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Oxo/Sulfidotungstate(VI) as Precursors to $W^{VI}O_2$, $W^{VI}OS$, and $W^{VI}S_2$ Complexes and W^{IV}−Dithiolene Chelate Rings

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Synthetic models leading to oxosulfidotungsten(VI) groups and dithiolene chelate rings have been investigated. The heterogeneous reaction systems $[WO_{4-n}S_n]^{2-}$/2Ph_3SiCl/Me_4phen ($n = 0-2$) in acetonitrile afford the complexes $[WQ_2(OSiPh_3)_2(Me_4phen)]$ (**1**−**3**) in the indicated yields containing the groups $W^{VI}O_2$ (**1**; 86%), $W^{VI}OS$ (**2**; 45%), and $W^{VI}S_2$ (**3**; 83%). In the crystalline state these complexes have imposed C_2 symmetry, with *cis*-oxo/sulfido and *trans*-silyloxide ligands. ^{1}H NMR spectra indicate that this stereochemistry is retained in solution. The colors of **2** (yellow, 367 nm) and **3** (orange, 451 nm) arise from LMCT absorptions at the indicated wavelengths. These results demonstrate that the silylation procedure previously introduced for the preparation of molecules with the $Mo^{VI}OS$ group (Thapper, et al. *Inorg. Chem.* **1999**, *38*, 4104) extends to tungsten. Methods for the formation of dithiolene chelate rings $MS_2C_2R_2$ in reactions with sulfide-bound M = Mo or W precursors are summarized. In a known reaction type, **3** and activated acetylenes rapidly form $[W^{IV}(OSiPh_3)_2(Me_4phen)(S_2C_2R_2)]$ (R = CO_2Me, **4**, 83%, and Ph, **5**, 98%). In a new reaction type not requiring the isolation of an intermediate, the systems $[MO_2S_2]^{2-}$/2Ph_3SiCl/Me_4phen/PhC≡CPh in acetonitrile afford **5** (68%) and $[Mo^{IV}(OSiPh_3)_2(Me_4phen)(S_2C_2Ph_2)]$ (**6**; 61%). Complexes **5** and **6** are isostructural, maintain the *trans*-silyloxide stereochemistry, and exhibit chelate ring dimensions indicative of ene-1,2-dithiolate coordination. Reductions in the −1.4 to −1.7 V range are described as metal-centered. It remains to be seen whether the oxo/sulfidotungsten(VI) groups in **1**−**3** eventuate in the active sites of tungstoenzymes. (Me_4phen = 3,4,7,8-tetramethyl-1,10-phenanthroline.)

Introduction

Coordination of the one or two pterin dithiolene cofactor ligands at the active sites of enzymes containing molybdenum[1−3] (excluding nitrogenase) and tungsten[4,5] necessitates the synthesis of new types of dithiolene complexes, if the properties of these sites are to be investigated using analogue molecules. Two issues in synthesis are immediately apparent: (i) development of routes to complexes whose dithiolene ligand(s) resemble the cofactor and are not necessarily available in the free form; (ii) introduction of the functionalities and other ligands present in enzyme sites, including $Mo^{IV}QR$ and and $Mo^{VI}O(QR)$ (Q = O, S, Se), $Mo^{VI}O_2$, and $Mo^{VI}OS$ inter alia, in complexes with the appropriate number of dithiolene ligands. Our recent research has emphasized synthesis of bis(dithiolene)molybdenum species with the foregoing functional units[6,7] and incorporation of the $Mo^{VI}OS$ group in six-coordinate (non-dithiolene) complexes.[8] The structural nature of tungsten sites is much less clear at this stage. Collective evidence from protein crystallography[9,10] and X-ray absorption spectroscopy[4,11] indicates bis(dithiolene) coordination and one or two presumably oxygenous ligands. In our development of molybdenum analogues, we have considered it advisable to prepare where possible related tungsten complexes,[12−14] should their coordination units eventuate as biologically relevant. Toward that end, we have recently reported a detailed X-ray absorption spectroscopic study of congeneric structurally defined bis(dithiolene)molybdenum and -tungsten complexes.[15] These results should be useful in identifying structural features of enzyme sites.

Closely associated with the preparation of dithiolene complexes is the synthesis of dithiolene ligands themselves, for which a number of methods are available.[16−19] One approach, summarized in Table 1, results in the closure of chelate rings in sulfide-bound precursors,[20−30] nearly always by reaction with

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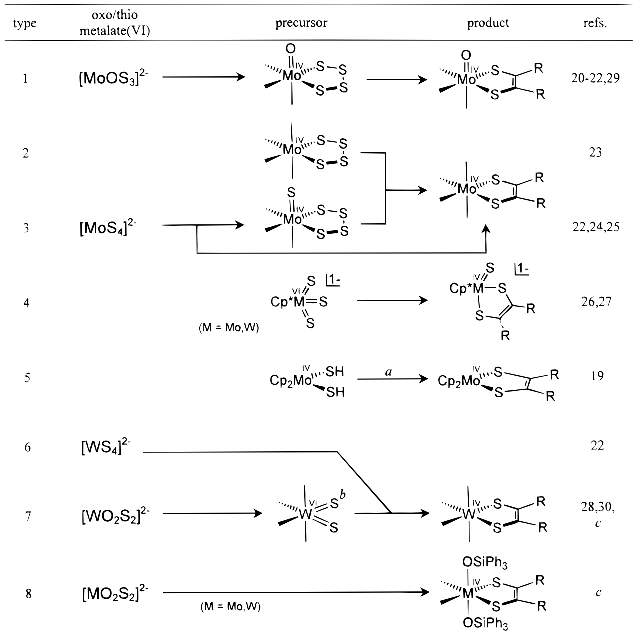
Table 1. Formation of Dithiolene Chelate Rings $MS_2C_2R_2$ (M = Mo, W) from Sulfido-Bound Precursors and Activated Acetylenes



[a] Reactant is ArC(O)CH(X)R (X = Br, tosyl). [b] Not derived from an oxosulfidotungstate in two cases.[28,30] [c] This work.

an activated alkyne. In these procedures, bound sulfur as sulfide, hydrosulfide, or tetrasulfide is directly incorporated into product chelate rings. This general method is useful for the formation of certain coordinated dithiolenes that are not available in free form. Here we report synthetic procedures leading to the introduction of the uncommon $W^{VI}OS$ and $W^{VI}S_2$ groups in six-coordinate molecules and dithiolene ring closure using the simple precursors $[MoO_2S_2]^{2-}$ and $[WO_2S_2]^{2-}$.

