 19.267(4)$ Å, $c = 16.652(5)$ Å, $\beta = 104.78(3)°$, monoclinic, $P2_1/n$, $Z = 4$.

Introduction

Biological, atmospheric, and geochemical sulfur transformations involve a wide range of reactions, many of which are formal oxidation−reduction processes.[1,2] Within these natural cycles the most common oxidation reactions involve S/S or S/O bond formation. Metal ions play important roles in many of these processes, and investigations into the oxidation of sulfur ligands should therefore impact upon studies related to these natural transformations.

The oxidations of sulfur bridges in anionic imido−dithiophosphato−carboxylato−sulfidomolybdenum(V) dimers such as $[Mo_2(NTo)_2(S_2P(OEt)_2)_2(\mu\text{-}O_2CMe)(\mu\text{-}S)_2]^-$ (**1**) have been previously reported;[3,4] those reactions yielded disulfide (S−S) and halosulfide (S−X) products. (In the structure diagrams shown, dithiophosphate groups are omitted for clarity. Abbreviations for organic groups are footnoted.[5]) With an interest in the oxygenation of sulfur sites to SO_x ligands, studies of the oxidation of μ-thiolate−μ-sulfide compounds $[Mo_2(NTo)_2(S_2P(OEt)_2)_2(\mu\text{-}O_2CMe)(\mu\text{-}SR)(\mu\text{-}S)]$, **2**, were undertaken and are reported presently. These rections have yielded the dimolybdosulfoxides $[Mo_2(NTo)_2(S_2P(OEt)_2)_2(\mu\text{-}O_2CMe)(\mu\text{-}SR)(\mu\text{-}SO)]$, **3**, and the dimolybdosulfones $[Mo_2(NTo)_2(S_2P(OEt)_2)_2(\mu\text{-}O_2CMe)(\mu\text{-}SR)(\mu\text{-}SO_2)]$, **4**. Taken together, these constitute a rare example[6,7] of the ability to isolate both μ-SO and μ-SO_2 products from the oxidation of a sulfide bridge. These complexes are also high-valent, d^1 systems; this is in distinct contrast to prior μ-SO and μ-SO_2 compounds which were predominantly organometallic, low valent, and of high d-electron count.[8−11]



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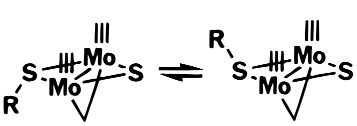

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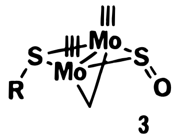

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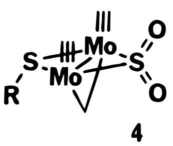

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During the course of these studies, the facile photoextrusion of SO from the SO_2 bridge was also observed, and these results are included herein.

Experimental Section

Reactions and manipulations were conducted open to air except as noted. $[Mo_2(NTo)_2(S_2P(OEt)_2)_2(O_2CMe)(SBz)(S)]$, **2** (R = Bz),[3] and $[Mo(NTo)(S_2P(OEt)_2)S]_4$[12] were prepared as previously reported. All commercial reagents were used as received. Silica gel for chromatography was 100−200 mesh (DAVISIL grade 644). Peracetic acid

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⊗ Abstract published in *Advance ACS Abstracts*, April 15, 1996.

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(5) Abbreviations used in this paper: Me, methyl; Et, ethyl; *t*-Bu, *tert*-butyl; Bz, benzyl; Ar, aryl; Ph, phenyl; To, *p*-tolyl; Cp, cyclopentadienyl; dppm, bis(diphenylphosphino)methane.

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S0020-1669(95)01518-7 CCC: $12.00

was commercial grade in dilute $MeCO_2H$; it assayed to be 47% total peroxide. *m*-Chloroperbenzoic acid was commercial grade which also contained *m*-chlorobenzoic acid; it assayed to be 84%. The peroxide assays were conducted by reaction with excess Ph_3P in $CDCl_3$ and quantitation by ^{31}P NMR spectroscopy; this method gave total peroxide equivalents and did not distinguish, for example, $MeCO_3H$ from H_2O_2, which was also present in the commercial reagent.

$^{31}P\{^1H\}$ and ^1H NMR spectra were obtained in $CDCl_3$ (except as noted) on a Varian XL-300 spectrometer (which was updated during this work with an Inova300 console) at 121 and 300 MHz or a Bruker AMX-500 spectrometer at 202 and 500 MHz; results are reported as downfield shifts from external 85% H_3PO_4 and internal Me_4Si. In the NMR data listed below, values for minor invertomers are given in parentheses where these could be distinguished; when four isomers were distinguishable, the major isomer is A, while the minor isomers are B−D (least abundant). Infrared data were obtained using a Mattson Galaxy Series FTIR 5000 spectrometer by diffuse reflectance on KBr powder mixtures. GC-MS data were obtained on a Hewlett-Packard 5890 Series II gas chromatograph with a Hewlett-Packard 5971A mass selective detector. Galbraith Laboratories, Inc. (Knoxville, TN) performed the elemental analyses.

Routine photolyses were conducted in an apparatus of local construction which consisted of four 20-W, 23-in., cool white fluorescent lamps. The lamps were arranged parallel and vertical, with the internal center of each lamp lying at the corners of a rectangle of dimensions 6.5 cm × 7.5 cm. The solution to be photolyzed was held centrally within the four lamps and parallel to the lamps; vertically, the solution center was near mid-length of the lamps.

All syntheses of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2(O_2CMe)(SR)(SO)]$, **3**, and of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2(O_2CMe)(SR)(SO_2)]$, **4**, were conducted under red light conditions.[3] Except during actual photolysis, these compounds were stored in the dark and were handled under red light conditions, even as solids.

$[Mo_2(NTo)_2(S_2P(OEt)_2)_2(O_2CMe)(SBz)(SO)]$, 3 (R = Bz). $[Mo_2(NTo)_2(S_2P(OEt)_2)_2(O_2CMe)(SBz)(S)]$, **2** (R = Bz; 0.3947 g, 0.400 mmol), and *m*-chloroperbenzoic acid (84%; 0.0869 g, 0.42 mmol) were dissolved separately in 4 mL of CH_2Cl_2, and both solutions were cooled in a CH_2Cl_2 slush bath (prepared from liquid nitrogen and CH_2Cl_2) for 0.5 h. Under red light, the solution of *m*-chloroperbenzoic acid was quickly poured into the solution of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2(O_2CMe)(SBz)(S)]$ while being stirred. Additional CH_2Cl_2 (4 mL) at the same temperature was used for complete transfer. When the slush bath warmed to −20 °C, the mixture was taken out of the bath and rotavapped. The residue was redissolved in a small volume of MeCN, and this was chromatographed on silica gel using MeCN as eluent. A flashlight was occasionally used to check the progress. The second colored band was collected, rotavapped, and redissolved in tetrahydrofuran (THF) (1 mL). $EtOH:H_2O$ (2:5, 11.5 mL) was used for precipitation. The slurry was filtered, and the product was vacuum dried, giving a dark-green powder (0.3032 g, 75%). ^{31}P NMR (ppm): (114.6, D), (114.2, C), (114.1, B), 113.6 (A). ^1H NMR (ppm): (7.71 br), 7.63 d (A), 7.48 t (A), 7.38 m (A), Bz−H; (6.86 br, D), (6.77 br, C), 6.56 d (A), 6.41 d (A), To−H; (4.43 s, B), 3.59 s (A), (3.29 s, C), $Bz-CH_2$; 3.9−4.4 m, $POCH_2$; (2.12 s, B), 2.04 s (A), $To-CH_3$; 1.57 s (A), O_2CCH_3; 1.38 t (A), 1.18 t (A), $POCCH_3$. Invertomer distribution: 67% A, 20% B, 10% C, 3% D. Selected IR bands (cm^{-1}): 1536 m, 1452 s, 1011 vs, 968 vs, 816 m, 791 m.

