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Synthesis, Structures, and Oxo Transfer Reactivity of Bis(dithiolene)tungsten(IV,VI) Complexes Related to the Active Sites of Tungstoenzymes

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Abstract: A series of bis(dithiolene)tungsten(IV,VI) complexes derived from benzene-1,2-dithiolate (bdt) has been prepared as an synthetic approach to pterin dithiolene-bound active sites of tungstoenzymes, one example of which, a archaeal oxidoreductase, has been established crystallographically (Chan et al. *Science* **1995**, *267*, 1463). With $[W^{IV}O(bdt)_2]^{2-}$ (**2**) as the starting compound, silylation with RR'_2SiCl afforded $[W^{IV}(bdt)_2(OSiRR'_2)]^{1-}$ (**4**). Oxidation of **4** with Me_3NO gave $[W^{VI}O(bdt)_2(OSiRR'_2)]^{1-}$ (**5**), also accessible by silylation of $[W^{VI}O_2(bdt)_2]^{2-}$ (**3**). Reaction of **3** or **5** with Me_3SiCl resulted in $[W^{VI}O(bdt)_2Cl]^{1-}$ (**6**), from which the unstable species $[W^{VI}O(bdt)_2L]^{1-}$ ($L = Bu^tO^-$, PhS^-) were generated in solution. Reductive oxo transfer of **6** with L′ = $P(OEt)_3$ or $Bu^tNC/P(OEt)_3$ gave $[W^{IV}(bdt)_2L'_2]$ (**8** and **9**). Sulfido complex $[W^{VI}S(bdt)_2(OSiRR'_2)]^{1-}$ (**12**) was obtained in the reaction systems **4**/$(PhCH_2S)_2S$ and **5**/$(Me_3Si)_2S$. Structures of $[WO(SPh)_4]^{1-}$ and $[W(bdt)_3]^{2-}$ and eight complexes of types **4**−**6**, **8**, **9**, and **12** were determined by X-ray crystallography. Complexes **4** and **5** are tungsten analogues of the desoxo Mo(IV) and monooxo Mo(VI) states of *Rhodobacter sphaeroides* DMSO reductase. Six types of reactivity, including oxygen atom transfer, are recognized by the synthesis and interconversion of the set of complexes. The potential biological relevance of these complexes to the structure and function of active sites in two families of tungstoenzymes is considered ($RR'_2 = Me_3$ (**4**); Bu^tMe_2 (**4** and **5**), Bu^tPh_2 (**4**, **5**, and **12**)).

Introduction

Recently, more than a dozen tungsten-containing enzymes have been isolated from hyperthermophilic archaea and bacteria[1,2] and have been classified into two major families.[2] Members of the aldehyde oxidoreductase (AOR) family catalyze the reaction $RCHO + H_2O \rightleftharpoons RCO_2^- + 3H^+ + 2e^-$. The enzyme from *Pyrococcus furiosus* (*Pf*, M_r 136 kDa, α_2) is the most thoroughly studied. It contains one tungsten atom and one $[Fe_4S_4]^{2+/1+}$ redox center per cluster and is the only tungsten enzyme for which an X-ray structure is currently available.[3,4] The tungsten atom is coordinated by two pterin dithiolene cofactor ligands in a distorted square pyramidal arrangement, and perhaps also by two oxygen ligands. However, oxygen ligation is not definitely established, owing to the heterogeneous nature of the tungsten center[5] and crystallographic difficulties in locating light atoms in the presence of a heavy scatterer.[4] The initial EXAFS analysis of dithionite-reduced *Pf* AOR, preceding the crystallographic results, revealed two W=O units at 1.74 Å, about three W−S bonds at 2.41 Å, and a possible W−O/N bond at 1.97 Å.[6] A second EXAFS study revealed one W=O (1.74 Å), four to five W−S (2.40 Å), and perhaps one W−O/N (1.97 Å) bond,[2] in improved agreement with the X-ray results. It is probable that the WO_2 form of the enzyme is inactive. The active enzyme has been examined in detail by MCD and EPR spectroscopies.[5]

The second family of tungstoenzymes consists of formate dehydrogenase (FDH) and N-formylmethanofuran dehydrogenase (FMDH). These enzymes catalyze the first step in the conversion of CO_2 to acetate and to methane in acetogens and methanogens, respectively.[2] On the basis of sequence data, F(M)DH enzymes have similarities to molybdoenzymes, including Mo−FDH, biotin S-oxide reductase, and DMSO reductase.[2] It has been suggested that their tungsten coordination units may be structurally similar to those found for DMSO reductase but with cysteinate or selenocysteinate in place of serinate.[2] X-ray crystallography of the *Rhodobacter sphaeroides* enzyme has established monooxo $Mo^{VI}O$ and desoxo Mo^{IV} site structures with one dithiolene ligand tightly bound, another asymmetrically coordinated ($Mo^{VI}O$) or virtually unbound (Mo^{IV}), and Mo−O·Ser ligation in both states.[7] EXAFS[8] and resonance Raman

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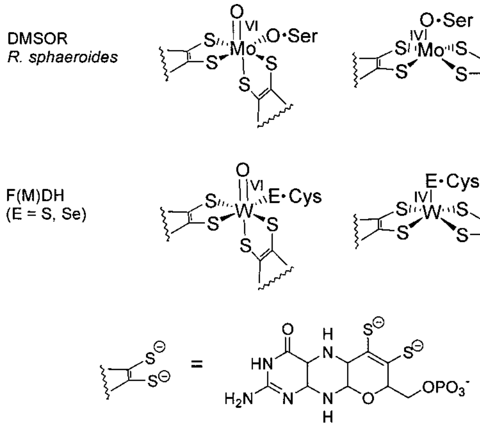

Figure 1. Schematic structures of the Mo^{IV} and $Mo^{VI}O$ sites of *R. sphaeroides* DMSO reductase depicted with tightly bound dithiolene chelate rings, possible structures of W−FM(D)H enzymes in two oxidation states, and the structure of the pterin dithiolene cofactor (nucleotide omitted).

spectroscopy[9] of this enzyme support the structures shown in Figure 1, in which two dithiolenes form tight chelate rings.[10] It might be conjectured that the tungsten coordination sites in F(M)DH resemble those depicted (Figure 1) in which cysteinate or selenocysteinate replaces serinate binding. Recently, bis(dithiolene) selenocysteinate coordination has been established for *Escherichia coli* Mo−FDH by crystallography[11a] and EXAFS analysis.[11b]

All molybdenum[12] and tungsten[2] enzymes of the hydroxylase or oxotransferase type contain at least one pterin dithiolene cofactor, sometimes with a nucleotide appended to the phosphate group. The cofactor structure is set out in Figure 1. The indicated dithiolene chelation mode has been established crystallographically for *Pf* AOR.[3,4] Although no bond distances were quoted, the depictions of the cofactor imply tight binding of the metal. In other tungstoenzymes, the number of cofactors bound to the metal has not been determined.

The existence of native metal−dithiolene coordination raises a new imperative for the examination of molybdenum and tungsten dithiolene complexes, particularly those with physiologically relevant coordination units. In this context, we have undertaken several investigations. In one study, the kinetics of oxygen atom transfer from $[MoO_2(mnt)_2]^{2-}$ (mnt = maleonitriledithiolate(2−)) to tertiary phosphine substrates as dependent on the stereoelectronic properties of the phosphines have been determined.[13] In another, the relative kinetics of oxo transfer from $[MO_2(mnt)_2]^{2-}$ (M = Mo, W) to tertiary phosphine and phosphite acceptors have been established, showing that transfer from the $Mo^{VI}O_2$ complex is more facile.[14] Additionally, we are addressing on a broader basis the synthesis of bis(dithiolene)molybdenum and -tungsten systems with the intent of approaching or attaining biological coordination units and accurate structural definition thereof, providing structural and spectroscopic calibrant molecules for native sites, and probing reactivity. Certain results have been briefly described.[15] Excluding organometallic compounds, about 20 tungsten dithiolenes have been previously prepared, the large majority being tris-complexes.[16] Some of these date from the discovery of dithiolene complexes and accompanying recognition of their noninnocent behavior in certain molecular oxidation states.[16a−d,17] Three monodithiolene species have been prepared.[18,19] Several sets of bis(dithiolene) complexes have been synthesized.[18,20,21] Indeed, preparation of $[WO(bdt)_2]^{2-,1-}$ and $[WO_2(bdt)_2]^{2-}$ (bdt = benzene-1,2-dithiolate(2−)) by Nakamura and co-workers,[20] and $[WO(mnt)_2]^{2-}$ and $[WO_2(mnt)_2]^{2-}$ by Sarkar and co-workers,[21] was stimulated by the discovery of tungstoenzymes. We have found the bdt complexes to be tractable precursors for further development of bis(dithiolene)tungsten chemistry relevant to the enzyme active site problem. The results of our investigation in this area are presented here.

Experimental Section

Preparation of Compounds. All reactions and manipulations were performed under a pure dinitrogen atmosphere using either modified Schlenk techniques or an inert atmosphere box. The compounds PhIO,[22] $PhI^{18}O$,[23] and Ph_2SeO[24] were prepared by literature methods. Other reagents were of commercial origin and were used as received. Acetonitrile was freshly distilled from CaH_2 and methanol from magnesium. Diethyl ether and THF were distilled from sodium and stored over 4 Å molecular sieves.

$(Et_4N)[WO(SPh)_4]$. A solution of 2.84 mL (27.7 mmol) of benzenethiol and 2.80 g (27.7 mmol) of Et_3N in 20 mL of acetonitrile was slowly added to a stirred solution of 2.49 g (5.53 mmol) of $WOCl_3(THF)_2$[25] in 20 mL of THF at −40 °C. The reaction was allowed to warm to room temperature and stirring was continued for 20 min. The violet solution was filtered and reduced in vacuo to a volume of 15 mL. To this solution was added a solution of 1.78 g (6.92 mmol) of Et_4NI in 80 mL of methanol, resulting in the precipitation of a dark solid. This material was collected by filtration, washed with methanol (3 × 10 mL), and dried in vacuo. The product was obtained as 3.70 g (87%) of a dark violet solid. Absorption spectrum (acetonitrile): λ_{max}

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(ϵ_M) 520 (3300) nm. IR (KBr): 948 cm^{-1} (ν_{WO}). FAB-MS$^-$: *m/z* 636 (M$^-$). Anal. Calcd for $C_{32}H_{40}NOS_4W$: C, 50.13; H, 5.26; N, 1.83; S, 16.72. Found: C, 50.21; H, 5.22; N, 1.86; S, 16.79. This compound has been previously reported,[26] but no explicit preparation was given. The Ph_4P^+ salt was prepared in 73% yield by the same procedure as for the Et_4N^+ salt.

