of liquid ammonia and $(NH_4)_2[PtCl_6]$.[16] The synthetic conditions for **2** are therefore rather unusual for producing NH_2^- and show that the acidity of the coordinated ammine ligands in the parent tetranuclear complex **1** is remarkably increased. The pH of the reaction solution was 2.1 and 2.6 before and after pyrazine addition, respectively. If pyrazine was not added, **2** was not obtained and only the starting material **1** was recovered in 39% yield on gradual evaporation of the solution to ca. two-thirds of the original volume. If the reaction solution plus pyrazine was concentrated to less than two-thirds, **1** and $[Pt^{II}{}_3Pt^{III}(NH_3)_8(C_4H_6NO)_4](NO_3)_5{\cdot}2H_2O$ (**3**)[6,18] were obtained as crystals besides **2**. These complexes were separated microscopically and identified by elemental analyses and UV-vis and ESR spectra.[3,6] No dimeric $[Pt^{II}{}_2(NH_3)_4(C_4H_6NO)_2]^{2+}$[5] or $[Pt^{III}{}_2(NH_3)_4(C_4H_6NO)_2X_2]^{2+}$[11] (X is an axial ligand) was obtained even when the solution was dried. The products obtained were not affected by the presence or absence of air during the preparation. Recrystallization of **2** from water or diluted H_2SO_4 (pH 2) by gradual evaporation at room temperature gave only **1** and **3**. Complex **2** is diamagnetic[19] and is almost instantaneously reduced to **1** and **3** when dissolved in water, which was confirmed by UV-vis and ESR spectra.[3,6] The visible transmittance spectrum of a microcrystalline sample of **2** shows very broad bands at 450 and 695 nm.

Regarding the formation route of **2**, it is improbable that deprotonation occurs on a coordinated ammine in $[Pt^{III}{}_2(NH_3)_4(C_4H_6NO)_2X_2]^{2+}$, which exists together with $[Pt^{II}{}_2(NH_3)_4(C_4H_6NO)_2]^{2+}$ in equilibrium with **1** in solution as a result of disproportionation reaction,[18] and the deprotonated dimeric Pt(III) complex further dimerizes to form **2** by axially substituting the ligand X with NH_2^-. Actually, addition of pyrazine to either $[Pt^{III}{}_2(NH_3)_4(C_4H_6NO)_2(NO_2)(NO_3)](NO_3)_2{\cdot}H_2O$[11] or $[Pt^{III}{}_4(NH_3)_8(C_4H_6NO)_4](SO_4)(ClO_4)_6$[3] at 0.1-2 times the equivalent amount in water did not give **2**. From the former solution, the dimeric Pt(III) complex with axially coordinated pyrazine was obtained,[20] whereas the latter complex was too unstable in neutral water and is easily reduced to **1** and **3**.[3] Therefore, deprotonation seems to occur only on **1**, which leads to the formation of **2** as follows:

$$\underset{\mathbf{1}}{3[Pt^{II}{}_2Pt^{III}{}_2(NH_3)_8(C_4H_6NO)_2]^{6+}} + 2NO_3^- \rightarrow \underset{\mathbf{2}}{[(NO_3)(NH_3)_2Pt^{III}(C_4H_6NO)_2Pt^{III}(NH_3)(\mu\text{-}NH_2)]_2{}^{4+}} + \underset{\mathbf{3}}{2[Pt^{II}{}_3Pt^{III}(NH_3)_8(C_4H_6NO)_2]^{5+}} + 2H^+ \quad (1)$$

Equation 1 is also supported by the fact that, on addition of pyrazine to **1**, the solution rapidly becomes blue ($\lambda_{max} = 680$ nm) due to formation of **3**.

Acknowledgment. This work was financially supported by the Japanese Ministry of Education, Science, and Culture (Grant-in-Aid for "Multiplex Organic Systems" (01649 08)). Financial support from the Asahi Glass Foundation is also acknowledged.

Supplementary Material Available: Tables of anisotropic thermal parameters (Table S1), detailed crystallographic data (Table S3), bond lengths (Table S4), and bond angles (Table S5) (5 pages); a listing of final structure factors (Table S2) (16 pages). Ordering information is given on any current masthead page.

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(19) The sample sometimes shows a weak ESR signal; however, this is due to contamination of **3**, which was confirmed by the *g* values.

(20) $[Pt^{III}{}_2(NH_3)_4(C_4H_6NO)_2(NO_2)(pyrazine)](NO_3)_3{\cdot}3H_2O$ was obtained. Anal. Calcd for $Pt_2C_{12}H_{34}N_{12}O_{16}$: C, 14.52; H, 3.46; N, 16.93. Found: C, 14.42; H, 3.50; N, 16.78.

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The Dithiocarbonate Route to 1,2-Dithiolene Complexes of Molybdenum and Tungsten

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Received May 23, 1990

Tetrathiapentalenedione, $C_2S_4(CO)_2$, reacts with MS_4^{2-} (M = Mo, W) to give $M(S_2C_2S_2CO_3)^{2-}$, isolated as PPh_4^+ salts. COS is the major coproduct of this transformation. The new tris(dithiolene) complexes were characterized by spectroscopic methods as well as a crystallographic study of $(PPh_4)_2[W(S_2C_2S_2CO)_3]$. $C_2S_4(CO)(CS)$ and WS_4^{2-} react to give $W(S_2C_2S_2CS)_3^{2-}$ together with $[W_2S_4(S_2C_2S_2CS)_2]^{2-}$. The same compounds can be obtained by the action of WS_4^{2-} on the cyclic bis(disulfide) $(S_2C_2S_2CS)_2$. Electrochemical studies show that $[M(S_2C_2S_2CE)_3]^{2-}$ (M = Mo, W; E = S, O) undergo two one-electron oxidations at mild potentials. $[Mo(S_2C_2S_2CO)_3]^0$ was prepared by the oxidation of the corresponding dianion with nitrosonium and ferrocenium salts. The neutral dithiolenes are soluble in nonpolar organic solvents and were characterized by IR and mass spectrometry. A methanol suspension of $[Mo(S_2C_2S_2CO)_3]^0$ reacts with methoxide followed by methyl or butyl iodide to give the new dithiolenes $[Mo(S_2C_2S_2R_2)_3]^0$. These species are less oxidizing than $[Mo(S_2C_2S_2CO)_3]^0$.