Experimental Section

Preparation of Compounds. $K_2[WO_3S]$[31] and $(NH_4)_2[MO_2S_2]$ (M = Mo, W)[32] were prepared as described. Other reagents were of commercial origin and were used as received. Tetrahydrofuran, diethyl ether, and hexanes were distilled from sodium, and acetonitrile and dichloromethane were distilled from CaH_2. These compounds were stored over 4 Å molecular sieves. In the preparations below, solvent removal and drying steps were performed in vacuo, and solids were separated by filtration.

$[WO_2(OSiPh_3)_2(Me_4phen)]$. A suspension of 0.163 g (0.500 mmol) of $K_2[WO_4]$ and 0.165 g (0.698 mmol) of 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4phen) in 15 mL of acetonitrile was stirred for 30 min, and 0.266 g (0.902 mmol) of Ph_3SiCl was added. The reaction mixture was refluxed for 4 h and reduced to dryness. The residue was washed with acetonitrile (2 × 10 mL) and redissolved in 150 mL of dichloromethane. The solution was filtered, and the filtrate was reduced to dryness. The residue was washed with acetonitrile (2 × 10 mL) and ether (2 × 10 mL), and dried to afford the product as 0.431 g (86%) of a white solid. An analytical sample was obtained by recrystallization from dichloromethane/acetone. IR (KBr): ν_{SiO} 949 (br), ν_{WO} 928, 905 cm^{-1}. Absorption spectrum (CH_2Cl_2): λ_{max} (ϵ_M) 285 (28 000), 307 (sh, 9000), 334 (1600) nm. FAB-MS: m/z 1002 (M^+). ^1H NMR ($CDCl_3$): δ 9.12 (s, 2,9-H, 1), 7.76 (s, 5,6-H, 1), 7.12 (t, Ph, 3), 7.07 (d, Ph, 6), 6.97 (t, Ph, 6), 2.52, 2.28 (2 s, Me, 3, 3). Anal. Calcd for $C_{52}H_{46}N_2O_4Si_2W$: C, 62.27; H, 4.62; N, 2.79. Found: C, 62.41; H, 4.71; N, 2.84.

$[WOS(OSiPh_3)_2(Me_4phen)]$. A suspension of 0.328 g (0.959 mmol) of $K_2[WO_3S]$ and 0.319 g (1.35 mmol) of Me_4phen in 20 mL of acetonitrile was stirred for 20 min. To the mixture was added 0.513 g (1.74 mmol) of Ph_3SiCl, resulting in a red-brown solution and a light orange precipitate within 10 min. The reaction mixture was stirred for 2 h. The solid was collected, washed with acetonitrile (3 × 10 mL) and ether (2 × 10 mL), and dissolved in 200 mL of THF. The orange solution was filtered, and the filtrate was reduced to dryness. The orange residue was redissolved in 10 mL of dichloromethane and loaded onto a silica gel column (3 × 10 cm) packed as a slurry in a 3:2 dichloromethane/hexanes (v/v) mixture, which was also used as the eluant. The first band, an orange compound identified as $[WS_2(OSiPh_3)_2(Me_4phen)]$, was dried and collected (0.144 g, 15%). A higher yield preparation of this compound has been developed (vide infra). The second band was dried and collected to give the desired product as 0.438 g (45%) of a yellow solid. IR (KBr): ν_{SiO} 933 cm^{-1} (br), ν_{WS} 480 cm^{-1}. Absorption spectrum (CH_2Cl_2): λ_{max} (ϵ_M) 285 (33 000), 307 (sh, 11 000), 335 (2100), 367 (560) nm. FAB-MS: m/z 1018 (M^+). ^1H NMR ($CDCl_3$): δ 9.73, 8.92 (2 s, 2,9-H, 1, 1), 7.79 (dd, 5,6-H, 2), 7.13 (t, Ph, 6), 7.06 (d, Ph, 12), 6.97 (t, Ph, 12), 2.55, 2.52, 2.35, 2.24 (4 s, 3,4,7,8-Me, 3, 3, 3, 3). Anal. Calcd for $C_{52}H_{46}N_2O_3SSi_2W$: C, 61.29; H, 4.55; N, 2.75; S, 3.15. Found: C, 61.46; H, 4.45; N, 2.77; S, 3.19.

$[WS_2(OSiPh_3)_2(Me_4phen)]$. A suspension of 0.158 g (0.500 mmol) of $(NH_4)_2[WO_2S_2]$ and 0.165 g (0.698 mmol) of Me_4phen in 20 mL of acetonitrile was stirred for 20 min, and 0.266 g (0.902 mmol) of Ph_3SiCl was added. The reaction mixture was stirred for 2 h; the orange solid was collected and washed with acetonitrile (2 × 10 mL). The solid was dissolved in 150 mL of dichloromethane, and the solution was filtered. The filtrate was reduced to dryness. The residue was washed with acetonitrile (2 × 10 mL) and ether (2 × 10 mL), and dried to afford the product as 0.428 g (83%) of an orange solid. IR (KBr): ν_{SiO} 928 (br), ν_{WS} 473 cm^{-1}. Absorption spectrum (CH_2Cl_2): λ_{max} (ϵ_M) 285 (38 000), 307 (sh, 14 000), 334 (5300), 451 (910) nm. ^1H NMR ($CDCl_3$): δ 9.42 (s, 2,9-H, 1), 7.82 (s, 5,6-H, 1), 7.14 (t, Ph, 3), 7.08 (d, Ph, 6), 6.98 (t, Ph, 6), 2.55, 2.28 (2 s, Me, 3, 3). Anal. Calcd for $C_{52}H_{46}N_2O_2S_2Si_2W$: C, 60.34; H, 4.48; N, 2.71; S, 6.20. Found: C, 60.35; H, 4.41; N, 2.69; S, 6.16.

