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Articles

Substitution and Oxidation Reactions of Bis(dithiolene)tungsten Complexes of Potential Relevance to Enzyme Sites

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Structurally characterized tungstoenzymes contain mononuclear active sites in which tungsten is coordinated by two pterin-dithiolene ligands and one or two additional ligands that have not been identified. In this and prior investigations (Sung, K.-M.; Holm, R. H. *Inorg. Chem.* **2000**, *39*, 1275; *J. Am. Chem. Soc.* **2001**, *123*, 1931), stable coordination units of bis(dithiolene)tungsten(IV,V,VI) complexes potentially related to enzyme sites have been sought by exploratory synthesis. In this work, additional members of the sets $[WL(S_2C_2Me_2)_2]^{2-,-}$ and $[WLL'(S_2C_2Me_2)_2]^{2-,-}$ have been prepared and structurally characterized. Tungsten(IV) complexes obtained by substitution are carbonyl displacement products of $[W(CO)_2(S_2C_2Me_2)_2]$ and include those with the groups $W^{IV}S$ (**4**), $W^{IV}(O_2CPh)$ (**5**), and W^{IV}(2-AdQ)(CO) (Q = S (**6**), Se (**7**); Ad = adamantyl). Those obtained by oxidation reactions contain the groups $W^{V}O$ (**9**), $W^{V}(QPh)_2$ (Q = S (**10**), Se (**11**)), $W^{VI}S(OPh)$ (**12**), and $W^{VI}O_2$ (**14**). The latter two complexes were obtained from W(IV) precursors using sulfur and oxygen atom transfer reactions, respectively. Complexes **4** and **9** are square pyramidal; **6**, **7**, **10**, and **11** are distorted trigonal prismatic with cis ligands LL′; and **12** and **14** are distorted octahedral. Complexes **4**, **10**, and **11** support three-membered electron transfer series. Attempts to oxidize **4** to the $W^{V}S$ complex results in the formation of binuclear $[W_2(\mu_2\text{-}S)_2(S_2C_2Me_2)_4]^{2-}$ having distorted octahedral coordination. The 21 known functional groups WL and WLL′ in mononuclear bis(dithiolene) complexes prepared in this and prior investigations are tabulated. Of those with physiological-type ligands, it remains to be seen which (if any) of these ligation modes are displayed by enzyme sites.

Introduction

We have demonstrated recently that the trigonal prismatic dicarbonyl−bis(dithiolene) complexes $[M(CO)_2(S_2C_2R_2)_2]$ (M = Mo, W; R = Me, Ph) are effective synthetic precursors to five- and six-coordinate bis(dithiolene) complexes of molybdenum[1,2] and tungsten.[3−5] One or, usually, two carbonyl groups are displaced under mild conditions in substitution reactions that afford a variety of previously unknown bis(dithiolene) complexes. In the case of tungsten, the complexes can be described as containing the mononuclear fragments $W^{IV,V}{=}Q$, $W^{IV}(OR)$, $W^{IV}(CO)(QR)$, $W^{VI}{=}O(OR)$ (Q = O, S; R = alkyl, aryl), and binuclear $W^{V}_2(\mu_2\text{-}S)_2$. Certain of these complexes serve as structural[6,7] and functional[2,5,8] representations of the catalytic sites of oxotransferase enzymes, especially members of the molybdenum DMSO reductase enzyme family[9] and the corresponding tungsten isoenzymes.[5,10]

Tungstoenzymes may be organized into two major families, AOR (aldehyde oxidoreductases) and F(M)DH (formate dehydrogenase, *N*-formylmethanofuran dehydrogenases).[11] In two members of the AOR family, the tungsten atoms are bound by two pterin-dithiolene cofactor ligands (S_2pd) and one or two light, presumably oxygen-donor, ligands as determined by crystallography.[12,13] Because of site heterogeneity and/or the difficulty of identifying light scatterers in the presence of tungsten, these ligands and the full coordination geometry have not been determined. Nothing is known concerning active site structures in the F(M)DH family. The best defined site at present is that in the tungsten isoenzyme of *Rhodobacter capsulatus* DMSO reductase, where the site formulation $[WO(O{\cdot}Ser)(S_2\text{-}pd)_2]$ in the oxidized enzyme is consistent with crystallographic and EXAFS results.[10] In view of the absence of fully defined binding sites in tungstoenzymes, we have continued exploratory synthesis in order to determine accessible coordination units of bis(dithiolene)tungsten complexes. Some of these may be relevant to enzymes, and others contribute to the further disclosure of tungsten−dithiolene chemistry,[3−5,14−18] a little-

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Chart 1. Designation of Tungsten Complexes and Abbreviations

$[W(CO)_2(S_2C_2Me_2)_2]$	**1**[3]
$[W^{IV}(OPh)(S_2C_2Me_2)_2]^{1-}$	**2**[4]
$[W^{IV}O(S_2C_2Me_2)]^{2-}$	**3**[3]
$[W^{IV}S(S_2C_2Me_2)_2]^{2-}$	**4**
$[W^{IV}(O_2CPh)(S_2C_2Me_2)_2]^{1-}$	**5**
$[W^{IV}(CO)(2\text{-AdS})(S_2C_2Me_2)_2]^{1-}$	**6**
$[W^{IV}(CO)(2\text{-AdSe})(S_2C_2Me_2)_2]^{1-}$	**7**
$[W^{V}_2(\mu_2\text{-S})_2(S_2C_2Me_2)_4]^{2-}$	**8**
$[W^{V}O(S_2C_2Me_2)]^{1-}$	**9**
$[W^{V}(SPh)_2(S_2C_2Me_2)_2]^{1-}$	**10**
$[W^{V}(SePh)_2(S_2C_2Me_2)_2]^{1-}$	**11**
$[W^{VI}S(OPh)(S_2C_2Me_2)_2]^{1-}$	**12**
$[W^{VI}O(OPh)(S_2C_2Me_2)_2]^{1-}$	**13**[5,8]
$[W^{VI}O_2(S_2C_2Me_2)_2]^{2-}$	**14**

2-Ad	2-adamantyl
bdt	benzene-1,2-dithiolate(2-)
mnt	maleonitriledithiolate(2-)
ndt	napthalene-2,3-dithiolate(2-)
S_2pd	pterin-dithiolene cofactor

explored area prior to the imperative provided by the discovery of tungstoenzymes.[11] As noted elsewhere,[4] we utilize the dimethyldithiolene ligand 1,2-$Me_2C_2S_2^{2-}$ because, like the pterin-dithiolene cofactor ligand, it is a dialkyldithiolene.

