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Syntheses of Metal Dithiolene Complexes from Thiometalates by Induced Internal Redox Reactions

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A variety of new and known transition metal dithiolene complexes has been synthesized from thiometalates via induced internal electron-transfer reactions. Treating MS_4^{2-} ($M = Mo, W$) with stoichiometric amounts of bis(trifluoromethyl)-1,2-dithiete ($(CF_3)_2C_2S_2$) results in rapid formation of the respective tris(dithiolene) complexes $M(tfd)_3^{2-}$ (tfd = $[(CF_3)_2C_2S_2]^{2-}$). These complexes are isostructural and adopt twisted trigonal prismatic coordination (ca. 18° from a perfect trigonal prism). Crystal data: $Mo(tfd)_3^{2-}$, monoclinic, space group $C2/c$, with $a = 18.905(4)$ Å, $b = 13.732(3)$ Å, $c = 17.101(3)$ Å, $\beta = 110.29(3)°$, and $Z = 4$; $W(tfd)_3^{2-}$, monoclinic, space group $C2/c$, with $a = 18.933(4)$ Å, $b = 13.728(3)$ Å, $c = 17.096(3)$ Å, $\beta = 110.26(3)°$, and $Z = 4$. In contrast, $Mo(tfd)_3$ (synthesized as reported previously) has nearly perfect trigonal prismatic coordination. Crystal data: hexagonal, space group $P6_3/m$, with $a = 9.6795(14)$ Å, $b = 9.6795(14)$ Å, $c = 13.951(3)$ Å, and $Z = 2$. Treating WOS_3^{2-} and $MoO_2S_2^{2-}$ with $(CF_3)_2C_2S_2$ results in the respective $MO(tfd)_2^{2-}$ complexes. These two complexes are isostructural and adopt square pyramidal coordination with four sulfur atoms forming the base and oxygen at the apex. Crystal data: $MoO(tfd)_2^{2-}$, monoclinic, space group $P2_1/n$, with $a = 12.184(2)$ Å, $b = 18.627(4)$ Å, $c = 15.482(3)$ Å, $\beta = 91.06(3)°$, and $Z = 4$; $WO(tfd)_2^{2-}$, monoclinic, space group $P2_1/n$, with $a = 12.200(2)$ Å, $b = 18.630(4)$ Å, $c = 15.463(3)$ Å, $\beta = 91.02(3)°$, and $Z = 4$. On the basis of spectroscopic evidence, the product from the reaction of ReS_4^- with $(CF_3)_2C_2S_2$ is proposed to be $\{Re[S_2C_2(CF_3)_2][S_3C_2(CF_3)_2]_2\}^-$. Influences of the nature of the oxidant on the ease with which thiometalates undergo induced internal electron-transfer reactions are discussed.

Introduction

Metal dithiolene complexes (metallo-1,2-enedithiolates) have attracted considerable attention since they were first reported.[1,2] While early interest focused primarily on the redox and optical properties of the complexes,[3−5] more recently the scope has expanded to areas ranging from bioinorganic chemistry to material science. Some dithiolene complexes have been reported as conducting[6−8] and magnetic materials;[9,10] others as solution lumophores.[11−16] It has been established that all molybdenum enzymes, except for nitrogenase, and all tungsten enzymes contain the pterin cofactor designated as Mo-co (or W-co) in which a metal−dithiolene structural motif is present.[17,18] Nickel bis(dithiolene) complexes have been used as molecular models for the nickel site in the active center of hydrodesulfurization catalysts.[19,20] The wide range of interest in this class of compounds has stimulated exploration of new methods to synthesize the complexes by convenient, high-yield reactions.[21−26]

The concept of induced internal electron-transfer reactions was first systematically applied to coordination compounds by Taube.[27] More recently, induced internal electron-transfer reactions involving tetrathiometalate anions of V, Mo, W, and Re

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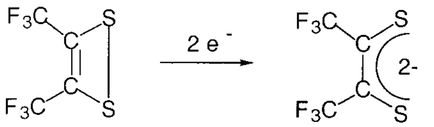
Scheme 1



have been established.[28-33] Reactions of VS_4^{3-}, MoS_4^{2-}, and ReS_4^- with certain oxidants yield products with the metal in oxidation states lower than those in the respective starting tetrathiometalates. Among those oxidants that have been used are organic disulfides (RSSR),[31] tetraalkylthiuram disulfides ($(R_2NCS_2)_2$),[30-32] dithiobenzoate disulfides ($(C_6H_5CS_2)_2$),[28] and alkylxanthogen disulfides ($(ROCS_2)_2$).[29]

A variety of methods for synthesizing metal dithiolene complexes has been developed.[25] However, each of these methods is limited only to certain types of complexes. Because of the wide scope of potential applications, there is continuing interest in alternative methods to prepare metal dithiolene complexes. In this paper, we report that, using an appropriate oxidant, induced internal redox reactions can serve as an entry into metal dithiolene complexes.

Bis(trifluoromethyl)-1,2-dithiete ($(CF_3)_2C_2S_2$), first prepared by Krespan,[34,35] is a two-electron oxidant.[36] Reduction of the dithiete gives 1,2-bis(trifluoromethyl)ethylene-1,2-dithiolate (Scheme 1, $(CF_3)_2C_2S_2^{2-} \equiv$ tfd). If $(CF_3)_2C_2S_2$ can be used as an oxidant for thiometalates, then induced internal redox reactions may provide a feasible route for making metal dithiolene complexes. Indeed, we have found that $(CF_3)_2C_2S_2$ reacts with tetrathiometalates and oxothiometalates to give dithiolene complexes, for which we report the resultant improved syntheses and structural characterizations. Some of these complexes reported are known, although most had not been crystallographically characterized.[37,38]

Experimental Section

All manipulations were carried out under an N_2 atmosphere using either drybox or standard Schlenk-line techniques. All solvents were of anhydrous grade purchased from Aldrich and were used as received. $(Et_4N)_2MS_4$ (M = Mo, W),[39] $(Et_4N)ReS_4$,[40] $(Et_4N)_2WOS_3$,[39] and $(Et_4N)_2MoO_2S_2$[39] were prepared according to literature methods. $(CF_3)_2C_2S_2$ was synthesized using the method of Krespan[34,35] by refluxing hexafluoro-2-butyne (Aldrich) with sulfur under atmospheric pressure.

Infrared spectroscopy was performed on a Mattson Galaxy Series 5000 FTIR spectrometer. Electronic spectra were recorded on a Hewlett-Packard 8543 Biochemical UV−vis system. NMR measurements were carried out on a Varian XL300 spectrometer. Mass spectra were obtained on a VG Analytical/Micromass ZAB2-SEQ mass spectrometer. Cyclic voltammograms were recorded using a BAS 100A electrochemical analyzer equipped with a Pt-disk working electrode, an Ag^+/Ag-wire reference electrode, and a Pt-wire auxiliary electrode. Bu_4NPF_6 was used as the supporting electrolyte. Potentials were referenced to the ferrocene/ferrocenium couple ($E_{1/2}$ = 0.40 V vs SCE in MeCN).[41]

Single-Crystal X-ray Diffraction. Data for single crystals of **1**−**5** were collected at 21 ± 2 °C with Mo Kα radiation on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined from 25 centered reflections. Six standard reflections monitored at intervals of every 3 h showed no significant change during the course of the data collection. Crystal data and details of data collection for all compounds are given in Table 1. In the solution and refinement of these structures, the SHELXTL 5.0 software package was used.[42] The initial solutions were obtained by heavy-atom methods, data were corrected for absorption with empirical methods, hydrogen atoms were assigned to calculated positions and refined according to a riding model, and the structures were refined on F_o^2 with full-matrix least-squares analysis. As typical in structures with perfluoromethyl groups, there is substantial oscillation around the $C-CF_3$ axes. Where applicable, each fluorine atom was considered to occupy two positions and the occupancy all three fluorine atoms on each perfluoromethyl group was refined as a group. Selected bond distances and angles for compounds **1**−**5** are given in Tables 2, 3, 6, 7, and 5, respectively. Additional crystal and experimental details, atom positions, anisotropic displacement parameters, and all bond lengths and angles are given in the Supporting Information.