$[W(OSiPh_3)_2(Me_4phen)(S_2C_2(CO_2Me)_2)]$. To a solution of 0.206 g (0.199 mmol) of $[WS_2(OSiPh_3)_2(Me_4phen)]$ in 10 mL of dichloromethane was added 0.043 g (0.302 mmol) of dicarbomethoxyacetylene, causing an immediate color change from orange to green-brown. The mixture was stirred for 1 h, and the solvent was removed. The residue was washed with ether (4 × 20 mL) and redissolved in 3 mL of dichloromethane. Addition of ether (20 mL) caused the product to crystallize as brown needles, which were collected, washed with ether (2 × 10 mL), and dried to afford the product as 0.195 g (83%) of a green-brown microcrystalline solid. IR (KBr): ν_{SiO} 904 (br) cm^{-1}. Absorption spectrum (CH_2Cl_2): λ_{max} (ϵ_M) 286 (33 000), 307 (sh, 15 100), 334 (sh, 3 500), 393 (650), 485 (320) nm. FAB-MS: m/z 1176 (M^+). ^1H NMR ($CDCl_3$): δ 9.13 (s, 2,9-H, 1), 7.97 (s, 5,6-H, 1), 7.10 (t, Ph, 3), 6.92 (t, Ph, 6), 6.74 (d, Ph, 6), 4.06 (s, CO_2Me, 3), 2.65, 2.27 (2 s, 3,4,7,8-Me, 3, 3). Anal. Calcd for $C_{58}H_{52}N_2O_6S_2Si_2W$: C, 59.18; H, 4.45; N, 2.38. Found: C, 59.21; H, 4.41; N, 2.26.

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Table 2. Crystal Data[a] for $W^{VI}Q_2$ (Q = O, S) and W^{IV}− and Mo^{IV}−Monodithiolene Complexes

	1	**2**	**3**	**5**·MeCN	**6**·C_5H_{12}[b]
empirical formula	$C_{52}H_{46}N_2O_4Si_2W$	$C_{52}H_{46}N_2O_3SSi_2W$	$C_{52}H_{46}N_2O_2S_2Si_2W$	$C_{68}H_{59}N_3O_2S_2Si_2W$	$C_{71}H_{56}MoN_2O_2S_2Si_2$
fw	1002.94	1019.00	1035.06	1254.33	1185.42
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	*C*2/*c*	*C*2/c	*C*2/*c*	$P\bar{1}$	*C*2/*c*
Z	4	4	4	2	4
a, Å	27.119(4)	16.710(2)	16.9351(1)	13.305(2)	19.068(1)
b, Å	10.017(1)	10.3575(6)	10.4963(1)	14.959(1)	19.316(1)
c, Å	16.547(1)	27.002(3)	26.8896(2)	17.549(1)	17.7183(9)
α, deg				109.330(7)	
β, deg	96.65(1)	103.518(9)	104.517(1)	103.81(1)	112.442(1)
γ, deg				106.667(8)	
V, Å^3	4465(1)	4543.8(7)	4627.18(6)	2934.4(5)	6032.0(5)
R1,[c] wR2[d]	0.0309, 0.0767	0.0305, 0.0760	0.0506, 0.1272	0.0291, 0.0612	0.0485, 0.1342

[a] Obtained with graphite-monochromatized Mo Kα (λ = 0.710 73 Å) radiation at 213 K. [b] Solvate modeled as a disordered pentane molecule. [c] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

[W(OSiPh$_3$)$_2$(Me$_4$phen)(S$_2$C$_2$Ph$_2$)]. Method A. To a solution of 0.206 g (0.199 mmol) of [WS$_2$(OSiPh$_3$)$_2$(Me$_4$phen)] in 10 mL of dichloromethane was added dropwise a solution of 0.0534 g (0.300 mmol) of diphenylacetylene in 5 mL of dichloromethane, causing an immediate color change from orange to deep red-brown. The mixture was stirred for 1 h, and the solvent was removed. The residue was washed with ether (4 × 20 mL) and dissolved in 3 mL of dichloromethane. Addition of ether (20 mL) induced crystallization of the product, which was collected, washed with ether (2 × 10 mL), and dried to afford the product as 0.237 g (98%) of a deep red-brown microcrystalline solid. IR (KBr): ν_{SiO} 918 (br) cm^{-1}. Absorption spectrum (CH$_2$Cl$_2$): λ_{max} (ϵ_M) 285 (39 300), 306 (22 800), 332 (sh, 9640), 350 (sh, 4150), 504 (835) nm. FAB-MS: *m*/*z* 1212 (M$^+$). ^{1}H NMR (CDCl$_3$): δ 9.16 (s, 2,9-H, 1), 7.99 (s, 5,6-H, 1), 7.60−6.84 (m, Ph, 20), 2.65, 2.27 (2 s, Me, 3, 3). Anal. Calcd for $C_{66}H_{56}N_2O_2S_2Si_2W$: C, 65.33; H, 4.65; N, 2.31; S, 5.29. Found: C, 65.18; H, 4.58; N, 2.24; S, 5.35.

Method B. A suspension of 0.064 g (0.203 mmol) of (NH$_4$)$_2$[WO$_2$S$_2$], 0.143 g (0.800 mmol) of diphenylacetylene, and 0.066 g (0.279 mmol) of Me$_4$phen in 10 mL of acetonitrile was stirred for 4 h. To the reaction mixture was added 0.106 g (0.359 mmol) of Ph$_3$SiCl, resulting in a red-brown solution and a deep brown precipitate within 30 min. The mixture was stirred for 4 h, and the solid was collected. This material was washed with acetonitrile and toluene (both 2 × 6 mL) and was dissolved in 30 mL of dichloromethane. The solution was filtered, and the filtrate was reduced to dryness. The residue was washed with acetonitrile and ether (both 2 × 6 mL) and dried to afford the product as 0.167 g (68%) of a deep red-brown solid, whose spectroscopic properties are identical with those of the product of method A.

