Synthesis and Reactivity Aspects of the Bis(dithiolene) Chalcogenide Series $[W^{IV}Q(S_2C_2R_2)_2]^{2-}$ (Q = O, S, Se)

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An improved synthetic route to the previously reported dicarbonyl complexes $[W(CO)_2(S_2C_2R_2)_2]$ (R = Ph (**1**), Me (**2**)) has been developed via the thermal reaction of $[W(CO)_3(MeCN)_3]$ and $[Ni(S_2C_2R_2)_2]$ in dichloromethane (60−70%). Complexes **1** and **2** are shown to be useful synthetic precursors by means of carbonyl ligand displacement. Reactions of **1** with Et_4NOH, Na_2S, and Li_2Se afford the previously unknown bis(dithiolene) series $[W^{IV}Q(S_2C_2Ph_2)_2]^{2-}$ (Q = O (**3**), S (**6**), Se (**7**), 65−76%). Complex **2** and Et_4NOH give $[W^{IV}O(S_2C_2Me_2)_2]^{2-}$ (**5**, 68%). Members of the series manifest absorption spectra that are strongly dependent on Q and redox potentials for $W^{IV}Q/W^{V}Q$ couples that are independent of Q. Reaction of **3** and **5** with MeI or EtI results in mono-S-alkylation as shown by the ^1H NMR spectra of $[WO(EtS_2C_2R_2)(S_2C_2R_2)]^{1-}$, which indicate a single stereoisomer with a diastereotopic methylene group. S-alkylation of **3** was further confirmed by the structure of the reaction product with MeI, $[WO(MeS_2C_2Ph_2)(S_2C_2Ph_2)]^{1-}$ (**8**, 65%), which reveals the exo stereoisomer with a pyramidal sulfur atom whose methyl carbon atom is displaced 1.27 Å from the chelate ring plane. Treatment of **3** with hard alkylating agents caused oxidation to $[W^{V}O(S_2C_2Ph_2)_2]^{-}$, independently prepared by reaction of **3** with iodine (78%). Sulfido complex **6** with soft alkylating agents such as MeI gave mixtures. Reaction of **6** with $C_7H_7^+$ resulted in electron transfer rather than alkylation and the formation of binuclear $[W^{V}_2(\mu\text{-}S)_2(S_2C_2Ph_2)_4]^{2-}$ (**11**, 53%). No alkylated species were isolated from selenido complex **7**; $[W(S_2C_2Ph_2)_3]$ (**13**) was identified as a reaction product. Electrochemical data and X-ray structural results for **1**, **2, 13** (trigonal prismatic), Et_4N^+ salts of **3**, **5**, **6** (square pyramidal), **8** (distorted square pyramidal), and **11** (distorted octahedral), and $(PhCH_2NEt_3)[W(S_2C_2Ph_2)_3]$ (distorted trigonal prismatic) are presented.

Introduction

The findings that molybdenum-[1,2] and tungsten-containing[3−5] oxotransferase and hydroxylase enzymes contain a universal pterin dithiolene cofactor, shown in Figure 1, has added new significance to the chemistry of dithiolene complexes of these elements, the first examples of which were prepared over 30 years ago.[6] Tungstoenzymes are isolated from hyperthermophilic archaeons and have been organized into two major families.[3,4] Those in the aldehyde oxidoreductase (AOR) family catalyze the reaction $RCHO + H_2O \rightleftarrows RCO_2H + 2H^+ + 2e^-$. Almost all other tungstoenzymes fall into the other major family, F(M)DH, which consists of two classes. The formate dehydrogenases (FDH) are responsible for the first step in the conversion of carbon dioxide to acetate in acetogenic bacteria. The *N*-formylmethanofuran dehydrogenases (FMDH) are implicated in the transformation of carbon dioxide to methane in methanogenic organisms. The structure of one enzyme, *Pyrococcus furiosus* AOR, has been determined crystallographically.[7−9] The active site consists of a tungsten atom chelated by two pterin dithiolene cofactor ligands and bound to two additional oxygenous ligands that could not be definitely identified. Recent EXAFS results of the dithionite-reduced enzyme corroborate the enzyme structure, revealing the interactions 4−5 W−S at 2.40 Å, 1 W−O at 1.75 Å, and a possible W−O/N at 1.97 Å.[4]

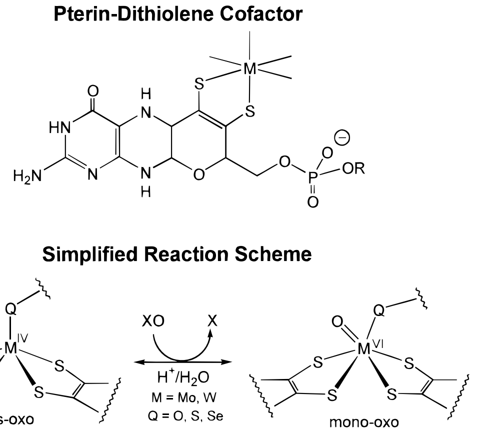

Figure 1. Structure of the pterin dithiolene cofactor coordinated to M = Mo, W (R absent or a nucleotide), and a simplified oxo transfer or hydroxylase reaction scheme for DMSOR and F(M)DH enzymes showing possible active site structures.

Enzymes of the F(M)DH family show little sequence homology with the AOR family and are more closely related to the molybdoenzymes of the DMSO reductase (DMSOR) family.[1,3,4] Members of the latter (which also include molybdenum-containing FDH and FMDH[1]) share certain active site common

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features, including coordination by *two* pterin dithiolene ligands and protein-based ligands that appears to vary with enzyme type: serinate for DMSOR[10−13] and cysteinate or selenocysteinate for FDH[14] and FMDH. Although there are structural discrepancies in active site coordination in the DMSOR family,[10−13,15] two features are constant: loss of an oxo ligand upon reduction from the Mo(VI) to the Mo(IV) state and retention of a protein ligand (serinate) in the oxidized and reduced enzymes. If these circumstances are generalized to molybdenum and tungsten enzymes of the DMSOR and F(M)-DH types, the simplified oxo transfer and hydroxylase reactions involving substrate/product X/XO depicted in Figure 1 emerge. As a result, desoxo and monooxo bis(dithiolene) complexes of the general types $[M^{IV}(S_2C_2R_2)_2(QR')]^{2-}$ and $[M^{VI}O(S_2C_2R_2)_2(QR')]^{2-}$, respectively, with M = Mo, W and Q = O, S, Se have potential significance in disclosing the fundamental structural, electronic, and reactivity properties of enzyme sites.

In seeking the foregoing complexes with Q = O, we have synthesized the series $[M^{IV}(bdt)_2(OSiR_3)]^{2-}$ and $[M^{VI}O(bdt)_2(OSiR_3)]^{2-}$, in which benzene-1,2-dithiolate is the dithiolene ligand, silyl oxide simulates serinate binding, and M = Mo[16,17] and W.[16,18] These complexes are obtained in good yield by direct silylation of the previously reported oxo species $[MO(bdt)_2]^{2-}$ and $[MoO_2(bdt)_2]^{2-}$ (M = Mo,[19,20] W[21]). Among the potential routes to complexes with alkoxide, thiolate, and selenoate ligands is alkylation of terminal chalcogenide ligands, with due recognition of the possibility of competing or exclusive dithiolene S-alkylation. This reaction is well precedented for reduced dithiolene complexes,[22−34] particularly for those with M = Ni, Pd, Pt, and Rh. Instances of alkylation of tungsten complexes, dimethylation of $[W(S_2C_2Ph_2)_3]^{2-}$ with methyl iodide[23] and $[W(bdt)_3]^{2-}$ with R_3O^+ (R = Me, Et),[34] have been reported. Investigation of the alkylation route requires the set $[MQ(S_2C_2R_2)_2]^{2-}$. Whereas complexes with Q = O and M = Mo[17,35] and W[18,21,36] are now readily accessible, those with Q = S and Se have not been previously described. Here we report the preparation of the complexes $[WQ(S_2C_2Ph_2)_2]^{2-}$, their reactivity with alkylating agents, X-ray structures, and related observations. This work is part of a more general investigation of the synthesis, structures, and reactivity properties of bis(dithiolene)molybdenum and -tungsten complexes relevant to enzyme sites.[16−18,37] Related molybdenum chemistry will be described separately.[38]

Experimental Section

Preparation of Compounds. All operations were performed under a pure dinitrogen atmosphere using Schlenk or inert atmosphere box techniques unless otherwise stated. Diethyl ether and THF were distilled from sodium/benzophenone, acetonitrile and dichloromethane were distilled from CaH_2, and methanol was distilled from magnesium. Other reagents were of commercial origin. Crystallizations were performed by a vapor diffusion method.