$(Et_4N)[WO(bdt)_2]$. A solution of 0.500 g (3.52 mmol) of benzene-1,2-dithiol[27] and 0.712 g (7.04 mmol) of Et_3N in 10 mL of acetonitrile was added slowly to a stirred solution of 0.792 g (1.76 mmol) of $WOCl_3(THF)_2$ in 10 mL of acetonitrile at −40 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 30 min. The solution was filtered and reduced in vacuo to a volume of 6 mL. The deep blue-green solution was treated dropwise with a solution of 0.565 g (2.20 mmol) of Et_4NI in 20 mL of methanol. The mixture was stirred for 30 min, and the black solid was collected by filtration. This material was washed with methanol (3 × 4 mL), and dried in vacuo to give 0.850 g (79%) of product as a black solid. Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 354 (sh), 455 (1000), 613 (3000) nm. IR (KBr): 949 cm^{-1} (ν_{WO}). FAB-MS$^-$: *m/z* 480 (M$^-$). Anal. Calcd for $C_{20}H_{28}NOS_4W$: C, 39.35; H, 4.62; N, 2.29; S, 21.00. Found: C, 39.22; H, 4.62; N, 2.36; S, 20.83. This compound has been prepared previously by a different method.[20]

$(Et_4N)_2[WO(bdt)_2]$. A solution of sodium acenaphthylenide was prepared from 0.110 g (4.78 mmol) of sodium and 0.750 g (4.93 mmol) of acenaphthylene in 75 mL of THF; the mixture was stirred until all of the sodium dissolved. A portion of this solution (60 mL) was added dropwise to a stirred solution of 2.00 g (3.28 mmol) of $(Et_4N)[WO(bdt)_2]$ in 30 mL of acetonitrile, resulting in a brown solution. The solution was allowed to warm to room temperature and was stirred for 1 h. The solution was reduced in vacuo to a volume of 15 mL, and was treated with a solution of 1.10 g (4.28 mmol) of Et_4NI in 80 mL of methanol. The resulting suspension was filtered to separate an orange-brown solid, which was washed with methanol (3 × 20 mL), acetonitrile (2 × 10 mL), and ether (2 × 10 mL), and dried in vacuo to give 1.60 g (66%) of product as an ochre solid. Absorption spectrum (acetonitrile): λ_{max} 326, 394, 466 nm. IR (KBr): 905 cm^{-1} (ν_{WO}). ES-MS$^-$: *m/z* 480 (M$^-$). ^{1}H NMR (anion + Cp_2Co, CD_3CN): δ 7.70 (d, 1), 6.70 (d, 1). Cobaltocene was added to reduce line broadening by electron transfer with $[WO(bdt)_2]^{1-}$ impurity. Anal. Calcd for $C_{28}H_{48}N_2OS_4W$: C, 45.40; H, 6.53; N, 3.78; S, 17.31. Found: C, 45.18; H, 6.44; N, 3.66; S, 16.99. This compound has been prepared previously by another method.[20]

$(Et_4N)_2[WO_2(bdt)_2]$. This compound was prepared by a published procedure, but few characterization details were given.[20] It was isolated in 75% yield as a light red-orange crystalline solid. Absorption spectrum (acetonitrile): λ_{max} 286 (sh), 324 (sh), 423, 482 nm. IR (KBr): 847, 887 cm^{-1} (ν_{WO}). FAB-MS$^-$: *m/z* 496 (M$^-$). ^{1}H NMR (anion, CD_3CN): δ 6.99 (d, 1), 6.52 (d, 1).

$(Et_4N)_2[W(bdt)_3]$. This compound was isolated as a byproduct in the synthesis of $(Et_4N)_2[WO(bdt)_2]$ and was extracted from it by washing the solid products with acetonitrile to give a red solution. Slow addition of ether by vapor diffusion to this solution afforded the compound as red crystals. Yields of up to 70% have been obtained, which apparently depend on the water content of the solvent. FAB-MS$^-$: *m/z* 604 (M$^-$). ^{1}H NMR (anion, CD_3CN): δ 7.57 (d, 1), 6.58 (d, 1). Anal. Calcd for $C_{34}H_{52}N_2S_6W$: C, 47.21; H, 6.06; N, 3.24; S, 22.24. Found: C, 47.09; H, 6.02; N, 3.30; S, 22.18.

$(Et_4N)[W(bdt)_2(OSiMe_3)]$. To a stirred solution of 100 mg (0.135 mmol) of $(Et_4N)_2[WO(bdt)_2]$ in 2 mL of acetonitrile was added 18.0 mg (0.170 mmol) of Me_3SiCl. The reaction mixture turned red and a red precipitate appeared. Stirring was continued for 2 h, the solvent was removed in vacuo, and the solid residue was washed with ether (3 × 3 mL). This material was dissolved in the minimum volume (∼6 mL) of THF/acetonitrile (3:1 v/v), the solution was filtered through Celite, and ether was introduced into the filtrate by vapor diffusion. The solid was separated and was collected by filtration, washed with ether (3 × 3 mL), and dried in vacuo to afford the product as 99 mg (90%) of red crystals. IR (KBr): 1250 (m), 1171 (m), 909 (vs, ν_{SiO}), 844 (s), 750 (s). MS-ES: *m/z* 553 (M$^-$). ^{1}H NMR (anion, CD_3CN): δ 7.96 (dd, 4), 6.98 (dd, 4), −0.21 (s, 9). Anal. Calcd for $C_{23}H_{37}NOS_4SiW$: C, 40.40; H, 5.45; N, 2.05; S. 18.76. Found: C, 40.26; H, 5.48; N, 2.01; S, 18.89.

$(Et_4N)[W(bdt)_2(OSiBu^tMe_2)]$. A solution of 50 mg (0.067 mmol) of $(Et_4N)_2[WO(bdt)_2]$ in 10 mL of acetonitrile was treated with 10 mg (0.066 mmol) of Bu^tMe_2SiCl, producing a red color. The reaction mixture was stirred for 1 h, and solvent was removed in vacuo. The residue was dissolved in 2 mL of THF, the solution was filtered through Celite, and the volume of the filtrate reduced to 1 mL. Ether (18 mL) was added very slowly to the filtrate, and the solution was allowed to stand overnight. Red crystals were collected by filtration, washed with ether (2 × 5 mL), and dried in vacuo to afford 35 mg (71%) of product. IR (KBr): 1250 (s), 1170 (m), 923 (vs, ν_{SiO}), 833 (m), 819 (m), 782 (s), 745 (s) cm^{-1}. FAB-MS$^-$: *m/z* 595 (M$^-$). ^{1}H NMR (anion, CD_3CN): δ 7.95 (dd, 4), 6.98 (dd, 4). 0.61 (s, 9), −0.26 (s, 6). Anal. Calcd for $C_{26}H_{43}NOS_4SiW$: C, 43.03; H, 5.97; N, 1.93; S. 17.67. Found: C, 43.19; H, 6.07; N, 1.87; S, 17.50.

$(Et_4N)[W(bdt)_2(OSiBu^tPh_2)]$. A suspension of 0.400 g (0.540 mmol) of $(Et_4N)_2[WO(bdt)_2]$ in 5 mL of acetonitrile was treated dropwise with 0.153 g (0.557 mmol) of Bu^tPh_2SiCl. The reaction mixture was stirred for 1 h, at which point it consisted of a red solution and a red-purple solid. The solid was separated by filtration, washed with acetonitrile (2 × 2 mL) and ether (2 × 5 mL), and dried in vacuo to give the product as 0.380 g (83%) of a red-purple solid. An analytical sample was recrystallized from acetonitrile/ether. Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 307 (21 100), 345 (6740), 420 (420), 553 (85) nm. IR (KBr): 1587 (m), 1554 (m), 1112 (s), 963 (vs, ν_{SiO}), 751 (s), 707 (s), 506 (s) cm^{-1}. ES-MS$^-$: *m/z* 595 (M$^-$). ^{1}H NMR (anion, CD_3CN): δ 8.00 (dd, 4), 7.36 (d, 4), 7.25 (t, 2), 7.08 (t, 4), 7.02 (dd, 4), 0.73 (s, 9). Anal. Calcd for $C_{36}H_{47}NOSiS_4W$: C, 50.87; H, 5.57; N, 1.65; S, 15.09. Found: C, 50.72; H, 5.61; N, 1.69; S, 15.18.

$(Et_4N)[WO(bdt)_2(OSiBu^tPh_2)]$. (a) Method 1. A stirred solution of 0.200 g (0.235 mmol) of $(Et_4N)[W(bdt)_2(OSiBu^tPh_2)]$ in 5 mL of acetonitrile was treated with 36 mg (0.48 mmol) of Me_3NO, resulting in an instantaneous color change from red to brown-green. The mixture was stirred for 1 h, the solvent was removed in vacuo, and the solid residue was extracted with 40 mL of THF. The green extract was filtered through Celite, evaporated to dryness, washed with ether (3 × 10 mL), and dried in vacuo to yield the product as 0.155 g (76%) of brown powder. An analytical sample as red crystals was obtained by vapor diffusion of ether into an acetonitrile/THF solution (1:5 v/v). Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 294 (14 300), 339 (sh, 7620), 375 (sh, 5250), 455 (3720), 600 (1610) nm. IR (KBr): 1109 (s), 933 (vs, ν_{SiO}), 888 (vs, ν_{WO}), 748 (s), 704 (s), 611 (s), 505 (s) cm^{-1}. FAB-MS$^-$: *m/z* 735 (M$^-$). ^{1}H NMR (anion, CD_3CN): δ 7.91 (dd, 4), 7.36 (m, 6), 7.23 (dd, 4), 6.87 (dd, 4), 1.06 (s, 9). Anal. Calcd for $C_{36}H_{47}NO_2SiS_4W$: C, 49.93; H, 5.47; N, 1.62; S, 14.81. Found: C, 50.11; H, 5.59; N, 1.73; S, 14.66.

(b) Method 2. A stirred solution of 0.200 g (0.264 mmol) of $(Et_4N)_2[WO_2(bdt)_2]$ in 2 mL of acetonitrile was treated with 80 mg (0.29 mmol) of Bu^tPh_2SiCl. The orange solution turned brown-green within a few seconds; stirring was continued for 1 h. The reaction mixture was worked up as in method 1 to afford 0.195 g (85%) of product. The spectroscopic properties were identical to those of the product of method 1. Anal. Found: C, 50.06; H, 5.55; N, 1.63; S, 14.69.