$[Mo_2(NTo)_2(S_2P(OEt)_2)_2(O_2CMe)(SBz)(SO_2)]$, 4 (R = Bz). Under red light, $MeCO_3H$ (47%; 63 μL, 0.44 mmol) was added to a solution of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2(O_2CMe)(SBz)(S)]$, **2**, (R = Bz; 0.0987 g, 0.100 mmol), in THF (1 mL). After being stirred for 1 min, the solution was treated with 1:1 $EtOH:H_2O$ (4 mL). The resulting precipitate was filtered and vacuum dried, giving a brown crystalline solid (0.0875 g, 84%). ^{31}P NMR (ppm): (112.2), 112.0. ^1H NMR (ppm): (7.74 br), 7.64 m, 7.50 t, 7.40 m, Bz−H; (6.94 br), 6.80 d, 6.39 d, To−H; (4.76 br), 3.55 s, $Bz-CH_2$; 3.9−4.3 m, $POCH_2$; 2.04 s, $To-CH_3$; 1.42 s, O_2CCH_3; 1.37 t, 1.16 t, $POCCH_3$. Invertomer ratio: 5. Selected IR bands (cm^{-1}): 1534 m, 1456 s, 1208 m, 1051 vs, 1011 vs, 968 s, 818 m, 793 m.

$[Mo_2(NTo)_2(S_2P(OEt)_2)_2(O_2CMe)(SBz)(O)]$, 5 (R = Bz). A solution of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2(O_2CMe)(SBz)(SO_2)]$, **4** (R = Bz; 0.2600 g, 0.255 mmol), in $CHCl_3$ (10 mL) in a long tube of 5 mm i.d. was photolyzed for 1.5 h. The solution was rotavapped; the residue was redissolved in a small volume of $CHCl_3$ and chromatographed on silica gel using $CHCl_3$ as eluent. The second orange band was collected and rotavapped. The residue was dissolved in CH_2Cl_2 (1 mL), and dodecane (6 mL) was added. This mixture was left standing for 2 days for slow precipitation. The slurry was filtered; the solid was washed ($C_{12}H_{26}$) and vacuum dried, giving a red-orange powder (0.2115 g, 85%). ^{31}P NMR (ppm): 110.3, (110.2). ^1H NMR (ppm): 7.57 d, 7.45 t, 7.35 m, Bz−H; (6.95 d), (6.73 d), 6.65 d, 6.51 d, To−H; 3.9−4.3 m, $POCH_2$; 3.54 s, $Bz-CH_2$; (2.20 s), 2.09 s, $To-CH_3$; 1.50 s, O_2CCH_3; 1.37 t, 1.21 t, $POCCH_3$. Invertomer ratio: 6.2. Selected IR bands (cm^{-1}): 1545 m, 1447 s, 1013 vs, 961 s, 816 s, 795 m.

The first band in the chromatography workup was separately identified as $[Mo_2(NTo)_2(S_2P(OEt)_2)_2(O_2CMe)(SBz)(S)]$, **2** (R = Bz).

$[Mo_2(NTo)_2(S_2P(OEt)_2)_2(O_2CMe)(SMe)(S)]$, 2 (R = Me). The synthesis follows that for **2** (R = Bz).[3] MeBr (40 mL gas, 1.6 mmol) was slowly added to a solution of $[Mo(NTo)(S_2P(OEt)_2)S]_4$ (0.8364 g, 0.500 mmol), $MeCO_2H$ (72 μL, 1.2 mmol), and Et_3N (148 μL, 1.2 mmol) in CH_2Cl_2. After being stirred for 15 min, the solution was rotavapped. The residue was dissolved in THF (10 mL). Precipitation was effected with 2:1 $EtOH:H_2O$ (30 mL), and the resulting slurry was filtered; the solid was washed (4:1 $EtOH:H_2O$) and vacuum dried to give an orange crystalline product (0.607 g, 67%). Anal. Calcd for $Mo_2C_{25}H_{40}N_2O_6P_2S_6$: C, 33.0; H, 4.4; N, 3.1. Found: C, 33.0; H, 4.3; N, 2.8. ^{31}P NMR (ppm): (115.2, 4 Hz downfield of major invertomer), 115.2. ^1H NMR (ppm): (6.71 d), (6.59 d), 6.57 d, 6.46 d, To−H; 4.0−4.3 m, $POCH_2$; (2.93 s), 2.27 s, SCH_3; (2.14 s), 2.08 s, $To-CH_3$; 1.32 t, 1.22 t, $POCCH_3$; 1.27 s, O_2CCH_3. Invertomer ratio: 5. Selected IR bands (cm^{-1}): 1545 m, 1449 s, 1011 vs, 964 s, 816 s, 797 m.

$[Mo_2(NTo)_2(S_2P(OEt)_2)_2(O_2CMe)(SMe)(SO)]$, 3 (R = Me). $[Mo_2(NTo)_2(S_2P(OEt)_2)_2(O_2CMe)(SMe)(S)]$, **2** (R = Me; 0.5900 g, 0.648 mmol), and *m*-chloroperbenzoic acid (84%; 0.1347 g, 0.656 mmol) were dissolved separately in 6.5 mL of CH_2Cl_2, and both solutions were cooled in a CH_2Cl_2 slush bath (prepared from liquid nitrogen and CH_2Cl_2) for 0.5 h. Under red light, the solution of *m*-chloroperbenzoic acid was added to the solution of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2(O_2CMe)(SMe)(S)]$ while being stirred; a rinse with CH_2Cl_2 (6.5 mL) at the same temperature was used for complete transfer. After being warmed to −20 °C, the mixture was taken out of the bath and rotavapped. The residue was redissolved in a small volume of MeCN and chromatographed on silica gel using MeCN as eluent. A flashlight was occasionally used to check the progress. The second colored band was collected, and this was rotavapped to a volume of ~20 mL. H_2O (20 mL) was added, and the solution was rotavapped until nearly all MeCN was removed. The resulting slurry was filtered. The product was vacuum dried, giving a dark green solid (0.3585 g, 60%). Anal. Calcd for $Mo_2C_{25}H_{40}N_2O_7P_2S_6$: C, 32.4; H, 4.4; N, 3.0. Found: C, 31.5; H, 4.4; N, 2.9. ^{31}P NMR (ppm): (114.7, D), (114.5, C), (114.4, B), 113.7 (A). ^1H NMR (ppm): (7.00 br, D), (6.86 br, C), (6.68 d, B), 6.57 d (A), To−H; 3.9−4.3 m, $POCH_2$; (3.28 br, D), (3.05 s, B), 2.31 s (A), SCH_3; (2.18 s, C), (2.11 s, B), 2.07 s (A), (2.02 s, D), $To-CH_3$; 1.51 s (A), (1.43 s, B), O_2CCH_3; 1.34 t (A), 1.17 t (A), $POCCH_3$. Invertomer distribution: 66% A, 20% B, 11% C, 3% D. Selected IR bands (cm^{-1}): 1532 m, 1452 s, 1011 vs, 968 vs, 816 s, 795 m.

$[Mo_2(NTo)_2(S_2P(OEt)_2)_2(O_2CMe)(SMe)(SO_2)]$, 4 (R = Me). Under red light, $MeCO_3H$ (47%; 0.25 mL, 1.8 mmol) was added to a solution of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2(O_2CMe)(SMe)(S)]$, **2** (R = Me; 0.3643 g, 0.400 mmol), in THF (4 mL). After being stirred for 1 min, the solution was treated with 1:1 $EtOH:H_2O$ (16 mL). The resulting precipitate was filtered and vacuum dried, giving a brown crystalline solid (0.3332 g, 88%). Anal. Calcd for $Mo_2C_{25}H_{40}N_2O_8P_2S_6$: C, 31.8; H, 4.3; N, 3.0; S, 20.4. Found: C, 31.8; H, 4.0; N, 2.9; S, 20.7. ^{31}P NMR (ppm): (112.8), 112.2. ^1H NMR (ppm): (6.91 d), 6.81 d, (6.48 d), 6.42 d, To−H; 3.9−4.3 m, $POCH_2$; (3.30 s), 2.32 s, SCH_3; (2.10 s), 2.06 s, $To-CH_3$; 1.36 s, O_2CCH_3; 1.34 t, 1.16 t, $POCCH_3$. Invertomer ratio: 5.5. Selected IR bands (cm^{-1}): 1535 m, 1454 s, 1209 m, 1051 vs, 1007 vs, 964 s, 816 m, 793 m.