$[W(CO)_2(S_2C_2Ph_2)_2]$. This procedure is an improved version of that originally described.[39] A solution of 2.78 g (5.12 mmol) of $[Ni(S_2C_2Ph_2)_2]$[40] and 1.00 g (2.56 mmol) of $[W(CO)_3(MeCN)_3]$[41] in 250 mL of dichloromethane was stirred for 3 h. Solvent was removed in vacuo, and the residue (air-stable) was eluted on a silica gel column in *n*-pentane/benzene (4:1 v/v). The dark violet eluant fraction was evaporated in vacuo to give 1.30 g (70%) of pure product whose identity was confirmed by comparison with previous UV−vis and IR spectroscopic data.[39]

$[W(CO)_2(S_2C_2Me_2)_2]$. A solution of 1.51 g (5.12 mmol) of $[Ni(S_2C_2Me_2)_2]$[40] and 1.00 g (2.56 mmol) of $[W(CO)_3(MeCN)_3]$ in 200 mL of dichloromethane was stirred for 3 d. The reaction mixture was worked up as in the preceding preparation to afford 0.72 g (59%) of product as a purple solid whose identity was confirmed by spectroscopic comparison.[39] ^{1}H NMR (C_6D_6): δ 2.33 (s).

$(Et_4N)_2[WO(S_2C_2Ph_2)_2]$. A solution of 100 mg (0.138 mmol) of $[W(CO)_2(S_2C_2Ph_2)_2]$ in 100 mL of THF was treated with 500 mg of a 25% solution (w/w) of Et_4NOH in methanol (0.85 mmol). The orange-red solid that immediately precipitated was isolated by filtration, washed with THF (3 × 10 mL), and recrystallized from acetonitrile/ether. The product was isolated as 96.7 mg (74%) of an orange-red crystalline solid. IR (KBr): ν_{WO} 886 cm^{-1}. FAB-MS$^-$: *m/z* 684 (M^-). λ_{max} (ϵ_M) (acetonitrile): 271 (33 000), 310 (sh), 350 (13 000), 449 (3300), 527 (2000) nm. Anal. Calcd for $C_{44}H_{60}N_2OS_4W$: C, 55.92; H, 6.40; N, 2.96; S, 13.57. Found: C, 54.96; H, 6.48; N, 3.34; S, 13.70.

$(Et_4N)_2[WO(S_2C_2Me_2)_2]$. A solution of 50.0 mg (0.105 mmol) of $[W(CO)_2(S_2C_2Me_2)_2]$ in 3 mL of THF was treated with 200 mg of a 25% w/w solution of Et_4NOH in methanol (0.34 mmol). The brown solid that separated after 1 min was collected by filtration, washed with

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THF (3 × 10 mL), and recrystallized from acetonitrile/ether to afford the product as 49.4 mg (68%) of a red-brown crystalline solid. IR (KBr): ν_{WO} 897 cm^{-1}. FAB-MS^-: *m/z* 436 (M^-). λ_{max} (ϵ_M) (acetonitrile): 386 (7400), 455 (3700), 562 (910), 702 (700) nm. Anal. Calcd for $C_{24}H_{52}N_2OS_4W$: C, 41.37; H, 7.52; N, 4.02; S, 18.40. Found: C, 41.30; H, 7.46; N, 4.07; S, 18.28.

$(Et_4N)[WO(S_2C_2Ph_2)_2]$. A stirred suspension of 51 mg (54 μmol) of $(Et_4N)_2[WO(S_2C_2Ph_2)_2]$ in 2 mL of acetonitrile was treated dropwise with 6.8 mg (27 μmol) of iodine in 1 mL of THF. Solvent was removed in vacuo, and the dark residue was redissolved in THF. The solution was filtered to remove Et_4NI. Ether was diffused into the filtrate, causing the product to separate as 34 mg (78%) of a purple crystalline solid. IR (KBr): ν_{WO} 940 cm^{-1}. FAB-MS^-: *m/z* 684 (M^-). λ_{max} (ϵ_M) (acetonitrile): 272 (33 000), 310 (sh), 721 (2700) nm. Anal. Calcd for $C_{36}H_{40}NOS_4W$: C, 53.07; H, 4.95; N, 1.72; S, 15.74. Found: C, 52.88; H, 4.90; N, 1.70; S, 15.82.

$(Et_4N)[WO(MeS_2C_2Ph_2)(S_2C_2Ph_2)]$. To a stirred solution of 150 mg (0.159 mmol) of $(Et_4N)_2[WO(S_2C_2Ph_2)_2]$ in 25 mL of acetonitrile was added 120 mg (0.845 mmol) of methyl iodide. Within 15 s, the original red solution turned light orange. Solvent was removed in vacuo and the residue was redissolved in a minimal volume of THF (ca. 5 mL). The solution was filtered and the filtrate was treated with 20 mL of ether. The orange solid which precipitated was collected by filtration, washed with ether (2 × 10 mL) and recrystallized from acetonitrile/ether. The product was obtained as 86.1 mg (65%) of an orange solid. IR (KBr): v_{WO} 927 cm^{-1}. FAB-MS^-: *m/z* 715 ($M^- + O$). λ_{max} (ϵ_M) (acetonitrile): 266 (31000), 318 (15000), 443 (1600), 562 (180) nm. ^1H NMR (CD_3CN): δ 2.69 (s, 3), 7.14−7.25 (m, 20), Anal. Calcd. for $C_{37}H_{43}NOS_4W$: C, 53.55; H, 5.22; N, 1.69; S, 15.45. Found: C, 53.50; H, 5.28; N, 1.76; S, 15.55.

$(Et_4N)_2[WS(S_2C_2Ph_2)_2]$. A suspension of 200 mg (0.276 mmol) of $[W(CO)_2(S_2C_2Ph_2)_2]$ and 212 mg (2.72 mmol) of Na_2S in 10 mL of acetonitrile was stirred vigorously for 1.5 h, during which time the solution turned brown. A solution of 91 mg (0.55 mmol) of Et_4NCl in 5 mL of acetonitrile was added. The resulting mixture was stirred for 10 min and was filtered. Ether (100 mL) was added to the filtrate, causing separation of a dark brown microcrystalline solid. This material was isolated by filtration, washed with ether (3 × 10 mL), and recrystallized from acetonitrile/ether. The product was obtained as 195 mg (74%) of a brown-green crystalline solid. FAB-MS^-: *m/z* 700 (M^-). λ_{max} (ϵ_M) (acetonitrile): 302 (34 000), 353 (17 000), 432 (sh, 4800), 559 (830), 618 (650) nm. Anal. Calcd for $C_{44}H_{60}N_2S_5W$: C, 54.99; H, 6.29; N, 2.91; S, 16.68. Found: C, 54.85; H, 6.21; N, 2.79; S, 16.83.

$(Et_4N)_2[W_2(\mu\text{-}S)_2(S_2C_2Ph_2)_4]$. Method 1. A solution of 12.3 mg (52 μmol) of tropylium hexafluorophosphate in 10 mL of acetonitrile was added dropwise to a solution of 50.0 mg (52 μmol) of $(Et_4N)_2[WS(S_2C_2Ph_2)_2]$ in 5 mL of acetonitrile. The reaction mixture was stirred for 1 h, the solvent volume was reduced in vacuo to ca. 3 mL, and 25 mL of ether was added. The dark solid which precipitated was isolated by filtration and recrystallized from acetonitrile/ether to give 23 mg (53%) of product as a dark crystalline solid. FAB-MS^-: *m/z* 700 (M^{2-}). λ_{max} (ϵ_M) (acetonitrile): 320 (27 000), 344 (sh), 406 (13 000), 492 (9600), 556 (8800) nm. ^1H NMR (CD_3CN): δ 7.05 (s). Anal. Calcd for $C_{72}H_{80}N_2S_{10}W_2$: C, 52.04; H, 4.85; N, 1.69; S, 19.29. Found: C, 51.78; H, 5.07; N, 1.64; S, 19.45.

Method 2. A stirred solution of 32.0 mg (33.3 μmol) of $(Et_4N)_2[WS(S_2C_2Ph_2)_2]$ in 1 mL of acetonitrile was treated dropwise with a solution of 4.2 mg (16 μmol) of iodine in 1 mL of THF. Upon the addition of 4 mL of ether, a dark solid formed, which was collected by filtration and redissolved in a minimal volume of acetonitrile. Vapor diffusion of ether into this solution over 2 d resulted in the separation of Et_4NI and dark brown crystals. The solid was collected by filtration and washed with methanol to remove Et_4NI. The remaining solid was recrystallized from acetonitrile/ether to afford the product as 13.4 mg (48%) of dark brown crystals. This material is spectroscopically identical to the product of method 1.