Experimental Section

Preparation of Compounds. All operations were carried out under a pure dinitrogen atmosphere using an inert atmosphere box or standard Schlenk techniques. Solvents were passed through the Innovative Technology solvent purification system prior to use. Lithium 2-adamantylthiolate was obtained from adamantane-2-thiol[19] by reaction with Bu^nLi at −78 °C. Bis(2-adamantyl)diselenide was obtained as described.[2] $(Et_4N)(SH)$ was recrystallized from acetonitrile/ether, and benzenethiol and benzeneselenol were distilled prior to use. Other reagents were commercial samples used as received. Solvent removal was performed in vacuo. Filtrations were through Celite; compounds were isolated by filtration unless otherwise stated. Abbreviations are given in Chart 1.

(1) W(IV) Complexes. $(Et_4N)_2[WS(S_2C_2Me_2)_2]$. To a dark violet solution of 198 mg (0.415 mmol) of $[W(CO)_2(S_2C_2Me_2)_2]$[3] in 1.5 mL of THF was added a solution of 135 mg (0.829 mmol) of $(Et_4N)(SH)$ in 1 mL of acetonitrile. An immediate reaction occurred, and the solution color changed from violet to green to brown. The solution was stirred for 1 h, and the solvents were removed. The resulting dark brown solid was dissolved in 2 mL of acetonitrile and filtered. THF (30 mL) was layered on the filtrate. The solid which separated was collected, washed with THF (3 × 3 mL), and dried to give the product as 185 mg (63%) of dark brown plates. IR (KBr): ν_{WS} 468 cm^{-1}. ^1H NMR (CD_3CN, anion): δ 2.66 (s, br, 12). Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 359 (6100), 400 (sh, 2000), 470 (700), 600 (400) nm. Anal. Calcd for $C_{24}H_{52}N_2S_5W$: C, 40.44; H, 7.35; N, 3.93; S, 22.49. Found: C, 40.32; H, 7,26; N, 3.84; S, 22.58.

$(Et_4N)[W(O_2CPh)(S_2C_2Me_2)_2]$. To a suspension of 38.2 mg (0.152 mmol) of $(Et_4N)(O_2CPh)$ in 1 mL of acetonitrile was added a dark violet solution of 72.1 mg (0.151 mmol) of $[W(CO)_2(S_2C_2Me_2)_2]$ in 3 mL of THF. The solution color changed to orange-brown immediately. After 1 h of stirring, the solution was filtered to remove an orange solid. Ether (60 mL) was layered on the filtrate. The solid that separated was collected, washed with ether (3 × 1 mL), and dried. The product was obtained as 38 mg (38%) of brown microcrystalline solid. IR (KBr): ν_{COO} 1444 cm^{-1}. ^1H NMR (CD_3CN, anion): δ 2.69 (s, 12), 7.36 (t, 2), 7.44 (t, 1), 7.71 (d, 2). Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 336 (4300), 394 (4000), 419 (sh, 3800), 491 (1000), 686 (510) nm. Anal. Calcd for $C_{23}H_{37}NO_2S_4W$: C, 41.13, H, 5.55; N, 2.09; S, 19.10. Found: C, 41.28; H, 5.43; N, 1.96; S, 19.16.

$(Et_4N)[W(CO)(2\text{-AdS})(S_2C_2Me_2)_2]$. To a suspension of 15.6 mg (89.5 μmol) of 2-AdSLi and 16.4 mg (99.0 μmol) of Et_4NCl in 1.5 mL of acetonitrile was added a dark violet solution of 41.0 mg (86.1 μmol) of $[W(CO)_2(S_2C_2Me_2)_2]$ in 2 mL of THF. An intense green color developed immediately. The solution was stirred for 10 min, and the solvents were removed. The dark green solid was dissolved in 2 mL of acetonitrile and filtered. Ether (60 mL) was added to the green filtrate, and the mixture was allowed to stand for 2 days. The solid was isolated, washed with ether (10 × l mL), and dried to afford the product as 37 mg (58%) of black blocklike crystals. IR (KBr): ν_{CO} 1931 cm^{-1}.^1H NMR (CD_3CN, anion): δ 1.41−2.14 (m, 14), 2.44 (s, 12), 4.91 (s, 1). Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 272 (10000), 342 (6600), 431 (8100), 607 (2900) nm. Anal. Calcd for $C_{27}H_{47}NOS_5W$: C, 43.48; H, 6.35; N, 1.88; S, 21.40. Found: C, 43.63; H, 6.46; N, 1.94; S, 21.56.

$(Et_4N)[W(CO)(2\text{-AdSe})(S_2C_2Me_2)_2]$. To a dark violet solution of 55.0 mg (0.116 mmol) of $[W(CO)_2(S_2C_2Me_2)_2]$ in 2 mL of THF was added a solution of 2-AdSeLi, which was generated in situ from the reaction of 24.9 mg (0.0581 mmol) of $(2\text{-AdSe})_2$ and 0.12 mL of a 1.0 M solution of $LiEt_3BH$ in THF. An intense green color developed immediately. The reaction mixture was stirred for 10 min and then treated with 22.4 mg (0.135 mmol) of Et_4NCl in 1 mL of acetonitrile, and the solvent was removed. The dark-green solid was dissolved in 2 mL of acetonitrile, and the solution was filtered. Ether (60 mL) was added to the green filtrate, causing the separation of a solid over 1 day. This material was isolated, washed with ether (3 × 1 mL), and dried to yield the product as 43 mg (47%) of black block-shaped crystals. IR (KBr): ν_{CO} 1923 cm^{-1}. ^1H NMR (CD_3CN, anion): δ 1.47−2.18 (m, 14), 2.46 (s, 12), 5.09 (s, 1). Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 280 (10000), 332 (6300), 359 (sh, 5900), 438 (7900), 625 (3300) nm. Anal. Calcd for $C_{27}H_{47}NOS_4SeW$: C, 40.91; H, 5.98; N, 1.77; S, 16.18; Se, 9.96. Found: C, 40.76; H, 6.46; N, 1.69; S, 16.25; Se, 10.06.

(2) W(V) Complexes. $(Et_4N)[WO(S_2C_2Me_2)_2]$. To an orange-yellow solution of 59.8 mg (85.8 μmol) of $(Et_4N)_2[WO(S_2C_2Me_2)_2]$[3] in 3 mL of acetonitrile was added dropwise a solution of 12.2 mg (48.1 μmol) of I_2 in 1 mL of THF. The solution color changed to blue immediately. The solution was stirred for 10 min, and the solvents were removed. The dark residue was dissolved in a minimal volume of THF, and the solution was filtered. Addition of ether to the filtrate gave the product as 19 mg (39%) of black crystalline solid. IR (KBr): ν_{WO} 896 cm^{-1}. Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 283 (sh, 1900), 312 (sh, 1500), 400 (3100), 505 (1300), 607 (5100) nm. EPR (DMF/acetonitrile): br, isotropic, $g_{av} = 1.995$. This compound was identified by its spectroscopic similarity to $[WO(S_2C_2Ph_2)_2]^-$,[3] and by an X-ray structure determination.