Introduction

The tetrathioanions of V, Mo, W, and Re are the most important molecular chalcogenides of these elements.[1] These MS_4^{n-} species are stoichiometrically simple, easily prepared, and synthetically versatile. They are precursors to low-dimensional materials,[2] and they are the building blocks for a variety of multimetallic inorganic[3-6] and organometallic[7] clusters. In addition to their use as metalloligands, the thiometalates have been shown to be reactive toward oxidants,[8-12] protons,[13-15] and main-group

Chart I

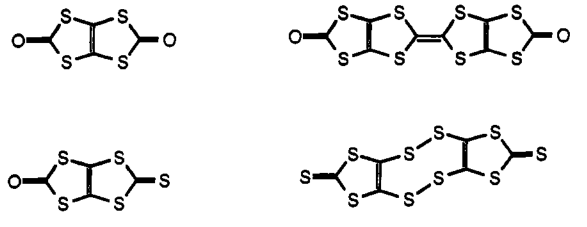

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Table I. Selected Distances (Å) and Angles (deg) for $(PPh_4)_2[W(S_2C_2S_2CO)_3]$

W–S1	2.399 (6)	W–S2	2.398 (6)
W–S3	2.385 (6)	S1–C1	1.74 (2)
S4–C1	1.74 (3)	S2–C2	1.72 (3)
S5–C2	1.75 (2)	S3–C3	1.73 (2)
S6–C3	1.73 (2)	S4–C4	1.75 (3)
S5–C4	1.76 (3)	S6–C5	1.73 (2)
C1–C2	1.34 (4)	C3–C3′	1.37 (3)
C4–O1	1.23 (3)	C5–O2	1.23 (4)
S1–W–S1′	153.0 (2)	S1–W–S2	82.1 (2)
S1–W–S2′	84.1 (2)	S1–W–S3	83.9 (2)
S1–W–S3′	117.0 (2)	S2–W–S2′	117.9 (2)
S2–W–S3	153.2 (2)	S2–W–S3′	83.1 (2)
S3–W–S3′	83.1 (2)		

electrophiles.[16] The action of electrophiles on MS_4^{2-} (M = Mo, W) often results in redox reactions wherein the metal formally undergoes reduction. The present paper provides new examples of such redox brought about by the reaction of the thiometalates with some dithiocarbonate esters. This new reaction constitutes ester cleavage coupled to the $M^{VI/IV}$ redox; this process defines a novel route to dithiolene complexes of molybdenum and tungsten.

The dithiolene ligands described in this paper are formally derivatives of ethylenetetrathiolate (Chart I). To emphasize this lineage, as well as to convey some structural information, we write their formulas as $(S_2C_2S_2CE)^{2-}$, where E = O or S. Complexes of these ligands have received considerable attention following reports on the metallic[17] and superconducting[18] properties of salts of $[Ni(S_2C_2S_2CS)_2]^{z-}$, where $z \leq 1$. Complexes of the type $[M(S_2C_2S_2CE)_3]^z$ have been studied only for the recent case of vanadium.[19-21] These inorganic anions are attractive precursors to molecular electronic materials because their sulfur-rich dithiolene backbone should promote the formation of extended interactions in the solid state, giving rise to cooperative phenomena. The present study extends our previous work on the reactions of thioanions with inorganic heterocycles.[16,22]

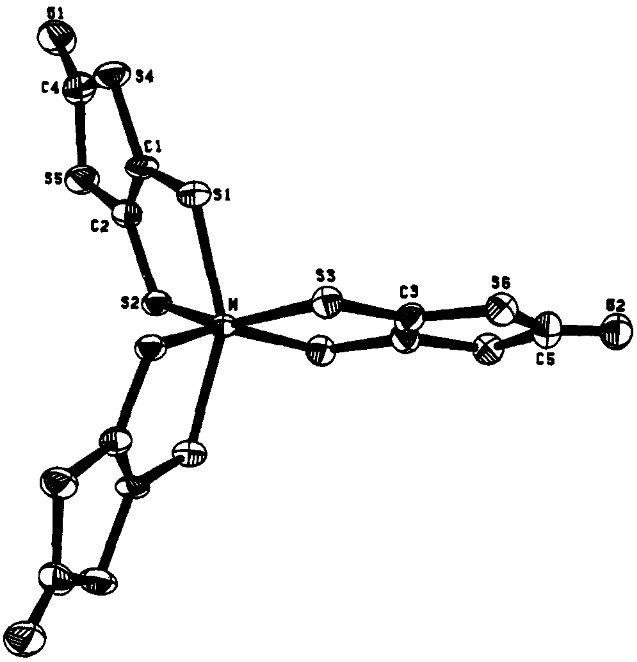

Figure 1. ORTEP plot of $[W(S_2C_2S_2CO)_3]^{2-}$ with thermal ellipsoids drawn at the 35% level.