$(Et_4N)_2[WSe(S_2C_2Ph_2)_2]$. A suspension of 200 mg (0.276 mmol) of $[W(CO)_2(S_2C_2Ph_2)_2]$ and 160 mg (1.72 mmol) of Li_2Se in 5 mL of acetonitrile was stirred vigorously for 1 d, during which a dark brown solution formed. A solution of 91 mg (0.55 mmol) of Et_4NCl in 3 mL of acetonitrile was added, and the resulting mixture was stirred for 10 min. The mixture was filtered; 150 mL of ether was added to the filtrate. The black solid which formed was isolated by filtration, washed with ether (3 × 10 mL), and recrystallized from acetonitrile/ether. The product was obtained as 211 mg (76%) of a brown-red crystalline product. FAB-MS^-: *m/z* 748 (M^-). Anal. Calcd for $C_{44}H_{60}N_2S_4SeW$: C, 52.43: H, 6.00; N, 2.78; Se, 7.83. Found: C, 52.28; H, 6.06; N, 2.83; Se, 7.95.

Chart 1

$[W(CO)_2(S_2C_2Ph_2)_2]$	**1**
$[W(CO)_2(S_2C_2Me_2)_2]$	**2**
$[WO(S_2C_2Ph_2)_2]^{2-}$	**3**
$[WO(S_2C_2Ph_2)_2]^{1-}$	**4**
$[WO(S_2C_2Me_2)_2]^{2-}$	**5**
$[WS(S_2C_2Ph_2)_2]^{2-}$	**6**
$[WSe(S_2C_2Ph_2)_2]^{2-}$	**7**
$[WO(MeS_2C_2Ph_2)(S_2C_2Ph_2)]^{1-}$	**8**
$[WO(EtS_2C_2Ph_2)(S_2C_2Ph_2)]^{1-}$	**9**
$[WO(EtS_2C_2Me_2)(S_2C_2Me_2)]^{1-}$	**10**
$[W_2(\mu\text{-}S)_2(S_2C_2Ph_2)_4]^{2-}$	**11**
$[W(S_2C_2Ph_2)_3]^{1-}$	**12**
$[W(S_2C_2Ph_2)_3]$	**13**

Designation of Tungsten−Dithiolene Complexes. These complexes are listed in Chart 1.

X-ray Structure Determinations. The nine compounds listed in Tables 1−3 were structurally characterized by X-ray crystallography and are henceforth referred to by the numerical designations in Chart 1. For simplicity, salts are denominated by anion number in this section. Suitable crystals of **1**, **2**, and **13** were obtained by slow evaporation of solutions of methanol/ether (1:1 v/v), benzene, and THF, respectively. All other crystals were obtained by vapor diffusion, where the first component specified is the parent solvent: DMF/THF for **3**; DMF/MeOBu^t for **5**; acetonitrile/THF for **6**; DMF/MeOBu^t for **8**; acetonitrile/ether for **11** and **12**. Crystals were mounted on glass capillary fibers in grease and cooled in a stream of dinitrogen (−60 °C). Diffraction data were obtained with a Siemens (Bruker) SMART CCD area detector system using ω scans of 0.3°/frame with 30, 45, or 60 s frames such that 1271 frames were collected for a full hemisphere of data. Cell parameters were determined using SMART software, and data reduction was performed with SAINT software which corrects for Lorentz polarization and decay. Absorption corrections were applied with SADABS on the basis of a method described by Blessing,[42] and cell parameter refinement was executed with SAINT software on all observed reflections for $3° \leq 2\theta \leq 50°$.

Space groups were assigned by statistics and successful refinement or by systematic absences using XPREP. Structures were solved by direct methods using SHELXS and refined by full-matrix least-squares methods on F^2. In general, asymmetric units contain one (**1**, **2**, **6**, **8**, **11**) or two (**3**, **12**) formula weights in addition to solvate molecules, except for **5** and **13** which contained one-half formula weight owing to imposed mirror symmetry and a 2-fold axis, respectively. Further, one-half formula weight of **11** is generated by an inversion center. One cation is disordered equally over two sites and was refined with an occupancy factor of 0.5 in each of **3**, **5**, **6**, and **11**. Sulfur atoms in **13** were disordered over two positions and were refined accordingly. All non-hydrogen atoms were described anisotropically with the exception of some solvate molecules (**3, 5**, **6**) and the carbon atoms of a disordered cation (**3**). In the final stages of refinement, hydrogen atoms were added at idealized positions and refined as riding atoms with a uniform value for U_{iso}. For **6**, **11**, and **13**, a weighting scheme that increased the contribution of lighter atoms to the structure factor amplitudes was used for improved goodness-of-fit values.[43] All structures were checked for missing symmetry by PLATON, and Supporting Information was prepared with use of XCIF. Crystallographic data and final agreement

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Table 1. Crystallographic Data[a] for $[W(CO)_2(S_2C_2R_2)_2]$ and $[WO(S_2C_2R_2)_2]^{2-}$ (R = Ph, Me)]

	$[W(CO)_2(S_2C_2Me_2)_2]$	$[W(CO)_2(S_2C_2Ph_2)_2]$	$(Et_4N)_2[WO(S_2C_2Ph_2)_2]\cdot{}^1/_2THF$	$(Et_4N)_2[WO(S_2C_2Me_2)_2]\cdot DMF$
formula	$C_{10}H_{12}O_2S_4W$	$C_{30}H_{20}O_2S_4W$	$C_{46}H_{62}N_2O_{1.5}S_4W$	$C_{27}H_{59}N_3O_2S_4W$
fw	476.29	724.55	981.08	769.86
cryst system	triclinic	monoclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	*Pnma*
Z	2	4	8	4
a, Å	7.0858(5)	13.3608(7)	17.3362(2)	17.6352(4)
b, Å	7.7923(6)	11.4546(6)	17.6679(3)	10.9691(2)
c, Å	13.587(1)	18.625(1)	30.9649(2)	20.2778(5)
α, deg	93.665(1)			
β, deg	94.437(1)	101.73(1)	103.592(1)	
γ, deg	95.724(1)			
V, Å	742.30(9)	2791.0(3)	9218.7(2)	3922.6(2)
θ range	3−50	3−50	3−50	3−50
R_1[b] (wR2)[c]	0.0260 (0.0589)	0.0261 (0.0642)	0.0414 (0.0973)	0.0341 (0.0855)

[a] Obtained with graphite-monochromated Mo Kα ($\lambda = 0.710\ 73$ A) radiation at 213 K. [b] $R_1 = \sum||F_o| - |F_c||/|F_o|$. [c] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Crystallographic Data[a] for $[WO(MeS_2C_2Ph_2)(S_2C_2Ph_2)]^-$, $[WS(S_2C_2Ph_2)_2]^{2-}$, and $[W_2S_2(S_2C_2Ph_2)_4]^{2-}$

	$(Et_4N)[WO(MeS_2C_2Ph_2)(S_2C_2Ph_2)]\cdot 2Bu^tOMe$	$(Et_4N)_2[WS(S_2C_2Ph_2)_2]\cdot THF$	$(Et_4N)_2[W_2S_2(S_2C_2Ph_2)_4]\cdot 3CH_3CN\cdot Et_2O$
formula	$C_{47}H_{67}NO_3S_4W$	$C_{48}H_{68}N_2OS_5W$	$C_{82}H_{99}N_5OS_{10}W_2$
fw	1006.11	1033.19	1858.96
cryst system	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
Z	4	4	2
a, Å	20.591(4)	10.7384(4)	11.7885(2)
b, Å	22.396(5)	19.0581(7)	15.9465(3)
c, Å	10.572(2)	23.7849(8)	23.7428(5)
α, deg			87.962(1)
β, deg	102.155(15)	98.926(1)	76.601(1)
γ, deg			79.402(1)
V, Å^3	4765.9(2)	4808.7(3)	4267.6(1)
θ range	3−50	3−50	3−50
R_1,[b] wR_2[c]	0.0446 (0.0979)	0.0423 (0.0938)	0.0428 (0.0936)

[a] Obtained with graphite-monochromatized Mo Kα ($\lambda = 0.710\ 73$ Å) radiation at 213 K. [b] $R_1 = \sum||F_o| - |F_c||/|F_o|$. [c] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 3. Crystallographic Data[a] for $[W(S_2C_2Ph_2)_3]^-$ and $[W(S_2C_2Ph_2)_3]$

	$(PhCH_2NEt_3)[W(S_2C_2Ph_2)_3]\cdot 0.5MeCN$	$[W(S_2C_2Ph_2)_3]$
formula	$C_{56}H_{52.5}N_{1.5}S_6W$	$C_{42}H_{30}S_6W$
fw	1123.71	910.87
cryst system	monoclinic	monoclinic
space group	$P2_1/c$	*C*2/*c*
Z	8	4
a, Å	19.580(4)	19.4108(8)
b, Å	23.655(6)	11.3257(5)
c, Å	21.797(6)	18.0304(8)
β, deg	91.96(1)	106.166(1)
V, Å^3	10090(4)	3807.1(3)
θ range	3−50	3−50
R_1[b] (wR_2)[c]	0.0289 (0.0722)	0.0314 (0.0573)

[a] Obtained with graphite-monochromated Mo Kα ($\lambda = 0.710\ 73$ Å) radiation at 213 K. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

factors are collected in Tables 1−3. (See paragraph at the end of this article for Supporting Information available.)