Synthesis of $(Et_4N)_2M(tfd)_3$ (M = Mo, W). These two compounds were prepared similarly. The synthesis of $(Et_4N)_2Mo(tfd)_3$ is given as an example. The tetrathiomolybdate $(Et_4N)_2MoS_4$ (0.2 g, 0.41 mmol) was dissolved in 30 mL of anhydrous acetonitrile to give an orange-red solution. To this solution was added dropwise with stirring 0.3 g of $(CF_3)_2C_2S_2$ (1.32 mmol). The color of the solution quickly changed to deep blue with precipitation of elemental sulfur. The mixture was stirred at room temperature for 30 min and filtered through a pad of Celite to remove sulfur. The volume of solution was reduced to ca. 5 mL under vacuum, and the concentrated solution was layered with ether and stored at 0 °C overnight. A dark blue solid was obtained (0.36 g, yield = 88%). X-ray-quality crystals were obtained by slow evaporation of a chloroform solution at room temperature.

$(Et_4N)_2Mo(tfd)_3$ (1). ^1H NMR (CD_3CN): δ 1.19 (t, J_{H-H} = 7 Hz), 3.13 (q). ^{19}F NMR (CD_3CN, $\delta(C_6F_6)$ = −163 ppm): δ −53 (s). IR (KBr): 2989 (w), 1533 (m), 1483 (m), 1458 (w), 1438 (w), 1394 (m), 1234 (s), 1159 (s), 1126 (s), 1019 (w), 999 (m), 893 (m), 840 (w), 784 (w), 715 (m), 692 (m) cm^{-1}. UV−vis (MeCN): 260, 290 (sh), 328, 622 nm. FAB$^-$/MS: m/z = 906 ($[M - Et_4N]^-$), 776 ($[M - 2Et_4N]^-$). CV: two reversible couples ($E_{1/2}$ = 0.28 V, − 0.28 V vs $Fc^{0/+}$ couple).

$(Et_4N)_2W(tfd)_3$ (2). ^1H NMR (CD_3CN): δ 1.20 (t, J_{H-H} = 7 Hz), 3.15 (q). ^{19}F NMR (CD_3CN, $\delta(C_6F_6)$ = −163 ppm): δ −52.7 (s). IR (KBr): 2987 (w), 1540 (m), 1484 (m), 1458 (w), 1438 (w), 1394 (m), 1253 (s, sh), 1232 (s), 1158 (s), 1125 (s), 998 (m), 889 (m), 840 (m), 783 (m), 713 (s), 693 (m) cm^{-1}. UV−vis (MeCN): 260, 291, 320 (sh), 433 (sh), 505, 566 (sh) nm. FAB$^-$/MS: m/z = 994 ($[M - Et_4N]^-$), 862 ($[M - 2Et_4N]^-$). CV: two reversible couples ($E_{1/2}$ = 0.22 V, − 0.11 V vs $Fc^{0/+}$ couple).

Synthesis of $(Et_4N)_2WO(tfd)_2$ (3). The dithiete $(CF_3)_2C_2S_2$ (0.17 g, 0.72 mmol) was added dropwise to a stirred solution of $(Et_4N)_2WOS_3$ in acetonitrile (0.2 g, 0.36 mmol). The color of the solution changed immediately from yellow to orange, with concomitant formation of elemental sulfur. The mixture was stirred for 2 h and filtered. The volume was reduced under vacuum, and the concentrated solution was layered with ether. Storing the mixture at 0 °C overnight resulted in the formation of a red solid (0.26 g, yield = 79%). X-ray-quality crystals were obtained by slow evaporation of an acetonitrile solution at room temperature. ^1H NMR (CD_3CN): δ 1.20 (t, J_{H-H} = 7.3 Hz), 3.16 (q). ^{19}F NMR (CD_3CN, $\delta(C_6F_6)$ = −163 ppm): δ −52.4 (s). IR (KBr): 2988 (m), 1550 (s), 1483 (s), 1395 (s), 1246 (vs), 1120 (vs), 1000 (s),

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Table 1. Crystallographic Data^a for Compounds **1**−**5**

	1	**2**	**3**	**4**	**5**
formula	$C_{28}H_{40}F_{18}MoN_2S_6$	$C_{28}H_{40}F_{18}N_2S_6W$	$C_{24}H_{40}F_{12}N_2OS_4W$	$C_{24}H_{40}F_{12}MoN_2OS_4$	$C_{12}F_{18}MoS_6$
fw	1034.92	1122.83	912.67	824.76	774.42
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	hexagonal
space group	$C2/c$	$C2/c$	$P2_1/n$	$P2_1/n$	$P6_3/m$
a (Å)	18.905(4)	18.933(4)	12.200(2)	12.184(2)	9.6795(14)
b (Å)	13.732(3)	13.728(3)	18.630(4)	18.627(4)	9.6795(14)
c (Å)	17.101(3)	17.096(3)	15.463(3)	15.482(3)	13.951(3)
α (deg)	90.00	90.00	90.00	90.00	90.00
β (deg)	110.29(3)	110.26(3)	91.02(3)	91.06(3)	90.00
γ (deg)	90.00	90.00	90.00	90.00	120.00
V (Å^{3})	4164.0(14)	4168.5(14)	3514.0(12)	3513.1(12)	1132.0(3)
Z	4	4	4	4	2
D_{calc} (g/cm^{3})	1.651	1.789	1.725	1.559	2.272
R^b	0.0454	0.0312	0.0456	0.0456	0.1036
$R_w{}^c$	0.1098	0.0691	0.0930	0.0988	0.2836

[a] Obtained with graphite-monochromatized Mo Kα (λ = 0.710 73 Å) radiation at 293(2) K. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$.

921 (s, $\nu_{W=O}$), 893 (s), 861 (s), 830 (s), 782 (s), 714 (s), 700 (s), 689 (s) cm^{-1}. FAB$^-$/MS: m/z = 782 ([M − Et_4N]$^-$), 652 ([M − $2Et_4N$]$^-$).