$(Et_4N)[W(SPh)_2(S_2C_2Me_2)_2]$. To a green-brown solution of 26.4 mg (41.0 μmol) of $(Et_4N)[W(OPh)(S_2C_2Me_2)_2]$[4] in 1.5 mL of acetonitrile was added 8.4 μL (81.8 μmol) of benzenethiol. Upon stirring of the reaction mixture, the solution changed to red-brown in 10 min. Solvent was removed, the dark brown oily residue was redissolved in 1 mL of acetonitrile, and the mixture was filtered. Ether (30 mL) was layered on the top of the filtrate. The solid which separated was collected, washed with ether, and dried to afford the product as 21 mg (67%) of

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Table 1. Crystallographic Data[a]

	$(Et_4N)[\mathbf{5}]$	$(Et_4N)[\mathbf{6}]$	$(Et_4N)[\mathbf{7}]$	$(Et_4N)_2[\mathbf{8}]\cdot CH_3CN$	$(Et_4N)[\mathbf{9}]$
formula	$C_{23}H_{37}NO_2S_4W$	$C_{27}H_{47}NOS_5W$	$C_{27}H_{47}NOS_4SeW$	$C_{34}H_{67}N_3S_{10}W_2$	$C_{16}H_{32}NOS_4W$
fw	671.63	745.81	792.71	1206.21	566.52
cryst syst	monoclinic	trigonal	trigonal	triclinic	tetragonal
space group	$P2_1/n$	$R3$	$R3$	$P\bar{1}$	$I\bar{4}2d$
Z	4	18	18	2	8
a, Å	8.934(1)	39.2057(1)	39.466(2)	11.516(7)	12.8552(2)
b, Å	23.801(2)	39.2057(1)	39.466(2)	14.901(9)	12.8552(2)
c, Å	12.980(2)	10.4603(1)	10.4482(8)	14.952(8)	27.3574(4)
α, deg				88.86(1)	
β, deg	105.33(1)			67.88(1)	
γ, deg				87.36(1)	
V, Å^3	2662.0(5)	13924.3(1)	14094(1)	2375(2)	4521.0(1)
d_{calc}, g/cm^3	1.676	1.601	1.681	1.687	1.665
2θ range, deg	3.4−56.6	2.1−56.6	2.1−56.6	2.7−50	3.5−55.3
GOF (F^2)	1.030	1.039	1.048	1.010	1.088
R1[b] (wR2[c])	0.0520 (0.1421)	0.0421 (0.0863)	0.0224 (0.0592)	0.0256 (0.0499)	0.0256 (0.0781)

[a] Obtained with graphite-monochromatized Mo Kα ($\lambda = 0.71073$ Å) radiation at 213 K. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

black rodlike crystals. Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 294 (sh, 12000), 397 (8300), 513 (6700), 608 (sh, 3900) nm. EPR (DMF/acetonitrile): v br, $g_{av} \sim 1.990$. Anal. Calcd for $C_{28}H_{42}NS_6W$: C, 43.74; H, 5.51; N, 1.82; S, 25.02. Found: C, 43.73; H, 5.45; N, 1.77; S, 25.11.

$(Et_4N)[W(SePh)_2(S_2C_2Me_2)_2]$. The preceding procedure was followed with use of benzeneselenol on a 97 μmol scale and gave the product as a black microcrystalline product (45%). Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 294 (sh, 12000), 397 (8300), 513 (6700), 608 (sh, 3900) nm. EPR (DMF/acetonitrile): br, $g_1 = 2.068$, $g_2 = 1.988$, $g_3 = 1.949$. This compound is isomorphous with the preceding compound and was identified by an X-ray structure determination.

$(Et_4N)_2[W_2(\mu\text{-}S)_2(S_2C_2Me_2)_4]$. Method a. To a green-brown solution of 32.5 mg (50.5 μmol) of $(Et_4N)[W(OPh)(S_2C_2Me_2)_2]$ in 1.5 mL of acetonitrile was added a solution of 14.5 mg (52.5 μmol) of Ph_3CSH in 1 mL of acetonitrile with stirring. The solution color turned dark brown over 1 h, after which the solvent was removed. The dark brown residue was dissolved in a minimal volume of acetonitrile, and the solution was filtered. Ether (60 mL) was added to precipitate a solid, which was isolated, washed with ether (3 × 1 mL), and dried to give the product as 24.0 mg (79%) of black microcrystalline solid. Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 337 (8900), 403 (7400), 490 (6700), 568 (5400) nm. Anal. Calcd for $C_{32}H_{64}N_2S_{10}W_2\cdot CH_3CN$: C, 33.85; H, 5.60; N, 3.48; S, 26.58. Found: C, 33.94; H, 5.54; N, 3.41; S, 26.46.

Method b. A green-brown solution of 58.7 mg (82.3 μmol) of $(Et_4N)_2[WS(S_2C_2Me_2)_2]$ in 2 mL of acetonitrile was treated with a solution of 10.1 mg (39.6 μmol) of I_2 in 1 mL of THF. The reaction mixture was stirred for 10 min, and solvent was removed. The dark brown residue was dissolved in a minimum volume of acetonitrile, and the mixture was filtered. Vapor diffusion of ether into the filtrate produced 18 mg (36%) of black solid. This material was contaminated with a slight amount of $(Et_4N)_2[W_2S_2(\mu\text{-}S)_2(S_2C_2Me_2)_2]$ (identified by an X-ray structure determination), which can be removed by washing with a minimal amount of acetonitrile/ether (1:3 v/v).

Method c. To a green-yellow suspension of the mixture of 18.3 mg (0.166 mmol) of Na_2S_2 and 51.8 mg (0.313 mmol) of Et_4NCl in 1 mL of acetonitrile was added a dark violet solution of 78.6 mg (0.165 μmol) of $[W(CO)_2(S_2C_2Me_2)_2]$ in 3 mL of THF. The color of the reaction mixture immediately changed to green, and became brown in 5 min. The mixture was stirred for 2 h, and solvent was removed. The resulting brown solid was redissolved in a minimal amount of acetonitrile and filtered. Ether (60 mL) was layered on the filtrate to yield a brown solid and pale blue supernatant over 2 days. The brown solid was recrystallized by vapor diffusion of ether into an acetonitrile solution. The solid was washed with ether (3 × 1 mL), and dried to afford the product as 63.3 mg (64%) of thin black plates.

The products from the three methods are spectroscopically identical.