Other Physical Measurements. All measurements were made under anaerobic conditions. Absorption spectra were recorded with a Perkin-Elmer Lambda 6 spectrophotometer. IR spectra were determined with a Nicolet Impact 400 FT-IR instrument. ^1H NMR spectra were obtained with a Bruker AM-400 spectrometer. Mass spectra were recorded on a JEOL SX-102 spectrometer; for FAB spectra, 3-nitrobenzyl alcohol was used as the matrix. Electrochemical measurements were performed with a PAR Model 263 potentiostat/galvanostat using a Pt working electrode and 0.1 M $(Bu_4N)(PF_6)$ supporting electrolyte in acetonitrile solution. Potentials were calibrated against the ferrocenium/ferrocene couple and are reported vs SCE.

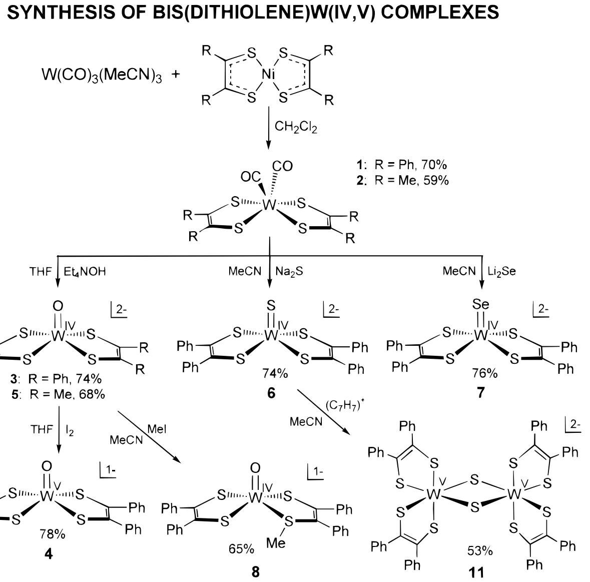

Figure 2. Scheme for the synthesis of complexes **1**−**8** and **11**. Complexes **9** and **10** (not shown) were produced by reactions analogous to that affording **8.**

Results and Discussion

Synthesis and Structures of Bis(dithiolene) Complexes. (a) Dicarbonyls. Syntheses of the tungsten complexes of interest in this work are outlined in Figure 2. Dicarbonyls **1** and **2** were originally described by Schrauzer et al.[39] in 1966 and were prepared by irradiation of a 1:1 mixture of $[W(CO)_6]$ and the

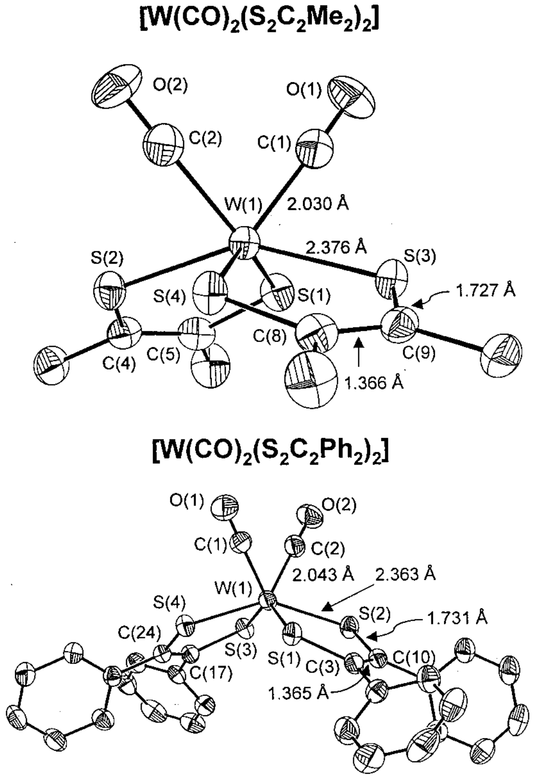

Figure 3. Structures of dicarbonyl complexes **1** (lower) and **2** (upper) showing 50% probability ellipsoids, atom labeling schemes, and selected mean bond distances.

bis(dithiolene) complex $[Ni(S_2C_2R_2)_2]$ (R = Me, Ph)[40] in benzene. Although this method was reproducible in our hands, consistently low yields (<15%) necessitated a better synthetic route. Irradiation was eliminated by substituting the more reactive $[W(CO)_3(MeCN)_3]$ for $[W(CO)_6]$. Also, the amount of the nickel starting material was increased such that reagents were utilized in the stoichiometry of reaction 1.

$$2[Ni(S_2C_2R_2)_2] + [W(CO)_3(MeCN)_3] \rightarrow [W(CO)_2(S_2C_2R_2)_2] + 2[Ni^{II}(S_2C_2R_2)] + 3MeCN + CO \quad (1)$$

Under these conditions, $[W(CO)_3(MeCN)_3]$ is subject to a four-electron oxidation effected by formal transfer of two (neutral) dithione ligands from the nickel reactant. The nickel byproduct is likely a Ni(II) dithiolate and is probably polymeric,[39] manifesting itself as a sparingly soluble brown solid. These modifications result in much improved yields for **1** (70%) and **2** (59%), greatly reducing other byproducts such as yellow-orange $[W(CO)_4(S_2C_2R_2)]$, which is a major contaminant in the synthetic method using irradiation.[39] Violet compounds **1** and **2** are air-stable and easily resolved by column chromatography. They are readily soluble in benzene and THF and only slightly soluble in methanol and acetonitrile.

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for $[W(CO)_2(S_2C_2Ph_2)_2]$ and $[W(CO)_2(S_2C_2Me_2)_2]$

	$[W(CO)_2(S_2C_2Ph_2)_2]$	$[W(CO)_2(S_2C_2Me_2)_2]$
W(1)−C(1)	2.044(4)	2.027(7)
W(1)−C(2)	2.043(4)	2.033(6)
W(1)−S(1)	2.360(1)	2.372(1)
W(1)−S(2)	2.370(1)	2.377(1)
W(1)−S(3)	2.359(1)	2.376(1)
W(1)−S(4)	2.363(1)	2.377(1)
W(1)−S_{av}	2.363(4)	2.376(2)
S−C_{av}	1.731(4)	1.727(3)
C−C_{av}[a]	1.365	1.366
C(1)−O(1)	1.123(5)	1.139(8)
C(2)−O(2)	1.134(5)	1.137(7)
W···S_4[b]	0.772	0.721
C(1)−W(1)−C(2)	83.4(2)	84.1(2)
S(1)-W(1)-S(2)[c]	81.10(3)	80.81(5)
S(3)-W(1)-S(4)[c]	80.90(3)	80.93(5)
θ_d[d]	128.9	132.8

[a] Chelate rings. [b] Distance of W atom to the S_4 mean plane. [c] Bite angle. [d] Dihedral angle between WS_2 planes.

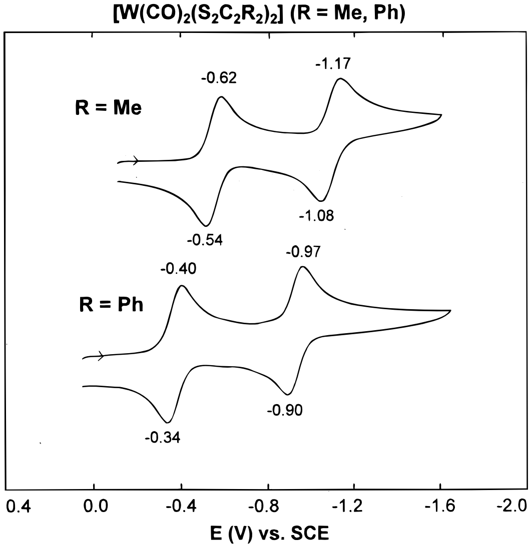

Figure 4. Cyclic voltammograms (100 mV/s) of dicarbonyl complexes **1** and **2** in acetonitrile solutions at ~25 °C. Peak potentials are indicated.