$[Mo_2(NTo)_2(S_2P(OEt)_2)_2(O_2CMe)(SMe)(O)]$, 5 (R = Me). A solution of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2(O_2CMe)(SMe)(SO_2)]$, **4** (R = Me; 0.2400 g, 0.255 mmol), in $CHCl_3$ (10 mL) in a long tube of 5 mm i.d. was photolyzed for 1.5 h. The solution was rotavapped; the residue was redissolved in a small volume of $CHCl_3$ and chromatographed on

Table 1. Crystallographic Data

	2	**3**	**4**	**5**
formula	$Mo_2S_6P_2O_6N_2C_{31}H_{44}\cdot 0.9CH_3OH$	$Mo_2S_6P_2O_7N_2C_{31}H_{44}$	$Mo_2S_6P_2O_8N_2C_{31}H_{44}$	$Mo_2S_5P_2O_7N_2C_{31}H_{44}$
fw	1018.93	1002.89	1018.88	970.83
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	13.604 (5)	12.535 (2)	12.591 (9)	13.731 (5)
b, Å	15.280 (4)	25.299 (9)	25.34 (1)	19.267 (4)
c, Å	12.502 (2)	13.989 (5)	14.048 (3)	16.652 (5)
α, deg	93.36 (2)			
β, deg	112.00 (2)	99.99 (2)	100.79 (4)	104.78 (3)
γ, deg	76.01 (2)			
T, °C	22 (1)	23 (1)	23 (1)	23 (1)
V, Å^3	2335 (1)	4369 (2)	4403 (3)	4259 (2)
Z	2	4	4	4
λ, Å	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)	0.710 93 (Mo Kα)	0.710 73 (Mo Kα)
ρ_{calcd}, g cm^{-3}	1.45	1.52	1.54	1.51
μ, cm^{-1}	9.13	9.75	9.70	9.50
R^a	0.040	0.037	0.043	0.039
$R_w{}^b$	0.042	0.037	0.043	0.040

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

silica gel using $CHCl_3$ as eluent. The second orange band was collected and rotavapped. The residue was dissolved in CH_2Cl_2 (1 mL), and dodecane (6 mL) was added. This mixture was left standing for 2 days for slow precipitation. The slurry was filtered; the solid was washed ($C_{12}H_{26}$) and vacuum dried, giving a red-orange powder (0.2026 g, 89%). Anal. Calcd for $Mo_2C_{25}H_{40}N_2O_7P_2S_5$: C, 33.6; H, 4.5; N, 3.1; S, 17.9. Found: C, 33.9; H, 4.6; N, 2.6; S, 18.2. ^{31}P NMR (ppm): (110.6), 110.5. ^{1}H NMR (ppm): (6.95 d), (6.73 d), 6.69 d, 6.56 d, To−H; 3.9−4.3 m, $POCH_2$; (2.80 s), 2.28 s, SCH_3; (2.20 s), 2.12 s, To-CH_3; 1.45 s, O_2CCH_3; 1.34 t, 1.21 t, $POCCH_3$. Invertomer ratio: 5.0. Selected IR bands (cm^{-1}): 1547 m, 1447 s, 1013 vs, 964 s, 818 m, 793 m, 775 m.

The first band in the chromatography work-up was separately identified as $[Mo_2(NTo)_2(S_2P(OEt)_2)_2(O_2CMe)(SMe)(S)]$, **2** (R = Me).

Photolysis Reactions. Several sample procedures were as follows. For photolysis in solution, **4** (R = Me; 9.4 mg, 10.0 μmol) in $CDCl_3$ (0.4 mL) in a sealed NMR tube was photolyzed for 1.5 h. The ^{31}P NMR spectrum was then obtained.

For photolysis in the solid state, solid **4** (R = Bz; 19.8 mg, 20.0 μmol) was sealed inside an NMR tube. The sample tube and the lamps were positioned horizontally with the solid dispersed along the length of the tube. The sample was photolyzed for 3.0 h. The tube was then broken open, $CDCl_3$ was added, and the ^{31}P NMR spectrum was obtained.

For photolysis with Ph_3P present, a solution of **4** (R = Bz, 10.6 mg, 10.4 μmol) and Ph_3P (40.9 mg, 0.156 mmol) in $CDCl_3$ (0.40 mL) was photolyzed 1.5 h in a septum-capped NMR tube under N_2. The ^{31}P NMR spectrum was then obtained.

For the reaction sequence involving photolysis and then dark reaction with Ph_3P, a solution of **4** (R = Me; 9.4 mg, 10.0 μmol) in $CDCl_3$ (0.4 mL) in a septum-capped NMR tube under N_2 was photolyzed 1.5 h. A solution of Ph_3P (10.5 mg, 40 μmol) in $CDCl_3$ (0.2 mL) was then syringed into the sample under N_2. The solution was left to stand for 1 h in the dark. The ^{31}P NMR spectrum was then obtained.

Photolysis using Corning band-pass filters was conducted using an apparatus of in-house construction. Results of the photolyses using filters 3-74 (412, 423), 3-68 (530, 546), 2-63 (582, 602), and 2-58 (631, 650) were compared to a reference reaction using a 9-54 filter. For comparison, the parenthetical values listed with the filters represent wavelengths (nm) for 10 and 80% transmittance relative to the 9-54 filter. The sample of **4** (R = Bz, 10.0 μmol) in $CDCl_3$ (0.40 mL) was photolyzed directly in a quartz NMR tube for 4.0 min using filtered light from a 650-W DVY lamp; the lamp-to-tube distance was 45 cm. Under these conditions, the reference reaction reached 68% completion.

Crystallography. Crystal data and experimental details are given in Table 1. Data were collected on an Enraf-Nonius CAD4 automated diffractometer with Mo Kα radiation (graphite monochromator), using the $\omega-2\theta$ scan technique; computations utilized the teXsan crystallographic software package.[13] Cell constants and orientation matrices were obtained from least-squares refinement. Absorption corrections, secondary extinction corrections, and Lorentz and polarization corrections were applied in each case. Scattering and anomalous dispersion factors were taken from ref 14. The structures were solved by Patterson methods and expanded using Fourier techniques. In each case, hydrogen atom positions were calculated and added to the structure factor calculations with B set to $1.2B_{eq}$ of the carbon atom to which each was bonded; hydrogen atom parameters were not refined. Each structure was refined by full-matrix, least-squares methods, minimizing $\Sigma w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F)]^{-1}$.

For **2** (R = Bz), an orange block crystal from CH_2Cl_2/MeOH measuring 0.46 × 0.40 × 0.36 mm was used for data collection. Three representative reflections were measured every 60 min; the standards decreased by 6.0% over the course of data collection, and a linear correction factor was applied. A partial, disordered methanol was present and was modeled as three C−O groups, each of 30% occupancy; hydrogens of the methanol were excluded.

For **3** (R = Bz), a green-black block crystal from CH_2Cl_2/*n*-hexane measuring 0.45 × 0.35 × 0.30 mm was used for data collection. Three representative reflections were measured every 60 min; no decay corrections were applied.

For **4** (R = Bz), an orange block crystal from C_6H_5Cl/*n*-dodecane measuring 0.40 × 0.30 × 0.30 mm was used for data collection. Three representative reflections were measured every 60 min; the standards decreased by 9.8% over the course of data collection, and a linear correction factor was applied.

For **5** (R = Bz), an orange block crystal from CH_2Cl_2/*n*-hexane measuring 0.55 × 0.50 × 0.41 mm was used for data collection. Three representative reflections were measured every 60 min; no decay corrections were applied. Several dithiophosphate ethyl groups were disordered and were modeled as follows: C(17)−C(18) was modeled as two groups in the ratio of 0.70:0.30; C(20) was modeled as two sites in the ratio of 0.75:0.25; C(21)−C(22) was modeled as two half-occupancy groups.

Selected results are given in Tables 2 and 3, and the structures are shown in Figures 1−4.

Results

For simplicity, the $[Mo_2(NTo)_2(S_2P(OEt)_2)_2(\mu\text{-}O_2CMe)(\mu\text{-}SR)(\mu\text{-}SO_x)]$ dimer groups will be designated $RSMo_2SO_x$, which indicates the thiolate bridge, the dimetal core, and the SO_x bridge; other ligands are invariant in the compounds described herein. Although various bonding modes are known for SO and SO_2,[6−11] the μ-SO and μ-SO_2 ligands described herein are μ_2-$\eta^1(S)$ unless otherwise specified.