Results

Synthesis of $[M(S_2C_2S_2CO)_3]^{2-}$. The starting substrate for this study is tetrathiapentalenedione (TPD, see Chart I), a colorless crystalline compound prepared in two steps from methyl dichloroacetate.[23] Treatment of acetonitrile solutions of TPD with organic salts of MoS_4^{2-} resulted in the formation of bright green homogeneous solutions, which give black-green microcrystals. A similar reaction occurred between WS_4^{2-} and TPD to give dark blue crystals of $(PPh_4)_2[W(S_2C_2S_2CO)_3]$ (**2**). The IR spectra feature pairs of $\nu_{C=O}$ bands at 1659 (s), 1609 (s) and 1664 (s), 1611 (s) cm^{-1} for **1** and **2**, respectively. The analytical data on these compounds and all of their derivatives were only fair, despite repeated recrystallizations. This problem appears to be related to the refractory nature of molybdenum and tungsten tetrathiooxalates, since other derivatives of TPD have given excellent microanalytical results.

Using vacuum-line techniques, we demonstrated that the WS_4^{2-} + 3 TPD reaction generates COS in nearly quantitative yield. The COS was identified by IR spectroscopy (gas phase[24]) and EIMS, as well as its physical properties.[25] Neither CO_2 nor CS_2 was detected. The reaction of TPD and $MoSe_4^{2-}$ gave **1** as the only soluble Mo-containing product. These results are consistent with the reaction in eq 1.

$$MS_4^{2-} + 3OCS_2C_2S_2CE \xrightarrow{25\ °C} [M(S_2C_2S_2CE)_3]^{2-} + S + 3COS \quad (1)$$

$$M = Mo, W;\ E = S, O$$

Structure of $(PPh_4)_2[W(S_2C_2S_2CO)_3]$. The structure of **2** consists of a hexacoordinate tungsten anion bound to three planar bidentate dithiolene ligands (Figure 1). Selected bond distances and angles are presented in Table I. Crystallographic symmetry

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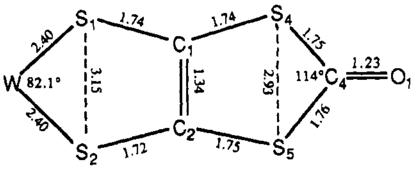
Table II. Electrochemical Data for Reversible Couples for $[M(dithiolene)_3]^n$ (M = Mo, W)

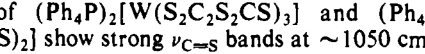
complex	$E_{1/2}$ (V vs Ag/AgCl) for n = -3/-2	-2/-1	-1/0	ref
$[Mo(S_2C_2(CN)_2)_3]^n$	-1.15	+0.49		31
$[Mo(S_2C_2(CF_3)_2)_3]^n$	-1.19	+0.36	+0.95	31
$[Mo(S_2C_2(CO_2Me)_2)_3]^n$		+0.02	+0.48	32
$[Mo(S_2C_2S_2CO)_3]^n$	-1.44	-0.02	+0.33	this work
$[Mo(S_2C_2S_2Bu_2)_3]^n$		-0.63	-0.30	this work
$[W(S_2C_2(CN)_2)_3]^n$	-1.52	+0.43		32
$[W(S_2C_2S_2CS)_3]^n$		+0.01	+0.31	this work
$[W(S_2C_2S_2CO)_3]^n$		-0.07	+0.27	this work

requires W to lie on a 2-fold axis, which bisects one of the $S_2C_2S_2CO$ ligands and relates the other two. The observed geometry closely resembles that for $(AsPh_4)_2[W(mnt)_3]$. The average W–S distance in the latter is 2.371 Å,[26] which is close to 2.394 Å for **2**. The transoid S–W–S angles, e.g., $\angle S_1$–W–S_1' = 153.0° and $\angle S_2$–W–S_3 = 153.2°, are intermediate with respect to the limiting angles of 136 and 180° for trigonal-prismatic and perfect octahedral geometry, respectively. In $(AsPh_4)_2[W(mnt)_3]$ the S–W–S angle is 156.4°. The $WS_2C_2S_2CO$ subunits are approximately planar. In contrast the VS_2C_2 rings are puckered in organic salts of $[V(S_2C_2S_2CS)_3]^{2-}$.[19,20] The dimensions of a representative chelate ring are shown as follows:



The C–C distances support the alkenedithiolate description of the ligand. The C–O distance of 1.23 Å is close to the double-bond value in organic esters.[27]

Extensions of the Reaction of MS_4^{2-} + Dithiocarbonate. The reaction between TPD and MS_4^{2-} is a new type of reaction for the thiometalates, and efforts were made to extend the scope of this transformation. The tetracyclic species $C_6S_8(CO)_2$ was found to be reactive toward WS_4^{2-}; however, the product was completely insoluble in common organic solvents. The thiocarbonyl $SCS_2C_2S_2CO$, available from the reaction of $[Zn(S_2C_2S_2CS)_2]^{2-}$ and phosgene,[28,29] reacted with $(PPh_4)_2WS_4$ to give $(PPh_4)_2[W(S_2C_2S_2CS)_3]$. Also formed in this reaction were small amounts of $(PPh_4)_2[W_2S_4(S_2C_2S_2CS)_2]$. The absence of ν_{CO} bands in the 1700–1600-cm^{-1} region of the IR spectra of these two products showed that the reactions occur exclusively at the carbonyl, not the thiocarbonyl. The optical properties of $(PPh_4)_2[W(S_2C_2S_2CS)_3]$ and $(PPh_4)_2[W(S_2C_2S_2CO)_3]$ are similar. The IR spectra of $(Ph_4P)_2[W(S_2C_2S_2CS)_3]$ and $(Ph_4P)_2[W_2S_4(S_2C_2S_2CS)_2]$ show strong $\nu_{C=S}$ bands at ~1050 cm^{-1}. The IR spectrum of the ditungsten compound shows an absorption at 513 cm^{-1} as a shoulder on a PPh_4^+ band; this is assigned as $\nu_{W=S}$. A proposed structure can be shown:



The same W–S–C anions can be prepared by the reaction of WS_4^{2-} with the tricyclic $[S_2C_2S_2CS]_2$.[30] An acetonitrile slurry of this cyclic bis(persulfide) quickly oxidizes $(PPh_4)_2WS_4$ to give salts of both $[W(S_2C_2S_2CS)_3]^{2-}$ and $[W_2S_4(S_2C_2S_2CS)_2]^{2-}$. Compared to the $WS_4^{2-}/SCS_2C_2S_2CO$ reaction, the WS_4^{2-} and $[S_2C_2S_2CS]_2$ reaction affords a greater amount of the $W_2S_4^{2+}$ derivative.

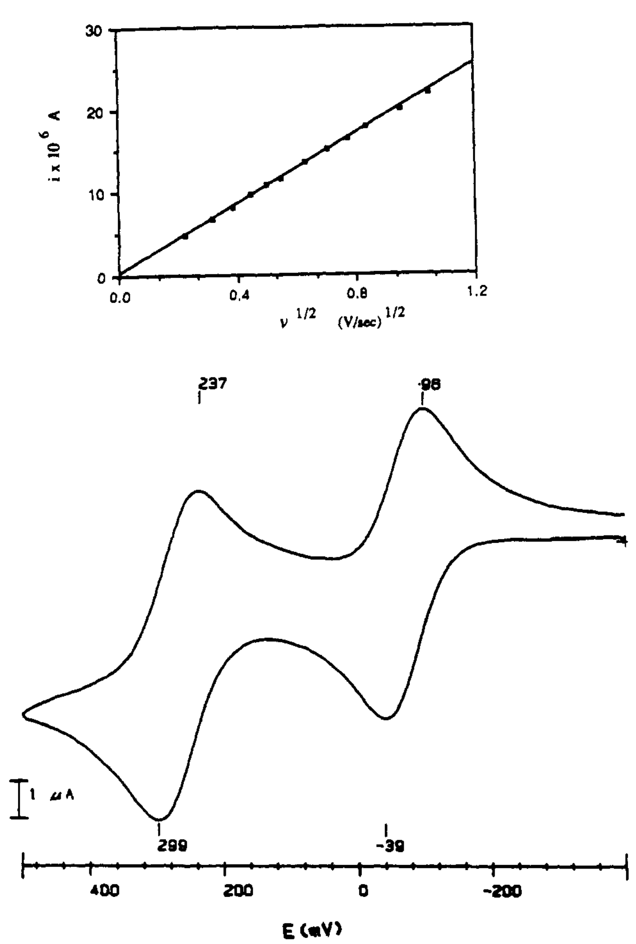


Figure 2. Cyclic voltammogram of a 10^{-3} M solution of $(PPh_4)_2[W(S_2C_2S_2CO)_3]$ in CH_2Cl_2, referenced to Ag/AgCl. The inset is a plot of i vs $\upsilon^{1/2}$ for the 2–/1– couple.

Electrochemical Studies. Cyclic voltammetry experiments show that $[M(S_2C_2S_2CO)_3]^{2-}$ (M = Mo, W) undergo two one-electron oxidations (Figure 2). For M = W and Mo, plots of $\upsilon^{1/2}$ vs i are linear for each of the reductions, indicating electrochemical reversibility for these processes. The $E_{1/2}$ values show that it is more difficult to oxidize $[Mo(S_2C_2S_2CO)_3]^{2-}$ than its tungsten analogue. Compared to literature values[31,32] of $E_{1/2}$ for first reductions of other tris(dithiolene) complexes (Table II), it appears that $S_2C_2S_2CO$ is a slightly poorer acceptor than $S_2C_2(CN)_2^{2-}$ (mnt^{2-}) and $S_2C_2(CF_3)_2^{2-}$ but similar to $S_2C_2(CO_2Me)_2^{2-}$. Cyclic voltammetry studies also show that $S_2C_2S_2CO^{2-}$ is a poorer acceptor than $S_2C_2S_2CS^{2-}$. Thus, $E_{1/2}$ for $[W(S_2C_2S_2CO)_3]^{2-/-}$ is ca. 80 mV milder than that for $[W(S_2C_2S_2CS)_3]^{2-/-}$.

Given the well-behaved electrochemistry of $[Mo(S_2C_2S_2CO)_3]^{2-}$, we subjected its solutions to bulk electrolysis. A coulommetry experiment at +500 mV vs Ag/AgCl demonstrated 2e$^-$/Mo stoichiometry for the oxidation. Evaporation of the electrooxidized solution followed by extraction with CS_2 gave a purple solution. Evaporation of this solution gave a purple solid that showed a molecular ion (M$^+$) in its field desorption mass spectrum.