[Mo(OSiPh$_3$)$_2$(Me$_4$phen)(S$_2$C$_2$Ph$_2$)]. A suspension of 0.115 g (0.504 mmol) of (NH$_4$)$_2$[MoO$_2$S$_2$], 0.356 g (2.00 mmol) of diphenylacetylene, and 0.165 g (0.698 mmol) of Me$_4$phen in 10 mL of acetonitrile was stirred for 4 h. Addition of 0.265 g (0.899 mmol) of Ph$_3$SiCl caused formation of a red-brown solution and a purple-brown precipitate within 30 min. The reaction mixture was stirred for 4 h, and the solid was collected, washed with acetonitrile (2 × 8 mL), and dissolved in 40 mL of dichloromethane. The solution was filtered, and the filtrate was reduced to dryness. The residue was washed with acetonitrile, toluene, and ether (all 2 × 8 mL) and dried to yield the product as 0.346 g (61%) of purple-brown solid. IR (KBr): ν_{SiO} 904 cm^{-1}. Absorption spectrum (CH$_2$Cl$_2$): λ_{max} (ϵ_M) 285 (39 200), 306 (sh, 21 100), 332 (sh, 9830), 360 (8670), 504 (2080) nm. ^{1}H NMR (CDCl$_3$): δ 8.76 (s, 2,9-H, 1), 8.07 (s, 5,6-H, 1), 7.69−6.80 (m, Ph, 20), 2.67, 2.26 (2 s, Me, 3, 3). Anal. Calcd for $C_{66}H_{56}MoN_2O_2S_2Si_2$: C, 70.46; H, 4.98; N, 2.49; S, 5.70. Found: C, 70.28; H, 5.10; N, 2.37; S, 5.56.

In the sections which follow, complexes are designated as shown in Chart 1.

X-ray Structure Determinations. Crystals of **1** (colorless blocks), **2** (yellow blocks), and **3** (red-orange blocks) were grown by slow evaporation of dichloromethane solutions. Crystals of **5**·MeCN (red-brown blocks) and **6**·C$_5$H$_{12}$ (deep red blocks) were produced by layering concentrated dichloromethane solutions with acetonitrile or pentane. Crystals were coated in oil and mounted on a Bruker CCD area detector instrument operated by the SMART software package. For each crystal, a hemisphere of data was collected at 213 K in 30 s frames and with ω scans of 0.3 deg/frame. The first 50 frames were recollected at the end of the data collection to monitor for significant decay, which was not detected for any compound. For all five structures, all data out to 2θ of 56° were used, allowing for a final resolution of 0.76 Å. Data reduction was performed with SAINT, which corrects for Lorentz polarization and decay. Absorption corrections were applied using SABABS. For compounds **1**, **2**, **3**, and **6**·C$_5$H$_{12}$, the space group was identified as *C*2/*c* on the basis of systematic absence analysis by the program XPREP and the successful structure solution and refinement. The space group of **5**·MeCN was selected as $P\bar{1}$ on the basis of anomalous scattering effects, as determined by the program XPREP, and by successful solution and refinement of the structure. Crystal parameters are collected in Table 2.

Chart 1. Compound Designations and Abbreviations

[WO$_2$(OSiPh$_3$)$_2$(Me$_4$phen)]	**1**
[WOS(OSiPh$_3$)$_2$(Me$_4$phen)]	**2**
[WS$_2$(OSiPh$_3$)$_2$(Me$_4$phen)]	**3**
[W(OSiPh$_3$)$_2$(Me$_4$phen)(S$_2$C$_2$(CO$_2$Me)$_2$)]	**4**
[W(OSiPh$_3$)$_2$(Me$_4$phen)(S$_2$C$_2$Ph$_2$)]	**5**
[Mo(OSiPh$_3$)$_2$(Me$_4$phen)(S$_2$C$_2$Ph$_2$)]	**6**

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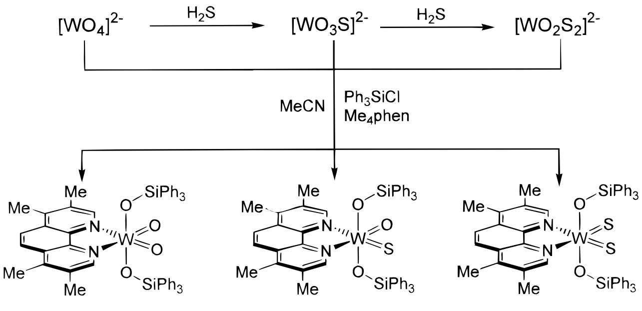
bdt	benzene-1,2-dithiolate(2-)
HB(Me$_2$pz)$_3$	tris(3,5-dimethylpyrazolyl)hydroborate(1-)
L-N$_2$S$_2$	N,N'-dimethyl-N,N'-bis(2-mercaptophenyl)-ethylenediamine(2-)
Me$_4$phen	3,4,7,8-tetramethyl-1,10-phenanthroline
phen	1,10-phenanthroline

All structures were solved by Patterson methods with SHELXTL and subsequently refined against all data by full-matrix least-squares on F^2. In the structure of **2**, the oxo and sulfido ligands as well as the Me$_4$phen ligand were disordered and refined with site occupancy factors of 0.5 for all atoms. The solvate in **6** was modeled as a disordered pentane molecule, and hydrogen atoms were not added. All non-hydrogen atoms were refined anisotropically, with the exception of the Me$_4$phen ligand in **2** and the pentane solvate in **6**. Hydrogen atoms were attached at idealized positions on carbon atoms and were refined as riding atoms with uniform isotropic thermal parameters. All structures converged in the final stages of refinement, showing no movement in atom positions. No residual electron density >1 e$^-$/Å^3 was observed upon convergence, with the exception of two electron density peaks of opposite sign symmetrically disposed around the tungsten atoms. These peaks, which were located within 1 Å of the tungsten and did not exceed 2e$^-$/Å^3, are due to the X-ray absorption properties of tungsten and could not be adequately corrected using SADABS. Bond distances and angles were not constrained in refinements. Use of the checking program PLATON did not identify any missing or higher



1 86 % **2** 45 % **3** 83 %

Figure 1. Scheme depicting the synthesis of oxo/sulfidotungstate(VI) complexes **1**−**3**.

symmetry. Final agreement factors are given in Table 2. (See the Supporting Information.)

Other Physical Measurements. Absorption spectra were obtained with a Varian Cary 50 Bio spectrophotometer. ^{1}H NMR spectra were obtained with Bruker AM 400N/500N spectrometers. Cyclic voltammograms were recorded at 100 mV/s with a PAR model 263 potentiostat/galvanostat using a platinum disk working electrode and 0.1 M $(Bu_4N)(PF_6)$ supporting electrolyte. Potentials are referenced to the saturated calomel electrode (SCE).