$(Et_4N)[WO(bdt)_2(OSiBu^tMe_2)]$. A solution of 50 mg (0.066 mmol) of $(Et_4N)_2WO_2(bdt)_2]$ in 0.5 mL of acetonitrile was treated with 10 mg (0.066 mmol) of Bu^tMe_2SiCl, resulting in an orange to brown-green color change. The solution was stirred for 30 min, the solvent was removed in vacuo, and the residue extracted with 2 mL of THF. The solution was filtered through Celite, and ether was added dropwise to the filtrate. The dark crystals that separated from the filtrate solution overnight were collected, washed with ether (2 × 5 mL), and dried in vacuo to give 45 mg (92%) of product as a dark brown-green solid. IR (KBr): 1244 (m), 1171 (m), 930 (vs, ν_{SiO}), 890 (vs, ν_{WO}), 835 (m), 821 (m), 778 (m), 752 (s) cm^{-1}. FAB-MS$^-$: *m/z* 611 (M$^-$). ^{1}H NMR

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(anion, CD_3CN): δ 7.22 (dd, 4), 6.85 (dd, 4), 0.93 (s, 9), 0.19 (s, 6). Anal. Calcd for $C_{26}H_{43}NO_2SiS_4W$: C, 42.10; H, 5.84; N, 1.89; S, 17.29. Found: C, 42.24; H, 5.88; N, 1.88; S, 17.44.

$(Et_4N)[WO(bdt)_2Cl]$. **(a) Method 1.** $(Et_4N)[WO(bdt)_2(OSiBu^tPh_2)]$ (0.250 g, 0.289 mmol) was dissolved in 15 mL of acetonitrile to form a dark green-black solution, to which was added 63 mg (0.58 mmol) of Me_3SiCl. The reaction mixture was stirred until it became deep purple (3 h), and 60 mL of ether was added. The black microcrystalline product that separated was collected by filtration, washed with ether (3 × 10 mL), and dried in vacuo to yield the product as 0.138 g (74%) of black solid. Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 290 (18 100), 351 (12 500), 499 (5100), 600 (3130) nm. IR (KBr): 1170 (m), 997 (m), 915 (vs, ν_{WO}), 835 (m), 765 (s) cm^{-1}. ES-MS: m/z 515 (M^-). ^1H NMR (anion, CD_3CN): δ 7.36 (dd, 1). 7.00 (dd, 1). Anal. Calcd for $C_{20}H_{28}ClNOS_4W$: C, 37.19; H, 4.37; Cl, 5.49; N, 2.17; S, 19.85. Found: C, 36.94; H, 4.33; Cl, 5.56; N, 2.20; S, 19.64. This procedure was also applied to $(Et_4N)[WO(bdt)_2(OSiBu^tMe_2)]$ on a 0.12 mmol scale; the product was obtained as 51 mg (66%) of red crystals.

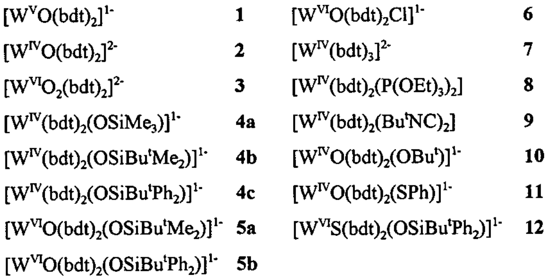
(b) Method 2. To a stirred solution of 200 mg (0.585 mmol) of $WOCl_4$[28] in 5 mL of acetonitrile was added 50.0 mg (0.585 mmol) of $LiOBu^t$ in portions. Within 1 min, the orange solution turned yellow and a white precipitate formed. Et_4NCl (100 mg, 0.585 mmol) was added to the reaction mixture followed by a solution of 90.0 mg (1.17 mmol) of $Li_2(bdt)$ in 1 mL of acetonitrile. The mixture was stirred for 5 min and filtered through Celite, and the filtrate taken to dryness in vacuo. The residue of black powder was washed with ether (4 × 4 mL) and 14 mL of THF/ether (2:5 v/v) and dried in vacuo, giving the product as 230 mg (60%) of a black solid. Spectroscopic properties were identical to those of the product of method 1.

$[W(bdt)_2(P(OEt)_3)_2]$. To a solution of 50 mg (0.077 mmol) of $(Et_4N)[WO(bdt)_2Cl]$ in 5 mL of acetonitrile was added 50 mg (0.30 mmol) of $P(OEt)_3$. The reaction mixture was stirred for 12 h, the solvent was removed in vacuo, and the dark residue was extracted with ether (2 × 10 mL). The yellow-orange extract was filtered, and the filtrate was reduced to dryness in vacuo, affording the product as 24 mg (39%) of orange crystalline solid. Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 339 (10 000), 411 (14 700) nm. ^1H NMR (CD_3CN): δ 8.20 (dd, 4), 7.20 (dd, 4), 3.81 (q, 12), 1.18 (t, 18). Anal. Calcd for $C_{24}H_{38}O_6P_2S_4W$: C, 36.19; H, 4.81; P, 7.78; S, 16.10. Found: C, 36.26; H, 4.88; P, 7.86; S, 16.19.

$[W(bdt)_2(Bu^tNC)_2]$. To a solution of 50 mg (0.077 mmol) of $(Et_4N)[WO(bdt)_2Cl]$ in 5 mL of acetonitrile was added 25 mg (0.30 mmol) of Bu^tNC followed by 15 mg (0.090 mmol) of $P(OEt)_3$. The reaction mixture was stirred for 1 h, during which time the color changed from purple to orange-brown and a dark microcrystalline product precipitated. Solvent was removed in vacuo and the dark residue was extracted with ether (10 × 10 mL). The orange-red extract was filtered and 20 mL of methanol was added to the filtrate. The volume of the solution was reduced to 3 mL, causing separation of a solid which was collected by filtration. This material was washed with methanol (2 × 1 mL) and dried in vacuo, giving the product as 27 mg (55%) of a red crystalline product. Absorption spectrum (acetonitrile): λ_{max} (ϵ_M) 352 (9100), 445 (15 100) nm. IR (KBr): 2151, 2128 (sh) cm^{-1} (ν_{NC}). ^1H NMR (CD_2Cl_2): δ 8.20 (dd, 4), 7.20 (dd, 4), 1.56 (s, 18). Anal. Calcd for $C_{22}H_{26}N_2S_4W$: C, 41.91; H, 4.16; N, 4.44; S, 20.34. Found: C, 41.82; H, 4.22; N, 4.36; S, 20.28.

$(Et_4N)[WS(bdt)_2(OSiBu^tPh_2)]$. This compound could be reproducibly prepared by two methods but was always obtained as a mixture. **(a) Method 1.** An acetonitrile solution of 20 mg (0.023 mmol) of $(Et_4N)[WO(bdt)_2(OSiBu^tPh_2)]$ in 1 mL of acetonitrile was treated with 6.0 μL (0.029 mmol) of $(Me_3Si)_2S$ (*caution*—stench). The reaction mixture was stirred for 12 h, during which it turned from green to brown. After 2 d of stirring, the solvent was removed in vacuo, and the residue was triturated with ether (2 × 5 mL) and dried in vacuo. An ^1H NMR analysis of the solid showed that it contained 60% desired product and 40% $[W(bdt)_2(OSiBu^tPh_2)]^{1-}$. The spectrum of the former in CD_3CN closely resembles that of $[WO(bdt)_2(OSiBu^tPh_2)]$: δ 7.88 (dd), 7.35 (m), 7.26 (dd), 6.87 (dd), 1.06 (s). IR (KBr): 915 cm^{-1} (ν_{SiO}). FAB-MS^-: m/z 751 (M^-). **(b) Method 2.** $(Et_4N)[W(bdt)_2(OSiBu^tPh_2)]$ (20 mg, 0.023 mmol) was added to a solution of 8.0 mg of $(PhCH_2S)_2S$ (0.029 mmol) in 1 mL of acetonitrile. The red solution turned brown and was stirred for 6 h; method 1 was then followed. The desired compound was obtained in a mixture of similar proportion to that of method 1. Although this compound could not be obtained pure in bulk quantity, dark violet crystals suitable for X-ray diffraction were grown from a DMF−ether solution.

Chart 1. Designation of Tungsten−Dithiolene Complexes



$[W^VO(bdt)_2]^{1-}$	**1**	$[W^{VI}O(bdt)_2Cl]^{1-}$	**6**
$[W^{IV}O(bdt)_2]^{2-}$	**2**	$[W^{IV}(bdt)_3]^{2-}$	**7**
$[W^{VI}O_2(bdt)_2]^{2-}$	**3**	$[W^{IV}(bdt)_2(P(OEt)_3)_2]$	**8**
$[W^{IV}(bdt)_2(OSiMe_3)]^{1-}$	**4a**	$[W^{IV}(bdt)_2(Bu^tNC)_2]$	**9**
$[W^{IV}(bdt)_2(OSiBu^tMe_2)]^{1-}$	**4b**	$[W^{IV}O(bdt)_2(OBu^t)]^{1-}$	**10**
$[W^{IV}(bdt)_2(OSiBu^tPh_2)]^{1-}$	**4c**	$[W^{IV}O(bdt)_2(SPh)]^{1-}$	**11**
$[W^{VI}O(bdt)_2(OSiBu^tMe_2)]^{1-}$	**5a**	$[W^{VI}S(bdt)_2(OSiBu^tPh_2)]^{1-}$	**12**
$[W^{VI}O(bdt)_2(OSiBu^tPh_2)]^{1-}$	**5b**		

$Ph_2Se^{18}O$. To a solution of 70 mg of NaOH in 0.100 mL of $H_2{}^{18}O$ (Icon, 98.7% ^{18}O) cooled in an ice bath was added 100 mg of Ph_2SeCl_2. The reaction mixture was stirred vigorously for 30 min in the ice bath and overnight at room temperature. The liquid was decanted, and the solid was washed with distilled water (2 × 1 mL) and hexane (2 × 1 mL) and dried in vacuo. Mass spectrometry showed the product to contain 62(3)% ^{18}O.

Oxo Transfer Reactions. These reactions, involving $(Et_4N)[W(bdt)_2(OSiBu^tPh_2)]$ (δ 0.73) as an oxo acceptor and $(Et_4N)[WO(bdt)_2(OSiBu^tPh_2)]$ (δ 1.06) as an oxo donor, were monitored in CD_3CN solutions by ^1H NMR. The mole percents of initial and final complexes are based on integration of Bu^t signals with the indicated chemical shifts and that of Bu^tPh_2SiOH (δ 0.98), which appeared in nearly all reaction systems owing to partial hydrolysis of the tungsten complexes by trace amounts of water.