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(13) *teXsan: Crystal Structure Analysis Package;* Molecular Structure Corp.: The Woodlands, TX, 1985, 1992.

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Table 2. Selected Bond Lengths (Å)

	2	3	4	5
Mo(1)−Mo(2)	2.8315 (9)	2.8689 (6)	2.9440 (6)	2.6688 (6)
Mo(1)−S(1)	2.443 (2)	2.441 (1)	2.452 (1)	2.444 (1)
Mo(1)−S(2)/O(7)[a]	2.342 (2)	2.428 (1)	2.427 (1)	1.942 (3)
Mo(1)−S(3)	2.518 (2)	2.514 (2)	2.502 (2)	2.529 (2)
Mo(1)−S(4)	2.548 (2)	2.523 (2)	2.505 (2)	2.541 (2)
Mo(1)−O(1)	2.206 (4)	2.174 (3)	2.184 (3)	2.201 (3)
Mo(1)−N(1)	1.723 (4)	1.726 (4)	1.733 (4)	1.741 (4)
Mo(2)−S(1)	2.443 (2)	2.447 (1)	2.457 (1)	2.447 (2)
Mo(2)−S(2)/O(7)[a]	2.347 (2)	2.429 (1)	2.420 (1)	1.941 (3)
Mo(2)−S(5)	2.519 (2)	2.514 (2)	2.502 (2)	2.537 (2)
Mo(2)−S(6)	2.538 (2)	2.523 (2)	2.507 (2)	2.560 (2)
Mo(2)−O(2)	2.194 (4)	2.165 (3)	2.175 (3)	2.206 (3)
Mo(2)−N(2)	1.719 (4)	1.726 (4)	1.725 (4)	1.726 (4)
S(1)···S(2)/O(7)[a]	3.860 (3)	3.937 (4)	3.885 (3)	3.456 (3)
S(1)−C(25)	1.852 (6)	1.856 (4)	1.840 (5)	1.865 (5)
S(3)−P(1)	1.986 (3)	1.989 (2)	1.987 (2)	1.996 (2)
S(4)−P(1)	1.990 (2)	1.993 (2)	1.995 (2)	1.989 (2)
S(5)−P(2)	1.988 (3)	1.989 (2)	1.993 (2)	1.994 (2)
S(6)−P(2)	1.991 (3)	1.992 (2)	1.989 (2)	1.990 (3)
O(1)−C(15)	1.254 (7)	1.247 (6)	1.262 (6)	1.264 (6)
O(2)−C(15)	1.258 (7)	1.268 (5)	1.245 (6)	1.253 (6)
N(1)−C(1)	1.380 (6)	1.387 (5)	1.384 (5)	1.376 (6)
N(2)−C(8)	1.378 (6)	1.390 (5)	1.385 (5)	1.389 (6)
S(2)−O(7)		1.515 (4)	1.467 (3)	
S(2)−O(8)			1.469 (4)	

[a] The bridge atom is S(2) for compounds **2**−**4** and O(7) for compound **5**.

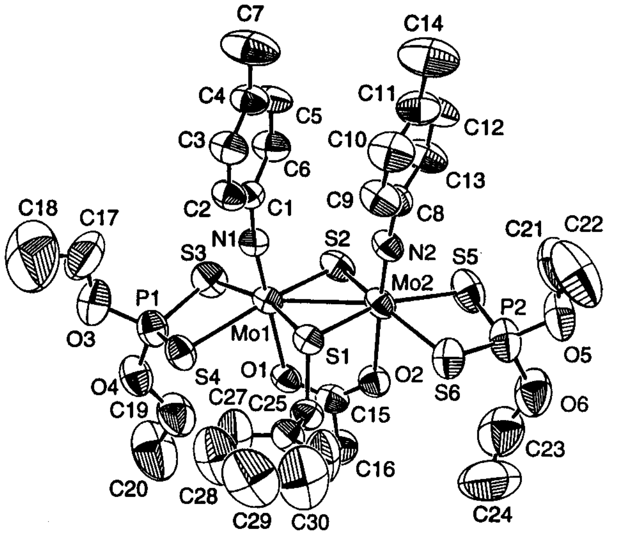
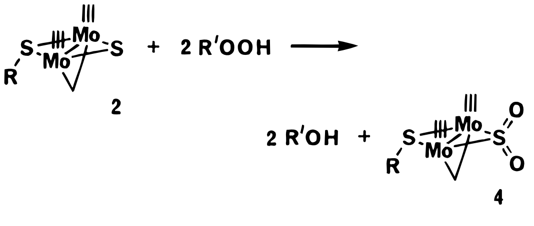


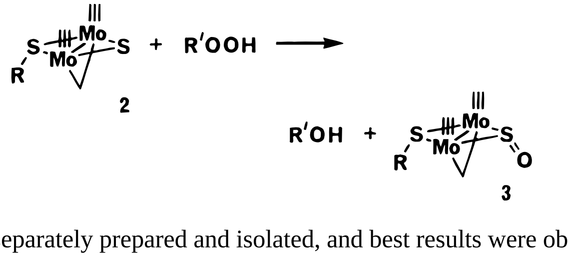
Figure 1. ORTEP view of [Mo$_2$(NTo)$_2$(S$_2$P(OEt)$_2$)$_2$(O$_2$CMe)(SBz)(S)], **2** (R = Bz).

The oxidation of the sulfide bridge of RSMo$_2$S, **2**, was investigated for R = Bz and Me. Using excess MeCO$_3$H, NMR spectra revealed quantitative oxygenation to μ-SO$_2$ products RSMo$_2$SO$_2$, **4**, eq 1, and high yields could be isolated with this



(1)

reagent. High solution yields were also observed using *m*-chloroperbenzoic acid, H$_2$O$_2$/HBF$_4$, or *t*-BuOOH/HBF$_4$. H$_2$O$_2$ or *t*-BuOOH alone gave no reaction, indicating the need for some acid catalysis. In a study by NMR spectroscopy using incremental additions of MeCO$_3$H, the formation of BzSMo$_2$SO$_2$, **4**, from sulfide BzSMo$_2$S, **2**, clearly proceeded by way of SO-bridged BzSMo$_2$SO, **3**, eq 2. This compound could be



(2)

separately prepared and isolated, and best results were obtained using near-stoichiometric amounts of *m*-chloroperbenzoic acid and low temperature (−95 °C). Higher temperatures generally gave more μ-SO$_2$ product. The ability to isolate μ-SO and μ-SO$_2$ products from oxidation of dimetal μ-S sites has limited precedence: [Mn$_2$Cp$_2$(CO)$_4$(μ-S)][6] and [Pd$_2$Cl$_2$(μ-dppm)$_2$(μ-S)][7] were successful, but others were not.[15−18] The more common parallel is with organic sulfide/sulfoxide/sulfone chemistry.[19,20]

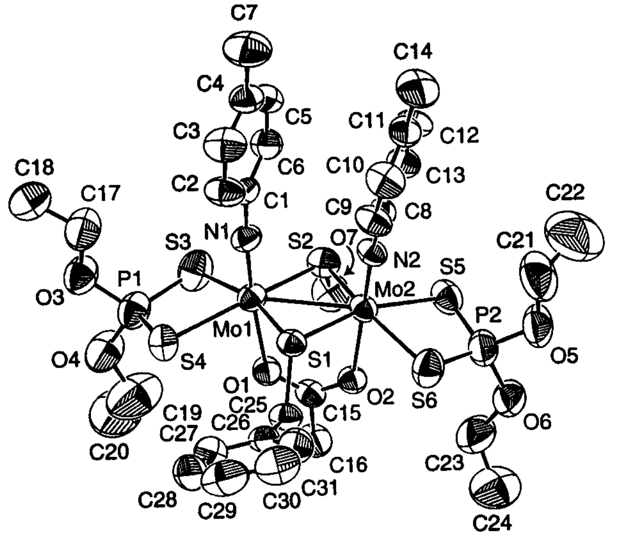


Figure 2. ORTEP view of [Mo$_2$(NTo)$_2$(S$_2$P(OEt)$_2$)$_2$(O$_2$CMe)(SBz)(SO)], **3** (R = Bz). This view clearly shows the pyramidicity of S(2).