Results and Discussion

Oxo/Sulfido Tungsten(VI) Complexes. (a) Synthesis and Properties. We have sought the tungsten analogues of the Mo^{VI} complexes $[MoO_2(OSiPh_3)_2(Me_4phen)]$ and $[MoOS(OSiPh_3)_2(Me_4phen)]$ recently prepared in this laboratory.[8] The preparation of the dioxo compound was based on the observation that Ag_2MoO_4 could be silylated to form coordinatively unsaturated $[MoO_2(OSiPh_3)_2]$.[33] The compound $K_2[MoO_3S]$ undergoes an analogous reaction which in the presence of Me$_4$phen affords a product containing the *cis*-MoOS group. This group in unperturbed form has proven to be synthetically elusive in five- and six-coordinate molecules, and is of significance because of its presence in the xanthine oxidase family of enzymes where it is obligatory to function.[1,2] We have verified the unexpected lack of reactivity of Ag_2WO_4 with Ph_3SiCl under forcing conditions.[33] However, as indicated in Figure 1, tungstate itself and oxosulfidotungstates can be silylated in reaction mixtures in acetonitrile at room temperature in the presence of a ligand which stabilizes a six-coordinate structure. The starting materials are $K_2[WO_4]$, $K_2[WO_3S]$, and $(NH_4)_2[WO_2S_2]$, all of which are insoluble but reactive as acetonitrile suspensions to give products **1**, **2**, and **3**, respectively, in overall reaction 1. The lower yield

$$[WO_{4-n}S_n]^{2-} + 2Ph_3SiCl + Me_4phen \rightarrow [WO_{2-n}S_n(OSiPh_3)_2(Me_4phen)] + 2Cl^- \ (n = 0-2) \quad (1)$$

of **2** is associated with difficulty in obtaining highly pure $K_2[WO_3S]$. We are aware of only one prior example of silylation of a $W^{VI}{=}O$ group.[12] The compounds were identified by analytical, spectroscopic, and X-ray structural results.

The ^{1}H NMR spectra of the Me$_4$phen portion of **1**−**3** in Figure 2 are characterized by downfield-shifted 2,9-H resonances owing to the inductive effect of the metal. The spectra of **1** and **3** are consistent with C_2 symmetry whereas the spectrum of **2** clearly reflects the absence of symmetry. This is particularly evident in the splitting of the 2,9-H signals by 0.81 ppm, larger than that observed in $[MoOS(OSiPh_3)_2(Me_4phen)]$ (0.66 ppm).[8] The mass spectrum of **2** in the parent ion region, shown in Figure 3, reveals a prominent parent ion peak and features consistent with the separate loss of one oxygen atom and one sulfur atom. Absorption spectra of the three complexes are shown in Figure 4. Complex **1** is a white solid with no visible absorption. Complex **2** is yellow and absorbs at λ_{max} (ϵ_M) = 367 (560) nm, while **3** is orange with λ_{max} (ϵ_M) = 451 (910) nm. The corresponding feature for orange $[MoOS(OSiPh_3)_2(Me_4phen)]$ is at 434 nm. This is the expected trend for LMCT bands, owing to the higher optical electronegativity of Mo^{VI} vs W^{VI}.[34]

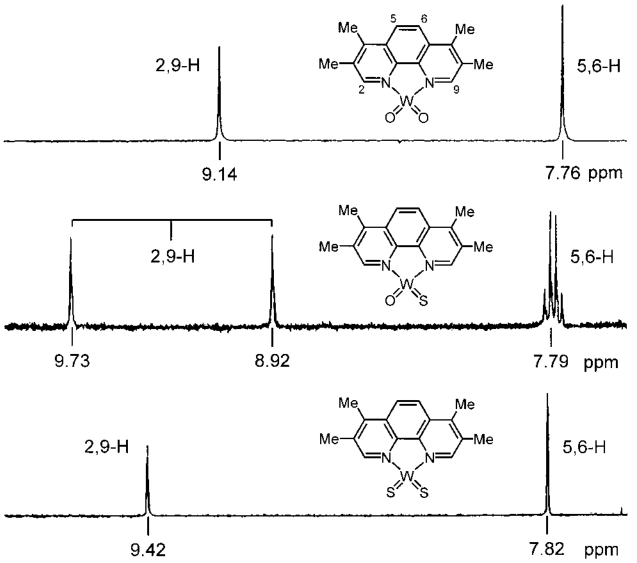


Figure 2. ^{1}H NMR spectra of the Me$_4$phen ligand in $[WO_2(OSiPh_3)_2(Me_4phen)]$ (top), $[WOS(OSiPh_3)_2(Me_4phen)]$ (middle), and $[WS_2(OSiPh_3)_2(Me_4phen)]$ (bottom) in $CDCl_3$ solutions. Chemical shifts are indicated.

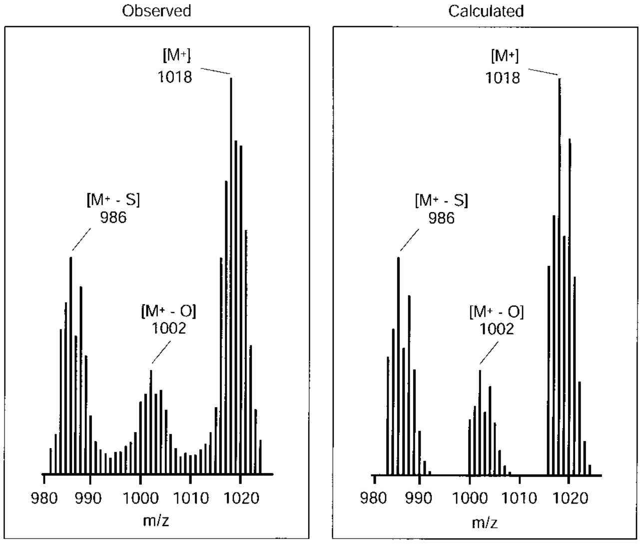


Figure 3. Observed and calculated FAB$^+$ mass spectra of $[WOS(OSiPh_3)_2(Me_4phen)]$ in the parent ion region.