^{18}O Transfer Reactions. (a) $(Et_4N)[W(bdt)_2(OSiBu^tPh_2)]$ (5.0 mg, 5.8 μmol) and $PhI^{18}O$ (5.0 mg, 23 μmol) were stirred in 0.5 mL of acetonitrile for 3 h. The solvent was removed in vacuo and the residue dried in vacuo. IR (KBr): 931 (Si−O), 895 ($W{=}^{16}O$), 848 ($W{=}^{18}O$). The ^1H NMR spectrum of the product is identical to that of $[WO(bdt)_2(OSiBu^tPh_2)]^{1-}$. In two experiments the ^{18}O product incorporation was 60(3<)% and 68(5)% by FAB-MS. (b) $(Et_4N)[W(bdt)_2(OSiBu^tPh_2)]$ (5.0 mg, 5.8 μmol) and $Ph_2Se^{18}O$ (3.0 mg, 12 μmol) were stirred in 0.5 mL of acetonitrile for 10 h. The previous procedure was followed, leading to 60(3)% ^{18}O product incorporation.

X-ray Structure Determinations. Reference is made to the numerical designation of complexes in Chart 1. The structures of the 10 compounds in Tables 1 and 2 were determined. Crystals of $(Ph_4P)[WO(SPh)_4]\cdot{}^3/_2DMF$ (black blocks), (Et_4N)[**4a**] (red plates), (Et_4N)[**4c**] (red-black blocks), (Et_4N)[**5a**]$\cdot{}^1/_2MeCN$ (orange-red plates), and $(Et_4N)_2$[**7**] (red plates) were obtained by slow diffusion of Bu^tOMe into saturated DMF ($(Ph_4P)[WO(SPh)_4]\cdot{}^3/_2DMF$) or acetonitrile solutions ((Et_4N)[**4a**], (Et_4N)[**4c**], (Et_4N)[**5a**]$\cdot{}^1/_2MeCN$), and $(Et_4N)_2$[**7**]. A similar procedure using Et_2O gave (Et_4N)[**6**] (red needles). Diffusion of Et_2O in 1:1 acetonitrile/THF solution gave (Et_4N)[**5b**] (black plates) and into a DMF solution afforded (Et_4N)[**12**] (violet elongated plates). Slow evaporation of an ether/methanol solution (2:1 v/v) produced **8** (orange needles), while **9** (red blocks) was obtained directly from the reaction mixture upon standing.

Diffraction data for $(Ph_4P)[WO(SPh)_4]\cdot{}^3/_2DMF$, (Et_4N)[**4c**], (Et_4N)[**5a**]$\cdot{}^1/_2MeCN$, (Et_4N)[**5b**], (Et_4N)[**6**], and **9** were collected on a Nicolet P3 diffractometer. Crystals were coated in grease, mounted on glass fibers, and cooled in a nitrogen stream. Refined cell parameters were obtained by least-squares fits of 30−50 machine-centered reflections (10° ≤ 2θ° ≤ 20°). Two check reflections were monitored during the data collections and showed no significant decay. Data reduction and corrections for scan speed, background, and Lorentz and polarization effects were applied by the program XDISK of the SHELXTL PLUS program suite. Empirical absorption corrections were applied with XPREP using variations in intensity in azimuthal (Ψ) data for 7−10 reflections with 2θ evenly spaced between 10° and 45°. The compounds (Et_4N)[**4a**], $(Et_4N)_2$[**7**], **8**, and (Et_4N)[**12**] were examined with a Siemens (Bruker) SMART CCD area detector instrument. Data

Table 1. Crystallographic Data[a] for Compounds Containing $[WO(SPh)_4]^-$, **4a**, **4c**, **5a**, and **5b**

	$(PPh_4)[WO(SPh)_4]\cdot{}^3/_2DMF$	(Et_4N)[**4a**]	(Et_4N)[**4c**]	(Et_4N)[**5a**]$\cdot{}^1/_2CH_3CN$	(Et_4N)[**5b**]
formula	$C_{48}H_{40}OPS_4W\cdot{}^3/_2HCONMe_2$	$C_{23}H_{37}NOS_4SiW$	$C_{36}H_{47}NOS_4SiW$	$C_{29}H_{47.5}N_{1.5}O_2S_4SiW$	$C_{36}H_{47}NO_2S_4SiW$
fw	1085.50	683.72	849.93	782.85	865.93
crystal system	triclinic	monoclinic	monoclinic	triclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/c$	Pn	$P\bar{1}$	$Pbca$
Z	2	4	2	4	8
a, Å	10.391(2)	9.9543(1)	10.616(2)	11.030(2)	10.662(2)
b, Å	15.430(3)	25.2280(3)	9.968(2)	17.581(4)	22.730(5)
c, Å	17.380(4)	11.8162(0)	17.804(4)	17.765(4)	31.414(6)
α, deg	63.78(3)			97.23(3)	
β, deg	89.75(3)	102.638(1)	96.02(3)	94.76(3)	
γ, deg	79.78(3)			95.91(3)	
V, Å^3	2451.6(9)	2895.47(5)	1873.6(6)	3383.3(12)	7613(3)
T, K	223	213	223	223	223
R^b ($R_w{}^c$)	0.0352 (0.0852)	0.0325 (0.0564)	0.0279 (0.0635)	0.0672 (0.1633)	0.0367 (0.0731)

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

Table 2. Crystallographic Data[a] for Compounds Containing **6**−**9** and **12**

	(Et_4N)[**6**]	$(Et_4N)_2\cdot$[**7**][d]	**8**	**9**	(Et_4N)[**12**]
formula	$C_{20}H_{28}ClNOS_4W$	$C_{34}H_{52}N_2S_6W$	$C_{24}H_{38}O_6P_2S_4W$	$C_{22}H_{26}N_2S_4W$	$C_{36}H_{47}NOS_5SiW$
fw	645.97	864.99	796.6	630.5	881.99
crystal system	monoclinic	orthorhombic	monoclinic	orthorhombic	triclinic
space group	$P2_1/c$	$Pbca$	$P2_1/c$	$Pna2_1$	$P\bar{1}$
Z	4	8	8	4	4
a, Å	10.156(2)	14.2662(2)	19.4060(0)	17.110(3)	10.2247(1)
b, Å	11.649(2)	17.5888(1)	16.7707(3)	16.380(3)	10.2247(1)
c, Å	20.055(4)	30.3401(5)	21.6413(1)	9.466(2)	39.6961(7)
α, deg					85.791(1)
β, deg	90.91(3)		116.514(1)		84.855(1)
γ, deg					69.668(1)
V, Å^3	2372.4(8)	7613.1(2)	6302.4(1)	2653.0(9)	3871.80(9)
T, K	223	213	213	223	213
R^b ($R_w{}^c$)	0.0419 (0.1017)	0.0431 (0.0716)	0.0358 (0.0534)	0.0281 (0.0653)	0.0910 (0.1822)

[a] Obtained with graphite-monochromatized Mo Kα ($\lambda = 0.71073$ Å) radiation. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = \{\sum[w(|F_o| - |F_c|)^2]/\sum[w|F_o|^2]\}^{1/2}$. [d] Crystalline $[Et_4N]_2[W^{IV}(bdt)_3]$ was also obtained in space group $C2/c$ with cell parameters $a = 19.267(2)$ Å, $b = 27.581(3)$ Å, $c = 17.852(3)$ Å, $\beta = 114.512(8)°$ by slow diffusion of 1,2-dimethoxyethane into a DMF solution.

were measured using ω scans of 3°/frame with 30 or 60 s frames such that 1271 frames were collected for a hemisphere of data. No decay in intensities was observed over the data collections. Cell parameters were retrieved using SMART software and refined using SAINT software on all observed reflections between 2θ of 3° and 56° ((Et_4N)[**4a**], $(Et_4N)_2$[**7**], **8**) or 45° ((Et_4N)[**12**]). Data reduction was performed with SAINT software, which corrects for Lorentz polarization and decay. Absorption corrections were applied using SADABS based on the method described by Blessing.[29]

Space groups were assigned on the basis of systematic absences with use of XPREP ((Et_4N)[**4a**], (Et_4N)[**4c**], (Et_4N)[**5b**], (Et_4N)[**6**], $(Et_4N)_2$[**7**], **8**, **9**). For $(Ph_4P)[WO(SPh)_4]\cdot{}^3/_2DMF$, ($Et_4N$)[**5a**]$\cdot{}^1/_2$MeCN, and ($Et_4N$)[**12**], space groups were assigned on the basis of statistics and successful structure solution and refinement. All structures were solved by direct methods using SHELXS and refined by full-matrix least-squares methods. All non-hydrogen atoms except those of the disordered DMF molecule in $(Ph_4P)[WO(SPh)_4]\cdot{}^3/_2DMF$ were refined anisotropically; hydrogen atoms were added at idealized positions and refined as riding atoms with a uniform value of U_{iso}. In the final stages of refinement of (Et_4N)[**5a**]$\cdot{}^1/_2$MeCN, (Et_4N)[**5b**], (Et_4N)[**6**], and **9**, a weighting scheme was used that increased the contribution of the lighter atoms to the structure factor amplitudes such that an improved goodness-of-fit value was obtained.[30] The asymmetric unit of $(Ph_4P)[WO(SPh)_4]\cdot{}^3/_2DMF$ contains 1.5 DMF solvate molecules, the nitrogen atom of one of which resides on an inversion center. The position requires site occupancy factors of 0.5 for the atoms of DMF and imposes disorder over the symmetry site. For **8**, one methylene group of a phosphite ligand was disordered over two positions, which were refined with 0.5 site occupancies. The methylene groups of the cation of (Et_4N)[**12**] were disordered, and were refined with variable occupancies of the carbon atoms determined as optimal fits by SHELXTL. All structures were checked for missing symmetry with the checking program PLATON (V: 120695). Supporting Information was prepared with use of XCIF.[31]

Other Physical Measurements. All measurements were made under anaerobic conditions. Absorption spectra were recorded on Perkin-Elmer Lambda 6 or Varian Cary 3 spectrophotometer. ^{1}H and ^{31}P NMR spectra were obtained with a Bruker AM 400 spectrometer. IR spectra were determined with use of a Nicolet Impact 400 FT-IR instrument. Mass spectra were recorded on a JEOL AX-505 (EI-MS), JEOL SX-102 (FAB-MS), and a Micromass Platform II (ES-MS) spectrometers. The matrix for FAB spectra was 3-nitrobenzyl alcohol.

Results and Discussion

This work constitutes the first systematic investigation of the synthetic and structural chemistry of tungsten-dithiolene complexes of any type. A synthesis and reactivity scheme is presented in Figure 2. Structures of 10 complexes are set out in Figures 3−7, selected metric data are collected in Tables 3−5. Complexes **1**−**3**[20] and**7**[16h] have been previously prepared, but by different methods, and their structures determined.[16i,20]

Synthesis and Structures of Bis(dithiolene)tungsten(IV,V,VI) Complexes. (a) Precursors. Complex **1** was first prepared by the ligand substitution reaction of $bdtH_2$ with $[WO(SPh)_4]^{1-}$,[20] which itself was obtained in unspecified yield from $[WOCl_4]^{1-}$ and Et_3N/PhSH.[26] In this work, the precursor complex was synthesized by the reaction of $[WOCl_3(THF)_2]$ and Et_3N/PhSH

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(31) See paragraph at the end of this article concerning Supporting Information available.