(3) W(VI) Complexes. $(Et_4N)_2[WO_2(S_2C_2Me_2)_2]$. To an orange-yellow solution of 59.6 mg (85.5 μmol) of $(Et_4N)_2[WO(S_2C_2Me_2)_2]$ in 3 mL of acetonitrile was added a solution of 9.7 mg (0.129 mmol) of Me_3NO in 1 mL of acetonitrile dropwise with stirring. An intense orange-red color developed in 3 min; the solution was stirred for 10 min. The solvent was removed, the red oily residue was dissolved in a minimal amount of acetonitrile/THF (1:3 v/v), and the mixture was filtered. Ether (60 mL) was layered on the filtrate. Over 1 day a crystalline solid separated and was collected, washed with ether (3 × 1 mL), and dried. The product was obtained as 40.2 mg (69%) of orange-red thin needles. IR (KBr): ν_{WO} 876, 833 cm^{-1}. ^{1}H NMR (CD_3CN, anion): δ 1.87 (s, 12). Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 370 (4300), 457 (2500) nm. Anal. Calcd for $C_{24}H_{52}N_2O_2S_4W$: C, 40.44; H, 7.35; N, 3.93; S, 17.99. Found: C, 40.27; H, 7.26; N, 3.84; S, 17.85.

$(Et_4N)[WS(OPh)(S_2C_2Me_2)_2]$. To a solution of 31.0 mg (48.2 μmol) of $(Et_4N)[W(OPh)(S_2C_2Me_2)_2]$ in 1 mL of acetonitrile was added a solution of 18.7 mg (67.2 μmol) of dibenzyl trisulfide in 1 mL of acetonitrile. The initial green-brown solution immediately turned red-brown. The reaction mixture was stirred for 10 min, and solvents were removed. The residual dark brown oil was dissolved in 1.5 mL of acetonitrile, and the solution was filtered. Ether (50 mL) was added to the dark red-brown filtrate. The solid which separated over 1 day was collected, washed with ether (3 × 1 mL), and dried, affording the product as 13 mg (40%) of black microcrystalline solid. IR (KBr): ν_{WS} 470 cm^{-1}. ^{1}H NMR (CD_3CN, anion): δ 2.29 (s, 12), 6.80 (t, 1), 6.94 (d, 2), 7.18 (t, 2). Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 290 (sh, 10000), 341 (11000), 370 (sh, 9500), 474 (5500) nm. Anal. Calcd for $C_{22}H_{37}NOS_5W$: C, 39.11; H, 5.52; N, 2.07; S, 23.73. Found: C, 38.97; H, 5.46; N, 2.03; S, 23.87.

In the sections which follow, tungsten complexes are referred to by the numerical designations in Chart 1.

X-ray Structure Determinations. The nine compounds listed in Tables 1 and 2 were structurally identified by X-ray crystallography. Single crystals were obtained by layering ether on the corresponding acetonitrile solutions at ambient temperature over a period of at least 1 day. Selected crystals were coated in silicone grease and mounted on a Siemens (Bruker) SMART CCD-based diffractometer equipped with an LT-2 low-temperature apparatus operating at 213 K. Mo Kα radiation ($\lambda = 0.71073$ A) was used for all data collection. Data were collected with ω scans of 0.3°/frame for 30 s, such that 1271 frames were collected for a hemisphere of data. The first 50 frames were re-collected at the end of the data collection to monitor for decay; no significant decay was detected for any compounds. Data only out to 2θ of 50° for $(Et_4N)[\mathbf{8}]\cdot CH_3CN$ were used because of the low-quality high-angle data while data out to 2θ of 55.9−56.6° was collected for the other compounds. Cell parameters were retrieved using SMART software and refined using SAINT software on all reflections. Data reduction was performed with SAINT software, which corrects for Lorentz polarization and decay. Absorption corrections were applied using SADABS. The space groups for all compounds were assigned unambiguously by analysis of symmetry and systematic absences

Table 2. Crystallographic Data[a]

	$(Et_4N)[\mathbf{10}]$	$(Et_4N)[\mathbf{11}]$	$(Et_4N)[\mathbf{12}]$	$(Et_4N)_2[\mathbf{14}]$
formula	$C_{28}H_{42}NS_6W$	$C_{28}H_{42}NS_4Se_2W$	$C_{22}H_{37}NOS_5W$	$C_{24}H_{52}N_2O_2S_4W$
fw	768.84	862.64	675.68	712.77
cryst syst	orthorhombic	orthorhombic	orthorhombic	monoclinic
space group	*Pbca*	*Pbca*	*Fdd*2	$P2_1/n$
Z	8	8	16	4
a, Å	13.2822(5)	13.326(2)	24.309(4)	11.1622(9)
b, Å	20.1469(7)	20.196(3)	20.528(4)	21.897(3)
c, Å	23.9424(9)	24.352(4)	21.720(4)	13.169(2)
β, deg				102.891(9)
V, $Å^3$	6406.9(4)	6554(1)	10838(3)	3137.6(6)
d_{calc}, g/cm^3	1.594	1.749	1.656	1.509
2θ range, deg	3.4−56.6	3.3−56.5	3.2−55.9	3.7−56.5
GOF (F^2)	1.001	1.044	0.953	1.131
$R1^b$ ($wR2^c$)	0.0453 (0.0912)	0.0459 (0.0916)	0.0311 (0.0798)	0.0630 (0.1200)

[a] Obtained with graphite-monochromatized Mo Kα ($\lambda = 0.71073$ Å) radiation at 213 K. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 3. Selected Bond Distances (Å) and Angles (deg)