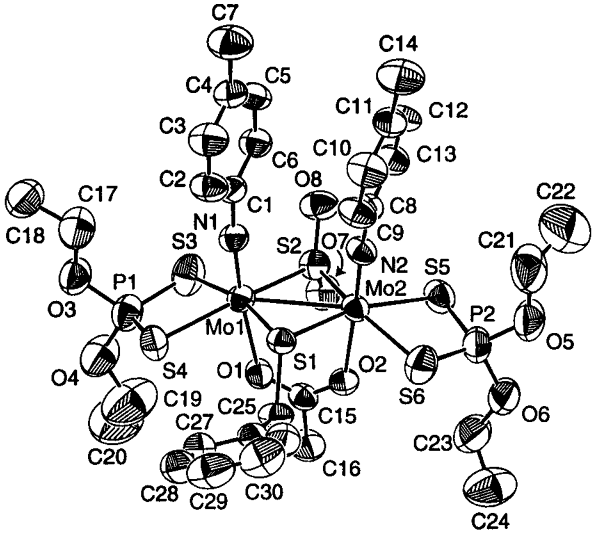


Figure 3. ORTEP view of [Mo$_2$(NTo)$_2$(S$_2$P(OEt)$_2$)$_2$(O$_2$CMe)(SBz)(SO$_2$)], **4** (R = Bz).

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Table 3. Selected Bond Angles (deg)

	2	**3**	**4**	**5**
S(1)−Mo(1)−S(2)/O(7)[a]	107.52 (6)	107.97 (5)	105.70 (5)	103.4 (1)
S(1)−Mo(1)−S(4)	88.74 (5)	88.71 (5)	90.17 (5)	89.28 (5)
S(2)/O(7)−Mo(1)−S(3)[a]	83.91 (6)	82.68 (5)	83.01 (5)	85.93 (9)
S(3)−Mo(1)−S(4)	77.86 (6)	78.85 (5)	79.28 (5)	78.52 (5)
O(1)−Mo(1)−N(1)	173.8 (2)	175.0 (2)	174.2 (2)	174.8 (2)
Mo(2)−Mo(1)−N(1)	96.3 (1)	94.0 (1)	94.3 (1)	97.5 (1)
Mo(2)−Mo(1)−O(1)	81.8 (1)	81.14 (9)	80.10 (9)	83.61 (9)
S(1)−Mo(2)−S(2)/O(7)[a]	107.35 (6)	107.74 (5)	105.76 (5)	103.3 (1)
S(1)−Mo(2)−S(6)	87.63 (6)	89.30 (5)	91.04 (5)	90.18 (5)
S(2)/O(7)−Mo(2)−S(5)[a]	84.62 (6)	82.32 (5)	82.24 (5)	85.8 (1)
S(5)−Mo(2)−S(6)	77.97 (7)	78.50 (5)	78.93 (6)	78.18 (5)
O(2)−Mo(2)−N(2)	173.7 (2)	178.6 (1)	177.2 (2)	176.2 (2)
Mo(1)−Mo(2)−N(2)	101.1 (2)	98.5 (1)	97.5 (1)	98.9 (1)
Mo(1)−Mo(2)−O(2)	82.3 (1)	81.33 (9)	80.42 (9)	84.88 (9)
Mo(1)−S(1)−Mo(2)	70.83 (4)	71.87 (4)	73.70 (4)	66.13 (4)
Mo(1)−S(1)−C(25)	111.1 (2)	111.2 (2)	112.2 (2)	109.8 (2)
Mo(2)−S(1)−C(25)	110.8 (2)	110.8 (2)	111.9 (2)	110.4 (2)
Mo(1)−S(2)/O(7)−Mo(2)[a]	74.30 (5)	72.41 (4)	74.80 (4)	86.8 (1)
Mo(1)−S(3)−P(1)	88.27 (8)	87.28 (7)	87.09 (7)	87.17 (7)
Mo(1)−S(4)−P(1)	87.32 (8)	86.95 (7)	86.83 (7)	86.97 (7)
Mo(2)−S(5)−P(2)	88.15 (9)	87.72 (7)	87.46 (7)	86.93 (7)
Mo(2)−S(6)−P(2)	87.6 (1)	87.38 (7)	87.42 (8)	86.50 (7)
S(3)−P(1)−S(4)	106.4 (1)	106.9 (1)	106.7 (1)	107.27 (9)
S(5)−P(2)−S(6)	106.2 (1)	106.4 (1)	106.2 (1)	107.8 (1)
Mo(1)−O(1)−C(15)	125.4 (4)	127.2 (3)	127.6 (3)	122.9 (3)
Mo(2)−O(2)−C(15)	125.3 (4)	126.7 (3)	128.0 (3)	121.7 (3)
Mo(1)−N(1)−C(1)	172.0 (4)	175.6 (4)	175.1 (4)	174.9 (4)
Mo(2)−N(2)−C(8)	176.1 (4)	172.3 (3)	174.4 (4)	171.8 (4)
Mo(1)−S(2)−O(7)		113.7 (2)	115.3 (2)	
Mo(2)−S(2)−O(7)		113.1 (2)	114.8 (2)	
Mo(1)−S(2)−O(8)			115.3 (2)	
Mo(2)−S(2)−O(8)			116.1 (2)	
O(7)−S(2)−O(8)			114.8 (2)	

[a] The bridge atom is S(2) for compounds **2**−**4**, and O(7) for compound **5**.

The isolated $RSMo_2SO$, **3**, products were not very stable, and decomposition was evident within a week of cold storage in the dark. Solution samples decomposed within days even under N_2. The $RSMo_2SO_2$, **4**, derivatives were indefinitely stable in the dark in air-exposed solution; these were, however, considerably light-sensitive.

All products were characterized by IR spectroscopy, NMR spectroscopy (^1H and ^{31}P), and elemental analyses or X-ray crystallography. IR spectra showed absorptions which are typical for the $[Mo_2(NTo)_2(S_2P(OEt)_2)_2(\mu\text{-}O_2CMe)]$ portion.[2,21−24] In addition, $RSMo_2SO_2$ displayed ν(SO) at 1208 and 1051 cm^{-1} (R = Bz) and 1209 and 1051 cm^{-1} (R = Me); SO_2 deformation bands could also be assigned at 529 (Bz) and 526 (Me) cm^{-1}. These values are consistent with those of prior μ-SO_2 complexes.[8] The ν(SO) band for $RSMo_2SO$ was not observed for either R = Me or Bz; the band was expected at lower wavenumbers and was presumed to be buried under the intense dithiophosphate bands in the vicinity. Values for ν(SO) in prior μ-SO complexes extend from 883 to 1100 cm^{-1}.[6,7,16,25−30] For those cases where analogous $M_2(\mu\text{-}SO)$ and $M_2(\mu\text{-}SO_2)$ complexes have been reported,[6,7,16,30] ν(SO) is of lower energy for μ-SO than for μ-SO_2 bridges. This parallels the pattern for organic sulfoxides and sulfones.[19,31,32]

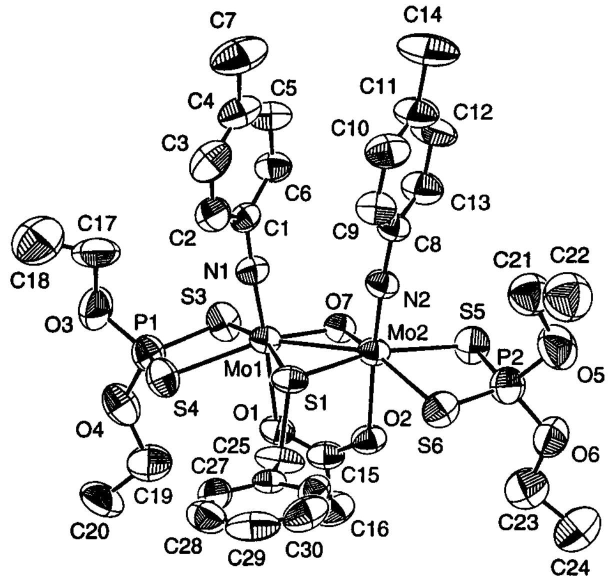

Figure 4. ORTEP view of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2(O_2CMe)(SBz)(O)]$, **5** (R = Bz).