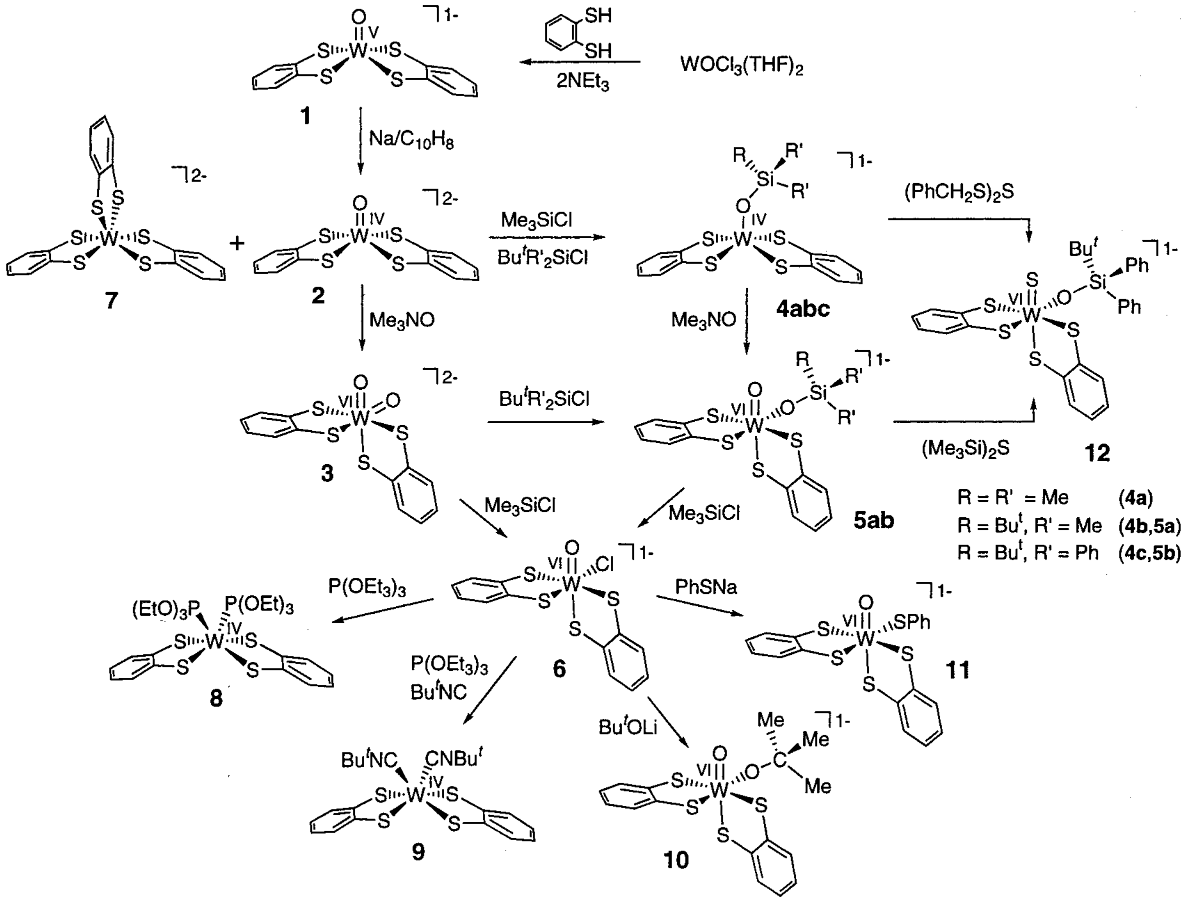

Figure 2. Scheme for the synthesis and reactions of bis(benzenedithiolato)tungsten complexes **1**−**12**.

in THF/acetonitrile and was isolated as two salts in 87% (Et_4N^+) and 73% (Ph_4P^+) yields. The structure of the Ph_4P^+ compound (Figure 3, Table 3) is distorted square pyramidal with an axial W−O1 bond length of 1.589(5) Å and a 0.765 Å displacement of the tungsten atom from the S(1−4) mean plane. Severe distortions from idealized C_{4v} symmetry are particularly evident in W−S bond distances, which span a range of 0.225 Å with a mean value of 2.46(9) Å. The phenyl rings are disposed on the oxo side of the S(1−4) plane with *o*-H···O1 distances of 2.883 Å (S1 ring) and 2.984 Å (S4 ring) suggestive of weak interactions. In contrast, the structure of $[MoO(SPh)_4]^{1-}$ (Ph_4As^+ salt) is regular with Mo−O and mean Mo−S bond lengths of 1.669(9) Å and 2.403(6) Å.[32]

We have found that **1** can be more conveniently and efficiently prepared by a procedure analogous to that for $[WO(SPh)_4]^{1-}$ with use of $bdtH_2/2Et_3N$. The compound (Et_4N)[**1**] was obtained in 79% yield. When reduced with sodium acenaphthylenide in THF/acetonitrile, this compound afforded $(Et_4N)_2$[**2**] in 66% yield. We have been unsuccessful in reproducing the reported reduction of **1** to **2** (71%) with $(Ph_4P)(BH_4)$.[20] Rigorously anhydrous and freshly distilled solvents and $bdtH_2$ are obligatory to obtaining high yields of **1** and **2**, both of which have square pyramidal stereochemistry.[20] Small amounts of water resulted in the formation of $[W(bdt)_3]^{1-,2-}$. Variable amounts of $(Et_4N)_2$[**7**] have been encountered in the preparation of **2** and can be separated by differential solubility in acetonitrile. The structure of **7** has been determined (Figure 3, Table 4). Metric parameters are unexceptional; as is the case for many tris(dithiolene) complexes,[16f,g,i,j,k,33] **7** closely

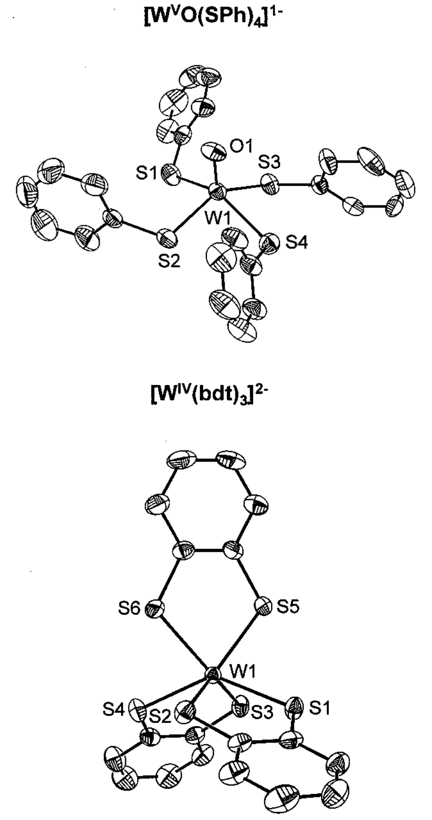

Figure 3. Structures of $[WO(SPh)_4]^{1-}$ (upper) and $[W(bdt)_3]^{2-}$ (**7**, lower), showing 50% probability ellipsoids and partial atom-labeling schemes.

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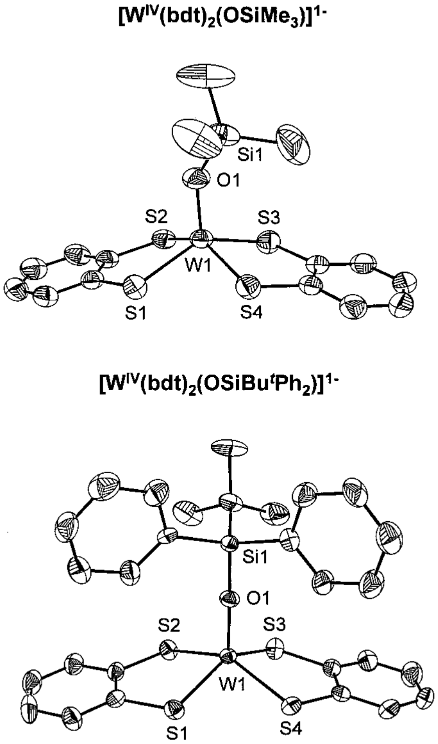
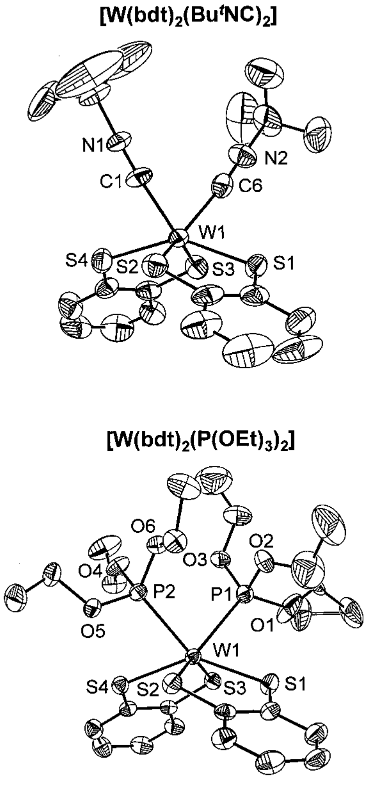

$[W^{IV}(bdt)_2(OSiMe_3)]^{1-}$

$[W^{IV}(bdt)_2(OSiBu^tPh_2)]^{1-}$

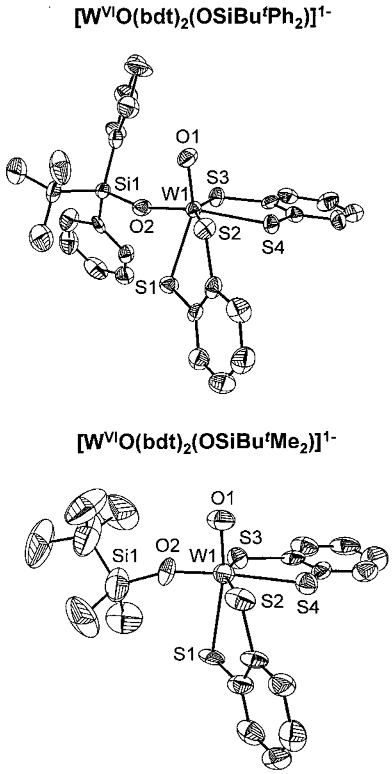
Figure 4. Structures of $[W(bdt)_2(OSiMe_3)]^{1-}$ (**4a**, upper) and $[W(bdt)_2(OSiBu^tPh_2)]^{1-}$ (**4c**, lower), showing 50% probability ellipsoids and partial atom-labeling schemes.