Although complexes **1** and **2** have been known for over 30 years, no structures have been reported. The structures of these complexes are set out in Figure 3; selected metric parameters are collected in Table 4. The complexes approach idealized trigonal prismatic (C_{2v}) geometry, as evidenced by the dihedral angles $\theta_d = 128.9°$ (**1**) and 132.8° (**2**) between the nearly planar chelate rings. Very little structural difference exists between **1** and **2**, which are effectively isostructural with isoelectronic $[WL_2(bdt)_2]$ (L = Bu^{t}NC, $P(OEt)_3$).[18] Both compounds display essentially identical chelate ring bite angles (81°). The average C═C distances (1.365 Å (**1**), 1.366 Å (**2**)) are slightly elongated from a true olefinic bond (1.33 Å), and average C−S distances (1.731 Å (**1**), 1.727 Å (**2**)) are significantly shortened compared with a typical C−S single bond (1.82 Å), indicating a ligand electron distribution intermediate between an enedithiolate and a dithione. Thus, reaction 1 can be interpreted as a four-electron oxidation of W(0) by the transfer of two dithione ligands from the nickel precursor, but the tungsten oxidation state in the product (W(II) or W(IV)) remains ambiguous.[44] Either formulation leads to the expectation that **1** and **2** should be reducible because the metal and/or the ligand system are not fully reduced. As shown in Figure 4, both **1** and **2** sustain two reversible reductions, with the potentials of **2** being more negative because of substituent effects.

Redox potentials are given in Table 5. The final reduction product is most reasonably formulated as the bis(enedithiolate) species $[W^{II}(CO)_2(S_2C_2Ph_2)_2]^{2-}$. This electron-transfer series will be the subject of further investigation to determine the nature of the electroactive orbital(s).

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(44) For a recent discussion of electron delocalization in tris(dithiolene)-tungsten complexes, cf.: Argyropoulos, D.; Lyris, E.; Mitsopolou, C. A.; Katakis, D. *J. Chem. Soc., Dalton Trans.* **1997**, 615.

Table 5. Redox Potentials and Stretching Frequencies for Bis(dithiolene)Tungsten Complexes

complex	$E_{1/2}$, V[a]	$\nu_{\mathrm{CO/WO}}$,[b] cm^{-1}
$[W(CO)_2(S_2C_2Me_2)_2]$	−0.58(70),[c] −1.13(90)	1951, 2020
$[W(CO)_2(S_2C_2Ph_2)_2]$	−0.37(60), −0.93(70)	1980, 2038
	$W^{IV/V}$, $W^{V/VI}$	
$[WO(S_2C_2Me_2)_2]^{2-}$	−0.91(80), −0.05(80)	897
$[WO(S_2C_2Ph_2)_2]^{2-}$	−0.62(80), (−0.21)[d]	886
$[WO(bdt)_2]^{2-}$[e]	−0.63	905
$[WO(mnt)_2]^{2-}$	0.09	935
$[WO(MeS_2C_2Ph_2)(S_2C_2Ph_2)]^{-}$	(0.04)[d]	927
$[WS(S_2C_2Ph_2)_2]^{2-}$	−0.62(80)	
$[W_2(\mu\text{-}S)_2(S_2C_2Ph_2)_4]^{2-}$	0.18(70), (0.39)[d]	

[a] $E_{1/2} = (E_{pc} + E_{pa})/2$, vs SCE. [b] KBr pellet. [c] ΔE_p (mV). [d] Irreversible. [e] Reference 21, DMF solution.

(b) W═Q Complexes (Q = O, S, Se). Compounds **1** and **2** serve as very useful starting materials for the exploration of bis(dithiolene) chemistry because the carbonyl ligands are readily replaced with anionic ligands (Figure 2). The majority of synthetic work employed **1**; insofar as it has been explored, the reactivity of **2** is comparable to that of **1**. Both compounds react rapidly with excess Et_4NOH in reaction 2 to give the oxo

$$[W(CO)_2(S_2C_2R_2)_2] + 2OH^- \rightarrow [WO(S_2C_2R_2)_2]^{2-} + H_2O + 2CO \quad (2)$$

complexes **3** and **5** in good yield. When the reaction is conducted in THF, the oxo product precipitates upon formation as the Et_4N^+ salt, thereby facilitating workup. When aqueous Et_4NOH is used, a significant amount of $(Et_4N)_2[W(S_2C_2Ph_2)_3]$ crystallizes as brown needles along with **3**. The compound was identified by an X-ray structure determination of $(Et_4N)_2[W(S_2C_2Ph_2)_3]\cdot 3MeCN$: monoclinic, space group $P2_1$, $a = 11.090(1)$ Å, $b = 32.277(2)$ Å, $c = 19.427(1)$ Å, $\beta = 103.84(1)°$. The structure was refined to $R_1 = 0.077$. Compounds **3** and **5**, as expected, have similar properties. Both are readily soluble in acetonitrile, DMF, and Me_2SO, are insoluble in weakly polar solvents such as THF, and are red (**3**) to red-brown (**5**) in color. Routes to other bis(dithiolene)$W^{IV}O$ complexes involving ligand substitution and reduction[21] and reaction of $[WO_2(CN)_4]^{4-}$ with protected dithiolenes in a protic medium[45] are available.

In a similar manner, sulfido complex **6** and selenido complex **7** were prepared in good yield by substitution of the carbonyl ligands of **1**. Because both the chalcogenide source and the starting material **1** are only slightly soluble in the reaction solvent (acetonitrile), reactions 3 and 4 are heterogeneous and

$$[W(CO)_2(S_2C_2Ph_2)_2] + Na_2S \rightarrow Na_2[WS(S_2C_2Ph_2)_2] + 2CO \quad (3)$$

$$[W(CO)_2(S_2C_2Ph_2)_2] + Li_2Se \rightarrow Li_2[WSe(S_2C_2Ph_2)_2] + 2CO \quad (4)$$

required several hours (**6**) to 1 day (**7**) to go to completion. Because of an unidentified reaction of chloride with **1**, 2 equiv of Et_4NCl was added only after the reactions were complete. These reactions were conducted under rigorously dry conditions.

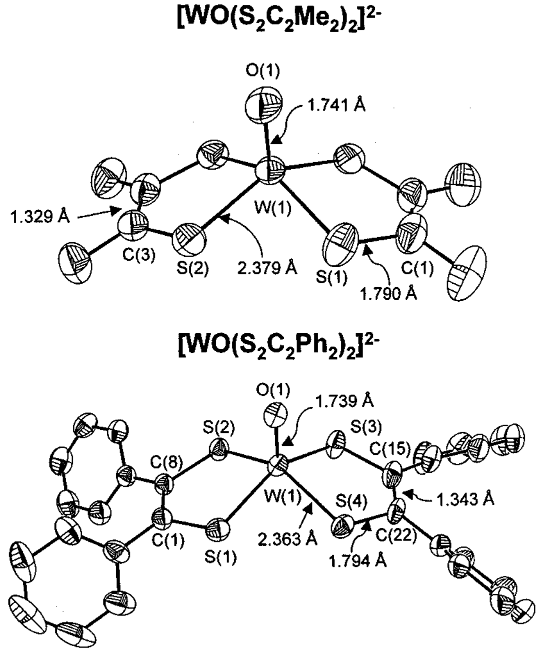

Figure 5. Structures of oxo complexes **3** (lower) and **5** (upper) showing 50% probability ellipsoids, atom labeling schemes, and selected mean bond distances. Complex **5** has an imposed mirror plane bisecting the chelate rings and containing the W═O group.

Small amounts of water were found to lead to significant contamination of the products with oxo complex **3** formed by hydrolysis.

Structures of oxo complexes **3** and **5** are shown in Figure 5; bond distance and angle data are summarized in Table 6. The oxo complexes belong to a growing number of square pyramidal species synthesized as possible analogues of sites in tungstoenzymes.[18,21,45,46] The shape of each complex is defined by dihedral angle $\theta_d \approx 129°$ between planar chelate rings and a 0.77 Å displacement of the tungsten atom from the S_4 mean plane in the direction of the oxo atom. The W═O bond distances are indistinguishable at 1.74 Å; the ν_{WO} values differ by 11 cm^{-1} (Table 5) and are in the range for related compounds (884−935 cm^{-1}).[21,45,46] The mean C−C distances of the chelate rings (1.343 Å (**3**), 1.329 Å (**5**)) and C−S distances (1.794 Å (**3**), 1.790 Å (**5**)) are more suggestive of an enedithiolate ring structure than are the corresponding distances in **1** and **2**. Other bond lengths and angles are unexceptional. The structure of sulfido complex **6** is presented in Figure 6; metric data are found in Table 7. This species is also square pyramidal with $\theta_d = 129°$ and a tungsten atom displacement of 0.80 Å. The W═S bond distance of 2.162(2) Å is typical of mononuclear W^{IV}═S complexes (range 2.10−2.19 Å[47−52]) and is marginally longer than that in isoelectronic $[WS(bdt)_2]^{2-}$ (2.146(2) Å).[53] Diffraction-quality crystals of $(Et_4N)_2[\mathbf{7}]$ thus far have not obtained.