	5	**6**	**7**	**8**[a]	**9**[b]	**10**	**11**	**12**[c]	**14**
W−O1	2.177(4)^d				1.724(6)^e			1.967(5)^f	1.741(5)^e
W−O2	2.172(4)^d								1.757(6)^e
W−S1	2.329(2)	2.372(2)	2.376(1)	2.382(2)	2.377(2)	2.367(2)	2.366(2)	2.456(2)^g	2.581(2)^g
W−S2	2.324(2)	2.381(2)	2.381(1)	2.453(2)	2.381(2)	2.368(2)	2.375(2)	2.408(2)	2.422(2)
W−S3	2.335(2)	2.400(2)	2.400(1)	2.432(2)		2.368(2)	2.367(2)	2.394(2)	2.586(2)^g
W−S4	2.322(2)	2.342(2)	2.341(1)	2.391(2)		2.374(2)	2.370(2)	2.400(2)	2.419(2)
W−S5		2.405(2)^f		2.346(2)^h		2.429(2)^f		2.151(2)^j	
W−S6				2.330(2)^{h,i}		2.430(2)^f			
W−Se1			2.532(1)				2.550(1)		
W−Se2							2.550(1)		
W···W				3.000(1)					
W−C1		2.024(6)	2.009(3)						
C1−O1		1.129(7)	1.145(4)						
S−C^k		1.741(7)	1.748(3)	1.737(7)	1.773(6)	1.742(2)	1.745(7)	1.745(8)	1.745(8)
C−C^{k,l}		1.337(9)	1.340(5)	1.330(9)	1.326(8)	1.34(1)	1.34(1)	1.34(1)	1.34(1)
Q−W−Q′ ^{m}	59.4(2)^d			100.16(5)		86.00(6)	86.48(2)	96.6(2)	100.2(3)
W−S−W				79.84(5)					
W−Q−C^f		118.4(2)	114.89(8)			113.3(2)	110.5(2)	136.4(4)	
S1−W−S2^n	81.71(6)	79.26(2)	81.26(3)	79.07(7)	82.62(6)^o	80.48(6)	80.29(6)	77.36(6)	78.06(7)
S3−W−S4^n	82.15(6)	81.18(5)	79.51(3)	78.92(6)		80.09(6)	80.54(6)	79.09(7)	78.40(7)
S1−W−S4^p	138.05(6)	137.96(6)	138.93(3)	158.92(5)	141.5(1)^q	122.68(7)	124.21(7)	92.13(7)	85.51(7)
S2−W−S3^p	141.04(6)	140.96(6)	140.81(3)	94.08(6)	144.5(1)^r	150.51(6)	151.24(6)	155.48(9)	90.83(7)
δ^s	0.805	0.822	0.814		0.755	0.870	0.849		
$\theta_d{}^t$	125.5	126.1	126.7	94.0	130.0	118.6	120.2	95.0	92.8

[a−c] One of the two anions in asymmetric unit; symmetry transformations used to generate equivalent atoms: [a] $-x + 2, -y + 1, z$. [b] $-x + 1, -y, z$ (anion); $-x + {}^1/_2, y, -z - {}^1/_4$ (cation). [c] $-x + 3, -y + 2, z$. [d] Bidentate benzoate ligand. [e] Terminal oxo ligand. [f] Unidentate ligand. [g] Trans to terminal oxo or sulfido ligand. [h] Bridging sulfido ligand. [i] S5A. [j] Terminal sulfido ligand. [k] Mean value. [l] Dithiolene chelate ring. [m] Angle between unidentate or bridging ligands; Q = O, S, Se. [n] Chelate ring bite angle. [o] S1−W−S2 and S1A−W−S2A are identical. [p] Transoid angle. [q] S1−W−S1A. [r] S2−W−S2A. [s] Perpendicular displacement of W atom from S_4 least-squares plane. [t] Dihedral angle between WS_2 planes.

determined by the program XPREP. Missing symmetry was checked by the program PLATON. Crystal parameters are given in Tables 1 and 2.

All structures were solved by direct methods with SHELXS-97 and subsequently refined against all data by full-matrix least squares on F^2 using SHELXL-97. Disorder in the cations was frequently encountered. All methylene groups and one methyl group of $(Et_4N)[\mathbf{12}]$, all methylene groups of one of the two cations in $(Et_4N)_2[\mathbf{13}]$, and all methylene groups of $(Et_4N)[\mathbf{5},\mathbf{9}]$ were disordered over two positions and were refined with a site occupancy factor of 0.5. All non-hydrogen atoms including the disordered cations were refined anisotropically. Hydrogen atoms were attached at idealized positions on carbon atoms in the final stages of refinement. All residual peaks near the highly absorbing tungsten atoms are within acceptable distances. Selected bond distances and angles are listed in Table 3.

Other Physical Measurements. All measurements were performed under anaerobic conditions. Absorption spectra were recorded with a Varian Cary 50 Bio spectrophotometer. ^1H NMR spectra were obtained with a Bruker AM500N or a Varian Mercury 400 spectrometers. IR spectra were measured with KBr pellets in a Nicolet Impact 400 or a Nicolet Nexus 470 FT-IR instruments. Cyclic voltammograms and differential potential voltammograms were recorded with a PAR model 263 potentiostat/galvanostat using Pt disk working electrode and 0.1 M Bu_4NPF_6 supporting electrolyte in MeCN solution. Potentials were directly measured with and referenced to the saturated calomel electrode (SCE). EPR spectra were recorded at ~4 K in DMF/acetonitrile (1:1 v/v) with a Bruker ESP 300 spectrometer. Spectral simulations were performed with WIN-EPR SimFonia v. 1.25 software.

Results and Discussion

In this investigation, we have sought to expand the basis set of stable coordination units in bis(dithiolene)W(IV,V,VI) complexes beyond those containing the foregoing mononuclear fragments WLL′ prepared in this laboratory.[3−5,18] The synthetic schemes in Figures 1 and 2 summarize reactions developed in this and in prior investigations. The structural data in Table 3 reveal the ranges of 1.33−1.34 and 1.74−1.77 Å for chelate ring C−C and S−C distances. These values are sufficiently close

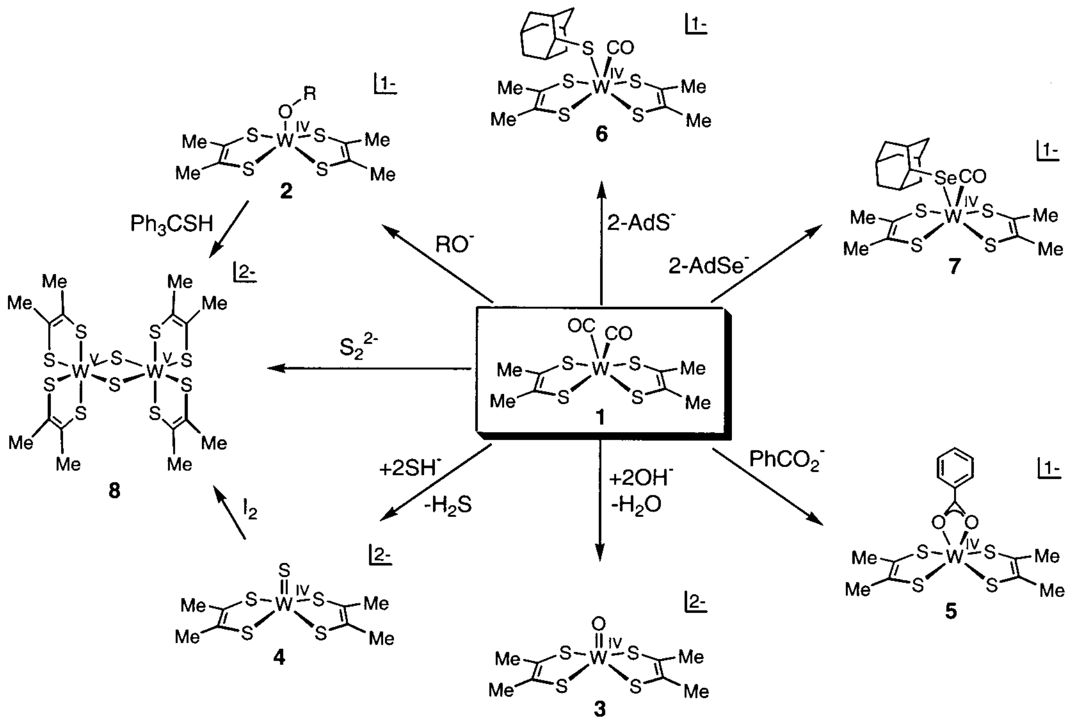

Figure 1. Scheme for the synthesis of bis(dithiolene)W(IV,V) complexes **2**−**8** by partial or complete substitution of the carbonyl ligands of **1**.