Isolation of $[Mo(S_2C_2S_2CO)_3]^0$. The oxidation of $[Mo(S_2C_2S_2CO)_3]^{2-}$ proceeds well with iodine, nitrosonium salts, and ferrocenium salts. Although all three reagents gave spectroscopically similar products in respectable yields, the ferrocenium oxidation gave fewer side products. Product isolation was facilitated by the fact that, unlike the precursor dianion, the blue-purple product is insoluble in acetonitrile. The product is quite

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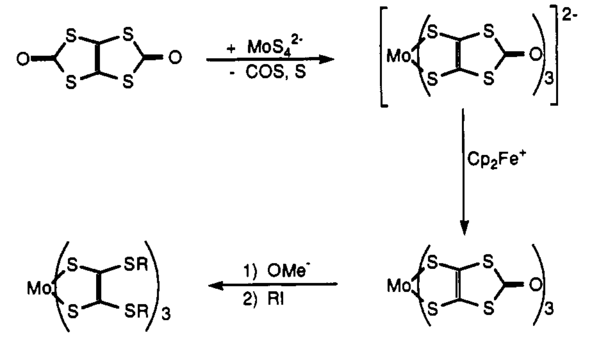
Scheme I



soluble in carbon disulfide, and this fact alone virtually requires that it is charge-neutral. A molecular ion is observed in its field desorption mass spectrum. Its IR spectrum is simple, and the ν_{CO} bands shift ~15 cm^{-1} to higher frequencies, relative to that of the starting dianion. The cyclic voltammetry of $[Mo(S_2C_2S_2CO)_3]^0$ was identical with that for the parent dianion.

Preparation of $Mo(S_2C_2S_2R_2)_3$ from $[Mo(S_2C_2S_2CO)_3]^0$. Although $[Mo(S_2C_2S_2CO)_3]^0$ is completely insoluble in methanol, a very dark green solution does form upon the addition of sodium methoxide. The nature of the resulting green species is not known although the formula $[Mo(S_2C_2S_2CO)_{3-n}(S_2C_2S_2)_n]^{2n-}$ is suggested by its reactivity. Treatment of the green solution with methyl iodide or butyl iodide gave blue-purple precipitates. The intensely purple butyl derivative was very soluble, and most of our efforts focused on this product. Its ^1H NMR spectrum consists of only a single set of butyl resonances. The microanalytical data and FD mass spectra support the formulation of these species as $[Mo(S_2C_2S_2R_2)_3]$ (R = Me, Bu). The IR spectra are very simple and lack absorptions characteristic in the 1500–1700-cm^{-1} region; thus, the molecule is devoid of carbonyls. Further synthetic evidence for the formulations comes from the observation of a mass spectral peak for $[Mo(S_2C_2S_2Me_2)_3]$ in the crude reaction mixture of the dithiocarbonate $(MeS)_2C_2S_2CO$ and MoS_4^{2-}. A cyclic voltammetry experiment on the hexabutyl derivative showed two reversible reduction waves at −0.3 and −0.63 V vs Ag/AgCl. These values are cathodically shifted by ca. 600 mV vs $[Mo(S_2C_2S_2CO)_3]^0$, consistent with the replacement of the electronegative CO groups by more strongly donating alkyl substituents.

Discussion

A new reaction has been discovered whereby electrophilic dithiocarbonates react with tetrathiometalates giving 1,2-dithiolene complexes. While the detailed mechanism was not investigated, we have established that the major coproduct of the reaction is COS. Sulfur is predicted to be released in the formation of the tris(dithiolene) complexes; the reaction of this sulfur with the starting MS_4^{2-} may explain the formation of small amount of dimetallic coproducts. The newly discovered reaction couples (thio)ester hydrolysis with oxidation reduction ($M^{VI} \rightarrow M^{IV}$).[33] The all-sulfur complex $[W(S_2C_2S_2CS)_3]^{2-}$ can be prepared from the trithiocarbonate or from the cyclic bis(persulfide) $[S_2C_2S_2CS]_2$. The condensation method is cleaner, possibly because the persulfide route generates more elemental sulfur as a byproduct. In terms of their stoichiometry, the Mo–C–S anions described in this paper are related to the perthiocarbonate complexes of molybdenum reported by Draganjac and Coucouvanis.[34]

The oxidation of $[M(S_2C_2S_2CO)_3]^{2-}$ activates the ester groups toward nucleophilic cleavage thereby opening the way to the compounds of the type $[M(S_2C_2S_2R_2)_3]^0$ (Scheme I). Since the parent $[Mo(S_2C_2S_2CO)_3]^{2-}$ is unreactive toward base, this transformation demonstrates redox activation of a hydrolysis process. Furthermore, the synthetic method implicates intermediates of the type $[Mo(S_2C_2S_2CO)_{3-n}(S_2C_2S_2)_n]^{2n-}$. While complexes containing bridging tetrathiooxalate ligands are well-known, monometallic compounds of the type $[L_nMS_2C_2S_2]^z$ have not been described.

Much attention has been focused on the formal reduction of the d^0 molybdenum, tungsten, rhenium, and vanadium metal centers when thiometalates are treated with oxidants.[8-10] As illustrated by this work, such changes in formal oxidation states are not caused by the action of an oxidant per se. Rather, reduction in the metal oxidation state occurs simply because the modified ligand set is less capable of stabilizing the Mo(VI) or W(VI) species.

Experimental Section

Materials. Tetrathiapentalene-2,5-dione (TPD),[23] 5-thioxotetrathiapentalene-2-one,[29] and C_6S_{10}[30] were prepared by the literature methods. Crude TPD was purified by recrystallization from hot CH_2Cl_2. Solvents were dried and freshly distilled before use. All reactions were carried out under a dinitrogen atmosphere. We have been unable to obtain accurate microanalytical data for all molybdenum tetrathiooxalates; analyses for sulfur were invariably low. The data presented are the best of multiple determinations.