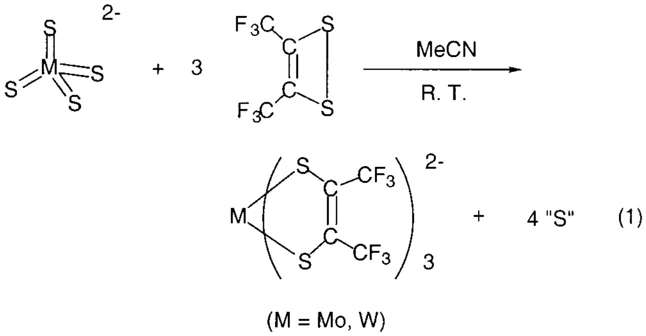
Synthesis of $(Et_4N)_2MoO(tfd)_2$ (4). The dithiete $(CF_3)_2C_2S_2$ (0.2 g, 0.88 mmol) was added dropwise to a stirred solution of $(Et_4N)_2MoO_2S_2$ in acetonitrile (0.2 g, 0.44 mmol). The yellow solution immediately became red-brown with the formation of elemental sulfur. The mixture was stirred at room temperature for 3 h and filtered to remove sulfur. The volume was reduced under vacuum, and the concentrated solution was layered with ether. Storing the mixture at 0 °C overnight gave a red solid (0.18 g, yield = 50%). X-ray-quality crystals were obtained by slow evaporation of an acetonitrile solution at room temperature. ^{1}H NMR ($CDCl_3$): δ 1.38 (t, J_{H-H} = 7.2 Hz), 3.44 (q). ^{19}F NMR ($CDCl_3$, $\delta(C_6F_6)$ = −163 ppm): δ −56.7 (s). IR (KBr): 2990 (m), 1543 (s), 1483 (s), 1396 (m), 1243 (vs), 1162 (sh), 1153 (s), 1114 (vs), 1000 (m), 917 (s, $\nu_{Mo=O}$), 872 (s), 831 (m), 782 (m), 706 (s), 688 (m) cm^{-1}. FAB$^-$/MS: m/z = 695 ([M − Et_4N]$^-$), 565 ([M − $2Et_4N$]$^-$).

Synthesis of Mo(tfd)$_3$ (5). This compound was synthesized according to the procedure of Davison et al. by refluxing $(CF_3)_2C_2S_2$ with Mo(CO)$_6$ in methylcyclohexane.[37] X-ray-quality crystals were obtained by slow diffusion of CH_2Cl_2 into a pentane solution of Mo(tfd)$_3$. ^{19}F NMR ($CDCl_3$, $\delta(C_6F_6)$ = − 163 ppm): δ −56.4 (s). IR (KBr): 1458 (w), 1259 (s), 1218 (s), 1179 (s), 1150 (s), 855 (w), 727 (s), 697 (s) cm^{-1}. UV−vis (pentane): 270 (sh), 387, 581 nm. FAB$^+$/MS: m/z = 775 (M$^+$).

Reaction of $(CF_3)_2C_2S_2$ with $ReS_4{}^-$. A solution of 0.4 g of $(Et_4N)ReS_4$ (0.9 mmol) in 50 mL of anhydrous acetonitrile was treated with 0.61 g of $(CF_3)_2C_2S_2$ (2.7 mmol) by dropwise addition. The purple solution immediately turned brown, and the formation of sulfur was observed during the course of the addition. After being stirred at room temperature for 2 h, the mixture was filtered through a pad of Celite, and the solvent was removed in vacuo. The resulting black solid was recrystallized from CH_3CN/Et_2O (0.57 g, 60% yield). ^{1}H NMR ($CDCl_3$): δ 1.18 (t, J_{H-H} = 7.5 Hz), 2.91 (q). ^{19}F NMR ($CDCl_3$, δ-(C_6F_6) = −163 ppm): δ −56.2 (s). IR (KBr): 2986 (w), 1561 (s), 1480 (s), 1455 (m), 1394 (m), 1236 (s), 1170 (s), 1153 (s), 996 (m), 888 (s), 843 (m), 781 (m), 712 (s), 694 (s), 522 (s), 372 (s) cm^{-1}. FAB$^-$/MS: m/z = 928 ([M − Et_4N]$^-$), 896 ([M − Et_4N − S]$^-$), 670 ([M − Et_4N − S − $(CF_3)_2C_2S_2$]$^-$).

Results and Discussion

Synthesis of Tris(dithiolene) Complexes. Treatment of tetrathiometalates $MS_4{}^{2-}$ (M = Mo, W) with stoichiometric amounts of $(CF_3)_2C_2S_2$ in acetonitrile at room temperature results in rapid formation of the dianionic tris(dithiolene) complexes (eq 1).



The reaction is fast, clean, and essentially quantitative. As monitored by ^{19}F NMR, varying the ratio of dithiete to tetrathiometalates (from 1 to 4 equiv) did not change the nature of the product; i.e., the tris(dithiolene) complex is formed as the exclusive product (albeit with different yields). Although intermediates are not observed, the reaction presumably proceeds via stepwise ligand displacement in which subsequent steps are much faster once the first equivalent of dithiete has reacted.

The nature of the redox in this reaction is worth comment. The formal oxidation state of metal in the tris(dithiolene) complexes is M^{IV}. Therefore, reacting the oxidant ($(CF_3)_2C_2S_2$) with the tetrathiometalate results in reduction of the metal from M^{VI} to M^{IV}. Concomitantly, the sulfide ligand is oxidized to form elemental sulfur. This internal electron transfer from sulfide ligand to metal is induced by the addition of the oxidant. Scheme 2 shows the electron balance for this reaction.

The redox properties of both $(Et_4N)_2Mo(tfd)_3$ (**1**) and $(Et_4N)_2W(tfd)_3$ (**2**) have been studied by polarography.[5,43] Cyclic voltammetry reveals two reversible redox couples, which are assigned to the M(tfd)$_3{}^{2-}$/M(tfd)$_3{}^-$ and M(tfd)$_3{}^-$/M(tfd)$_3$ couples, respectively. The redox potentials indicate that the neutral forms of these complexes are mild oxidants. The oxidizing properties have been employed to make the anions.[37,38] On the basis of the redox potentials, Mo(tfd)$_3$ is slightly more oxidizing than W(tfd)$_3$ ($E_{1/2}$ = 0.28 V (Mo) vs 0.22 V (W) for the 0/−1 couple). This difference in redox potential is consistent with the trends in the reactivities of these compounds in oxidizing hydrazines.[37]

Although tris(1,2-bis(trifluoromethyl)ethylene-1,2-dithiolato) complexes of Mo and W, such as M(tfd)$_3$ and M(tfd)$_3{}^{2-}$ (M = Mo, W), have been prepared previously via different routes,[37] these preparations require multiple steps and prolonged reaction times and the yields are usually low. For example, the reported two-step synthesis of W(tfd)$_3{}^{2-}$ involves more than 3 days

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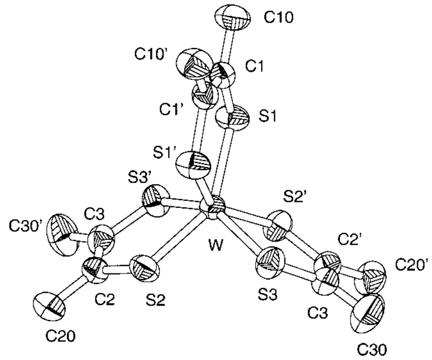

Figure 1. ORTEP drawing of $W(tfd)_3^{2-}$ (**2**). Fluorine atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. $Mo(tfd)_3^{2-}$ (**1**) is isostructural with **2**.