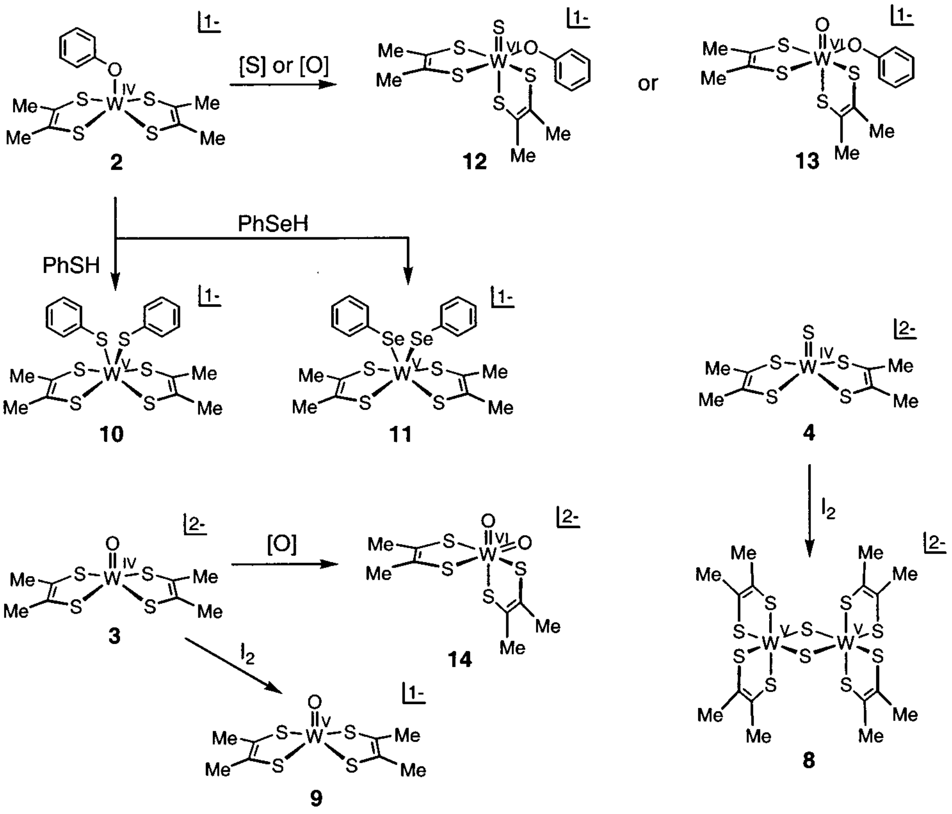

Figure 2. Scheme for the synthesis of bis(dithiolene)W(V,VI) complexes **9**−**14** by oxidation reactions of W(IV) complexes **2**, **3**, and **4**. [O] = Me$_3$NO; [S] = (PhCH$_2$S)$_2$S.

to the typical distances (sp^2)C═C(sp^2) = 1.331(9) Å and S−C(sp^2) = 1.751(17) Å[20] to allow description of the ligand as an ene-1,2-dithiolate and assignment of tungsten oxidation states in the sections that follow. This is the case for all bis(dithiolene)molybdenum and -tungsten complexes thus far examined with the exception of dicarbonyls.[21] In considering the structures of reaction products, nearly all metric parameters

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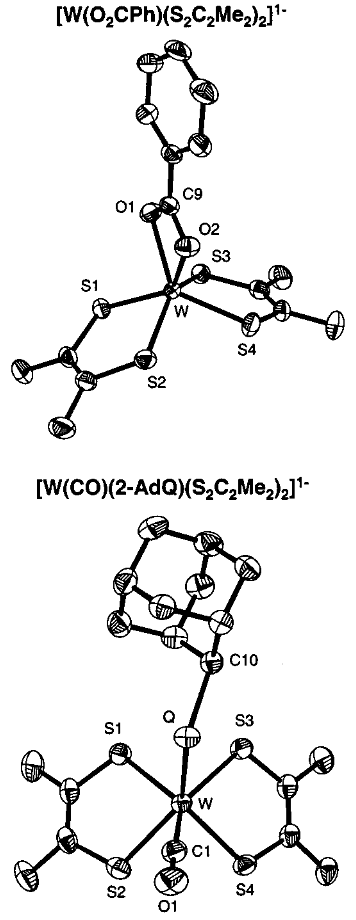

$[W(O_2CPh)(S_2C_2Me_2)_2]^{1-}$

$[W(CO)(2\text{-}AdQ)(S_2C_2Me_2)_2]^{1-}$

Figure 3. Structures of the W(IV) complexes **5** (upper) and **6**/**7** (lower; Q = S, Se) showing 50% probability ellipsoids and a partial atom-labeling scheme; **6** and **7** are isostructural.

(Table 3) are normal and are not explicitly discussed. Attention is directed toward molecular stereochemistry.

Tungsten(IV). All complexes have been prepared by displacement of one or two carbonyl groups from the readily prepared dicarbonyl precursor **1** (Figure 1). While depicted for simplicity as a bis(ene-1,2-dithiolate) complex, our recent experimental and theoretical work shows that **1** and its molybdenum analogue are highly delocalized, noninnocent species without clear-cut metal and ligand oxidation levels.[21] Both carbonyls are readily displaced by alkoxide or phenolate to afford **2**, by hydroxide to form oxo complex **3**, by hydrosulfide to form sulfido complex **4**, and by benzoate to yield **5**. Structures of square pyramidal **2**,[4] **3**,[3] and $[WS(S_2C_2Ph_2)_2]^{2-}$,[3] closely related to **4**, are available elsewhere. As seen in Figure 3, benzoate complex **5** is six-coordinate. The tungsten atom is displaced by 0.805 Å from the S_4 mean plane toward the benzoate ligand which is bound by two equivalent W−O interactions at 2.175 Å with a O−W−O angle of 59.4(2)°. The dihedral angle $\theta_d = 125.5°$ between WS_2 planes and the transoid S−W−S angles of 138° and 141° (involving sulfur atoms in different chelate rings) are close to the values of 120° and 136°, respectively, for trigonal prismatic geometry. In this sense, **5** closely resembles precursor **1**[3] and is the first example of a tungsten dithiolene carboxylate.