^1H and ^{31}P NMR spectra revealed all appropriate resonances and demonstrated the presence of conformational isomers associated with inversion at the thiolate sulfur bridge. Sulfur

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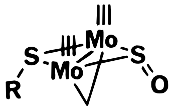
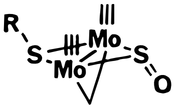
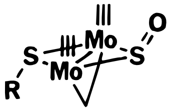
invertomers have been previously demonstrated for various μ-thiolate−μ-sulfide dimers $RSMo_2S$, **2**; these are depicted pictorially in the structure diagram for **2** (see Introduction) and are designated distal and proximal on the basis of the position of the sulfur substituent relative to the arylimido rings. Distal and proximal spectroscopic assignments are based on prior methods.[3] For $RSMo_2SO$, four isomers were observed in the NMR spectra; this indicated additional isomers associated with a pyramidal SO bridge. The isomers were spectroscopically assigned as orientations A−D. The isomer distributions in $CDCl_3$ were similar for both R = Me (66% A, 20% B, 11% C, and 3% D) and R = Bz (67% A, 20% B, 10% C, and 3% D). The distal/proximal preference for SO invertomers was 6.4 (Me) and 6.7 (Bz), while the ratio for SR invertomers was 3.5 (Me) and 3.4 (Bz). In $(CD_3)_2CO$, the isomer distributions were 54% A, 22% B, 17% C, and 7% D for R = Me and 59% A, 21% B, 15% C, and 5% D for R = Bz; the distal/proximal ratios were 3.1 (Me) and 4.2 (Bz) for SO invertomers and 2.5 (Me) and 3.0 (Bz) for SR invertomers. (The spectra showed good consistency for the ratio measurements which were believed valid within ±0.5.) Thus, the SO ratio was more sensitive to solvent than the SR ratio. Attempts to examine inversion ratios in other solvents were thwarted by poor solubility or inadequate separation of isomer resonances.



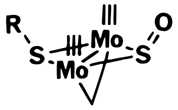
3A



3B

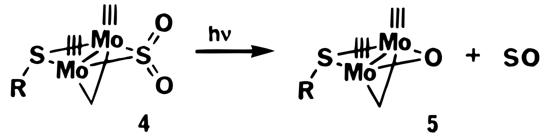


3C



3D

Photochemistry. The $RSMo_2SO_2$, **4**, products are modestly sensitive to normal lighting in solution and in the solid state, and samples were handled under red light. Direct photolysis of $MeSMo_2SO_2$ in $CDCl_3$ in a sealed tube for 1.5 h using fluorescent lights produced 11% of the sulfide $MeSMo_2S$, **2**, and 89% of a new product. Sometimes traces (<2%) of a third product could be observed, but this product was never identified. Similar results were obtained for photolysis in air-exposed solution and for photolysis of $BzSMo_2SO_2$. The major photoproduct could be isolated from larger scale reactions, but this defied spectroscopic identification. X-ray crystallography was necessary for definitive identification (see below), and the compound proved to be oxo-bridged $RSMo_2O$, **5** (R = Me or Bz). This suggested the loss of one formal equivalent of SO during the reaction, eq 3.

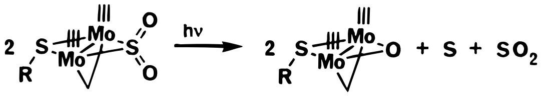


(3)

4 **5**

Although intermolecular pathways could be envisioned, a unimolecular mechanism for extrusion of free SO was demonstrated through several studies, some of which employed Ph_3P.[33] As a control, there was no reaction of $BzSMo_2SO_2$ with Ph_3P in the dark, even after 5 days. Photolysis of $RSMo_2SO_2$ (R = Bz or Me) for 1.5 h in the presence of 15- or 16-fold Ph_3P gave clean production of the oxide $RSMo_2O$, **5**, with no formation of the sulfide $RSMo_2S$, **2**. One equivalent of Ph_3PS and 1 equiv of Ph_3PO were also obtained. These results represented complete reaction as per eq 3 with quantitative interception of SO by Ph_3P.

When the photolysis and phosphine steps were separated, the results clearly differed. Photolysis of $MeSMo_2SO_2$ alone in $CDCl_3$ followed afterward by treatment with 4 equiv of Ph_3P in the dark yielded 89% oxide $MeSMo_2O$ and 10% sulfide $MeSMo_2S$, analogous to the cases of $RSMo_2SO_2$ as first indicated above. In addition, a sizable amount of Ph_3PS was observed, but only a trace (<1%) of Ph_3PO was present. In a separate experiment, the vapor phase was sampled after photolysis and SO_2 was identified by GC-MS analysis. These results indicated that eq 3 was yet the major and initial reaction, but this was followed by the characteristic disproportionation[34,35] of SO to S + SO_2, as given overall by eq 4. Post-addition of Ph_3P produced Ph_3PS from reaction with elemental sulfur, but not with SO_2. (Reaction of Ph_3P with SO_2 is not significant at room temperature without a catalyst.[36])



(4)

4 **5**

The formation of some sulfide $RSMo_2S$, **2**, in these reactions indicated that a second, minor pathway also existed for the fate of SO. This minor route involved SO or one of its disproportionation intermediates acting as a reducing agent for unreacted $RSMo_2SO_2$ to give $RSMo_2S$; this yielded more SO_2 and less elemental sulfur as predicted for eq 4 alone. In the photolysis of $MeSMo_2SO_2$ followed afterward by addition of Ph_3P, the observed amount of Ph_3PS corresponded to the observed distribution of $MeSMo_2S$, **2**, and $MeSMo_2O$, **5**, as calculated for these two pathways. The reduction involved oxygen abstraction and implied the intermediacy of $RSMo_2SO$. This compound was never observed, however, which therefore required that its own reduction to $RSMo_2S$ was fast. This was tested by photolyzing $BzSMo_2SO_2$ in the presence of $MeSMo_2SO$ (10 mol %): complete conversion of $MeSMo_2SO$ to $MeSMo_2S$ was realized before all $BzSMo_2SO_2$ had reacted. This was true despite the sluggish reactivity of $RSMo_2SO$ by itself (see below). Thus, SO (or one of its disproportionation intermediates) was indeed abstracting oxygen from $RSMo_2SO$ in a facile process.

The photolysis reaction was also investigated in the solid state. Photolysis of solid $BzSMo_2SO_2$ for 3 h produced 91% oxide $BzSMo_2O$ and 8% sulfide $BzSMo_2S$. The results were strongly indicative of a unimolecular extrusion of free SO: crystallography of $BzSMo_2SO_2$ revealed no close contacts which could suggest an intermolecular process in the solid state.

Since fluorescent lights provide visible and some UV radiation, an attempt was made to estimate the spectral region for the photoextrusion. Filter studies were conducted for solution photolysis of $BzSMo_2SO_2$ utilizing visible-cutoff filters; the reactions were compared to a reference using a 9-54 filter

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which transmits well below 300 nm. Photolysis using a 3-74 filter gave a slight (~10%) decrease in reaction, while 3-68 and 2-63 filters slowed the reaction substantially, ~50 and ~80%, respectively. A 2-58 filter eliminated the reaction completely. These results clearly showed the photolysis to be a visible light process and suggested that the photolysis band was in a region near 500 nm. The UV−vis spectrum of $BzSMo_2SO_2$ revealed a weak band at ~550 nm ($\epsilon = 140\ M^{-1}\ cm^{-1}$) and an inflection at ~470 nm ($\epsilon = 1010\ M^{-1}\ cm^{-1}$); these rode the tails of strong absorptions at higher energies and were not well-resolved. By comparison, UV−vis spectra of $BzSMo_2S$, $BzSMo_2SO_2$, and $BzSMo_2O$ revealed only one band in this region at 496 nm ($\epsilon = 1560\ M^{-1}\ cm^{-1}$), 578 nm ($\epsilon = 381\ M^{-1}\ cm^{-1}$), and ~520 nm ($\epsilon = 290\ M^{-1}\ cm^{-1}$), respectively; these, too, lay on higher energy absorption tails.

The μ-SO complexes were photoreactive, but very weakly: the process was extremely slow and was incomplete after 48 h. In all cases, the sulfide $BzSMo_2S$ was obtained, but other products were also observed, none of which could be identified. Reactions incorporating Ph_3P produced variable amounts of Ph_3PO and Ph_3PS, but $BzSMo_2O$ was not observed; this suggested other modes of sulfur release from dimer components. Overall, the results did not provide sufficient product accountability for useful conclusions.