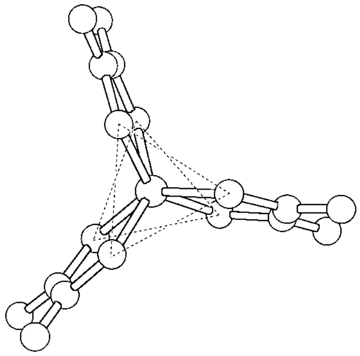

Figure 2. "Top" view of $Mo(tfd)_3^{2-}$ (**1**) indicating the twist from a perfect trigonal prism (16°).

Scheme 2

$4\ S^{2-} \rightarrow 4\ \text{"S"}$	eight-electron oxidation
$M^{VI} \rightarrow M^{IV}$	two-electron reduction
$3\ (CF_3)_2C_2S_2 \rightarrow 3\ [(CF_3)_2C_2S_2]^{2-}$	six-electron reduction

of refluxing of $W(CO)_6$ with $(CF_3)_2C_2S_2$ in an organic solvent to form $W(tfd)_3$ and reduction of $W(tfd)_3$ with hydrazine (a toxic and cancer suspect material) to form $W(tfd)_3^{2-}$. The total yield is less than 30%. The present synthesis provides a fast and convenient route to directly synthesize dianionic tris(dithiolene) complexes in high yield.

Crystal and Molecular Structure of $M(tfd)_3^n$ ($n = -2$, M = Mo, W; $n = 0$, M = Mo). The crystal structure of $[Fe(C_5Me_5)_2]_2Mo(tfd)_3$ has been reported by Miller et al.[38] To our knowledge, no crystal structure has been reported for $W(tfd)_3^{2-}$ or $M(tfd)_3$ (M = Mo, W). We have determined the crystal and molecular structure of $(Et_4N)_2W(tfd)_3$ (Figure 1). For comparison, we also determined the structure of $(Et_4N)_2Mo(tfd)_3$. The Mo and W anions are isostructural and are distorted by a "twist" from a perfect trigonal prism.[44] Figure 2 is a view from the "top" of the trigonal prism indicating that one equilateral triangle formed by three "upper" sulfur atoms is twisted away from the equilateral triangle formed by the three "lower" sulfur atoms. The twist angle is ca. 16°. The chelate ring formed by the metal and the dithiolene ligand is almost perfectly planar.

Crystallographic data are listed in Table 1. Selected bond lengths and angles for **1** and **2** are listed in Tables 2 and 3, respectively. The average bond lengths and angles are normal compared to those of other dithiolene complexes. Table 4 lists the mean interatomic distances and angles for these and related complexes.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $(Et_4N)_2Mo(tfd)_3$ (**1**)

Distances			
Mo−S(1)	2.3695(12)	S(3)−C(3)	1.734(5)
Mo−S(1′)	2.3696(12)	C(1)−C(1′)	1.339(8)
Mo−S(2)	2.3745(12)	C(1)−C(10)	1.498(6)
Mo−S(2′)	2.3746(12)	C(2)−C(3′)	1.334(7)
Mo−S(3)	2.3806(13)	C(2)−C(20)	1.490(7)
Mo−S(3′)	2.3805(13)	C(3)−C(2′)	1.334(7)
S(1)−C(1)	1.738(4)	C(3)−C(30)	1.515(7)
S(2)−C(2)	1.741(5)		
Angles			
S(1)−Mo−S(1′)	79.95(6)	S(1′)−Mo−S(3′)	123.34(5)
S(1)−Mo−S(2)	146.16(4)	S(2)−Mo−S(3′)	80.54(5)
S(1′)−Mo−S(2)	84.30(4)	S(2′)−Mo−S(3′)	83.87(5)
S(1)−Mo−S(2′)	84.30(4)	S(3)−Mo−S(3′)	146.98(7)
S(1′)−Mo−S(2′)	146.16(4)	C(1)−S(1)−Mo	110.64(14)
S(2)−Mo−S(2′)	123.01(7)	C(2)−S(2)−Mo	109.8(2)
S(1)−Mo−S(3)	123.34(5)	C(3)−S(3)−Mo	109.5(2)
S(1′)−Mo−S(3)	83.45(5)	C(1′)−C(1)−S(1)	119.38(13)
S(2)−Mo−S(3)	83.87(5)	C(3′)−C(2)−S(2)	119.7(3)
S(2′)−Mo−S(3)	80.54(5)	C(2′)−C(3)−S(3)	120.4(3)
S(1)−Mo−S(3′)	83.45(5)		

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $(Et_4N)_2W(tfd)_3$ (**2**)

Distances			
W−S(1)	2.3680(12)	S(3)−C(3)	1.738(5)
W−S(1′)	2.3680(12)	C(1)−C(1′)	1.336(8)
W−S(2)	2.3714(12)	C(1)−C(10)	1.509(6)
W−S(2′)	2.3715(12)	C(2)−C(3′)	1.340(7)
W−S(3)	2.3753(14)	C(2)−C(20)	1.499(7)
W−S(3′)	2.3753(14)	C(3)−C(2′)	1.340(7)
S(1)−C(1)	1.740(4)	C(3)−C(30)	1.496(8)
S(2)−C(2)	1.748(5)		
Angles			
S(1)−W−S(1′)	80.21(6)	S(1′)−W−S(3′)	83.29(5)
S(1)−W−S(2)	83.88(4)	S(2)−W−S(3′)	80.85(5)
S(1′)−W−S(2)	146.07(4)	S(2′)−W−S(3′)	83.71(5)
S(1)−W−S(2′)	146.07(4)	S(3)−W−S(3′)	146.97(7)
S(1′)−W−S(2′)	83.88(4)	C(1)−S(1)−W	110.37(14)
S(2)−W−S(2′)	123.58(7)	C(2)−S(2)−W	109.6(2)
S(1)−W−S(3)	83.29(5)	C(3)−S(3)−W	109.7(2)
S(1′)−W−S(3)	123.48(5)	C(1′)−C(1)−S(1)	119.52(14)
S(2)−W−S(3)	83.70(5)	C(3′)−C(2)−S(2)	119.8(4)
S(2′)−W−S(3)	80.84(5)	C(2′)−C(3)−S(3)	120.0(4)
S(1)−W−S(3′)	123.49(5)		

Table 4. Comparison of Mean Bond Lengths (Å) and Angles (deg) for Tris(dithiolene) Complexes

	Mo $(tfd)_3$	Mo $(bdt)_3$	Mo $(tfd)_3^{2-}$	Mo $(mnt)_3^{2-}$	W $(tfd)_3^{2-}$	W $(mnt)_3^{2-}$
Distances						
M−S	2.353(3)	2.367(6)	2.375(5)	2.374(7)	2.371(5)	2.371(7)
S−C	1.695(10)	1.727(6)	1.736(3)	1.74(2)	1.743(3)	1.73(2)
C═C	1.36(2)	1.41(1)	1.332(2)	1.33(2)	1.337(2)	1.32(2)
S−S (intra)	3.09(2)	3.110(8)	3.07(3)	3.12(2)	3.07(3)	3.12(2)
S−S (inter)	3.07(2)	3.09(2)	3.18(2)	3.19(8)	3.16(2)	3.19(8)
Angles						
S−M−S (intra)	82.2(2)	82.1(4)	80.2(3)	82.4(5)	80.6(3)	82.0(5)
S−M−S (trans)	135.7(2)	136(1)	146.5(4)	156(2)	146.4(4)	156(2)
References						
	this work	46	this work	44	this work	44

The crystal structure of $[Fe(C_5Me_5)_2]Mo[S_2C_2(CF_3)_2]_3$ has

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[44] Brown, B. F.; Stiefel, E. I. *Inorg. Chem.* **1973**, *12*, 2140.