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Table 6. Selected Interatomic Distances (Å) and Angles (deg) for $[WO(S_2C_2R_2)_2]^{2-}$ (R = Ph, Me)[a] and $[WO(MeS_2C_2Ph_2)(S_2C_2Ph_2)]^{-}$

	$[WO(S_2C_2Ph_2)_2]^{2-\,a}$	$[WO(S_2C_2Me_2)_2]^{2-}$	$[WO(MeS_2C_2Ph_2)(S_2C_2Ph_2)]^{-}$
W(1)−O(1)	1.739(4)	1.741(5)	1.716(4)
W(1)−S(1)	2.361(2)	2.377(1)	2.365(2)
W(1)−S(2)	2.364(1)	2.381(1)	2.372(2)
W(1)−S(3)	2.365(2)		2.341(2)
W(1)−S(4)	2.372(1)		2.356(2)
W(1)−S_{av}	2.363(4)	2.379	
S(1)−C(1A)			1.808(6)
S−C	1.794(4)[b]	1.790[b]	1.779(7)−1.816(6)
C−C_{av}[c]	1.343	1.329	1.336
W···S_4[d]	0.766	0.769	0.737
O(1)−W(1)−S_{av}	108.9(4)	108.86	99.7(2)−115.0(2) (range)
S(1)−W(1)−S(2)[e]	82.48(5)	81.07(7)	82.87(6)[f]
S(3)−W(1)−S(4)[e]	82.46(5)	81.97(6)	81.11(6)
θ_d,[g] θ_{twist}[h]	129.0, 0.2	129.5, 0.0	127.6, 19.4

[a] For R = Ph, values are for one of two dianions in the asymmetric unit. [b] Average value. [c] Chelate ring. [d] Distance of W atom to the S_4 mean plane. [e] Bite angle. [f] Angles at S(1): W(1)−S(1)−C(1A) 121.7(2)°, W(1)−S(1)−C(1) 111.7(2)°, C(1)−S(1)−C(1A) 103.2(3)°. [g] Dihedral angle between WS_2 planes. [h] Twist angle of dithiolene ligands with respect to each other measuring distortion away from an idealized square pyramid.

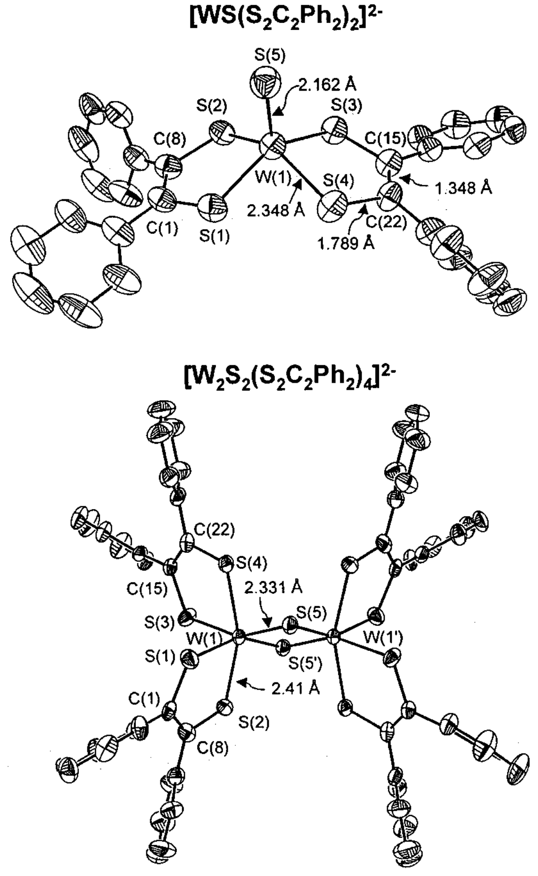

Figure 6. Structures of sulfido complexes **6** and **11** showing 50% probability ellipsoids, atom labeling schemes, and selected mean bond distances. Complex **11** has an imposed symmetry center.

Identification of this compound as containing a $W^{IV}{=}Se$ species rests on elemental analysis. Acetonitrile solutions of **7** are markedly sensitive to trace water, which convert it to oxo complex **3**. Solution properties of **7** have not proven to be adequately reproducible and are not reported. The series of dithiolene complexes $[WQ(S_2C_2R_2)_2]^{2-}$ (Q = O, S, Se) has not been previously prepared. We are unaware of any such set of W=Q complexes with constant ligands, although a series with the trans Q=W=Q group (Q = S, Se, Te) is known.[54] Terminal metal chalcogenide complexes have been treated by Parkin.[55]

Table 7. Selected Interatomic Distances (Å) and Angles (deg) for $[WS(S_2C_2Ph_2)_2]^{2-}$ and $[W_2S_2(S_2C_2Ph_2)_4]^{2-}$

	$[WS(S_2C_2Ph_2)_2]^{2-}$	$[W_2S_2(S_2C_2Ph_2)_4]^{2-}$
W(1)−S(5)	2.162(2)	2.331[a]
W(1)−S(1)	2.345(2)	2.434(2)
W(1)−S(2)	2.353(2)	2.389(2)
W(1)−S(3)	2.346(2)	2.433(2)
W(1)−S(4)	2.346(2)	2.400(2)
W(1)−S_{av}[b]	2.348(3)	2.41(2)
S−C_{av}	1.789(6)	1.740(9)
C−C_{av}[c]	1.348	1.366
W(1)···S_4[d]	0.797	
W(1)···W(1′)		2.9904(6)
S(5)−W(1)−S_{av}	109.8(5)	
S(1)−W(1)−S(2)[e]	82.10(6)	78.82(6)
S(3)−W(1)−S(4)[e]	82.15(5)	79.03(6)
W(1)−S(5)−W(1′)		79.81(6)
S(5)−W(1)−S(5′)		100.19(6)
θ_d,[f] θ_{twist}[g]	129.4, 1.2	

[a] Average value for W(1)−S(5) and W(1)−S(5′). [b] Excluding bridging distances. [c] Chelate rings. [d] Distance of W atom to the S_4 mean plane. [e] Bite angle. [f] Dihedral angle between the WS_2 planes in chelate rings. [g] Twist angle of dithiolene ligands with respect to each other measuring distortion from an idealized square pyramid.

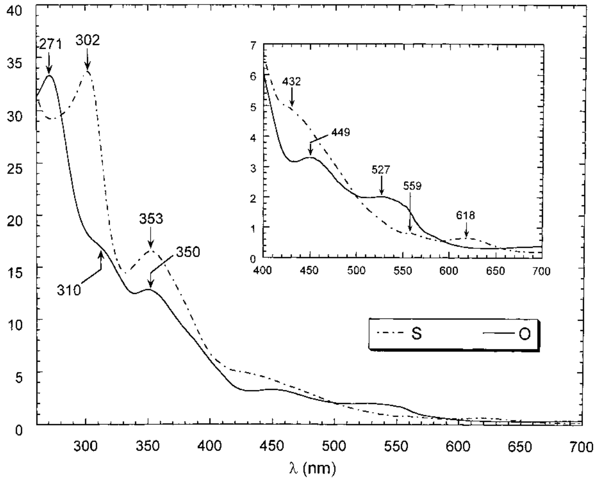

Figure 7. Absorption spectra of the series $[WQ(S_2C_2Ph_2)_2]^{2-}$ (Q = O (**3**), S (**6**)) in acetonitrile solutions. Band maxima are indicated.

The pair $[WQ(S_2C_2R_2)_2]^{2-}$ (Q = O, S) reveals certain spectroscopic and electrochemical aspects of interest. First, the absorption spectra in Figure 7 are quite distinct from each other and consist of series of bands, most of which shift to lower energy in the order S > O. The clearest progression occurs with

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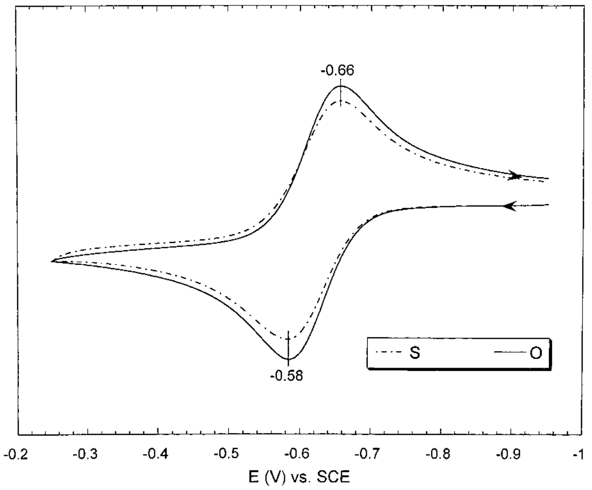

Figure 8. Cyclic voltammograms (100 mV/s) of the series $[WQ(S_2C_2Ph_2)_2]^{2-}$ (Q = O (**3**), S (**6**)) in acetonitrile solutions at −25 °C. Peak potentials are indicated.