$[W(bdt)_2(Bu^tNC)_2]$

$[W(bdt)_2(P(OEt)_3)_2]$

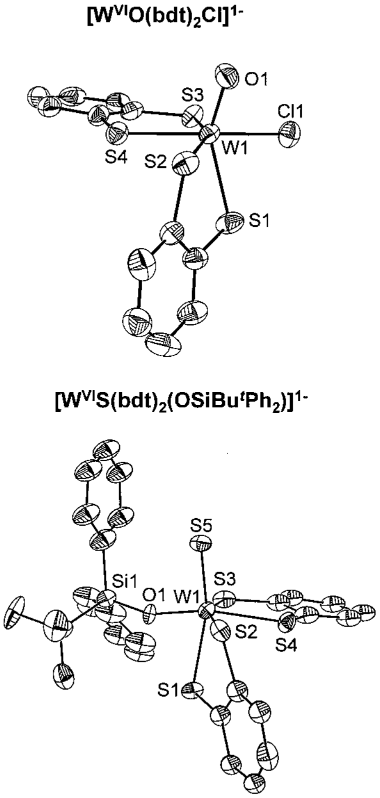
Figure 5. Structures of $[W(bdt)_2(Bu^tNC)_2]$ (**9**, upper) and $[W(bdt)_2(P(OEt)_3)_2]$ (**8**, lower), showing 50% probability ellipsoids and partial atom-labeling schemes.

approaches trigonal prismatic geometry, with an average twist angle of 3.5°.[34] The complex exhibits in acetonitrile two chemically reversible redox steps at −0.48 and 0.34 V vs SCE


$[W^{VI}O(bdt)_2(OSiBu^tPh_2)]^{1-}$

$[W^{VI}O(bdt)_2(OSiBu^tMe_2)]^{1-}$

Figure 6. Structures of $[WO(bdt)_2(OSiBu^tPh_2)]^{1-}$ (**5b**, upper) and $[WO(bdt)_2(OSiBu^tMe_2)]^{1-}$ (**5a**, lower), showing 50% probability ellipsoids and partial atom-labeling schemes.


$[W^{VI}O(bdt)_2Cl]^{1-}$

$[W^{VI}S(bdt)_2(OSiBu^tPh_2)]^{1-}$

Figure 7. Structures of $[WO(bdt)_2Cl]^{1-}$ (**6**, upper, 50%) and $[WS(bdt)_2(OSiBu^tPh_2)]^{1-}$ (**12**, lower, 30%), showing the indicated probability ellipsoids and partial atom-labeling schemes.

corresponding to the formation of $[W(bdt)_3]^{1-,0}$, which have been prepared earlier.[16b,h]

(b) Desoxo W(IV) and Monooxo W(VI). (i) Preparations. We have sought bis(dithiolenes) of these types by silylation of

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[34] Calculated from interatomic distances: Larsen, E.; La Mar, G. N.; Wagner, B. E.; Parks, J. E.; Holm, R. H. *Inorg. Chem.* **1972**, *11*, 2652.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for Square Pyramidal $[W^{IV,V}OS_4]^{1-}$ Complexes

	$[W^VO(SPh)_4]^{1-}$	$[W^{IV}(bdt)_2(OSiMe_3)]^{1-}$	$[W^{IV}(bdt)_2(OSiBu^tPh_2)]^{1-}$
W−S1	2.446(2)	2.341(1)	2.334(2)
W−S2	2.358(2)	2.350(1)	2.333(2)
W−S3	2.437(2)	2.334(1)	2.329(2)
W−S4	2.583(2)	2.331(1)	2.335(2)
$W-S_{av}$	2.46(9)	2.339(8)	2.333(3)
W−O1	1.589(5)	1.836(3)	1.844(6)
W−O1−Si1		145.3(2)	176.0(4)
O1−W−S1	100.1(2)	110.0(1)	108.1(2)
O1−W−S2	108.2(2)	109.1(1)	107.1(2)
O1−W−S3	110.8(2)	109.0(1)	108.5(2)
O1−W−S4	111.6(2)	106.3(1)	108.0(2)
θ_1[a]		129.2	131.1
θ_2[b]		14.7	17.7
$W - S_{\text{mean plane}}$[c]	0.765	0.746	0.717

[a] θ_1 = angle between planes defined by WS_2 atoms. [b] θ_2 = angle between planes defined by WS_2 and S_2C_2 ligand atoms. [c] $W - S_{\text{mean plane}}$ = displacement of W atom from least-squares S_4 plane.

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for Trigonal Prismatic $[W^{IV}(bdt)_2L_2]$ Complexes

	$[W^{IV}(bdt)_3]^{2-}$	$[W^{IV}(bdt)_2(Bu^tNC)_2]$	$[W^{IV}(bdt)_2(P(OEt)_3)_2]$[a]
W−S1	2.398(1)	2.354(2)	2.363(1)
W−S2	2.375(1)	2.353(3)	2.361(1)
W−S3	2.393(1)	2.362(3)	2.347(1)
W−S4	2.392(1)	2.353(3)	2.374(1)
W−X1[b]	2.396(1)	2.086(11)	2.453(1)
W−X2[b]	2.391(1)	2.080(12)	2.459(1)
X1−W−X2[b]	80.78(4)	80.6(4)	83.35(4)
S1−W−S2	80.90(4)	82.02(13)	82.02(4)
S1−W−S4	80.89(4)	81.97(10)	82.14(4)
θ_1[c]		129.4	128.3
θ_2[d]		4.9	4.1
$W - S_{\text{mean plane}}$[e]		0.759	0.775

[a] Data for one of two molecules in the asymmetric unit. [b] X = S, C, or P. [c] θ_1 = angle between planes defined by WS_2 atoms. [d] θ_2 = angle between planes defined by WS_2 and S_2C_2 ligand atoms. [e] $W - S_{\text{mean plane}}$ = displacement of W atom from least squares S_4 plane.

Table 5. Selected Interatomic Distances (Å) and Angles (deg) for W(VI) Complexes

	$[W^{VI}O(bdt)_2(OSiBu^tPh_2)]^{1-}$	$[W^{VI}O(bdt)_2(OSiBu^tMe_2)]^{1-}$[a]	$[W^{VI}S(bdt)_2(OSiBu^tPh_2)]^{1-}$[a]	$[W^{VI}O(bdt)_2Cl]^{1-}$
W−S1	2.489(2)	2.554(4)	2.490(5)	2.450(2)
W−S2	2.429(2)	2.388(4)	2.371(5)	2.419(2)
W−S3	2.410(2)	2.417(4)	2.382(5)	2.416(2)
W−S4	2.427(2)	2.439(4)	2.440(5)	2.408(2)
W−X1[b]	1.723(5)	1.729(10)	2.163(5)	1.728(5)
W−X2[c]	1.907(5)	1.835(12)	1.939(11)	2.436(2)
W−X2−Si1	161.5(3)	163.9(9)	158.1(8)	
X1−W−X2	95.0(3)	94.8(5)	98.0(4)	89.0(2)
X1−W−S1	145.6(2)	155.3(3)	154.1(2)	142.6(2)
X1−W−S2	81.1(2)	81.3(4)	82.7(2)	83.4(2)
X1−W−S3	104.6(2)	105.4(4)	104.4(2)	108.7(2)
X1−W−S4	103.8(2)	99.2(4)	101.5(2)	103.8(2)
X2−W−S4	153.8(2)	158.3(4)	155.5(4)	155.23(6)
S2−W−S3	153.86(8)	158.2(2)	156.3(2)	154.24(7)

[a] Data for one of two anions in the asymmetric unit. [b] X1 = O or S. [c] X2 = O−Si or Cl.

oxo complexes in the corresponding oxidation states. Treatment of a slurry of **2** with 1.05−1.25 equiv of the chlorosilanes RR'_2SiCl in acetonitrile resulted in silylation of the oxo ligand and formation of the red W(IV) complexes **4a**, **4b**, and **4c** (Figure 2), isolated in 71−90% yields as Et_4N^+ salts. Similarly, silylation of **3** with 1.03−1.14 equiv of $Bu^tR'_2SiCl$ in acetonitrile afforded the brown-green monooxo W(VI) species **5a** and **5b** in 85−92% yield, also as Et_4N^+ salts. Alternatively, (Et_4N)[**5b**] (76%) was prepared by the oxo transfer reaction of **4c** and Me_3NO in acetonitrile. The compounds **5** are brown-green noncrystalline solids giving dark green solutions in acetonitrile or THF, and light red solids when crystalline. Treatment of **3** with Me_3SiCl in acetonitrile did not lead to a mono silyl oxide product, but instead resulted in chloride substitution and the formation of black (Et_4N)[**6**] (74%). This compound can be more simply prepared in procedures not directly requiring **3**. The reaction system $WOCl_4/LiOBu^t/2Li(bdt)_2$ resulted in a 60% yield;[35] silylation of **5b** gave **6** in 74% yield.

While silylation of Mo═O and W═O groups is not an extensively investigated reaction type, a number of stable Mo^V-$(OSiR_3)/Mo^VO(OSiR_3)$,[36] $Mo^{VI}O(OSiR_3)$,[37] $Mo^{VI}O_2(OSiR_3)$,[38]

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[35] The role of $LiOBu^t$ in the reaction system is unclear, but **6** is not formed in its absence.

[36] (a) Wilson, G. L.; Kony, M.; Tiekink, E. R. T.; Pilbrow, J. R.; Spence, J. T.; Wedd, A. G. *J. Am. Chem. Soc.* **1988**, *110*, 6923. (b) Xiao, Z.; Young, C. G.; Enemark, J. H.; Wedd, A. G. *J. Am. Chem. Soc.* **1992**, *114*, 9194. (c) Xiao, Z.; Gable, R. W.; Wedd, A. G.; Young, C. G. *J. Am. Chem. Soc.* **1996**, *118*, 2912. (d) Xiao, Z.; Bruck, M. A.; Enemark, J. H.; Young, C. G.; Wedd, A. G. *JBIC* **1996**, *1*, 415.

[37] Arzoumanian, H.; Corao, C.; Krentzien, H.; Lopez, R.; Teruel, H. *J. Chem. Soc., Chem. Commun.* **1992**, 856.