(b) X-ray Structures. Complexes **1**−**3** crystallize in monoclinic space group *C*2/*c* (Table 2). Structures are set out in Figure 5, from which it is seen that all three have the same overall stereochemistry and considerable similarity in metric details. Oxo/sulfido ligands are mutually cis and cis to the silyloxide ligands, which are mutually trans. Each molecule has imposed C_2 symmetry at the tungsten special position. Selected dimensions of these molecules are collected in Table 3. Taking **3** as

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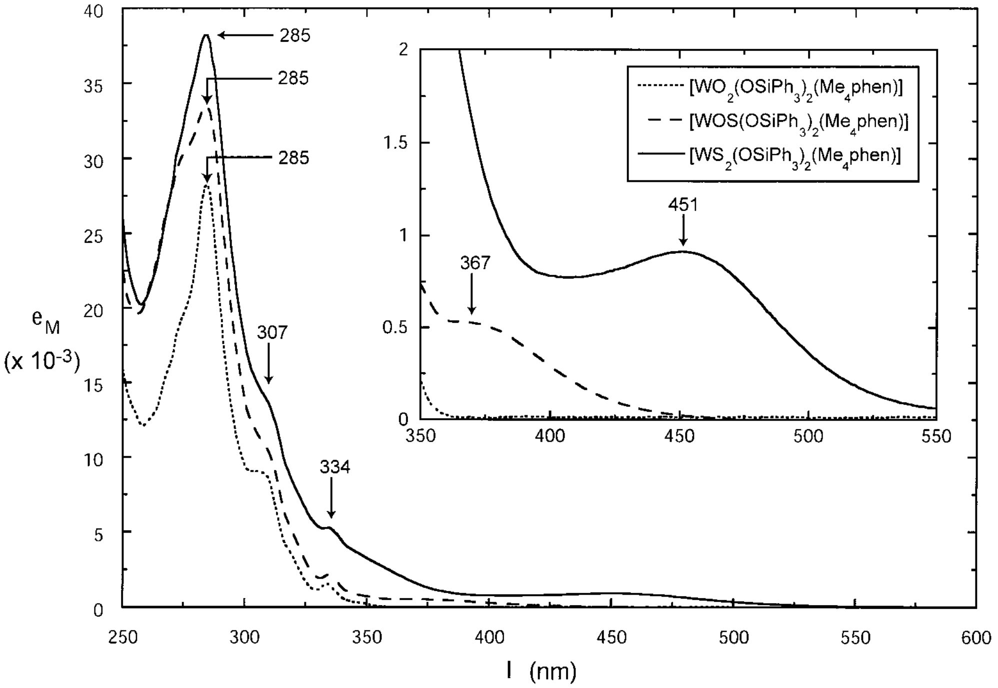

Figure 4. UV−vis spectra of [$WO_2(OSiPh_3)_2(Me_4phen)$], [$WOS(OSiPh_3)_2(Me_4phen)$], and [$WS_2(OSiPh_3)_2(Me_4phen)$] in dichloromethane solutions. Band maxima are indicated.

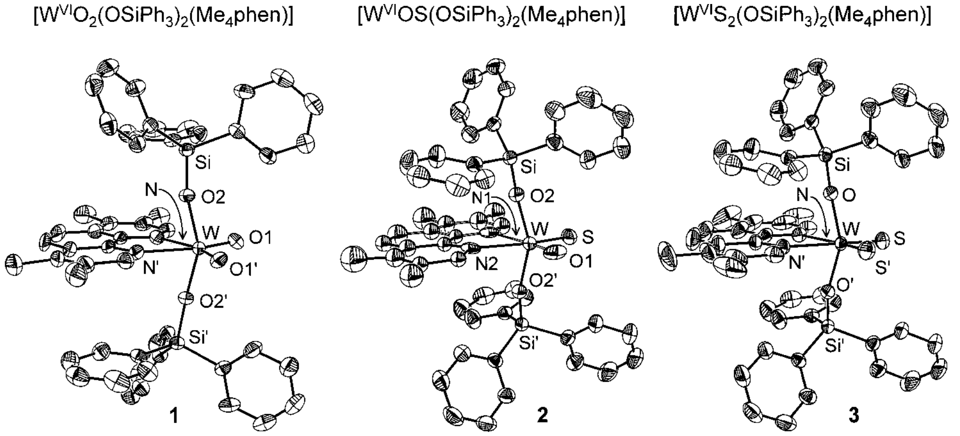

Figure 5. Structures of [$WO_2(OSiPh_3)_2(Me_4phen)$], [$WOS(OSiPh_3)_2(Me_4phen)$], and [$WS_2(OSiPh_3)_2(Me_4phen)$], showing 50% probability ellipsoids and atom-labeling schemes. Primed and unprimed atoms are related by a 2-fold axis.

Table 3. Selected Distances (Å) and Angles (deg) for Oxo/Sulfido Complexes **1**−**3**

	1	2[a]	3
W═O	1.733(2)	1.689(6)	
W═S		2.222(2)	2.160(1)
W−O_{Si}	1.926(2)	1.924(2)	1.923(3)
W−N_O	2.322(3)	2.37(3)	
W−N_S		2.32(4)	2.345(4)
Si−O	1.609(2)	1.625(4)	1.625(4)
Q−W−Q′	106.3(2)	103.7(3)	106.16(9)
O_{oxo}−W−O_{Si}	98.1(1)	97.0(2)	
S−W−O_{Si}		94.99(9)	99.1(1)
O_{Si}−W−O_{Si}	152.9(1)	153.0(1)	152.7(2)
N−W−N′	70.0(1)	68.6(2)	69.4(2)
W−O−Si	158.7(2)	153.6(1)	153.3(2)

[a] Disordered structure; see the text.

an example, sulfido ligands form a S−W−S angle of 106.2° owing to charge repulsion. For the same reason, the silyloxide groups are bent back from the sulfido ligands such that the O−W−S angle is 99.1°; the W−O−Si angle is 153.3(2)°. The displacement of the silyloxide groups is in the direction of the Me_4phen ligands. Comparable distortions from octahedral coordination are observed in **1** and **2**, in the corresponding molybdenum complexes,[8] and in numerous five- and six-coordinate complexes containing the *cis*-$M^{VI}O_2$ group.