Physical Measurements. Electronic spectra were measured with a Hewlett Packard 8452A diode-array spectrophotometer; peak maxima (λ_{max}) are reported in nanometers. IR spectra were recorded as KBr pellets with a Perkin-Elmer 1750 infrared Fourier transform spectrometer. Cyclic voltammetry was performed with a BAS 100 electrochemical analyzer. All the electrochemical measurements were carried out at room temperature under a nitrogen atmosphere with CH_2Cl_2 solutions of the complexes in 0.1 M Bu_4NPF_6 (TBAHP) as a supporting electrolyte. Potentials are referred to an Ag/AgCl electrode with *IR* compensation. A platinum disk and platinum wire were used as the working electrode and auxiliary electrode, respectively. Mass spectra for molybdenum compounds refer to the ^{96}Mo isotopomer.

$(PPh_4)_2[Mo(S_2C_2S_2CO)_3]$ (1). A solution of 0.852 g (0.945 mmol) of $(PPh_4)_2MoS_4$ in 30 mL of CH_3CN was treated with 0.590 g (2.84 mmol) of TPD, added as a solid. The solution assumed a bright green color in minutes. After a further 10 min, the solution was filtered in air and the filtrate was evaporated to give a green oil. The green oil was triturated with 10 mL of acetone. The crystalline solid was collected by filtration, washed with Et_2O, and dried in air. The product can be recrystallized by dissolution in CH_2Cl_2, dilution with acetone, and concentration in vacuo. Yield: 840 mg (68%). Anal. Calcd for $C_{57}H_{40}O_3P_2S_{12}Mo$: C, 52.05; H, 3.07; S, 29.22. Found: C, 51.76; H 3.07; S, 29.24. IR (KBr, cm^{-1}): 1660, 1610 ($\nu_{C=O}$). UV-vis (CH_2Cl_2): 766 (sh), 642, 430 (sh), 346.

$(PPh_4)_2[W(S_2C_2S_2CO)_3]$ (2). A 250-mL Schlenk flask was charged with 2 g (2.02 mmol) of $(PPh_4)_2WS_4$ and 1.26 g (6.06 mmol) of TPD followed by 50 mL of CH_3CN. After 2 min, the color of the solution had changed from orange to blue and dark blue crystals started to precipitate. After a further 15 min, the solution was filtered in air. The crystalline solid was extracted with ca. 500 mL of CH_3CN, leaving behind a brown CH_2Cl_2-soluble solid. The filtrate was concentrated to ca. 10 mL to give dark blue crystals. Recrystallization of this product from CH_3CN/Et_2O or CH_2Cl_2/Et_2O gave 2.14 g of dark blue crystals (76%). Anal. Calcd for $C_{57}H_{40}O_3P_2S_{12}W{\cdot}0.5CH_3CN$: C, 48.93; H, 3.05; S, 27.00; N, 0.49. Found: C, 48.18; H, 3.04; S, 27.09; N, 0.58. IR (KBr, cm^{-1}): 1655, 1611 ($\nu_{C=O}$). UV-vis (CH_2Cl_2): 704, 590, 356.

Isolation of COS from the Reaction of $(Ph_4P)_2WS_4$ and TPD. All manipulations were performed on a high-vacuum line. A flask containing a magnetic stir bar, 0.3 g (0.3028 mmol) of $(Ph_4P)_2WS_4$, and 0.189 g (0.908 mmol) of TPD was charged with 20 mL of degassed CH_3CN. The system was isolated from the vacuum and allowed to warm to room temperature. A dark blue coloration appeared after 10 min. After 30 min, the volatiles were fractionated under dynamic high vacuum through a dry ice/acetone trap and a liquid-N_2 trap. The contents of the liquid-N_2 trap were warmed with a dry ice/acetone bath, and the volatiles were collected as a white solid in a liquid-N_2-cooled trap. The yield of the gas was 0.98 mmol, determined by pressure/volume measurements assuming ideal gas behavior and 100% purity. The gas was characterized with FT-IR spectroscopy and EIMS as carbonyl sulfide (COS). CO_2 and CS_2 were not observed. Compound 2 was isolated in 75% yield together with some insoluble red-brown solid.

Reaction of $MoSe_4^{2-}$ with TPD. A solution of 0.185 g (0.170 mmol) of $(PPh_4)_2MoSe_4$ in 20 mL of CH_3CN to give a purple solution was treated with 0.106 g (0.509 mmol) of TPD. The solution color changed to brown (10 min) followed by the formation of a red-brown crystalline

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(33) The analogous reaction of ReS_4^- with TPD also affords dithiolenes: Yang, X. Ph.D. Thesis, University of Illinois at Urbana-Champaign, 1990.

(34) Coucouvanis, D.; Draganjac, M. *J. Am. Chem. Soc.* **1982**, *104*, 6820. Coucouvanis, D.; Patil, P. R.; Kanatzidis, M. G.; Detering, B.; Baenziger, N. C. *Inorg. Chem.* **1985**, *24*, 24. Coucouvanis, D.; Hadjikyriacou, A.; Draganjac, M.; Kanatzidis, M. G.; Ileperuma, O. *Polyhedron* **1986**, *5*, 349.

Table III. Crystallographic Data for $(PPh_4)_2[W(S_2C_2S_2CO)_3]$ (**2**)

$C_{57}H_{40}O_3P_2S_{12}W$	fw 1403.46
a = 21.064 (4) Å	space group $C2/c$ (No. 15)
b = 14.606 (3) Å	λ = 0.71073 Å
c = 21.693 (9) Å	ρ_{calcd} = 1.431 g/cm^3
β = 102.56 (2)	μ = 22.67 cm^{-1}
V = 6513 (5) Å^3	transm coeff = 0.872–0.589
Z = 8 (4)	$R(F_o)$ = 0.067
T = −25 °C	$R_w(F_o^2)$ = 0.100

solid. The yellow-green solution was filtered under N_2 and diluted with 20 mL of Et_2O. Green platelike crystals (50 mg) were isolated and identified as $(PPh_4)_2[Mo(S_2C_2S_2CO)_3]$ by UV–vis spectroscopy.