Earlier we reported the synthesis and structures of the set of complexes $[Mo(2\text{-}AdQ)(S_2C_2Me_2)_2]^-$, intended as representations of the Mo(IV) sites in DMSO reductase (Q = O), assimilatory nitrate reductase (Q = S), and formate dehydrogenase (Q = Se).[2] In our parallel development of molybdenum and tungsten dithiolene chemistry, we are interested in obtaining an analogous tungsten series. The square pyramidal complex $[W(2\text{-}AdO)(S_2C_2Me_2)_2]^-$ is readily prepared.[5] Reaction of **1** with 1−5 equiv of 2-adamantylthiolate or 2-adamantylselenolate gave only the monocarbonyl **6** or **7**. These results are consistent with that obtained in the reaction of **1** with highly hindered 2,4,6-triisopropylbenzenethiolate, from which the monocarbonyl complex was obtained.[4] Complexes **6** and **7** are isostructural (Figure 3). From θ_d and transoid S−W−S angles (Table 3), they are described as trigonal prismatic. We consider the W−S (2.405(2) Å) and W−Se (2.532(1) Å) bond lengths, much longer than the W−O distance in $[W(2\text{-}AdO)(S_2C_2Me_2)_2]^-$ (1.826(4) Å),[5] to reduce steric interactions between the adamantyl and carbonyl groups to the point where the monocarbonyls are stable. This aspect, together with higher W−CO than Mo−CO bond dissociation energies,[22] leads to the relative stability of the tungsten monocarbonyls, a matter discussed in more detail elsewhere.[4]

Table 4. Redox Potentials for W(VI/V), W(V/IV), and W(IV/III) Couples in Acetonitrile

complex	$E_{1/2}$, V[a] (ΔE_p, mV) W(VI/V)	W(V/IV)	W(IV/III)
$[W(CO)(2\text{-}AdS)(S_2C_2Me_2)_2]^-$			−1.53 (100)
$[W(CO)(2\text{-}AdSe)(S_2C_2Me_2)_2]^-$			−1.55 (110)
$[WO(S_2C_2Me_2)_2]^{2-}$ [b]	−0.05 (80)	−0.91 (80)	
$[WS(S_2C_2Me_2)_2]^{2-}$	−0.13 (80)[c]	−0.89 (90)	
$[W(SPh)_2(S_2C_2Me_2)_2]^-$	−0.18 (80)	−0.93 (70)	
$[W(SePh)_2(S_2C_2Me_2)_2]^-$	−0.21 (80)	−0.93 (150)	

[a] $E_{1/2} = (E_{pc} + E_{pa})/2$, scan rate 100 mV/s, vs SCE. [b] Reference 3. [c] Quasi-reversible.

Tungsten(V). Complexes in this oxidation state have been prepared by oxidation of W(IV) species with iodine (Figure 2). Redox potentials for four complexes are given in Table 4, and two cyclic voltammograms showing the existence of three-member electron transfer series based on **4** and **10** are presented in Figure 4. The low-potential oxo complex **3** is readily converted to **9** by treatment with iodine. It has the standard square pyramidal structure in Figure 5, observed for **3**[3] and related complexes such as $[WO(bdt)_2]^-$.[14] The redox potentials for **3** and sulfido complex **4** are nearly identical, as is the case with $[WQ(S_2C_2Ph_2)_2]^{2-}$ (Q = O, S).[3] When an analogous oxidation reaction was attempted with **4**, binuclear sulfide-bridged **8** was obtained instead of the desired mononuclear product. The complex can also be prepared in two other ways: oxidation of **1** with Na_2S_2 (Figure 1) and the reaction of **2** with Ph_3CSH, where we assume that the incipient triphenylmethyl carbocation is the likely oxidant as a W−S bond is developed and a S−C bond is compromised. This complex is characterized by a W···W interaction at 3.000(1) Å and distorted octahedral coordination (Figure 5). It is isostructural with $[Mo_2(\mu_2\text{-}S)_2(S_2C_2R_2)_4]^{2-}$ (R = Me,[1] CO_2Me[23]) and $[W_2(\mu_2\text{-}S)_2(S_2C_2R_2)_4]^{2-}$ (R = Ph,[3] CO_2Et[24]). $[W_2(\mu_2\text{-}S)_2(S_2C_2Ph_2)_4]^{2-}$ was obtained by the oxidation of $[WS(S_2C_2Ph_2)_2]^{2-}$ with tropylium ion.[3] We are unaware of any mononuclear dithiolene species containing either the $Mo^V{=}S$ or the $W^V{=}S$ group, the stability of bridged structures being prevalent.

In reactions intended to effect substitution of the phenolate ligand in **2** by proton transfer, this complex was treated with

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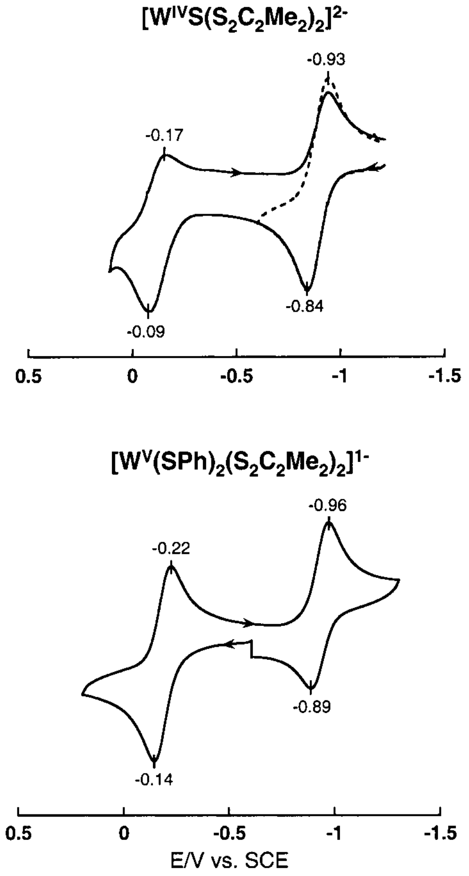


Figure 4. Cyclic voltammograms (100 mV/s) for complexes **4** (upper) and **10** (lower) in acetonitrile at ~25 °C. Peak potentials are indicated.