The imposed symmetry requires that a crystal of **2** contain a 1:1 mixture of identical molecules that differ only in the relative disposition of the $W^{VI}OS$ group. The disorder problem is the same as that described at length for [$MoOS(OSiPh_3)_2(phen)$] and [$MoOS(OSiPh_3)_2(Me_4phen)$][8] and was treated in the same way. The two $Mo^{VI}OS$ compounds are isomorphous, and the latter is nearly isometric, with **2**. To obtain accurate bond distances, free of disorder, in the two molybdenum compounds, Mo EXAFS analyses were carried out. The results were the same for both compounds (Mo═O, 1.71−1.72 Å; Mo═S, 2.19 Å).[8] We have not carried out a similar analysis for **2**. Here our primary aim was the preparation of a $W^{VI}OS$ complex by the silylation method.

Whereas five- and six-coordinate complexes containing the $W^{VI}O_2$ group are unexceptional, those containing the $W^{VI}OS$ and $W^{VI}S_2$ groups are less common. Complexes with the W^{VI}-

OS group include $[WOS(NCS)_4]^{2-}$,[35] $[(C_5Me_5)WOS(R)]$ (R = Me, CH_2SiMe_3),[36] $[(HB(Me_2pz)_3)WOS(L)]$ (L = Cl,[37] (−)mentholate[28]), and $[WOS(L{-}N_2S_2)]$.[38] Of these, $[WOS(L{-}N_2S_2)]$ is described as disordered; accurate structures are available for $[WOS(NCS)_4]^{2-}$ and $[(HB(Me_2pz)_3)WOS((-)\text{-mentholate})]$. Those with the $W^{VI}S_2$ group include three Schiff base complexes,[39] $[(HB(Me_2pz)_3WS_2(L)]$ (L = Cl,[37] OPh[28]), $[WS_2(PMe_3)_2(\eta^2\text{-}OCHPh)]$,[40] $[(C_5Me_5)WS_2(SR)]$,[26,27] and $[WS_2(L{-}N_2S_2)]$.[38] Given that the W=S bond distance range defined by these complexes and $[W^{VI}S(OSiBu^tPh_2)(bdt)_2]$[12] is 2.11−2.19 Å, it is probable that the value from the refinement of disordered **2** (Table 3) is artifactually long.

Dithiolene Ring Closure. While a number of dithiolene ligands are available in uncomplexed form as ene-1,2-dithiolate salts, such as $Na_2(S_2C_2(CN)_2)$, $Na_2(S_2C_2H_2)$, and $Li_2(bdt)$, and can be used as such in synthesis, others are not available in this condition. Dithiolenes protected as, e.g., thiophosphate[41] and 1,3-dithiolium or 1,3-dithiol-2-one derivatives,[42] can be deprotected under reaction conditions leading to complex formation. Summarized in Table 1 is a different general method with eight reaction types for chelate ring formation in molybdenum and tungsten dithiolenes. Here one or more ene-1,2-dithiolate rings are closed in reactions of sulfide-bound precursors with suitably activated alkynes RC≡CR, usually with R = aryl, COAr, $CONH_2$, or CO_2R'. Reaction type 5 employs a different closure reagent. Although the matter has not been proven by isotope labeling, it is entirely probable that the sulfur atoms in the product chelate ring are those present in the reactant. Two other procedures, involving the reactions of $[MS_4]^{2-}$ with the thiocarbonates $C_2S_4(CO)(CQ)$ (Q = O, S),[43] and $[MS_{4-n}O_n]^{2-}$ ($n = 0{-}2$) with the dithiete $(CF_3)_2C_2S_2$,[44] are not included in Table 1 because the origin of all chelate ring sulfur atoms is less certain.

The eight reaction types are represented generally, ancillary ligands usually being omitted, to emphasize chelate ring formation. The first demonstration that a dithiolene ring could be closed in this manner was the reaction of $(RC_5H_4)_2TiS_5$ with dicarbomethoxyacetylene.[45] This was followed by formation of bis- and tris(dithiolene)molybdenum complexes by reaction types 1−3. Five procedures start with readily accessible tetrasulfido- or oxosulfidometalates(VI). In reaction type 1, for example, $[MoOS_3]^{2-}$ is converted to $[MoO(S_4)_2]^{2-}$, which reacts with bis(phenacyl)acetylene to afford $[MoO(S_2C_2(COPh)_2)_2]^{2-}$ (39%).[20] The general method has been applied much less frequently to the synthesis of tungsten complexes. Reaction type 6 with dicarbomethoxyacetylene gives $[W(S_2C_2(CO_2Me)_2)_3]^{2-}$ (43%).[20] In procedure 7, the $W^{VI}S_2$ group reacts with alkynes to afford products in yields as high as 86%.[30] In these cases, the group was not derived from an oxosulfidotungstate(VI) starting material. Evidently, $Mo^{IV}(S_4)$ and $W^{VI}S_2$ are functionally equivalent groups in reactions with activated alkynes. Reactions involving the former group do not change the oxidation state, whereas those of the latter result in reduction to W^{IV}.

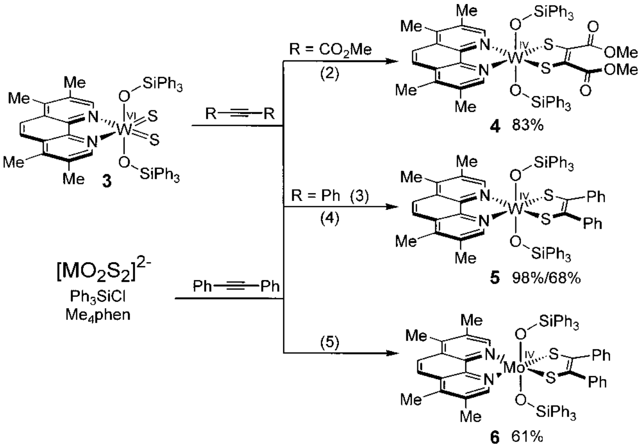

Figure 6. Scheme depicting the formation of dithiolene chelate rings in W^{IV} and Mo^{IV} complexes **4**−**6** using precursors with coordinated sulfide.