[38] Huang, M.; DeKock, C. W. *Inorg. Chem.* **1993**, *32*, 2287.

and $Mo^{VI}S_3(OSiR_3)$[39] species have been formed in this way. The only examples of silylation of a W═O group of which we are aware are in the systems $[(C_5Me_5)_2WO]/Me_3SiCl$[40a] and $[(MeC_5H_4)_2WO/Me_3SiX$ (X = Cl, I).[40b] In the first system, the initial reaction product is $[(C_5Me_5)_2W(OSiMe_3)Cl]$, which reacts with a second equivalent of Me_3SiCl to give $[(C_5Me_5)_2WCl_2]$ or slowly disproportionates in the absence of the silyl reagent to form $[(C_5Me_5)_2WO]$ and $[(C_5Me_5)_2WCl_2]$. In the second sytem, $[(MeC_5H_4)_2W(OSiMe_3)Cl]$ was detected and $[(MeC_5H_4)_2WI_2]$ was formed rapidly and quantitatively. These reactions proceed with formation of $(Me_3Si)_2O$. The formation of **5ab** proceeds by reaction 1. Steric features are sufficient to prevent reaction with a second equivalent of $Bu^tR'_2SiCl$ (R′ = Me, Ph), but not with less hindered Me_3SiCl which in reaction 2 forms **6**. When reaction 3 is carried out with one equivalent of Me_3SiCl, the characteristic green-black color of **6** develops instantly, indicating that reaction of the silyl reagent with bound silyl oxide is faster than any other process. Complexes **5ab**, and also **4abc**,

$$[WO_2(bdt)_2]^{2-} + Bu^tR'_2SiCl \rightarrow [WO(bdt)_2(OSiBu^tR'_2)]^{1-} + Cl^- \quad (1)$$

$$[WO(bdt)_2(OSiBu^tR'_2)]^{1-} + Me_3SiCl \rightarrow [WO(bdt)_2Cl]^{1-} + Me_3SiOSiBu^tR'_2 \quad (2)$$

$$[WO_2(bdt)_2]^{2-} + 2Me_3SiCl \rightarrow [WO(bdt)_2Cl]^{1-} + (Me_3Si)_2O + Cl^- \quad (3)$$

are stable for at least 2−3 days in anaerobic anhydrous acetonitrile solutions at ambient temperature. While there is visual indication of a reaction between the W^VO complex **1** and Me_3SiCl, thus far we have been unable to isolate a pure silyl oxide or chloride complex. Stabilization of monooxo W(VI) complexes **5ab** appears to require suitably hindered silyl oxide ligands. There are several prior examples (including Mo^VO species) related to reaction 2, in which bound silyl oxide rather than oxo acts as a nucleophile toward a further equivalent of Me_3SiCl, resulting in a chloride rather a silyl oxide product.[36d,41]

Complex **12** was prepared by the reaction of 1.10 equiv of $(Me_3Si)_2S$ with **5b** in acetonitrile, or by an oxidative addition reaction of **4c** and 1.26 equiv of $(PhCH_2S)_2S$. Either method afforded **12** and **4c** as a byproduct or unreacted material. Increased amounts of either sulfur reagent resulted in increased amounts of **4c** in the mixture, suggesting a reductive decomposition of **12**.[42] We have not been able to devise an effective bulk separation of (Et_4N)[**4c**] and (Et_4N)[**12**], which is the sulfido analogue of **5b**. Indeed, complex **12** is easily recognized by its ^1H NMR similarity to **5b**. Although a bulk quantity of pure (Et_4N)[**12**] was not achieved, a small quantity of single crystals suitable for structure determination (vide infra) was obtained by slow crystallization from a DMF/ether solution of the mixture.

Two other desoxo W(IV) complexes, **8** and **9**, were readily prepared by reduction of chloro complex **6** in reactions 4 and 5 conducted in acetonitrile. Triethyl phosphite is an effective

$$[WO(bdt)_2Cl]^{1-} + 3(EtO)_3P \rightarrow [W(bdt)_2(P(OEt)_3)_2] + (EtO)_3PO + Cl^- \quad (4)$$

$$[WO(bdt)_2Cl]^{1-} + 2Bu^tNC + (EtO)_3P \rightarrow [W(bdt)_2(Bu^tNC)_2] + (EtO)_3PO + Cl^- \quad (5)$$

oxo acceptor in these reactions at ambient temperature while Ph_3P shows slow reactivity at 60 °C. The associated reaction system $[WOCl_4]/Ph_3P$ affords *trans*-$[WCl_4(PPh_3)_2]$.[43] Complexes **8** and **9** are related to the bis(dithiolene) dicarbonyl $[W(S_2C_2Me_2)_2(CO)_2]$, prepared by the photochemical reaction of $W(CO)_6$ and $[Ni(S_2C_2Me_2)_2]$.[18]

(ii) Structures. From the structures of **4a** and **4c** (Figure 4, Table 3), it is immediately apparent that these are desoxo W(IV) complexes. They adopt a square-pyramidal stereochemistry with the tungsten atoms strongly displaced from the least-squares S(1−4) planes (by 0.72 Å (**4c**) and 0.75 Å (**4a**)) in the direction of axial silyl oxide ligands. This displacement is further emphasized by the dihedral angles θ_1 between WS_2 coordination planes. As is common with dithiolene complexes, there are small folds in the chelate ring structures along the S···S vectors that are made evident by the dihedral angles θ_2. Mean W−S bond distances in the two complexes are indistinguishable and average to 2.336 Å. The W−O−Si angle is **4a** is bent (145.3(2)°) whereas in **4c** it is nearly linear (176.0(4)°), an effect ascribed to the larger steric bulk of the silyl oxide ligand in the latter complex. The complexes **8** and **9** approach the trigonal prismatic stereochemistry of **7** (Figure 5, Table 4). In **9**, the W−C bond distances of 2.08(1) Å and 2.09(1) Å are comparable to those in other W(IV) isonitrile complexes.[44] The nearly linear C−N−C bond angles of 174(1)° indicate little π back-bonding, which would result in a bent configuration. Close similarities in the out-of-plane displacements of the tungsten atom and the dihedral angles θ_1 emphasize the structural relationship between five-coordinate **4a**,**b**,**c** and six-coordinate **8** and **9**. Structures of the latter resemble that of the isoelectronic bis(diselenolene) complex $[W(Se_2C_6H_4)_2(CO)_2]$.[45]

The structures of **5a** and **5b** (Figure 5, Table 5) confirm the monooxo W(VI) formulation. These complexes are irregularly distorted from octahedral, although several features normal to oxo species are present. The W═O bond lengths are in the range of those in $[WO_2(bdt)_2]^{2-}$ [20] and $[WO_2(mnt)_2]^{2-}$ [21] (1.70−1.74 Å). The trans effect of O1 renders the W−S1 bonds significantly longer than W−S(2−4), the effect being larger in **5a**. The angles O1−W−X where X = O, S cis to the oxo ligand are larger than 90° (except for X = S2), owing to electrostatic repulsion. Trans bond angles at tungsten are less than 180° by 22−34°, an effect due in part to the restricted bite distance of the rigid bdt ligand. The structure of **6** (Figure 7, Table 5) is similar in all respects to those of **5a** and **5b** except for the replacement of silyl oxide by chloride in the W−Cl bond of length 2.436(2) Å. The stereochemistry and metric pattern of **5b** extends to its sulfido analogue **12** (Figure 7, Table 5). The W−S5 bond length of 2.163(5) Å is consistent with other recent determinations of W^{VI}═S bond lengths.[46] Compared to their

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[39] Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 1831.

[40] (a) Parkin, G.; Bercaw, J. E. *Polyhedron* **1988**, *7*, 2053. (b) Luo, L.; Lanza, G.; Fragalà, Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 3111.

[41] Stavropoulos, P.; Bryson, N.; Youinou, M.-T.; Osborn, J. A. *Inorg. Chem.* **1990**, *29*, 1807.

[42] This situation appears related to the outcome of a silylation reaction of a $Mo^{VI}O_2$ complex resulting in reduction to Mo^VO, possibly according to the reaction $[Mo^{VI}O_2L] + (Me_3Si)_2S \rightarrow [Mo^VO(OSiMe_3)L] + {}^1/_2(Me_3SiS)_2$.[36a.]

[43] Drew, M. G. B.; Page, E. M.; Rice, D. A. *J. Chem. Soc., Dalton Trans.* **1983**, 61.

[44] Rabinovich, D.; Parkin, G. *Inorg. Chem.* **1995**, *34*, 6341.

[45] Heckmann, G.; Wolmershäuser, G. *Chem. Ber.* **1993**, *126*, 1071.

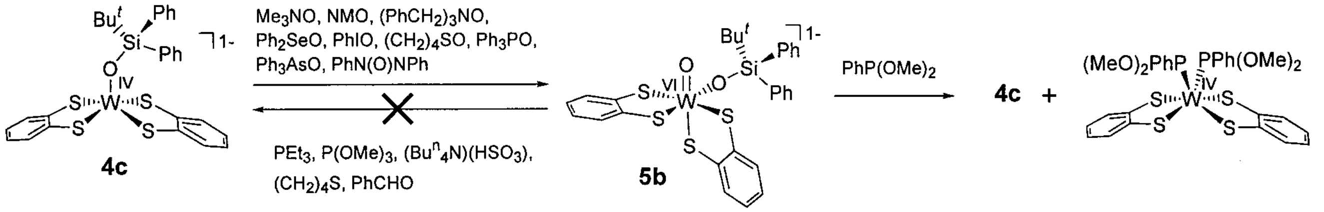

Figure 8. Summary of the oxo transfer reactivity of $[W(bdt)_2(OSiBu^tPh_2)]^{1-}$ (**4c**) and $[WO(bdt)_2(OSiBu^tPh_2)]^{1-}$ (**5b**) (NMO = *N*-methylmorpholine *N*-oxide).

$Mo^{VI}O$ counterparts, $W^{VI}O$ complexes are relatively common. Excluding organometallics and peroxides, the principal classes are halides,[47] alkylidenes,[48] and alkoxides/silyl oxides.[49] No $W^{VI}O$ or $W^{VI}S$ dithiolenes have been previously prepared.

Reactivity. The following reactivity types of bis(dithiolene) complexes have thus far been demonstrated and are summarized in Figure 2: (i) oxidative oxo transfer of **2** and **4bc** with Me_3NO to give **3**[20] and **5ab**, respectively; (ii) oxo ligand silylation resulting in the conversions **2** → **4abc** and **3** → **5ab**; (iii) silylation of coordinated silyl oxide in **3** (in situ) and **5b** with Me_3SiCl resulting in chloride complex **6**; (iv) oxidative sulfur transfer of **4c** with $(PhCH_2S)_2S$ to afford sulfido complex **12**; (v) oxo/sulfido replacement in the conversion of **5b** to **12** with $(Me_3Si)_2S$;[50] (vi) reductive oxo transfer reactions of **6** with $(EtO)_3P$ leading to **8** and **9**, respectively. In addition, two other reactions involving displacement of chloride in **6** have been observed. Treatment of this complex in acetonitrile with 1.0 equiv of $LiOBu^t$ resulted in the formation of an intense green solution. The ^1H NMR spectrum showed clean formation of alkoxide complex **10**. Attempted isolation of this product led to $(Et_4N)_2$[**7**], indicating reductive decomposition of **10**.[51] Similarly, reaction of **6** with 1.0 equiv of NaSPh led to an immediate color change to red-purple and then blue. When monitored by ^1H NMR, the reaction was found to produce thiolate complex **11**,[52] which rapidly decomposed to **1**, which has a characteristic blue chromophore. This compound was isolated and demonstrated by X-ray crystallography to be (Et_4N)-[**1**].[53] While the chloride ligand in **6** is susceptible to substitution, the reaction products are unstable to reduction, in contrast to the silyl oxide complexes **5ab**.