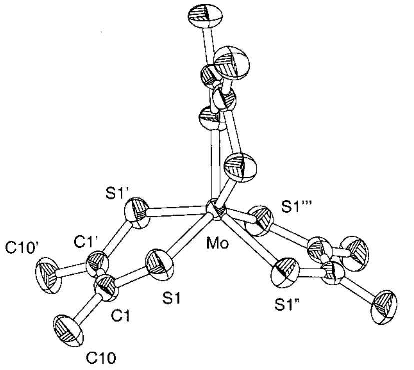

Figure 3. ORTEP drawing of Mo(tfd)$_3$ (**5**). Fluorine atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for Mo(tfd)$_3$ (**5**)

Distances			
Mo−S(1)	2.355(4)	C(1)−C(1′)	1.37(3)
S(1)−C(1)	1.695(14)	C(1)−C(10)	1.54(2)
Angles			
S(1)−Mo−S(1′)	82.0(2)	C(1′)−C(1)−C(10)	126.0(11)
S(1)−Mo−S(1″)	81.7(2)	C(1′)−C(1)−S(1)	120.5(5)
S(1′)−Mo−S(1″)	135.65(7)	C(10)−C(1)−S(1)	113.1(13)
C(1)−S(1)−Mo	106.7(5)		

also been reported.[38] The monoanion adopts a nearly perfect trigonal prismatic coordination, and the metal−ligand chelates are planar. In contrast, the geometry of the dianion in $[Fe(C_5Me_5)_2]_2Mo[S_2C_2(CF_3)_2]_3$ is significantly distorted from trigonal prismatic, which was attributed to crystal packing effects.[38]

For comparison, we determined the crystal and molecular structure of the neutral molecule Mo(tfd)$_3$ (**5**) (Figure 3). As anticipated, this complex adopts an almost perfect trigonal prismatic coordination, but the metal−ligand chelate rings are bent. The dihedral angle is ca. 18°. Crystallographic data and selected bond lengths and angles are listed in Tables 1 and 5, respectively.

The differences between the structures of Mo(tfd)$_3^{2-}$ and Mo(tfd)$_3$ are of interest. Both structures are shown in Figure 4 for comparison. The neutral complex adopts an almost perfect trigonal prismatic coordination with bent metal−dithiolene chelate rings. In contrast, in the dianion, the bend is absent and the coordination geometry around the metal is a twisted trigonal prism.

Bending of the metal−ligand chelate ring has been observed in other transition metal tris(dithiolene) complexes, especially in high-valent metal complexes.[45−48] However, the bending has been reported mostly in tris(dithiolene) complexes with dithiolene ligands such as $[(S_2C_2H_2)^{2-}]$[45] and $[(S_2C_6H_4)^{2-}]$.[46,47] The current example indicates that such bending persists in complexes with electron-withdrawing ligands such as $[(CF_3)_2C_2S_2]^{2-}$. Our results provide an opportunity to compare the structures of the neutral and the dianionic tris(dithiolene) complexes with the same, relatively bulky ligand.

The bending in Mo(tfd)$_3$ can be explained using the theoretical studies of Harris et al. on the tris(dithiolene) complexes.[49] Using $Mo(S_2C_2H_2)_3$ as a model, these calculations indicate that, in the D_{3h} limit (perfect trigonal prism), the HOMO is a nonbonding a$_2'$ combination of ligand π_v orbitals and the LUMO (a$_1'$) consists primarily of the metal d_{z^2} orbital. This orbital arrangement is in agreement with the earlier studies.[50] The derived level ordering is consistent with a description of the complex in which each dithiolene ligand is formally dianionic (reduced) and the Mo center is formally Mo^{VI}-4d^0. In this description, all of the metal 4d orbitals are unoccupied. The calculated energy difference between the HOMO and the LUMO is very small. In D_{3h} symmetry, no mixing is possible between the HOMO and the LUMO. However, bending of the chelate ring reduces the symmetry to C_{3h}, which allows the HOMO and the LUMO to mix, forming a bonding (a′) and an antibonding (a′) orbital. The ligand π_v orbitals are no longer orthogonal to the metal d_{z^2} orbital; instead they bend toward the metal d_{z^2} orbital. The bending effectively increases the bonding interaction of the ligand π_v orbitals and the metal d_{z^2} orbital, while concomitantly decreasing the antibonding interactions between the adjacent sulfur atoms among the ligands (although this likely is a minor factor). In complexes with additional electrons, e.g., Mo(tfd)$_3^{2-}$, the a$_1'$ orbital (previous LUMO) is populated and the driving force for bending is considerably less or nonexistent. The calculation suggests that the bulk of the ligand is only a secondary factor in determining whether the chelate ring bends,[49] which is consistent with our results. Our results suggest that the electron-withdrawing properties of the substituents on the dithiolene ligands may not be a major factor, either.

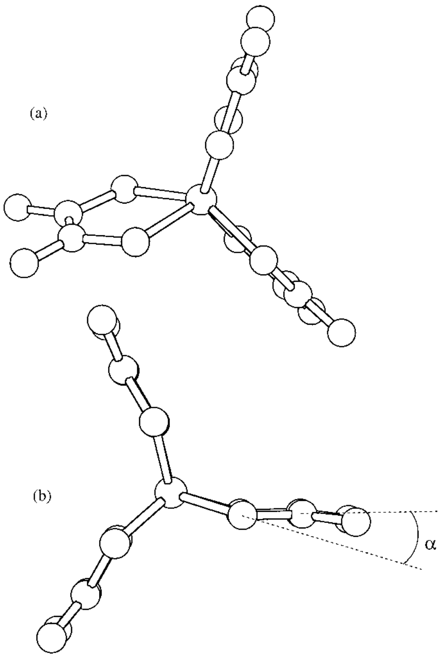

Figure 4. Comparison of the structures of (a) Mo(tfd)$_3^{2-}$ (**1**) and (b) Mo(tfd)$_3$ (**5**). The three metal−ligand chelate rings in **5** bend away from the plane by ca. 18°. Fluorine atoms are omitted for clarity.