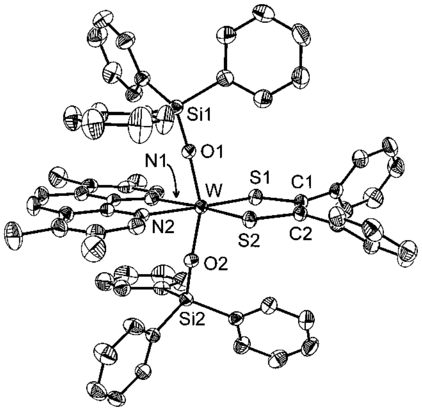

Figure 7. Structure of $[W^{IV}(OSiPh_3)_2(Me_4phen)(S_2C_2Ph_2)]$ showing 50% probability ellipsoids and the atom-labeling scheme. The structure of the corresponding molybdenum complex is essentially identical.

We provide here several examples of the formation of dithiolene rings using $[MO_2S_2]^{2-}$ starting materials and the reactions in Figure 6. Complex **3**, derived from $[WO_2S_2]^{2-}$ (Figure 1), reacts instantly with dicarbomethoxyacetylene or diphenylacetylene in reactions 2 and 3 to afford monodithiolene complexes **4** and **5**, respectively, in high yield. These reactions are new examples of type 7, first demonstrated by Young and co-workers.[28,30] Even more convenient are reactions 4 and 5, in which intermediate species need not be isolated. These reactions lead to complexes **5** and **6** in good yield; they constitute the current examples of reaction type 8.

The structures of both **5** and **6** have been determined. Because the complexes are isostructural and virtually isometric, only the structure of **5**, presented in Figure 7, is reported. Selected bond angles and distances are given in Table 4. Comparison with precursor **3** (Figure 2) reveals a closely related stereochemistry, which includes the direction of bending of the *trans*-silyloxide groups toward the Me_4phen ligand. Using average values where appropriate, the largest dimensional changes upon formation of **5** are a 0.15 Å increase in the W−S distance and a 22.2° decrease in the S−W−S angle as a consequence of chelate ring formation. Removal of the trans influence of the sulfido ligand results in a 0.09 Å decrease in the W−N distance. Other changes

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Table 4. Selected Bond Distances (Å) and Angles (deg) for $[W(OSiPh_3)_2(Me_4Phen)(S_2C_2Ph_2)]$

W−S1	2.306(1)	W−S2	2.308(1)
W−N1	2.253(2)	W−N2	2.257(2)
W−O1	1.905(2)	W−O2	1.893(2)
Si1−O1	1.627(2)	Si2−O2	1.630(2)
C1−C2	1.341(4)	C2−S2	1.804(3)
C1−S1	1.807(3)	N1−W−N2	73.73(8)
S1−W−S2	83.99(3)	O1−W−S2	97.92(6)
O1−W−S1	100.05(6)	O2−W−S2	97.79(6)
O2−W−S1	97.35(6)	N2−W−O1	80.99(8)
N1−W−O1	80.99(8)	N2−W−O2	80.20(8)
N1−W−O2	82.19(8)	W−O2−Si2	161.7(1)
W−O1−Si1	163.4(1)		
O1−W−O2	157.63(8)		

of bond angles at tungsten are <5°. The localization of significant structural changes to the WS_2 fragment presumably contributes to the rapidity of reactions 2 and 3. The chelate ring C−C and C−S distances are very close to the expected values for double (1.33 Å) and single (1.82 Å) bonds, respectively, indicating that the ligand is best formulated as an enedithiolate. The corresponding distances in **6** are 1.344(5) and 1.784(3) Å. Therefore, the chemically reversible reductions ($i_{pc}/i_{pa} \approx 1$) at −1.45 V (**6**) and −1.62 V (**5**) in dichloromethane are interpreted as metal-centered $M^{IV/III}$ processes. The order $E(W) < E(Mo)$ is consistent with this assignment.

Summary

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

(1) The readily available oxo/sulfidotungstates $[W^{VI}O_{4-n}S_n]^{2-}$ ($n = 0-2$) in the presence of a chelating ligand are effective precursors in a silylation method for the formation of the six-coordinate complexes $[WQ_2(OSiPh_3)_2(Me_4phen)]$, containing the $W^{VI}O_2$, $W^{VI}OS$, and $W^{VI}S_2$ groups.

(2) The complexes in (1) have crystallographically imposed C_2 symmetry, with *cis*-oxo/sulfido and *trans*-silyloxide ligands, and are isostructural with their molybdenum analogues, including the S/O and Me_4phen positional disorder encountered in the structure of $[WOS(OSiPh_3)_2(Me_4phen)]$.

(3) The complex $[WS_2(OSiPh)_2(Me_4phen)]$ reacts immediately with two activated alkynes, resulting in dithiolene ring closure and formation of $[W^{IV}(OSiPh)_2(Me_4phen)(S_2C_2R_2)]$ (R = CO_2Me, Ph; reaction type 7). The product retains the *trans*-silyloxide stereochemistry. Localization of significant structural changes to the WS_2 fragment presumably contributes to the facility of these reactions.

(4) Dithiolene ring closure occurs in the reaction systems $[MO_2S_2]^{2-}/2Ph_3SiCl/Me_4phen/PhC{\equiv}CPh$ to afford the products $[M^{IV}(OSiPh)_2(Me_4phen)(S_2C_2Ph_2)]$ (M = Mo, W; reaction type 8). These are the same as or analogous to those in (3), and are obtained in high yield without requiring the isolation of an intermediate.

These results are part of an ongoing investigation of the synthesis of new types of mono- and bis(dithiolene) complexes of molybdenum[6−8] and tungsten[12,13] with functional units the same as, or analogous to, those present in enzymes.[1−4] They demonstrate the viability of the silylation method, introduced earlier for molybdenum complexes,[8] in the formation of oxo/sulfidotungsten(VI) groups. The procedures in (1) and (3)/(4) are potentially extendable to the formation of complexes with different ancillary ligands and variously substituted dithiolene rings, respectively. Owing to the absence of five- or six-coordinate complexes containing the $Mo^{VI}S_2$ group, reaction type 7 is currently restricted to the formation of monodithiolene−W(IV) complexes. It remains to be seen whether the active sites of tungstoenzymes contain the oxo/sulfido groups in Figure 1 and other ligation modes recently achieved in this laboratory,[12−14] including $W^{IV}OR$ and $W^{VI}O(OR)$.

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

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