Crystal Structures. The crystal structures of $BzSMo_2SO$ and of $BzSMo_2SO_2$ were undertaken to more fully characterize the bridge units. The structure of $BzSMo_2SO$ is particularly valuable since the μ-SO linkage is not well-characterized crystallographically: only three structures were located in the literature, and two of these were disordered within the SO unit.[6,7,29] The structure of oxide $BzSMo_2O$ was undertaken for definitive identification, as indicated above. With that of $BzSMo_2S$, the crystal structures herein provide an interesting comparison of μ-S, μ-SO, μ-SO_2, and μ-O units within otherwise identical complexes.

The results are presented for the Mo_2SO and Mo_2SO_2 features and then for the comparison of the four compounds as a whole. All structures are shown in Figures 1−4. Selected metrical results are listed in Tables 2 and 3.

The SO bridge is revealed in the structure of $BzSMo_2SO$ to be a symmetric, pyramidal Mo_2SO unit, consistent with the observation of invertomers in solution. The sum of the angles at S(2) is 299.2(5)°; this can be compared to the sum of 293.9(5)° for the thiolate sulfur bridge, S(1). O(7) and the benzyl group are in distal orientations, consistent with the major solution isomer. The S(2)−O(7) bond length is 1.515(4) Å; this is longer than SO itself (1.481 Å[34]) and longer than the SO bond of organic sulfoxides (typical range, 1.47−1.49 Å[37,38]) but still much shorter than the sum of single bond radii (1.70 Å[39]). Any comparison to other μ-SO complexes is very limited. The crystal structures for $[Pd_2Cl_2(dppm)_2(SO)]$[7] and analogous $[Ni_2Cl_2(dppm)_2(SO)]$[29] revealed pyramidal M_2SO units, but both were disordered in the location of the O atom with respect to the two possible pyramidal orientations. The crystal structure of $[Cp_2Mn_2(CO)_4(SO)]$[6] was not disordered, but the Mn_2SO group was planar and was therefore incapable of that disorder. The planar SO bond length in $[Cp_2Mn_2(CO)_4(SO)]$ was 1.504(4) Å, similar to that for pyramidal SO in the present structure. The lack of disorder in $BzSMo_2SO$ can be attributed to the gross inequivalence of the two orientations, as reflected also in the solution isomer distribution. The $S(2)Mo_2$ angle in $BzSMo_2SO$ is 72.41(4)° and is much smaller than the range of 90.4(3)−130.78(7)° for SM_2 angles in the three complexes cited; none of the others, however, was a metal−metal bonded system.

The structure of $BzSMo_2SO_2$ clearly reveals the SO_2 bridge with perpendicular SO_2 and Mo_2S groups. The SO_2 angle is 114.6(2)°, and the $S(2)Mo_2$ angle is 74.80(4)°. The SO bond lengths are identical: 1.466(4) and 1.465(4) Å. These are longer than the bonds of SO_2 itself (1.431 Å[40]) but similar to SO bond lengths in organic sulfones (typical range, 1.41−1.47 Å[37,38]). The SO bonds of $BzSMo_2SO_2$ are shorter than that in the above $BzSMo_2SO$ complex; this is in direct parallel to the pattern of shorter SO bonds in sulfones than in sulfoxides.[37,38] Direct SO/SO_2 comparisons using other metallovariants are limited due to the lack of μ-SO structures, although both $[Pd_2Cl_2(dppm)_2(SO_x)]$ $x = 1$ (disordered)[7] and 2[15] have been reported. Comparisons can be made, however, between the Mo_2SO_2 structural features of $BzSMo_2SO_2$ and those of other M_2SO_2 systems. Ten crystal structures of dinuclear complexes with equivalent, metal−metal bonded sites have been previously reported;[41−50] one of these was a lower-valent molybdenum complex, $[Mo_2(CN)_8(S_2)(SO_2)]^{4-}$.[45] The SO bond lengths and the SM_2 angle in $BzSMo_2SO_2$ are well within the ranges, 1.44(1)−1.495(6) Å and 69.6(1)−79.84(7)°, respectively, of those prior ten structures. The M−S bond lengths of $BzSMo_2SO_2$ (2.427(1), 2.420(1) Å), however, are long compared to the prior range of 2.169(1)−2.369(8) Å. The SO_2 angle in $BzSMo_2SO_2$ is at the wide end of the range of 107.5(3)−114.3(2)°. If the structural pool is extended to SO_2-bridged dimers with inequivalent metal sites (four more structures[30,51,52]), then only $[(Me_5Cp)Ni(SO_2)(CO)_3W(MeCp)]$[52] exceeds $BzSMo_2SO_2$ in M−S bond length (2.441(1) Å for W−S) and only $[(Et_3P)BrPd(SO_2)PdCp(Et_3P)]$[51] exceeds $BzSMo_2SO_2$ in SO_2 angle (116.0(1)°).

The results of the comparison of the four structures reported herein are now described. The structure of μ-thiolate−μ-sulfide $BzSMo_2S$ is considered the reference structure; it is similar to those of related μ-sulfide complexes with a perthiolate (RSS^-) bridge, $EtSSMo_2S$,[53] a thiohydroxylamide (H_2NS^-) bridge, H_2NSMo_2S,[24] and, a thiooximate ($RCH{=}NS^-$) bridge, $Me_3CCHNSMo_2S$.[24] A few common features are as follows. The imido linkages are linear, and the acetate ligand bridges symmetrically. The SMo_2S cores are nearly planar; for

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$BzSMo_2S$ the dihedral angle for MoS_2 planes is 179.7(1)°. Metal bonds to tricoordinate S(1) are longer than those to sulfide S(2); this has been attributed to π effects.[54] The Mo−S(dithiophosphate) bond lengths are inversely correlated to Mo−S(bridge) bond lengths, demonstrating a greater trans influence for the sulfide bridge, S(2), than for the functionalized sulfur bridge, S(1).

Generalities for the present four compounds include linear imido groups, symmetric acetate bridges, and nearly planar SMo_2S cores, but Mo−S(2) bond lengths are substantially affected. In all compounds, the benzyl thiolate group is in the distal orientation, corresponding to the major solution isomer.

Structural changes associated with the conversion of μ-S to μ-SO reveal an expansion of the SMo_2S core. The Mo−Mo bond lengthens and S(2) moves out; the latter is evidenced by longer Mo−S(2) bonds and a larger cross-core S(1)···S(2) distance while Mo−S(1) bond lengths are unchanged. Some coligand-to-metal bond lengths decrease: Mo−O(acetate) bond lengths decrease and Mo−S(dithiophosphate) bonds trans to SO shorten. The latter indicates a weakened trans influence for SO. The results overall are consistent with reduced donating properties of SO vs S, which relaxes the SMo_2S core and shortens some coligand distances. The SMo_2S core remains planar, with a dihedral angle of 178.9(1)° for MoS_2 planes.

These trends are not consistently maintained on proceeding to the SO_2-bridged structure, which renders interpretation difficult. The Mo−Mo bond lengthens substantially, but the cross-core S(1)···S(2) distance shortens and is now intermediate to those in the μ-S and μ-SO structures. The Mo−S(2) bond lengths involving SO_2 remain the same as for SO. The thiolate Mo−S(1) bond lengths are modestly longer in $BzSMo_2SO_2$. The MoS_2 dihedral angle is 177.9(1)°. All Mo-S(dithiophosphate) bond lengths in $BzSMo_2SO_2$ are at least slightly contracted, and all are virtually equal, which indicates that there is no trans influence of μ-SO_2 relative to that of μ-SBz.

In this comparison of μ-S, μ-SO, and μ-SO_2 structures, some reference can be made to the series $[Pd_2Cl_2(dppm)_2(SO_x)]$, $x = 0-2$,[7,15] although, as noted above, these were not metal−metal bonded complexes and the SO structure was disordered. Similar to the case of the present series, some structural features for the Pd complexes fit a trend, while others were inconsistent.[7] The most notable feature for current comparison is that Pd−S bond lengths varied consistently and decreased in the series: Pd−S (2.298(5), 2.298(5) Å) > Pd−SO (2.268(8), 2.277(8) Å) > Pd−SO_2 (2.234(4), 2.241(4) Å, two independent molecules). This trend is in direct contrast to the present $BzSMo_2SO_x$ results, for which Mo−S bond lengths were the shortest with μ-S.