While the above argument explains the bending of the chelate ring in the neutral complex and the lack of bending in the dianion, the question still remains as to why the dianion adopts a *twisted* trigonal prismatic structure. Since the first observation of a discrete trigonal prismatic coordination in $Re(S_2C_2Ph_2)_3$,[51] a host of factors, such as (a) ligand constraint, (b) ligand field stabilization energy, (c) inter-donor atom bonding, (d) proper matching of the ligand and metal orbital energies, (e) the

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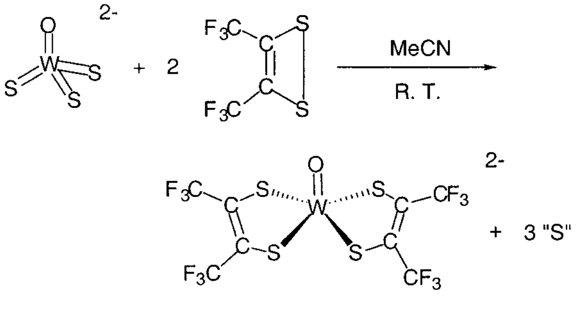
Scheme 3

$3\ S^{2-} \rightarrow 3\ \text{"S"}$	six-electron oxidation
$W^{VI} \rightarrow W^{IV}$	two-electron reduction
$2\ (CF_3)_2C_2S_2 \rightarrow 2\ [(CF_3)_2C_2S_2]^{2-}$	four-electron reduction

symmetry of ligand π orbitals, and (f) the overall charge of the complex have been suggested as important factors influencing the formation of trigonal prismatic, octahedral, or “in-between” geometries. Both experimental[52] and theoretical[53,54] studies aimed at understanding trigonal prismatic versus octahedral coordination geometry have been reported. It seems that the mixing of ligand-localized, filled σ orbitals (HOMO) with empty, π-type orbitals (LUMO) in a d^0 system can result in stabilization of a trigonal prismatic structure relative to an octahedral structure, which is predicted on the basis of the valence shell electron pair repulsion model. However, no adequate explanation for the *twisted* trigonal prismatic coordination has been offered.

Recently, the structures of early transition metal hexaacetylides have been reported.[55] In the case of $Ta(C{\equiv}CSi^tBu_3)_6^-$, a twisted trigonal prismatic structure was observed. The twist angle from the trigonal prism is ca. 18°. Theoretical studies using $Ta(C{\equiv}CH)_6^-$ as a model suggest that it is energetically easy to twist up to ~20° if the ligand is sterically demanding. The observed twist angle of 18° can apparently mitigate any interligand steric repulsive effects in $Ta(C{\equiv}CSi^tBu_3)_6^-$. However, in the case of $Mo(tfd)_3^{2-}$, interligand repulsion should not be a major factor since the ligands are not very bulky. Moreover, inspection of the crystal lattices did not suggest any significant packing effects. Further investigations, both experimental and theoretical, would be required to understand the difference in the structures of neutral, monoanionic, and dianionic tris(dithiolene) complexes.

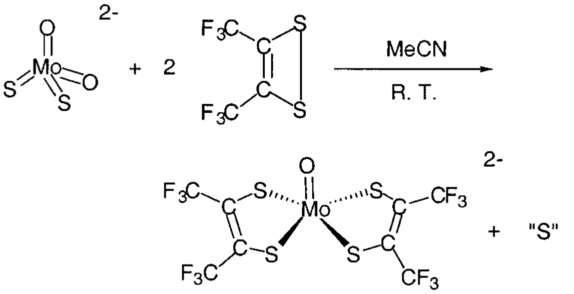
Synthesis of $(Et_4N)_2WO(tfd)_2$ (3). Treating $(Et_4N)_2WOS_3$ with $(CF_3)_2C_2S_2$ in acetonitrile at room temperature results in rapid formation of $(Et_4N)_2WO(tfd)_2$ in good yield (eq 2). The complex was isolated as an orange solid. In this reaction, adding the oxidant induced the electron transfer from the sulfido ligand to tungsten. Electron balance for this reaction is shown in Scheme 3. The ratio of $(CF_3)_2C_2S_2$ to WOS_3^{2-} has been varied. When 2 equiv or less of $(CF_3)_2C_2S_2$ is used, $(Et_4N)_2WO(tfd)_2$ is the only product as revealed by ^{19}F NMR. However, if more than 2 equiv of $(CF_3)_2C_2S_2$ is used, the formation of $W(tfd)_3$ can be observed by ^{19}F NMR.



(2)

$(Et_4N)_2WO(tfd)_2$ shows a characteristic W=O stretch at 921 cm^{-1} ($\nu_{W=O}$) in the IR spectrum. This frequency can be compared with those of similar compounds: $(Et_4N)_2WO(bdt)_2$ (905 cm^{-1}),[56] $(Et_4N)_2WO(mnt)_2$ (935 cm^{-1}).[57] Clearly, the more electron-withdrawing the substituent on the dithiolene, the higher the W=O stretching frequency. This trend can be readily rationalized in terms of the electron-withdrawing capability of the substituent on the dithiolene ligand, which enhances π-bonding of the oxo ligand with W d_{xz} and d_{yz} orbitals by decreasing the dithiolene electron donation to the metal. The metal−oxo stretching frequency therefore may provide important structural information for both enzymatic and model systems. In the biological systems, once the M−O stretch is established in the M(IV) oxidation state (M = Mo, W), the electron-withdrawing effect of the pyranopterin dithiolate could be compared to that of the model compounds.

Synthesis of $(Et_4N)_2MoO(tfd)_2$ (4). This compound can be synthesized from $(Et_4N)_2MoO_2S_2$. Treatment of $(Et_4N)_2MoO_2S_2$ with 2 equiv of $(CF_3)_2C_2S_2$ in acetonitrile results in rapid formation of $(Et_4N)_2MoO(tfd)_2$ in a moderate yield (eq 3). The isolated product is an orange solid. In this reaction, the internal electron transfer from sulfide to Mo is again induced by adding an external oxidant, $(CF_3)_2C_2S_2$. The yield of the reaction is relatively low, and the missing oxygen has not been accounted for in eq 3. One possibility is that the oxo ligand is hydrolyzed or protonated by adventitious water. The loss of one oxygen atom in the product in the reaction of oxo complexes of Mo and W is not unprecedented.[22,26,62]



(3)

Varying the ratio of $(CF_3)_2C_2S_2$ to $(Et_4N)MoO_2S_2$ revealed that $(Et_4N)_2MoO(tfd)_2$ is the major product when 2 equiv of dithiete or less is used. However, when more than 2 equiv of the dithiete is used, a significant amount of $(Et_4N)_2Mo(tfd)_3$ is formed. In the IR spectrum, a band at 917 cm^{-1} characteristic of $\nu_{Mo=O}$ is observed. This stretching frequency falls in the range of typical $\nu_{Mo=O}$ values for compounds in this class: $(Et_4N)_2MoO(bdt)_2$ (903 cm-1),[58] $(Et_4N)_2MoO[S_2C_2(COOMe)_2]_2$ (914 cm^{-1}),[59] $(Bu_4N)_2MoO(mnt)_2$ (940 cm^{-1}).[60] The trend in the Mo=O stretching frequency can again be explained by the electron-withdrawing properties of the substituent on the dithiolene ligand.

Crystal and Molecular Structure of $MO(tfd)_2^{2-}$ (M = Mo, W). The two anions are isostructural and adopt a square

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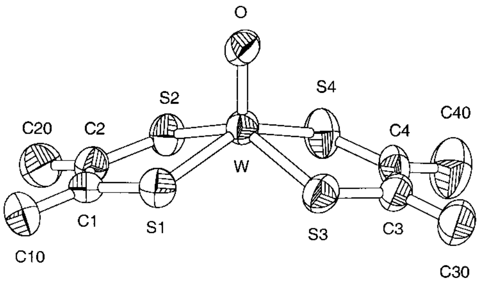


Figure 5. ORTEP drawing of $WO(tfd)_2^{2-}$ (**3**). Fluorine atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. $MoO(tfd)_2^{2-}$ (**4**) is isostructural with **3**.