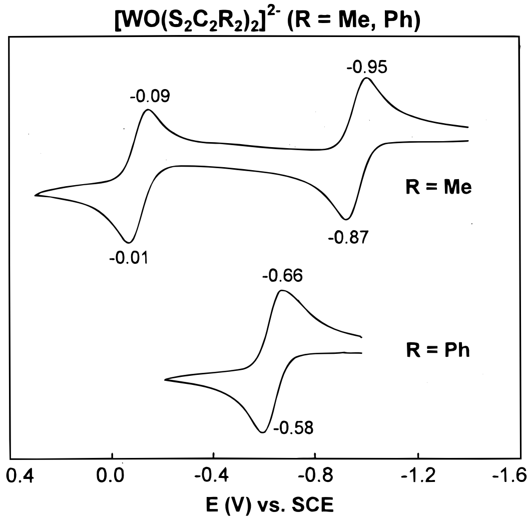

Figure 9. Cyclic voltammograms (100 mV/s) of $[WO(S_2C_2R_2)_2]^{2-}$ (R = Ph (**3**), Me (**5**)) in acetonitrile solutions at −25 °C. Peak potentials are indicated.

the most intense features at 271 (**3**) and 302 (**6**) nm, and are assigned to Q → W charge-transfer bands. The spectral trend is expected as the chalcogenide ligand becomes softer and more polarizable and has been observed with Mo/WQ$_2$ complexes.[56,57] The feature at 350 nm is independent of the chalcogenide and is likely a dithiolene → W charge transfer. Second, potentials of the reversible redox couples $[WQ(S_2C_2R_2)_2]^{-/2-}$ shown in Figure 8 are independent of Q (Table 5). Absorption spectra of sulfido complex **6** in the supporting electrolyte solution were identical before and after the voltammetric measurement, indicating no significant conversion to **3**. The electroactive orbital in the $W^{IV/V}$ redox step is expected to be d_{xy} (ground configuration $5d_{xy}{}^2$) and is implicated in in-plane π-bonding with the dithiolene sulfur atoms. However, interaction of this orbital with the filled valence s and p orbitals of the Q ligands is restricted by symmetry, leading to the observed behavior. Third, as demonstrated in Figure 9, oxo complex **5** supports the three-member electron-transfer series (5) at the potentials −0.91 and −0.05 V (Table 5). Chemical oxidation at a mild potential affords a potentially feasible route to the bis(dithiolene)$W^{VI}O$ portion of an enzyme site (Figure 1), which is subject to additional ligation as evidenced by the prior isolation of $[WO(bdt)_2(OSiR_3)]$.[16,18] An analogous redox series has been observed with certain $[MoO(S_2C_2R_2)_2]^{2-}$ complexes at similar potentials when R = alkyl.[17] The series was not realized with **3**, whose potentials are shifted ca. 300 mV positive of those of **5** because

$$[W^{VI}O(S_2C_2Me_2)_2] \rightleftharpoons [W^{V}O(S_2C_2Me_2)_2]^{1-} \rightleftharpoons [W^{IV}O(S_2C_2Me_2)_2]^{2-} \quad (5)$$

of a substituent effect. Perhaps for this reason, the $W^{VI}O$ complex is unstable, causing the second oxidation at $E_{pa} = 0.21$ V to be irreversible.

Chemical oxidation in the series $[WQ(S_2C_2Ph_2)_2]^{2-}$ has also been examined (Figure 2). Treatment of **3** with 0.5 equiv of iodine yields the purple $W^{V}O$ complex **4**, isoelectronic with $[WO(bdt)_2]^-$ whose square pyramidal structure has been demonstrated.[21] Reaction of **6** under the same conditions did not afford $[WS(S_2C_2Ph_2)_2]^-$, although this species apparently has been observed by cyclic voltammetry (Figure 8). Instead, binuclear sulfido-bridged complex **11** was obtained. To avoid difficulties in the separation of $(Et_4N)_2[\mathbf{11}]$ and Et_4NI, recourse was taken to tropylium as the oxidant. The product was isolated in 53% yield as a dark brown crystalline solid from reaction 6.

$$2[WS(S_2C_2Ph_2)_2]^{2-} + 2C_7H_7{}^+ \rightarrow [W_2(\mu\text{-}S)_2(S_2C_2Ph_2)_4]^{2-} + (C_7H_7)_2 \quad (6)$$

The structure of **11** is presented in Figure 6 and metric data are listed in Table 7. The complex is centrosymmetric with distorted octahedral coordination and a rhomboidal $W_2(\mu\text{-}S)_2$ bridging unit with average W−S distance of 2.311 Å, typical of the unit $W^{V}{}_2(\mu\text{-}S)_2$.[58−66] The W−W distance of 2.990 Å falls outside the range 2.78−2.84 Å for the subset of $W_2(\mu\text{-}S)_2$ species with six-coordinate W(V),[64−67] indicating weak or negligible direct metal−metal bonding. The complex shows a reversible oxidation at 0.18 V followed by an irreversible step (Table 5). It should be noted that dianion **11** is not isostructural with $[Mo_2S_2(S_2C_2Ph_2)_4]$, which is more oxidized by two electrons. The bridging unit in this molecule is $Mo_2(\mu\text{-}\eta^4\text{-}S_2)(\mu\text{-}RS)_2$, involving persulfide and sulfur atoms from different dithiolene ligands configured in the form of an Mo_2S_4 pseudooctahedron with the seven-coordinate metal atoms at opposite vertexes.[68] Because isoelectronic molybdenum and tungsten complexes nearly always have the same structure, the second

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oxidation step of **11** presumably results in the formation of coordinated persulfide concomitant with a structure change, accounting for the irreversibility of the process. Last, oxidation of selenido complex **7** was also attempted with stoichiometric amounts of iodine and tropylium. However only brown, intractable material was obtained which could not be characterized.

Alkylation Reactions. The series $[WQ(S_2C_2Ph_2)_2]^{2-}$ presents the possibilities of alkylation at the terminal chalcogenide and/or the dithiolene sulfur atoms which, from bond distances, are incorporated in chelate rings with considerable eneditholate character. At the outset, we note examples of alkylation of coordinated thiolate and selenolate by methyl iodide in strictly analogous molecules in the rate order $Co^{III}SR < Co^{III}SeR$,[69] the same as that of free PhS^- and $PhSe^-$ toward methyl iodide,[70] and alkylation of terminal $Mo^{VI}{=}O$,[71] $M^{VI}{=}S$ (in $MS_{3,4}$ species, M = Mo, W),[72−75] and $S{=}Mo^{IV}{=}S$[76] groups with retention of the alkoxide or alkanethiolate ligand. None of the latter reactions involved species with terminal oxo or sulfido *and* thiolate ligands. As already noted, $M^{IV}O$ and $Mo^{VI}O_2$ bdt complexes can be O-silylated to form stable products.[16−18] S-silylation of these complexes is improbable because of the ca. 50 kcal/mol difference between Si−O and Si−S bonds.[77] With this brief background, the alkylation reactions of **3** and **5**−**7** were examined.

Treatment of oxo complex **3** with 1 equiv of the soft alkylating agents MeI, EtI, or $PhCH_2Br$ in acetonitrile and the hard alkylating agents $MeSO_3Me$ in acetonitrile or CF_3SO_3Me in dichloromethane resulted in a mono-S-alkylated product. S-methylated complex **8** was isolated from reaction 7 in 65%

$$[WO(S_2C_2Ph_2)_2]^{2-} + MeI \rightarrow [WO(MeS_2C_2Ph_2)(S_2C_2Ph_2)_2]^{-} + I^{-} \quad (7)$$

yield as an orange solid, which showed a S−Me signal at δ 2.69. Similarly, **3** and **5** when reacted with 1 equiv of EtI afforded mono-S-ethyl products **9** and **10**, respectively, whose ^1H NMR spectra are set out in Figure 10. Two multiplets (δ 3.2−4.0) for each complex are consistent with diastereotopic methylene groups owing to the presence of a chiral sulfur atom[78] and one conformational isomer. The lack of symmetry of **10** is reflected by the four ring methyl resonances centered at δ 2.32. Inversion at sulfur is slow, unlike the behavior of certain alkylated dithiolene complexes.[25,30,31] Variable-temperature ^1H NMR experiments on **8**−**10** in acetonitrile did not reveal any stereodynamic processes up to ca. 340 K. Use of an excess (2−10 equiv) of the preceding alkylating agents did not result in mutiple alkylations of either **3** and **5** when the reaction systems were monitored by ^1H NMR. The hard alkylating agents Et_3O^+ in dichloromethane and $C_7H_7^+$ or Ph_3C^+ in acetonitrile as BF_4^- salts in stoichiometric quantities effected electron transfer, giving **4** as the main product.