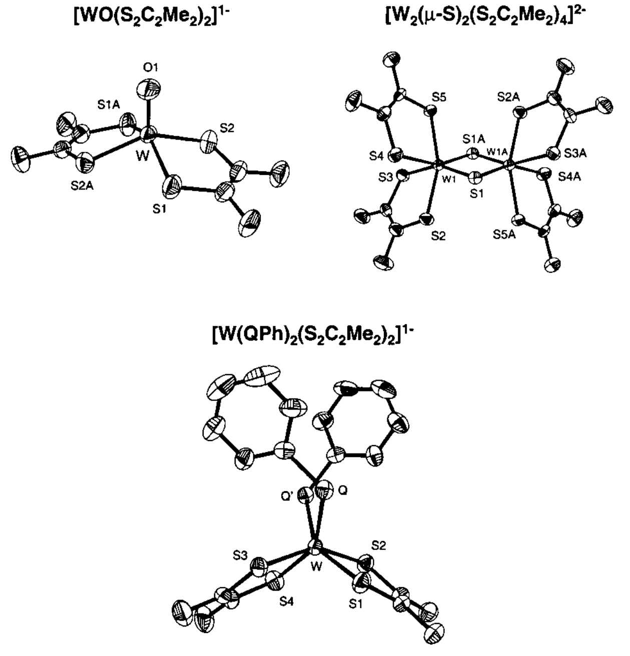


Figure 5. Structures of the W(V) complexes **9** and **8** (upper) and **10**/**11** (lower; Q = S, Se) showing 50% probability ellipsoids and a partial atom-labeling scheme; **10** and **11** are isostructural.

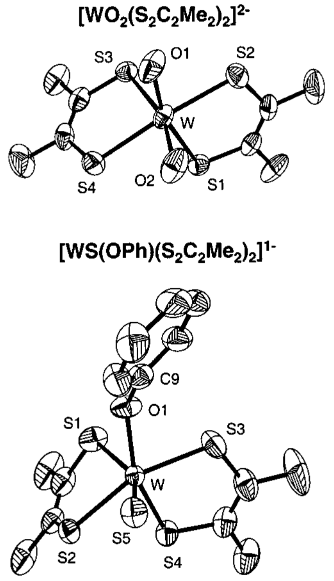
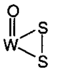
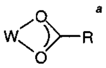


Figure 6. Structures of the W(VI) complexes **14** (upper) and **12** (lower) showing 50% probability ellipsoids and a partial atom-labeling scheme.

Table 5. Functional Groups in Mononuclear Bis(dithiolene)W(IV,V,VI) Complexes

Ox. State	Group				Refs
W(VI)	$\mathrm{\overset{O}{\overset{\|}{W}}{=}O}$ [a]	$\mathrm{\overset{O}{\overset{\|}{W}}{-}Cl}$	$\mathrm{\overset{O}{\overset{\|}{W}}{-}OR}$	$\mathrm{\overset{O}{\overset{\|}{W}}{-}OSiR_3}$	14, 15, 18, 28; 18; 5, 8; 18
		$\mathrm{\overset{S}{\overset{\|}{W}}{-}OR}$ [a]	$\mathrm{\overset{S}{\overset{\|}{W}}{-}OSiR_3}$		18, 18, 15
W(V)	W=O	$\mathrm{\overset{SR}{\overset{\mid}{W}}{-}SR}$ [a]	$\mathrm{\overset{SeR}{\overset{\mid}{W}}{-}SeR}$ [a]		3, 4,18
W(IV)	W=O	$\mathrm{W{-}OSiR_3}$	W—OR	 [a]	3, 4, 16, 18; 18; 4, 5
	W=S [a]	$\mathrm{\overset{CO}{\overset{\mid}{W}}{-}SR}$ [a]			3, 4
	W=Se [b]	$\mathrm{\overset{CO}{\overset{\mid}{W}}{-}SeR}$ [a]			3, 4
	$\mathrm{W(CO)_2}$ [c]	$\mathrm{W(CNR)_2}$ [c]	$\mathrm{W(P(OR)_3)_2}$ [c]		3, 21; 18; 18

[a] This work. [b] Not proven by a structure determination. [c] Ambiguous oxidation state.

benzenethiol or benzeneselenol. With 1 equiv of either compound in acetonitrile, the methyl resonance of **2** (δ 2.61) decreased in intensity by one-half; with 2 equiv, the resonance was abolished. On a preparative scale, **10** was obtained in 67% yield and **11** in 45% yield using 2 equiv of the reagents. These compounds are isostructural (Figure 5) and represent a new type of tungsten dithiolene complex. From transoid angles and θ_d values (Table 3), the complexes exhibit a distorted trigonal prismatic stereochemistry with the thiolate or selenolate ligands in cis positions. The overall stereochemistry is quite similar to that of **1**, **6**, and **7**. When compared with distances in PhQQPh (Q = S, 2.03 Å;[25,26] Q = Se, 2.29 Å[27]), the corresponding separations in **10** (3.31 Å) and **11** (3.49 Å) and Q−W−Q angles (Table 3) make clear that the ligands are monoanions, leading

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to a W(V) formulation. As shown by the results in Table 4 and Figure 4, complexes **10** and **11** reducible to W(IV) and oxidizable to W(VI) in reversible reactions at essentially identical potentials. EPR spectra of **9**−**11** at 4 K were broad and uninformative (Experimental Section).

Tungsten(VI). This oxidation state was achieved by the atom transfer reactions in Figure 2. Reaction of oxo complex **3** with Me_3NO affords dioxo complex **14**. Treatment of **2** with dibenzyl trisulfide affords sulfido complex **12**. The structures of **14** and **12** are set out in Figure 6. Complex **14** has a distorted octahedral stereochemistry and is essentially isostructural with $[WO_2(bdt)_2]^{2-}$ [14,28] and$[WO_2(mnt)_2]^{2-}$.[15] Complex **12** is congeneric with **13** and isostructural with it and $[WS(OSiBu^tPh_2)(bdt)_2]^-$.[18] Neither **12** nor **13** shows reversible reduction to W(V).

Summary. The research has afforded, by a combination of substitution and oxidation reactions, a new set of bis(dithiolene)-tungsten complexes composed of **4**−**12** and **14**, some of which are precedented structural types. The results of this and prior exploratory synthetic investigations are summarized in Table 5, which enumerates the 21 functional groups WL and WLL′ thus far stabilized in mononuclear bis(dithiolene) complexes and supplants an earlier version.[4] Conspicuously absent is the group $W^{VI}OS$, which has been stabilized in complexes with other ligands.[29−34] Despite multiple attempts, we have not been able to obtain a pure salt of $[WOS(S_2C_2Me_2)_2]^{2-}$. It remains to be seen which (if any) of the groups in Table 5 with physiological-type ligands eventuate in tungstoenzymes. Among the candidates are $W^{IV}O$, $W^{V}O$, and $W^{VI}O_2$, which appear in **3**, **9**, and **14**, respectively. We are continuing synthetic and reactivity studies, with current emphasis on the latter three species whose Et_4N^+ salts are water-soluble, an unusual property for bis(dithiolene)-tungsten complexes.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of the nine compounds in Tables 1 and 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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