Table 6. Selected Bond Distances (Å) and Bond Angles (deg) for $(Et_4N)_2W(O)(tfd)_2$ (**3**)

	Distances		
W−O	1.714(5)	S(4)−C(4)	1.775(11)
W−S(1)	2.357(2)	C(1)−C(2)	1.316(12)
W−S(2)	2.359(2)	C(3)−C(4)	1.329(14)
W−S(3)	2.353(3)	C(1)−C(10)	1.494(14)
W−S(4)	2.353(2)	C(2)−C(20)	1.509(13)
S(1)−C(1)	1.770(9)	C(3)−C(30)	1.49(2)
S(2)−C(2)	1.779(9)	C(4)−C(40)	1.50(2)
S(3)−C(3)	1.762(10)		
	Angles		
O−W−S(3)	108.5(2)	S(1)−W−S(2)	82.66(8)
O−W−S(4)	109.0(2)	C(1)−S(1)−W	107.9(3)
S(3)−W−S(4)	82.78(9)	C(2)−S(2)−W	107.1(3)
O−W−S(1)	110.1(2)	C(4)−S(4)−W	107.3(4)
S(3)−W−S(1)	85.16(9)	C(3)−S(3)−W	107.7(4)
S(4)−W−S(1)	140.87(8)	C(2)−C(1)−S(1)	120.0(7)
O−W−S(2)	106.6(2)	C(1)−C(2)−S(2)	120.8(7)
S(3)−W−S(2)	144.83(9)	C(4)−C(3)−S(3)	120.3(7)
S(4)−W−S(2)	86.17(8)	C(3)−C(4)−S(4)	120.2(7)

Table 7. Selected Bond Distances (Å) and Bond Angles (deg) for $(Et_4N)_2Mo(O)(tfd)_2$ (4)

	Distances		
Mo−O	1.684(3)	S(4)−C(4)	1.770(5)
Mo−S(1)	2.365(2)	C(1)−C(2)	1.325(8)
Mo−S(2)	2.3663(14)	C(3)−C(4)	1.328(8)
Mo−S(3)	2.3704(14)	C(1)−C(10)	1.502(9)
Mo−S(4)	2.371(2)	C(2)−C(20)	1.510(8)
S(1)−C(1)	1.759(6)	C(3)−C(30)	1.518(7)
S(2)−C(2)	1.763(6)	C(4)−C(40)	1.490(8)
S(3)−C(3)	1.762(5)		
	Angles		
O−Mo−S(3)	110.75(13)	S(1)−Mo−S(2)	82.16(6)
O−Mo−S(4)	107.67(14)	C(1)−S(1)−Mo	107.9(2)
S(3)−Mo−S(4)	82.28(5)	C(2)−S(2)−Mo	107.1(2)
O− Mo−S(1)	108.55(14)	C(4)−S(4)−Mo	107.4(2)
S(3)−Mo−S(1)	84.87(5)	C(3)−S(3)−Mo	107.7(2)
S(4)−Mo−S(1)	143.79(6)	C(2)−C(1)−S(1)	119.8(4)
O−Mo−S(2)	109.62(12)	C(1)−C(2)−S(2)	121.0(4)
S(3)−Mo−S(2)	139.63(6)	C(4)−C(3)−S(3)	120.8(4)
S(4)−Mo−S(2)	86.06(5)	C(3)−C(4)−S(4)	121.1(4)

pyramidal structure. The four sulfur atoms of the dithiolene ligands form the basal plane, with the oxygen at the apex. An ORTEP drawing of the W anion is given in Figure 5. Crystallographic data and selected bond lengths and angles are listed in Tables 1, 6, and 7, respectively. For $WO(tfd)_2^{2-}$, the W−O distance is 1.713(5) Å, somewhat shorter than that in $WO(bdt)_2^{2-}$ (1.727(9) Å).[61] The trend in W−O distance is consistent with the trend of $\nu_{W=O}$ in the IR spectrum; i.e., the shorter and presumably stronger bond has the higher stretching frequency (921 cm^{-1} for $WO(tfd)_2^{2-}$ vs 905 cm^{-1} for $WO(bdt)_2^{2-}$). Other bond lengths and angles are unexceptional. For $MoO(tfd)_2^{2-}$, the Mo−O distance is 1.687(3) Å, somewhat longer than that of $MoO(mnt)_2^{2-}$ (1.67 Å).[60] The trend in Mo−O distance is also consistent with the trend of $\nu_{Mo=O}$ in the IR spectrum; i.e., the shorter bond has the higher stretching frequency (917 cm^{-1} for $MoO(tfd)_2^{2-}$ vs 940 cm^{-1} for $MoO(mnt)_2^{2-}$). Other bond lengths and angles are normal (Table 8).

One feature worth noting is the nonplanar nature of the metal−dithiolene chelate ring. Almost all other oxo bis(dithiolene) complexes reported have planar chelate rings. Sterically, CF_3 is not a very bulky substituent; and a "side view" of the structure reveals no steric hindrance toward a planar chelate ring. Moreover, examination of the crystal lattices suggests that the "bend" is not an effect of crystal packing. The planar nature of the chelate rings in the mnt or bdt analogues is probably due to the π character of the substituent group. A planar chelate ring would maximize the π interaction between these more conjugated dithiolene ligands and the metal d orbitals.

Reaction of $(CF_3)_2C_2S_2$ with ReS_4^-. The reaction of the dithiete with tetrathioperrhenate, $(Et_4N)ReS_4$ (eq 4), leads to the isolation of a rhenium product in moderate yield (60%). Negative-ion FAB/MS reveals the anion to contain one rhenium, three dithiolenes, and two additional sulfur atoms. Two structures, which are internal redox isomers, seem most likely (Chart

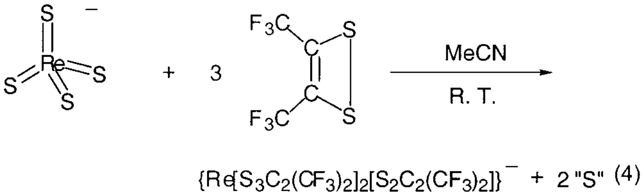
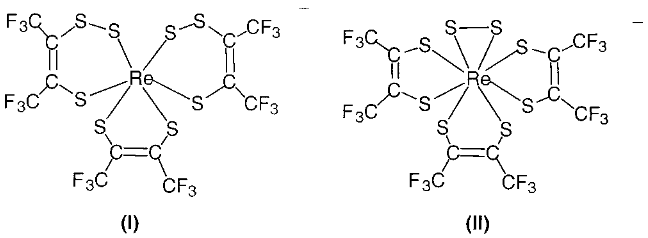