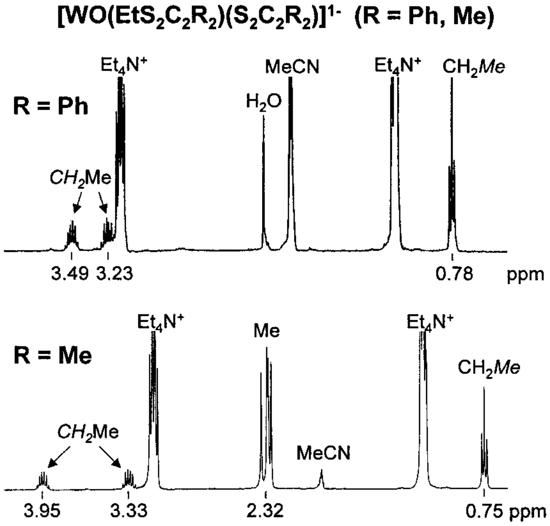

Figure 10. ^1H NMR spectra of monoalkylated complexes **9** (upper, isolated sample) and **10** (lower, generated in situ) in CD_3CN solutions. Signal assignments are indicated.

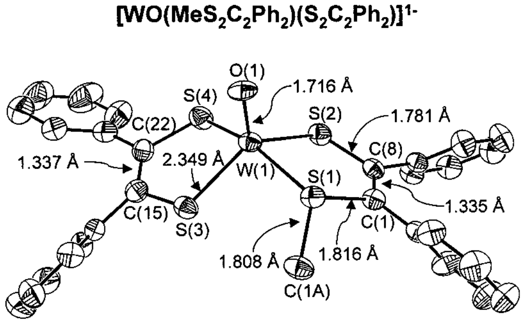

Figure 11. Structure of complex **8** showing 50% probability ellipsoids, atom labeling scheme, and selected bond distances. The W−S distance in the dithiolene ring is the average of two values.

S-alkylation was confirmed by the crystal structure of **8** provided in Figure 11; selected metric data are contained in Figure 6. Unlike square pyramidal precursor **3**, the chelate rings of **8** are not coplanar but are twisted relative to each other by ca. 20°, resulting in a large range of O−W−S angles (99.7(2)−115.0(2)°). The alkylated ring is displaced ca. 0.02 Å further from the tungsten atom, with the two W−S distances in the ring (2.365(2), 2.372(2) Å) essentially the same. The pyramidal stereochemistry at S(1) is indicated by bond angles and the 1.27 Å displacement C(1A) from the mean plane of its chelate ring. Atom deviations from the least-squares mean plane of that ring range from 0.004 Å (W) to 0.032 Å (C8); atom S(1) is displaced by 0.008 Å from this plane. The crystal is racemic and contains exclusively the exo stereoisomer, enantiomers of which are related by an inversion center. The behavior observed here is analogous to the monoalkylation of $[OsN(bdt)_2]^-$, which occurs at a sulfur atom.[79,80] The structure of [OsN(Mebdt)(bdt)] reveals the exo isomer only.[80]

Alkylation of sulfido complex **6** with ≥ 1 equiv of soft reagents did not proceed cleanly. When monitored by ^1H NMR,

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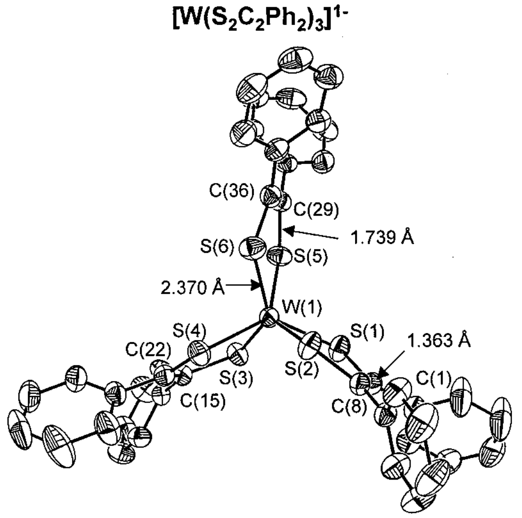

Figure 12. Structure of complex **12** showing 50% probability ellipsoids, atom labeling scheme, and selected mean bond distances. The structure of **13** (not shown) is closely related. Selected mean bond distances (Å) and angles (deg) for **12**/**13**: W−S 2.370(8), 2.41(1)/2.316(8); transoid S−W−S 136(3), 145.2(6)/136(1); twist angle 5.1, 14.5/1.6 (calculated as described[82]). The data for **12** include two inequivalent complexes in the asymmetric unit.

reactions gave product mixtures which, despite multiple attempts, were not resolved into one or more pure components. With hard alkylating agents, **6** was cleanly converted to **11**, as in reaction 6. Treatment of selenido complex **7** with 1 equiv of soft alkylating agents generated one species. With ethyl iodide and benzyl bromide, no diastereotopic splitting was found, suggesting a Se-alkylated product. Workup of this material afford the neutral tris(dithiolene) **13** as the only identifiable product. Similarly, reaction of **7** with 1−2 equiv of $C_7H_7^+$ or Ph_3C^+ in acetonitrile resulted in the crystallization of **13** from the reaction mixture.

Treatment of the W(V) complexes **4** and **11** with soft alkylating agents in acetonitrile gave no reaction. Reaction of **4** with 1 equiv of CF_3SO_3Me in dichloromethane gave green **12** as the major product. Both **4** and **11** with $C_7H_7^+$ or Ph_3C^+ in dichloromethane afforded crystalline **13**.

Tris(dithiolene) Complexes. The formation of **12** and **13** emphasizes what we frequently encounter in this and related work, *viz.*, the facile formation of $[M(S_2C_2R_2)_3]^{0,-,2-}$ as reaction sinks. Because these species and closely related complexes, which have been known for decades,[6,39,81] are not of special interest in this work, we do not detail the foregoing reaction systems. However, we have identified **12** and **13** through a combination of absorption spectra[81] and crystal structures (Table 3). The structure of **12** is shown in Figure 12; that of **13** is quite similar. Limited data are given in the figure to demonstrate that the complexes approach the trigonal prismatic limit, for which the twist angle[82] between opposite parallel S_3 faces is 0° and the transoid S−W−S angle is 136°. The octahedral values are 60° and 180°, respectively. Complex **13** closely approaches trigonal prismatic. Seven other $[M(S_2C_2R_2)_3]^{0,-,2-}$ structures have been described, showing a range of coordination geometries between octahedral and trigonal prismatic limits.[83−87]

Summary

The following are the principal results and conclusions of this investigation.

1. Bis(dithiolene) dicarbonyl complexes **1** and **2** are accessible in 60−70% yield by the thermal reaction of $[W(CO)_3(MeCN)_3]$ and 2 equiv of $[Ni(S_2C_2R_2)_2]$ (R = Ph, Me), a substantial improvement in convenience and yield over a published method requiring irradiation.[39] These complexes possess distorted trigonal prismatic stereochemistry.

2. Complex **1** is subject to rapid carbonyl ligand displacement with Et_4NOH, Na_2S, and Li_2Se to afford the previously unknown series $[W^{IV}Q(S_2C_2Ph_2)_2]^{2-}$ (Q = O, S, Se). Square pyramidal structures have been demonstrated for **3** and **6**, and chelate ring bond distances are strongly suggestive of enedithiolate character. Complexes **3** and **6** have absorption spectra strongly dependent on Q; redox potentials for the couples $[W^{IV}Q(S_2C_2Ph_2)_2]^{-,2-}$ are independent of Q.

3. Reaction of oxo complexes **3** and **5** with the soft alkylating agents R′X results in exclusive mono-S-alkylation, as demonstrated by the ^1H NMR spectra of **9** and **10** (R′ = Et) which are consistent with a single stereoisomer having a diastereotopic methylene group. The crystal structure of **8** (R′ = Me) reveals a coordinated pyramidal alkylated sulfur atom and exo stereochemistry, which presumably applies to **9** and **10** as well.

4. Sulfido complex **6** and selenido complex **7** thus far have not afforded isolable pure products with soft alkylating agents. With other electrophiles such as tropylium, **6** was oxidized to the binuclear W(V) complex **11** whereas **7** afforded the tris(dithiolene) **13** as the identifiable product.

The results in parts 3 and 4 necessitate a different route to the putative active site analogues $[M^{VI}O(QR')(S_2C_2R_2)_2]$ (M = W and, by implication, Mo). Alternate routes are currently under investigation, including additional types of carbonyl substitution reactions of **1** and **2** and their molybdenum counterparts.[38] Otherwise, the present results are pertinent to the basic chemistry of protein-bound tungsten sites with two pterin dithiolene cofactor ligands.

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Supporting Information Available: X-ray crystallographic data in CIF format for the nine compounds in Tables 1−3. This material is available free of charge via the Internet at http://pubs.acs.org.

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