In the comparison of structural variations in organic sulfides, sulfoxides, and sulfones,[37] the angles at S are narrowest for sulfoxides; this pattern is also obtained in the current series for S(2).

The crystal structure of the oxide-bridged $BzSMo_2O$ reveals a gross contraction of the SMo_2O core relative to the above SMo_2S cores, as to be expected. The shortness of the Mo−O(7) bond lengths along with the much shorter Mo−Mo bond account for the greatest differences. Mo−S(1) bond lengths are again unaffected, however, and overall these remained very consistent in all four compounds. The SMo_2O core is nearly planar (MoSO dihedral angle, 173.2(1)°), albeit less planar than the SMo_2S cores in the above structures. The disparity in Mo−S(dithiophosphate) bonds indicates a greater trans influence for μ-O than for μ-SR.

Discussion

Peroxide oxygenation of the bridge sulfide within $RSMo_2S$ **2** proceeded cleanly without evidence of reaction at other ligand sites including the thiolate. When taken with the observation of the product distribution obtained with limiting peroxide equivalents, it is seen that oxygenation reactivity follows the sequence S > SO ≫ SR. Although steric factors for SBz may have blocked access to the thiolate site, these would have been much smaller for SMe. The S > SO comparison and the use of acidic peroxide reagents are consistent with a mechanism involving nucleophilic sulfur and electrophilic oxidant.[1] The sulfide bridge of complexes $RSMo_2S$, **2**, has proven somewhat electron-rich in other recent studies.[4,55]

The classical description[8,9] of the bonding of SO_2 to a metal involves neutral SO_2 acting as σ-donor and π-acceptor and a metal with a moderate or high d-electron count to allow for back-donation into the π-accepting LUMO of SO_2. In some instances, the SO_2^{2-} unit has been invoked,[18,49,56] which is the extreme of π-acidity to the point of $2e^-$ reduction of the SO_2 unit at the expense of d-electrons. While this distinction has indefinite boundaries, clearly in the present case a μ-SO_2^{2-} complex with Mo(V) (d^1) is the appropriate description, as opposed to neutral μ-SO_2 with Mo(IV) (d^2). Despite the formal distinction, structural differences within the M_2SO_2 unit are modest between $BzSMo_2SO_2$ and 14 other structures previously reported for metal−metal bonded dimers. All of the 14 other compounds were lower valent and of higher d-electron count, regardless of the formalism invoked.

By analogy, the SO^{2-} bridge is invoked for $RSMo_2SO$. Structurally, there is a clear distinction between pyramidal and planar M_2SO units, although there are too few structures of either case for useful comparison. The parallel of the dimolybdosulfoxide $RSMo_2SO$ to organic sulfoxides is evidenced by the pyramidicity of the Mo_2SO unit, the inversion isomerization at sulfur, and even the solvent effect[57] on isomer preference.

Although the emphasis of this work had been on $S/SO/SO_2$ bridge conversions, it was of interest to determine whether there would be any influence on the thiolate bridge of the dimetal core. The latter, however, proved to be very insensitive to the changes, even for the μ-O complex. The constancy of the thiolate did allow a comparison of the trans influence of the $S/SO/SO_2/O$ bridges: as determined by Mo-S(dithiophosphate) bond lengths, the structural trans influence was in the order μ-S ≥ μ-O > μ-SO ≥ μ-SO_2 = μ-SBz. The μ-S vs μ-O relationship is similar to that seen in crystal structures of dithiophosphatomolybdenum dimers containing one S and one O bridge: in some cases, Mo−S(dithiophosphate) bonds trans to μ-S are longer, while in other cases the bond lengths are similar to those trans to μ-O.[58]

The most unusual feature of the current series of complexes is the facile photoextrusion of SO from the SO_2 bridge of the dimolybdosulfones $RSMo_2SO_2$. Thermal or photolytic extrusion of SO_2 has been established from a variety of $-(SO_2)-$, units including cyclic sulfones and some M_2SO_2 complexes.[8,9,31,32,59−62]

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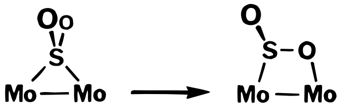
The extrusion of free SO from the $-(SO)-$ unit is known for sulfoxides.[32,60−66] Although the emphasis here is on bridge linkages, loss of SO_2 from terminal SO_2 ligands and loss of SO from terminal SO ligands have also been reported.[8,9,67,68] Despite these, the extrusion of SO from SO_2 units is not well-documented. The dissociation of SO_2 itself can give SO + O, but this is a high-energy process thermally or photolytically.[34,69] The release of SO from sulfenes ($R_2C{=}SO_2$) and cyclic sulfinate esters has been suggested in some studies.[70−72]

Although the present photoextrusion is extremely unusual, a mechanism can be proposed based on the following background. The SO_2 bridge can occur as μ_2-η^2(*S*,*O*) between two metal sites; this has been demonstrated crystallographically in $[Mo(CO)_2(PPh_3)(C_5H_5N)(SO_2)]_2$.[73] The analogy for organic compounds is sulfinate esters, RS(O)OR. Thermal and/or photochemical isomerization of cyclic sulfones to cyclic sulfinate esters has been demonstrated,[61,62] although the reverse also occurs for acyclics.[59] In the general area of metal$-SO_2$ studies, albeit not involving SO_2 as a μ_2 bridge, the terminal η^1(*S*)-SO_2 ligand of the monomeric complex $[Ru(NH_3)_4Cl(SO_2)]^+$ photoisomerizes to η^2(*S*,*O*) even in the solid state.[74] Another example is the recent proposal that the terminal SO_2 ligand can undergo $\eta^2-\eta^1$ (pyramidal and planar) isomerization to electronically buffer the metal during exchange of coligands.[75]

Based on the metal and organic background for $\eta^1-\eta^2$ isomerization, the photoextrusion of SO from $RSMo_2SO_2$ is proposed to proceed through a μ_2-η^2(*S*,*O*) intermediate, eq 5, which then extrudes SO to form the oxide $RSMo_2O$, 5, eq 6. In this scheme, eq 5 is the photoprocess and eq 6 is a thermal step. The inverse combination of thermal eq 5 and photoequation 6 is less favored but cannot be eliminated; this would necessitate an equilibrium for eq 5 which is very far to the left in order to escape detection by NMR spectroscopy (down to −50 °C) and in order to maintain reasonable thermal parameters in the crystal structure of $BzSMo_2SO_2$.



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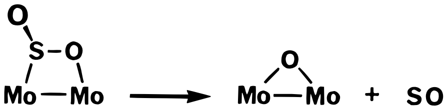

(6)

The elusive nature of SO has impeded studies of its chemistry under normal conditions. The present reactions identify an oxygen abstraction reactivity toward SO_2 and SO ligands. The ability of SO to abstract oxygen has been reported in other situations: its own disproportionation involves abstraction of O from its dimer $(SO)_2$; SO also reduces organic *N*-oxides.[76]

In the many cases of SO extrusion from organic sulfoxides and the subsequent reactions of SO, the question of spin state has been of interest but it has been very contentious. Although the ground state for SO is a triplet, this and its low-energy singlet state have been invoked for various mechanisms involving either concerted or stepwise pathways.[61,65,77] Given that background, and the facile spin conversion available to SO,[78] there is sufficient ambiguity to refrain from any spin-state projections for the present system.

The observed photoextrusion of SO from the SO_2 bridge further extends the versatility of this important ligand. It is reasonable to expect that this behavior will be observed thermally or photolytically for other μ-SO_2 complexes (η^1 or η^2) or for (mono)metallosulfones $M-(SO_2)-R$ or their sulfinate isomers $M-O-S(O)-R$. This may not be as well-favored, however, with lower valent, higher d-electron systems. Indubitably, the oxophilicity of the high-valent molybdenum(V) contributes driving force for the present process.

Acknowledgment. This work was supported by research awards from the National Science Foundation, the Kentucky EPSCoR Program, and the University of Louisville.

Supporting Information Available: Tables of full crystallographic parameters, positional and displacement parameters, bond lengths, and bond angles (27 pages). Ordering information is given on any current masthead page.

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