$(PPh_4)_2[W(S_2C_2S_2CS)_3]$ and $(PPh_4)_2[W_2S_4(S_2C_2S_2CS)_2]$. Method A. A 250-mL Schlenk flask was charged with 0.264 g (0.265 mmol) of $(PPh_4)_2WS_4$, 0.18 g (0.8 mmol) of C_4S_5O, and 20 mL of CH_3CN. After 2 min of stirring, the color of the solution had changed from orange to dark red brown. After 1 h the solution was filtered under N_2 to remove a small amount of precipitate and the filtrate was layered with 30 mL of Et_2O. After 48 h the orange crystalline solid was collected and filtrate "A" was saved. The orange solid was recrystallized from CH_3CN/Et_2O to give 15 mg of orange-brown crystals of $(PPh_4)_2[W_2S_4(S_2C_2S_2CS)_2]$. Filtrate "A" was layered with 40 mL of Et_2O to afford 120 mg of purple crystals contaminated with small amounts of orange brown solid. The orange contaminant was removed by hand. Anal. Calcd for $C_{57}H_{40}P_2S_{15}W$: C, 47.16; H, 2.78; S, 33.10. Found: C, 47.53; H, 2.91; S, 32.98. IR (KBr, cm^{-1}): 1050 ($\nu_{C=S}$). UV–vis (CH_3CN): 686, 574, 478, 380 (s), 318. Anal. Calcd for $C_{54}H_{40}P_2S_{14}W_2 \cdot CH_3CN$: C, 41.82; H, 2.70; N, 0.87. Found: C, 42.07; H, 3.00; N, 0.67. IR (KBr, cm^{-1}): 1059, 513 ($\nu_{W=S}$). UV–vis (CH_3CN): 460, 358 (sh).

Method B. A solution of $(PPh_4)_2WS_4$ in 30 mL of acetonitrile was treated with 0.079 g (0.202 mmol) of C_6S_{10}. The solution turned red purple immediately. The mixture was stirred at room temperature for 1 h, filtered, and layered with 50 mL of ether. After 2 days 30 mg of purple crystals of $(PPh_4)_2[W(S_2C_2S_2CS)_3]$ was formed. A further 50 mg was obtained by diluting the filtrate with more ether. Yield: 54%. The mother liquid was concentrated and layered with Et_2O to obtain 60 mg of yellow brown microcrystalline $(PPh_4)_2[W_2S_4(S_2C_2S_2CS)_2]$. Yield: 45%. Both compounds were identified by UV–vis spectroscopy.

$[Mo(S_2C_2S_2CO)_3]$. Method A. A 0.005-g sample of $(Ph_4P)_2[Mo(S_2C_2S_2CO)_3]$ (5 mg) was dissolved in 10 mL of 0.1 M NBu_4BF_4 dichloromethane. The auxiliary and working electrodes were a platinum wire and plate, respectively. A saturated calomel electrode was used as the reference electrode. The potential was set at +500 mV. The electrolysis was conducted for 30 min under N_2 with constant stirring. The solution was then evaporated to dryness, and the solid was rinsed with CH_3CN to remove salts. The resulting purple solid was characterized by FDMS (22 mA): m/e 636 (M^+).

Method B. A solution of 0.150 g of $NOBF_4$ (1.28 mmol) in 40 mL of MeCN was added rapidly to a stirred solution of 0.87 g of $(Ph_4P)_2[Mo(S_2C_2S_2CO)_3]$ (0.66 mmol) in 50 mL of MeCN. The reaction mixture was stirred for 30 min and then filtered. The brown/purple solid was then extracted with CS_2 to give a deep purple solution. CS_2 was removed under vacuum, and the dark purple solid obtained was recrystallized from C_6H_6/hexanes and dried under vacuum. Yield: 0.32 g (76%). Anal. Calcd for $C_9O_3S_{12}Mo$: C, 16.98; H, 0.0. Found: C, 17.80; H, 0.32. IR (KBr, cm^{-1}): 1688, 1628 ($\nu_{C=O}$). UV–vis (C_6H_6): 732, 488. FDMS (20 mA): m/e 636 (M^+).

Method C. To a solution of 1.63 g (1.24 mmol) of $(Ph_4P)_2[Mo(S_2C_2S_2CO)_3]$ in 50 mL of MeCN was added 0.816 g (2.46 mmol) of Cp_2FePF_6. After 3 h the reaction mixture was filtered and the residue was washed with cold MeCN. The solid was extracted into CS_2 and filtered. The concentrated solution was diluted with ether and cooled to −20 °C. The fine black-blue powder was dried in vacuum. Yield: 0.72 g (91%).