Noting the occurrence of oxo transfer reactions i and vi above, we examined this type of reactivity using other substrates and the complexes **4c** and **5b**. The observed reactivity is summarized in Figure 8; reactions were monitored by ^1H NMR. Complex **5b** was tested with six potential oxo acceptors; no clean reaction was observed in five cases. Only the strongly basic phosphinite $PhP(OMe)_2$ in large excess (≥80 equiv) afforded demonstrable oxo tranfer. This reagent has been previously shown to reduce $[WO_2(mnt)_2]^{2-}$ in a clean oxo transfer reaction.[14] Reaction 6 was monitored by ^1H NMR (60 °C) and spectrophotometry (25 °C). The weak band of **5b** at

$$[WO(bdt)_2(OSiBu^tPh_2)]^{1-} + PhP(OMe)_2 \rightarrow [W(bdt)_2(OSiBu^tPh_2)]^{1-} + PhP(O)(OMe)_2 \quad (6)$$

600 nm slowly decreased in intensity as product bands at 345 and 417 nm grew in. These features are analogous to the intense 339 and 411 nm bands of **8**. The NMR spectrum was consistent with the formation of $[W(bdt)_2(PhP(OMe)_2)_2]$, which was further demonstrated by FAB-MS (*m/z* 804, M^+). The formation of $PhP(O)(OMe)_2$ was confirmed by ^{31}P NMR. With 80 equiv of phosphinite at 60 °C after 24 h, 30% of **5b** remained unreacted and 30% was converted to **4c**. Amounts were determined by NMR signal integration. In this and subsequent relatively slow reaction systems, departures from tungsten complex material balance, are due to hydrolysis of **5b** by trace water before or during oxo transfer. With the evident lack of reactivity of **5b**, occasioned presumably by the difficulty of the W^{VI}/W^{IV} reduction,[14] attention was directed to the oxo acceptor propensity of **4c**.

Summarized in Table 6 are the oxo transfer properties of **4c** in reaction 7 with some 10 substrates XO covering nearly

$$[W(bdt)_2(OSiBu^tPh_2)]^{1-} + XO \rightarrow [WO(bdt)_2(OSiBu^tPh_2)]^{1-} + X \quad (7)$$

entirely the thermodynamic scale of oxo transfer reactivity.[54] A broad range of reactivity is encountered. Tertiary amine oxides, which are near the top of the scale, react quickly and relatively cleanly. Trimethylamine *N*-oxide, *N*-methylmorpholine *N*-oxide, and Ph_2SeO gave quantitative conversions. The slow reactivity of the strong oxo donor PhIO arises from its sparing solubility in acetonitrile. Using $PhI^{18}O$ and $Ph_2Se^{18}O$, oxo transfer was demonstrated from isotope shifts of W=O stretching frequencies and FAB-MS of the products (cf. Experimental Section). Interestingly, **4c** is capable of reducing Ph_3PO, although forcing conditions (60 °C) are required to achieve an appreciable reaction rate. On the thermodynamic reactivity scale, the gaseous couples $Me_3N + {}^1/_2O_2 \rightarrow Me_3NO$ (−2 kcal/mol),[15] $Ph_2Se + {}^1/_2O_2 \rightarrow Ph_2SeO$ (−17 kcal/mol,

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(46) (a) Eagle, A. A.; Harben, S. M.; Tiekink, E. R. T.; Young, C. G. *J. Am. Chem. Soc.* **1994**, *116*, 9749. (b) Barnard, K. R.; Gable, R. W.; Wedd, A. G. *JBIC* **1997**, *2*, 623.

(47) (a) Page, E. M.; Rice, D. A.; Hagen, K.; Hedberg, L.; Hedberg, K. *Inorg. Chem.* **1987**, *26*, 467. (b) Arnaudet, L.; Bougon, R.; Ban, B.; Lance, M.; Nierlich, M.; Vigner, J. *Inorg. Chem.* **1993**, *32*, 1142. (c) Lu, Y.-J.; Beer, R. H. *Polyhedron* **1996**, *15*, 1667.

(48) (a) Wengrovious, J. H.; Schrock, R. R.; Churchill, M. R.; Missert, J. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 4515. (b) Churchill, M. R.; Rheingold, A. L. *Inorg. Chem.* **1982**, *21*, 1357. (c) Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 7213.

(49) (a) Cotton, F. A.; Schwotzer, W.; Shamshoum, E. S. *J. Organomet. Chem.* **1985**, *296*, 55. (b) Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1991**, *30*, 4465. (c) Chisholm, M. H.; Cook, C. M.; Folting, K.; Streib, W. E. *Inorg. Chim. Acta* **1992**, *198*, 63. (d) Persson, C.; Oskarsson, Å.; Andersson, C. *Polyhedron* **1992**, *11*, 2039. (e) Heppert, J. A.; Dietz, S. D.; Eilerts, N. W.; Henning, R. W.; Morton, M. D.; Takusagawa, F. *Organometallics* **1993**, *12*, 2565.

(50) For the related $W^{VI}O_2/W^{VI}S_2$ conversion with the same reagent, cf: Yu, S.-B.; Holm, R. H. *Inorg. Chem.* **1989**, *28*, 4385.

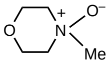
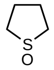
(51) The formation of **7** may result from intramolecular hydrogen abstraction from the Bu^t group with elimination of isobutene and transient formation of an W^V−OH species. The latter itself, or by bimolecular condensation to form water, could supply the protons necessary for decoordination of bdt, which can function as a ligand and as a reductant when bound or free. Use of NaOMe led to a mixture of **2** and **7**, again requiring a reductive pathway.

(52) ^1H NMR of **11** (CD_3CN): δ 6.90 (4, dd), 7.12 (1, t), 7.32 (2, d), 7.40 (4, dd), 7.75 (2, d).

(53) (Et_4N)[**1**] crystallizes in monoclinic space group $P2_1/n$ with a = 7.7645(1) Å, b = 16.5852(3) Å, c = 27.0389(4) Å, and β = 94.089(1)° at 213 K. The structure was solved to the point of compound identification but was not fully refined. The structure of (Ph_4P)[**1**] is available.[20]

(54) Holm, R. H.; Donahue, J. P. *Polyhedron* **1993**, *12*, 571.

Table 6. Oxo Transfer Reactivity of $[W^{IV}(bdt)_2(OSiBu^tPh_2)]^{1-}$ with Substrates XO[a]

XO	equiv	T, °C	time	**5b** formed (%)	**4c** remaining (%)
Me_3NO	2	20	<10 min	100	0
	10	20	<10 min	99	0
$(PhCH_2)_3NO$	1	20	15 h	84	9
PhN=N(O)Ph	3	60	2 d	64	23
Ph_2SeO	10	20	<10 min	100	0
PhIO (insol.)	5	20	12 h	95	0
Ph_3AsO	20	60	15 h	45	0
Ph_3PO	80	60	2 d	60	37
	3	60	21 h	35	55
Me_2SO	60	60	5 d	9	57
	25	20	25 h	21	71
	40	60	21 h	40	50

[a] Conditions: $(Et_4N)[W(bdt)_2(OSiBu^tPh_2)]$ (1 equiv, ~3 mM) in CD_3CN solution; reactions analyzed by ^1H NMR.

estimated),[55] and $Ph_3P + {}^1/_2O_2 \rightarrow Ph_3PO$ (−74 kcal/mol) with the indicated ΔH values indicate the large spread in oxo donor ability. Amine oxides are among the more reactive donors while phosphine oxides are near the bottom of the scale. From these results, **4c** emerges as a strong, albeit sluggish, oxo acceptor in the couple **4c** + $^1/_2O_2$ → **5b** for which $\Delta H \lesssim -74$ kcal/mol. The oxo transfer chemistry of tungsten is relatively little developed compared to that of molybdenum, which is the most extensive of any element. The small body of tungsten-mediated oxo transfer reactions preceding this work is summarized elsewhere.[14,56]

Biological Relevance. Because the (partial) coordination unit of only one tungsten enzyme, *Pf* AOR, is defined and the number of pterin cofactors bound in other enzymes is not generally established, we can at present speak only of the potential relevance of the complexes studied here. However, if members of the AOR enzyme family are structurally related, as seems likely,[2] bis(dithiolene) coordination is pervasive and the species in Figure 2 may be viewed in that context. The complexes **4a**−**c** and **8**/**9** provide the initial structural representations of bis(dithiolene) desoxo W(IV) five- and six-coordinate stereochemistry. Complexes **5a**,**b** and **6** serve the same function for the monooxo W(VI) state. In a stereochemical (but not electronic) sense, silyl oxide or chloride simulate binding of hydroxide and protein-bound ligands, should the latter eventuate in either family of enzymes. Complex **12** fulfills a similar purpose for any site containing the $W^{VI}{=}S$ group. Consequently, these molecules may be useful auxiliaries in X-ray absorption edge and EXAFS studies[2,6] and resonance Raman examination[5] of tungsten enzyme sites. Simple oxo transfer reactivity, as established here and exemplified in biology by, e.g., molybdenum DMSO reductases,[12] is not yet known as a function of tungstoenzymes. The reaction catalyzed by the AOR family, minimally $RCHO + [O] \rightleftharpoons RCOOH$, as with the molybdoenzyme xanthine oxidase,[12] must have a different mechanism. Indeed, molybdenum aldehyde oxidases belong to the xanthine oxidase enzyme family, and in the oxidized state contain the $Mo^{VI}OS$ group.[12] While we do not discount an all-oxygen ligand group such as $W^{VI}O(OH)$, conceivably a W^{VI}-OS group or a protonated form (e.g., $W^{VI}O(SH)$) may intervene in oxidized AOR enzymes. Bis(dithiolene)tungsten species of these types and the sites shown in Figure 1 that may apply to the F(M)DH family based on sequence homologies[57] represent attractive objectives for both their structural and functional properties. Synthesis of such compounds is now in progress in this laboratory. An account of bis(dithiolene)molybdenum complexes related to the tungsten group presented here is forthcoming.[58]

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Supporting Information Available: Crystallographic data for the 10 compounds in Tables 1 and 2, including intensity collections, positional, and thermal parameters, interatomic distances and angles, and calculated hydrogen atom positions (96 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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