Table 8. Comparison of Mean Bond Lengths (Å) and Angles (deg) for Oxo−Bis(dithiolene) Complexes $M(O)L_2^{2-}$ (M, L)

	complex							
	Mo, bdt	Mo, sdt	Mo, dct[a]	Mo, mnt	Mo, tfd	W, bdt	W, mnt	W, tfd
				Distances				
M−O	1.699(6)	1.700(5)	1.686(6)	1.67	1.687(3)	1.726(8)	1.73(2)	1.713(5)
M−S	2.388(2)	2.374(12)	2.380(4)	2.38	2.368(4)	2.372(3)	2.378(5)	2.356(4)
S−S (intra)	3.17	3.13(1)	3.16		3.109(2)	3.14	3.16(5)	3.113(5)
S−S (inter, cis)	3.25	3.22(5)	3.21		3.21 (3)	3.24	3.23(9)	3.20(3)
				Angles				
S−M−S (intra)	83.1(1)	82.4(3)	83.1		82.1(1)	82.9(1)	83.7(5)	82.7(1)
S−M−S (trans)	143.7(1)		142.1		142(2)	143.3(1)	144(3)	143(2)
				References				
	b	22	*c*	58	this work	60	57	this work

[a] dct = $[S_2C_2(COOMe)_2]^{2-}$. [b] Boyde, S.; Ellis, S. R.; Garner, C. D.; Clegg, W. *J. Chem. Soc., Chem. Commun.* **1986**, 1541. [c] Coucouvanis, D.; Hadjikyriacou, A.; Toupadakis, A.; Koo, S.-M.; Ileperuma, O.; Graganjac, M.; Salifoglou, A. *Inorg. Chem.* **1991**, *30*, 754.

Chart 1



(I) (II)

1). In structure **I**, Re has a formal oxidation state of $\mathrm{Re^{V}}$, and the reaction involves induced internal redox. For structure **II**, the reaction involves a pure ligand redox reaction as Re remains formally $\mathrm{Re^{VII}}$.

^{19}F NMR reveals only a singlet at δ -56.2 ppm, even at temperatures as low as -40 °C, suggesting that the structure is either highly symmetrical or, more likely, fluxional in solution. Treating the product with sulfur-abstracting reagents such as $\mathrm{PPh_3}$ results in the formation of $\mathrm{SPPh_3}$, as indicated by ^{31}P NMR ($\delta(\mathrm{SPPh_3}) = 44.0$ ppm). However, the nature of the rhenium-containing species after sulfur abstraction has not been established.

In the IR spectrum, the complex shows bands of medium intensity at 372 and 523 cm^{-1}, which are tentatively assigned as $\nu_{\mathrm{Re-S}}$ and $\nu_{\mathrm{S-S}}$ stretching vibrations. In the negative-ion mass spectrum, fragments resulting from the loss of one sulfur and from the loss of $[\mathrm{S} + (\mathrm{CF_3})_2\mathrm{C_2S_2}]$ have been observed.

Molecular mechanics calculations (MM2) suggest a nearly perfect octahedral coordination for structure **I**, while structure **II** has an eight-coordination sphere with a mirror plane. While no severe steric congestion is suggested for either structure, the calculated total energy of structure **I** (218 kcal/mol) is significantly less than that of structure **II** (558 kcal/mol).

The "trithiolene" ligand suggested in structure **I** has precedent in molybdenum chemistry. In the X-ray crystal structure of the trithiolene complex $\mathrm{Cp_2MoS_3C_2}$(2-quinoxaline)(C(O)Me), the S$-$Mo$-$S bite angle is ca. 88°, significantly larger than that in the corresponding dithiolene complex $\mathrm{Cp_2MoS_2C_2}$(2-quinoxaline)(C(O)Me) (82°).[62] Thus the trithiolene ligand has minimal geometric constraints in octahedral coordination, which may reduce the total energy of the complex compared to the structurally more crowded eight-coordinate structure **II**. Moreover, an analogous compound, $\mathrm{Re(S_2CPh)(S_3CPh)_2}$, is formed from a very similar reaction involving induced internal redox.[28]

To date, attempts with different cations, such as $\mathrm{Ph_4P^+}$, $\mathrm{PPN^+}$, $\mathrm{BzEt_3N^+}$, etc., to obtain X-ray-quality crystals have failed, although efforts are still underway. However, on the basis of the discussion above and the strong tendency of $\mathrm{ReS_4^-}$ to undergo induced internal redox reactions, we favor structure **I** over structure **II** for the product.

Concluding Remarks

We have devised an improved method for synthesizing selected metal dithiolene complexes starting from thiometalates and employing induced internal redox reactions. This strategy has been extended to oxothiometalates, yielding oxo-containing dithiolene complexes. This single-step synthesis is convenient and fast, and the yield is generally very good to satisfactory.

Induced internal electron-transfer reactions of thiometalates have been extensively studied over the last two decades.[28−33] When organic disulfides such as RSSR and $\mathrm{(R_2NCS_2)_2}$ are used as oxidants, the ease with which the thiometalates undergo induced internal redox reactions was found to correlate with the energy of the first LMCT band in the electronic spectrum of the thiometalates.[63] For example, when treated with stoichiometric amount of $\mathrm{(R_2NCS_2)_2}$, $\mathrm{MoS_4^{2-}}$ undergoes an internal redox reaction to form $\mathrm{Mo^{V}(S_2)(S_2CNR_2)_3}$. However, under the same conditions, $\mathrm{WS_4^{2-}}$ undergoes a *ligand redox* reaction to form $\mathrm{W^{VI}S(S_2)(S_2CNR_2)_2}$. Similarly, $\mathrm{MoO_2S_2^{2-}}$ also undergoes a ligand redox reaction to form $\mathrm{Mo^{VI}O(S_2)(S_2CNR_2)_2}$.[64] The first LMCT bands of these thiometalates are as follows:[65] $\mathrm{MoS_4^{2-}}$, 21 300 cm^{-1}; $\mathrm{WS_4^{2-}}$, 25 300 cm^{-1}; $\mathrm{MoO_2S_2^{2-}}$, 25 450 cm^{-1}. Clearly, the lower the LMCT, the easier it is for the thiometalate to undergo induced internal redox reactions. Thereby the position of the first LMCT band can be used as a spectroscopic indicator of the facility with which internal electron transfer can occur in chemical reactions.

However, the results reported in this paper suggest that, by choice of a different (and presumably stronger) oxidant, the extent to which internal electron-transfer reactions occur can be increased. Both $\mathrm{(CF_3)_2C_2S_2}$ and $\mathrm{(R_2NCS_2)_2}$ are strong oxidants. For example, $\mathrm{(CF_3)_2C_2S_2}$ can oxidize some metals such as nickel to $\mathrm{Ni[S_2C_2(CF_3)_2]_2}$ (formally Ni(IV))[66] and refluxing $\mathrm{(R_2NCS_2)_2}$ with nickel powder gives $\mathrm{Ni(S_2CNR_2)_2}$ (formally Ni(II)). Therefore an important conclusion of this study is that the *nature of the oxidant* can also greatly influence the reactivity of thiometalates toward induced internal electron-transfer reactions. The stronger oxidant increases the ability of the ligand to reduce the metal center.

Recently, a tungstoprotein, acetylene hydratase, was revealed to contain tungsten with a pterin dithiolene cofactor.[67] Sarkar et al. have reported that $\mathrm{WO(mnt)_2^{2-}}$ serves as a functional model for this acetylene hydratase.[68] We are currently investigating the possible reactivity of $\mathrm{MO(tfd)_2^{2-}}$ (M = Mo, W) toward alkynes to determine if they also serve as functional models for this reaction.

Acknowledgment. Mr. B. Liang and Mr. G. Dechert are thanked for experimental assistance.

Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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