$[Mo(S_2C_2S_2R_2)_3]$ (R = Me, Bu). A solution of 0.35 g (6.5 mmol) of NaOMe in 20 mL of MeOH was added to a stirred slurry of 1 g (0.8 mmol) of $[Mo(S_2C_2S_2CO)_3]$ in 20 mL of MeOH. The Mo complex dissolved to give a green solution, which was then treated with an excess of alkyl iodide (ca. 1 mL), and the reaction solution was allowed to stand for 12 h. The resulting clear solution was decanted from the dark precipitate. The solid was then extracted with CH_2Cl_2 (4 × 30 mL, R = Me) or hexanes (20 mL, R = Bu). Removal of the solvent afforded the product as dark purple powder. The butyl compound was further purified by chromatography on silica gel, eluting initially with hexanes followed by hexane/dichloromethane. The dark purple band was recrystallized by dissolution in benzene followed by the addition of methanol. Yields were 10–20% (R = Me) and 15–25% (R = Bu). Data for R = Me are as follows. Anal. Calcd for $C_{12}H_{18}MoS_{12}$: C, 22.42; H, 2.82. Found: C, 21.49; H, 2.74. FDMS: m/e 642 (M^+). ^{1}H NMR ($CDCl_3$): 1.53 ppm/(s). UV–vis ($CHCl_3$): 350, 526. Data for R = Bu are as follows. Anal. Calcd for $C_{30}H_{54}MoS_{12}$: C, 40.24; H, 6.08. Found: C, 39.89; H, 6.20. ^{1}H NMR (C_6D_6): 3.22 (m, 2 H), 1.48 (m, 2 H), 1.16 (m, 2 H), 0.66 ppm (m, 3 H). FDMS (20 mA): m/e 894 (M^+). UV–vis (C_6H_6): 342, 528.

Table IV. Atomic Coordinates for Non-Hydrogen Atoms for the Anion in $(PPh_4)_2[W(S_2C_2S_2CO)_3]$

	x/a	y/b	z/c
W	0.0	0.0315 (1)	0.25
S1	−0.0450 (3)	−0.0068 (4)	0.3392 (3)
S2	−0.0925 (3)	−0.0532 (4)	0.1948 (3)
S3	0.0504 (3)	0.1537 (4)	0.3158 (3)
S4	−0.1623 (3)	−0.1123 (5)	0.3616 (3)
S5	−0.2060 (3)	−0.1531 (5)	0.2266 (4)
S6	0.0482 (3)	0.3613 (4)	0.3096 (3)
P	0.6192 (3)	−0.0529 (4)	0.6253 (3)
O1	−0.2745 (9)	−0.189 (1)	0.3123 (10)
O2	0.0	0.509 (2)	0.25
C1	−0.114 (1)	−0.073 (2)	0.312 (1)
C2	−0.133 (1)	−0.092 (2)	0.250 (1)
C3	0.022 (1)	0.255 (1)	0.278 (1)
C4	−0.224 (1)	−0.157 (2)	0.302 (1)
C5	0.0	0.425 (2)	0.302 (1)

X-ray Crystallography. Dark blue crystals of $(Ph_4P)_2[W(S_2C_2S_2CO)_3]$ were grown from CH_3CN solutions by layering with Et_2O. A crystal with dimensions 0.1 × 0.1 × 0.2 mm was mounted to a thin glass fiber with epoxy and used for data collection. Crystallographic data are listed in Table III.

Data were collected at −25 °C, and no significant intensity variation was observed. The intensities were corrected for Lorentz and polarization effects as well as anomalous dispersion effects. The structure was solved by Patterson methods with SHELXS-86; the correct tungsten atom position was automatically determined from a vector map, and partial structure expansion revealed positions for 16 non-hydrogen atoms. A subsequent weighted difference Fourier summation gave positions for the remaining nonhydrogen atoms. The highest peaks in the final difference Fourier map indicated the presence of a highly disordered solvate molecule in the crystal lattice about the 2-fold symmetry axis. This solvate appeared to be a mixture of acetonitrile and diethyl ether. Attempts to refine a disorder model for the solvate were unsuccessful. A final analysis of variance between the observed and calculated structure factors showed a slight dependence on the structure factor amplitude and an inverse dependence on sine θ. The final atomic coordinates are listed in Table IV.

Acknowledgment. This research was supported by the Department of Energy through Grant DOE-DE-ACO2-76ER01198 (for support of G.K.W.F.) and the National Science Foundation through Grant CHE 87-11460.

Registry No. **1**, 133985-56-5; **2**, 133985-58-7; TPD, 64394-45-2; $(PPh_4)_2MoS_4$, 14348-10-8; $(PPh_4)_2WS_4$, 14348-11-9; COS, 463-58-1; $(PPh_4)_2MoSe_4$, 112988-66-6; $(PPh_4)_2[W(S_2C_2S_2CS)_3]$, 133985-60-1; $(PPh_4)_2[W_2S_4(S_2C_2S_2CS)_2]$, 133985-62-3; C_4S_5O, 64433-03-0; C_6S_{10}, 127807-76-5; $S_2C_2S_2CO^{2-}$, 111016-08-1; $[Mo(S_2C_2S_2CO)_3]$, 133985-63-4; $[Mo(S_2C_2S_2CO)_3]^{3-}$, 133985-64-5; $[Mo(S_2C_2S_2CO)_3]^-$, 133985-65-6; $[Mo(S_2C_2S_2Bu_2)_3]^-$, 133985-66-7; $[W(S_2C_2S_2CS)_3]^-$, 133985-67-8; $[W(S_2C_2S_2CO)_3]^-$, 133985-68-9; $[Mo(S_2C_2S_2Bu_2)_3]^{2-}$, 133985-69-0; $[W(S_2C_2S_2CS)_3]$, 133985-70-3; $[W(S_2C_2S_2CO)_3]$, 133985-71-4; $[Mo(S_2C_2S_2Me_2)_3]$, 71081-62-4; $[Mo(S_2C_2S_2Bu_2)_3]$, 134004-62-9.

Supplementary Material Available: Tables of bond distances, bond angles, and thermal parameters (3 pages); a table of structure factors (11 pages). Ordering information is given on any current masthead page.